Rotational Spectroscopy and Observational Astronomy of Prebiotic Molecules

Thesis by

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Abstract

It is now widely believed that prebiotic molecules were delivered to the early Earth by planetesimals and their associated interplanetary dust particles. Yet the formation pathways for these molecules are not clear. Amino acids and sugars have been found in carbonaceous chondrites, but only much simpler species have been detected in the interstellar medium (ISM). Prebiotic organics could have formed in the ISM and been directly incorporated into planetesimals, or simpler species could have formed in the ISM and then been incorporated into planetesimals, undergone further processing, and been delivered to Earth. Limits on interstellar chemistry must therefore be established through observational astronomy before potential prebiotic formation pathways can be assessed. These observations require laboratory spectroscopic investigation of the species of interest.

This thesis is an interdisciplinary study involving laboratory rotational spectroscopy and astronomical observations of several key prebiotic molecules. The laboratory work has focused on obtaining the rotational spectra of the simplest three-carbon ketose sugar, 1,3-dihydroxyacetone, and its structural isomers methyl glycolate and dimethyl carbonate, as well as aminoethanol, the predicted interstellar precursor to alanine. The pure rotational spectral analysis of the low-lying torsional states of the simplest α-hydroxy aldehyde, glycolaldehyde, has also been completed. The original Balle-Flygare Fourier transform microwave spectrometer was used to obtain the microwave spectra, while both the Jet

Propulsion Laboratory and Caltech direct absorption flow cell spectrometers were used for additional direct absorption millimeter and submillimeter studies.

The results of these laboratory experiments were used to guide observational searches with the Caltech Submillimeter Observatory, the Owens Valley Millimeter Array, and the Green Bank Telescope toward the hot core sources Sgr B2(N-LMH), Orion Hot Core/Compact Ridge, and W51 e1/e2. Evidence has been found for the presence of dihydroxyacetone and methyl glycolate in Sgr B2(N-LMH).

These results have important implications for interstellar grain surface chemistry, and proposed additions to grain surface chemical models are also discussed. Reactions involving surface radicals and molecules containing carbonyl groups can efficiently compete with the simple grain surface reactions included in previous models. Such aldehyde abstraction reactions should be considered as pathways to complex carbonyl-containing species on interstellar grain surfaces.

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Chapter 1

Introduction

1.1 Prebiotic Interstellar Chemistry

It is now widely believed that molecules that could have played a central role in the development of biological systems were delivered to the early Earth by planetesimals and their associated interplanetary dust particles [5]. Yet the degree of complexity reached by prebiotic organic chemistry before the formation of planetesimals and its impact on the evolution of planetary surfaces remains a mystery. Nearly 140 molecules, mostly organic, have been discovered in the interstellar medium (ISM), principally toward so-called hot molecular cores where the radiation and/or shocks from newly formed stars evaporates grain mantles and drives a complex gas-grain chemistry [3]. Approximately 50 of these compounds have been seen in the comae of comets, and many biologically-related monomers, including amino acids and sugars, have also been detected in carbonaceous chondrites [6–8].

The chemical processes leading to the formation of these prebiotic molecules are not fully understood. Aqueous alteration of simple organic species within the meteorite parent body is a viable explanation for the existence of the more complex species. The large enrichment of deuterium in the carbonaceous components of chondrites is not explainable by known or plausible solar system processes, however, and suggests an interstellar origin for the species

present therein, or at least their immediate precursors [3, 9].

There are two possible mechanisms for the formation of these molecules, the first being that a variety of prebiotic species were formed before our planetary system was assembled, integrated into planetesimals, and introduced to the Earth through interplanetary dust and comet or meteorite impacts. Alternatively, the planetesimals could have formed from interstellar dust grains whose mantles contained much simpler organic species. More complex prebiotic chemistry could then follow in the parent body, with the products ultimately being delivered to the early Earth through impact.

1.2 Grain Surface and Hot Core Chemistry

Interstellar grain surfaces are processed by charged particles, UV radiation, and radiative heating, and laboratory studies have shown that various combinations of these processes produce a highly complex mixture of organic species with molecular weights into the hundreds of atomic mass units (amu, see [10, 11]). Early chemical models considered complex molecule formation on grains [12], but current theoretical models of grain surface chemistry concentrate largely on the precursors to the more complex compounds, such as simple alcohols and aminoalcohols [3]. Many potential grain surface reaction pathways are eliminated by the conditions imposed on these models, greatly simplifying the possible products of grain synthesis and eliminating the possibility for much larger organics to form on the grain surfaces. Gas phase theoretical models of the chemistry in hot protostellar cores involving the products of grain surface reactions are therefore required to explain the formation of substantially larger organics under interstellar conditions.

A hot core is a region of dust and gas around a newly formed star where the temperature is sufficient to thermally evaporate grain mantles but low enough that organics remain stable

in the gas phase. The temperature of a hot core is typically ∼100–300 K. A schematic diagram of a hot core is shown in Figure 1.1.

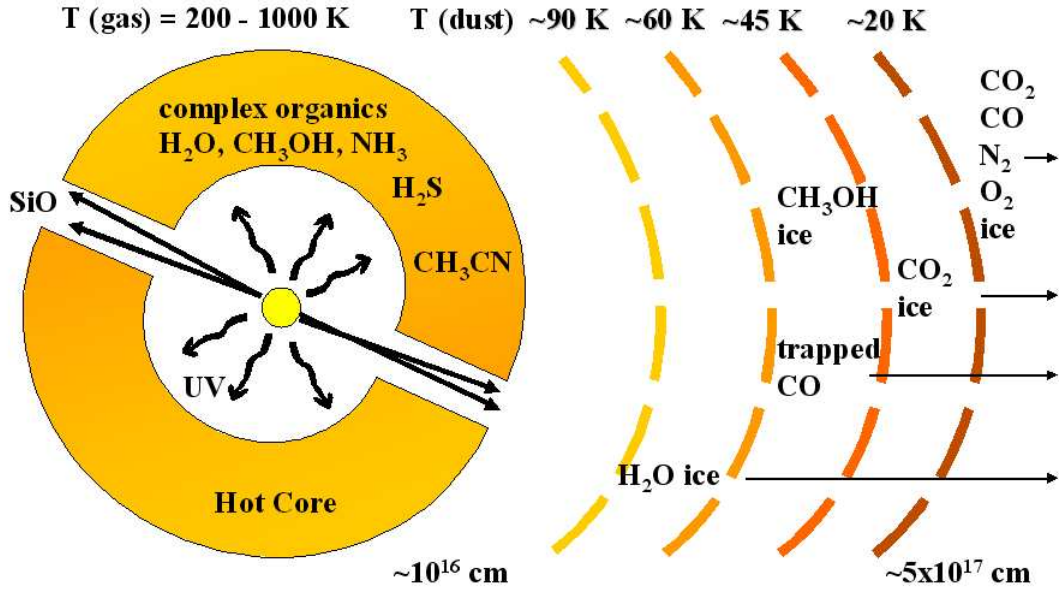

Figure 1.1: Schematic diagram of a hot core, adapted from [1]. The indicated size scale is that appropriate for a hot core surrounding a high mass protostar. 'Hot corinos' have also been detected around low mass protostars and have similar temperature profiles but are much less massive and smaller in size [2].

Current models assume that species such as alcohols and aminoalcohols undergo gas phase reactions in hot cores to form more complex prebiotic species. It has recently been shown, however, that gas phase pathways are insufficient for the production of organics such as ethanol (CH_3CH_2OH) and methyl formate (CH_3OCHO) [13, 14]. Recent observations have also reopened the possibility for complex molecule formation on grains. Glycolaldehyde, ($CHOCH_2OH$), the simplest two-carbon (2C) α-hydroxy aldehyde, has recently been detected toward the galactic center Sagittarius B2(N) molecular cloud complex [15]. The glycolaldehyde emission is spatially extended by $\geq 60''$ around the Sgr B2(N-LMH)

hot core [16], a conclusion reinforced by the low excitation temperature of the centimeter-wave transitions recently detected with the Green Bank Telescope (GBT, [17]). While the more compact emission gives a rotational temperature of ∼50 K, the extended emission lines yield a rotational temperature of ∼8 K, indicating that glycolaldehyde is likely sub-thermally excited after liberation from grain surfaces. Similar properties are exhibited by ethanol and acetaldehyde (CH_3CH_2OH & CH_3CHO, [18, 19]). Glycolaldehyde is closely related to polyhydroxylated aldehydes, or aldoses (sugars), which are produced biologically via glycolysis and used in the production of ATP. The presence of a species so closely related to aldoses could potentially link grain surface pathways to prebiotic interstellar chemistry.

The sugars and other polyhydroxylated organic species observed in meteorites are present in similar concentrations to amino acids, indicating that these species might form from similar processes. The most likely route to amino acids in the ISM is gas phase ion-molecule reactions. This possible link between hot core gas phase chemistry and the formation of α-hydroxy compounds stands in stark contrast to the grain surface production indicated by the glycolaldehyde observations, but it should be stressed that neither the formation of glycolaldehyde nor any other sugar-related species can be explained by existing grain surface or gas phase hot core chemical models. Detailed laboratory and observational investigations of both predicted grain surface precursors and more complex prebiotic species are clearly required before interstellar prebiotic chemistry can be understood.

1.3 Thesis Overview

This thesis is an interdisciplinary study involving laboratory rotational spectroscopy and astronomical observations of several key prebiotic molecules. The laboratory work has focused on obtaining the rotational spectra of the three-carbon (3C) ketose

sugar, 1,3-dihydroxyacetone ($CO(CH_2OH)_2$), and its structural isomers methyl glycolate (CH_3OCOCH_2OH) and dimethyl carbonate ($CH_3OCOOCH_3$). The pure rotational spectral analysis of glycolaldehyde's low-lying torsional states has also been completed. Additional laboratory studies involved the simple grain surface species aminoethanol ($NH_2CH_2CH_2OH$), the predicted precursor to the amino acid alanine. The original Fabry-Perot cavity pulsed Fourier transform microwave (FTMW) spectrometer, or Balle-Flygare instrument, was used to obtain the microwave spectra, while both the Jet Propulsion Laboratory (JPL) and Caltech Direct Absorption Flow Cell spectrometers were used for additional direct absorption millimeter and submillimeter studies.

The results of these laboratory experiments were used to guide observational searches with the Caltech Submillimeter Observatory (CSO), the Owens Valley Millimeter Array (OVRO), and the Green Bank Telescope (GBT). A combination of microwave, millimeter, and submillimeter spectral line searches and spatial imaging has been conducted. The Sgr B2(N-LMH) high mass hot core was the primary target for these observations, as it is found to have among the highest column densities of large organics ever detected. Other high mass hot cores targeted in these studies include the Orion Hot Core/Compact Ridge and W51 e1/e2.

These spectroscopic and observational studies have led to a revised theory for the formation of complex molecules on grains. The importance of reactions involving surface radicals and molecules containing carbonyl groups has been demonstrated, and suggestions for the adaptation of grain surface chemical models have been developed.

The techniques used for the laboratory and observational studies are outlined in Chapters 2 and 3, respectively. Detailed information on the FTMW instrument is given in Appendix A, while details on the Caltech Direct Absorption Flow Cell Spectrometer are

given in Appendix B. The spectroscopic and observational results for each molecule are presented in Chapters 4–7. An overview of the programs used for spectral fitting is given in Appendix C, while the files used for fitting the spectrum of each molecule are presented in Appendices E–I. The implications of the results of these studies for interstellar grain surface chemistry will be discussed in Chapter 8.

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Chapter 2

Experimental Laboratory Methods

2.1 Introduction

Prebiotic monomers are expected to have strong torsional transitions in the terahertz (THz) frequency range. Due to experimental limitations in this range, however, rotational spectral lines searches are more straightforward at microwave, millimeter, and submillimeter wavelengths. The OVRO and CSO observatories cover spectral ranges of 88–116 GHz / 210–270 GHz and 200–900 GHz, respectively, and so these frequency ranges were the highest priority target ranges for laboratory studies. Predictions from microwave spectral data are often required before millimeter and submillimeter spectra can be assigned. Microwave spectral information was available in the literature for all species but dihydroxyacetone and dimethyl carbonate. A Fabry-Perot cavity pulsed Fourier-Transform MicroWave (FTMW) spectrometer, also known as a Balle-Flygare instrument, was used for the microwave investigation of these two molecules. The spectral prediction derived from the microwave study of a species then served as the basis for further millimeter and submillimeter studies with the JPL and Caltech Direct Absorption Flow Cell Spectrometers. Overviews of the FTMW and direct absorption techniques are presented below.

2.2 Spectroscopic Techniques

2.2.1 Pulsed Fourier Transform Microwave Spectroscopy

Fourier-Transform microwave spectroscopy, developed by Balle and Flygare in 1971 [20], is an extremely sensitive method for high resolution rotational spectroscopy. This technique utilizes a pulsed molecular nozzle for adiabatic expansion of the species of interest into vacuum, which cools the sample to rotational temperatures of 1–4 K, and a Fabry-Perot cavity for polarization of resonant transitions of the species of interest. A pulse of microwave radiation is introduced into the cavity, exciting the molecules. After the pulse dies away, the molecules emit coherent radiation at their resonant frequencies. A superheterodyne detector is used to collect the time-domain free induction decay (FID), and the Fourier transform of this record gives the frequency-domain spectrum.

A schematic diagram of the current configuration of the original FTMW instrument is presented in Figure 2.1 (adapted from [21]). A signal of frequency ν is generated by the master oscillator (MO). The MO signal is upconverted by 30 MHz in a single sideband (SSB) mixer, and this signal is then coupled into the cavity upon the opening of a PIN diode. The radiation is pulsed into the cavity by the opening and shutting of this PIN diode, which is controlled by the timing control circuit. This timing control circuit also controls the molecular pulse valve. The pulse of radiation passes through the coupling iris of the Fabry-Perot cavity. The molecular nozzle pulses a beam of molecules into the cavity at the same time. The incident radiation excites the molecules, and they emit radiation at a transition frequency offset from the microwave pulse by Δ ($\sim$ 500 kHz). This emission is longer-lived than the incident radiation trapped in the cavity, but much weaker, and sets up a standing wave in the cavity. When the switch is again opened to the cavity, some

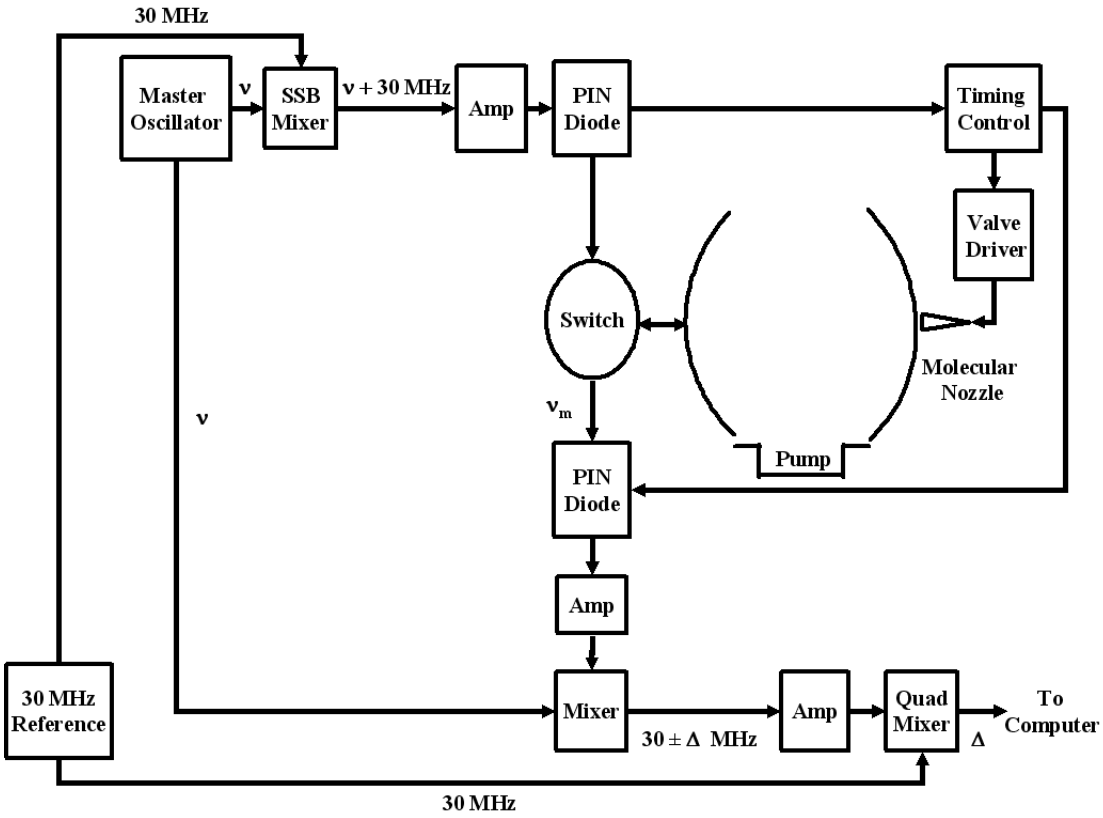


Figure 2.1: Schematic diagram of an FTMW instrument.

of the emitted radiation plus residual incident radiation passes through the same coupling iris, through an isolator, and through a second PIN diode, which is opened only after the majority of the MO radiation pulse has rung down. The radiation, at a frequency ν_m, is amplified and then mixed with the MO signal to yield a frequency $30 \pm \Delta$ MHz. This signal is then mixed with the 30 MHz signal in a quadruture mixer, producing signals near frequency Δ, the widths of which are determined by the finesse of the cavity. The output of this quadruture mixer is two signals, the upper and lower sidebands, which are separated in phase by 90°. These signals are then processed by a computer. The power spectrum is recorded in the time-domain, and the computer then performs the Fourier transform of this spectrum to obtain the final spectrum in the frequency-domain. Cavity pressures on

the order of 10^{-6} torr are maintained with a diffusion pump located below the spectral chamber.

This technique is much more sensitive than standard direct absorption experiments due to the superheterodyne detection and the high finesse of the cavity. The detection scheme lowers the 1/f noise considerably, allowing for detection of much weaker lines than those observable in direct absorption experiments. In addition, pressure broadening effects are eliminated, greatly decreasing the linewidths observed and therefore increasing the resolution. Line widths are limited by Doppler broadening and Doppler splitting due to the angular distribution of the molecules as they pass into the cavity. Although each transition is split into two lines that are sometimes tens of kHz apart, spectral linewidths of 1.4 kHz can be achieved for long-lived species.

The original FTMW instrument has recently been moved to the Blake labs at Caltech. Detailed operating procedures as well as a description of the changes made to the spectrometer since its relocation to Caltech are outlined in Appendix A. This instrument has a frequency range of 2–18 GHz, but Balle and Flygare noted in their original paper that these techniques " ... should also be easily applied to far-infrared and higher frequencies [20]." FTMW instruments based on this original design have been extended up to 40 GHz. Coaxial pulsed-jet instruments have been developed for the millimeter and submillimeter ranges, but these are not FT cavity experiments [22]. FT instruments in the millimeter, submillimeter, and terahertz ranges should have only slightly lower cavity finesse and will have wider cavity modes, enabling wider frequency coverage and therefore much faster data acquisition than traditional FTMW techniques, but no millimeter or far-IR FT instruments have yet been developed. The slow progress is in part due to the fact that, until very recently, very few intense tunable far-IR sources were available. Recent advancements in observational

astronomy have motivated development of new tunable sources in the far-IR, however, and a prototype FT-FIR instrument is currently being developed in the Blake labs.

2.2.2 Direct Absorption Flow Cell Spectroscopy

Direct absorption flow cell spectrometers were developed as a straightforward means of obtaining broadband spectral coverage for molecules with reasonably strong rotational spectra. A schematic diagram of this type of spectrometer is shown in Figure 2.2.

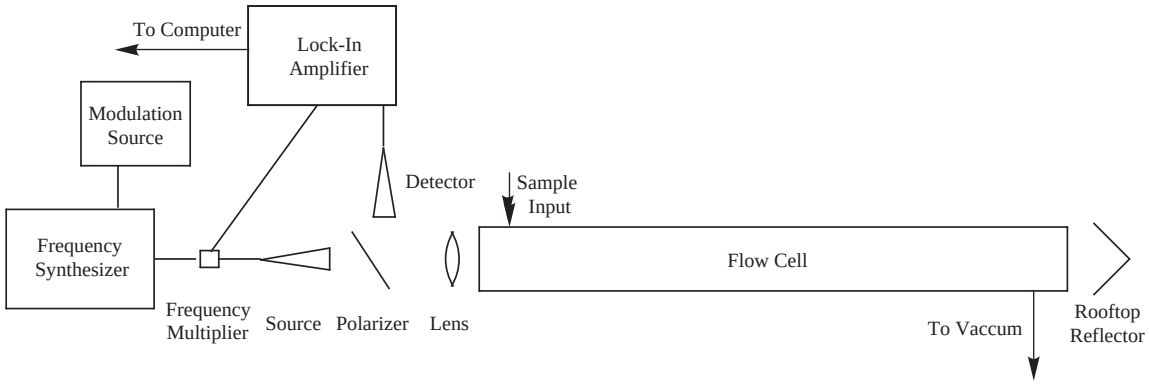


Figure 2.2: Schematic diagram of the Caltech Direct Absorption Flow Cell Spectrometer.

The general flow design involves a long quartz cell with a sample inlet on one end and a vacuum line on the opposite end. The pump is used to maintain a constant flow of gas phase species. Microwaves are generated by a frequency synthesizer that is controlled by a computer and swept through a given frequency range at a designated frequency interval. This radiation is then frequency modulated and multiplied to the desired frequency range by an active multiplier chain. It is emitted from a waveguide horn and passed through a polarizer and teflon lens to focus the coherent radiation into the flow cell. The cell acts as a dielectric waveguide, propagating the waves to the opposite end of the cell where they reflect off of a rooftop reflector. The rooftop changes the polarization by 90 degrees and

transmits the radiation back through the flow cell. The molecules present in the flow cell absorb this radiation as it passes through the cell, and the double-pass nature of the setup increases the amount of absorption and therefore the signal-to-noise ratio. After passing back through the cell, the radiation is then deflected off of the input polarizer and detected by either a Schottky diode detector or an InSb hot electron bolometer at 90 degrees to the source. A lock-in amplifier is used to narrow the detection bandwidth and amplify and rectify the 2f (second-derivative) signal. The resultant DC signal is then sent to a computer that is equipped with a GPIB card for analog to digital conversion. The signal is processed and recorded as a function of frequency.

Two of such spectrometers were used in these studies, one in the Laboratory for Microwave, Millimeter, and Submillimeter Spectroscopy at the Jet Propulsion Laboratory (JPL) and one in the Blake labs at Caltech. The details of the JPL spectrometer are outlined in reference [23]. The Caltech Direct Absorption Flow Cell Spectrometer is comprised of two cells, two detectors, and various combinations of multiplier chain components such that complete spectral coverage is achieved in the 80–120 GHz (3 mm) and 225–360 GHz (1 mm) spectral regions. The specific instrumentation used with this spectrometer as well as detailed operating procedures are outlined in Appendix B.

Two aspects of this design enable extensive spectroscopic studies of the species of interest. First, while most spectra are obtained at room temperature, both low and high temperature experiments are possible with the JPL spectrometer and the 1 mm setup at Caltech due to cooling jackets around the outsides of the cells. This allows for temperature variations, which are quite useful for molecules with large vibrational partition functions when only ground state vibrational spectra are desired or for molecules with very low vapor pressure. Secondly, this apparatus has very wide spectral range capabilities. Broadband,

fixed-tuned coverage of >100 GHz is easily achievable with current multiplier chain sources. Addition of frequency multipliers to the existing setup is limited only by the availability of appropriate power amplifiers in the frequency ranges desired.

Despite the straightforward nature of this experiment, it does have some disadvantages for extended spectroscopic studies. Although the signal to noise ratio for highly populated states is good for this setup, low abundance isotopologues and less populated states are not easily observed. Also, difficulties arise in resolution due to the Doppler and pressure broadening of the signal. Typical linewidths are on the order of 0.5–1 MHz. Such spectral features as hyperfine splittings often remain unresolved in the resultant spectra from this type of apparatus. Also, an extended amount of time is required to obtain a spectrum over a wide frequency range, making static cell experiments difficult, and so large quantities of sample are required to maintain a constant flow of a species for study over wide spectral ranges. While this method is straightforward in nature and allows extended spectral coverage, other spectroscopic techniques can be utilized that require fewer chemicals and less time or that have higher sensitivity.

Chapter 3

Observational Astronomy

3.1 Observational Requirements for Interstellar Detections

Many members of the astrochemistry community dedicate a significant portion of their allocated observing time to the search for complex organic molecules in hot cores. While many hot cores have been identified, systematic spectral line surveys have only been conducted toward a handful of sources (see [4, 24, 25]). Perhaps the best known hot core is Sgr B2(N-LMH), which is found to have among the highest column densities of large organics ever detected [14]. Line confusion is very high in this source, however, due to the large number of species present therein. The observed abundances of complex species in the Orion Hot Core and Compact Ridge have therefore been widely used as the basis for existing hot core models [3] since the line confusion is greatly decreased due to the lower temperatures and narrower line profiles of these hot cores relative to Sgr B2(N-LMH). This increased possibility of a definitive detection of complex molecules in Orion combined with the observed molecular richness of Sgr B2(N-LMH) make these sources the primary targets for complex molecule searches in hot cores. Other less widely studied sources that display similar chemical complexity include the W51 e1/e2 hot cores and the low mass hot corino recently discovered toward IRAS 16293-2422.

The search for molecules in hot cores is most often limited by the availability of laboratory spectral information. For example, ∼55% of the lines observed in the recent 3 mm survey of the Sgr B2(N-LMH) source remain unidentified [4]. Yet searches for many of even the simplest species found in primitive solar system materials have not been undertaken, and quite often the observed lines for these molecules are below the RMS limit for existing surveys. In addition, hot core sources are plagued with line confusion. Indeed, the confusion limit is often reached before the desired RMS level. Added to these factors is the ongoing debate within the field as to how many lines are required before one can claim a complex molecule detection, and this number seems to only be increasing. Complex molecule searches are only feasible if there are spectral windows within which the molecule has several strong lines and that are clear of line confusion.

The recent debate over the reported detection of glycine in the Sgr B2(N-LMH) source [26] has led to the development of a set of "essential criteria for establishing the identification of a new interstellar molecule [27]." These criteria are:

1. Rest frequencies for the molecule should be known to high accuracy.
2. Detected transitions should be consistently observed at the same source velocity.
3. Correction for beam dilution should be handled systematically.
4. The relative line intensities should be consistent with a given rotational temperature or quantitative physical source model.
5. Confirming transitions between connected states should be detected.

The high resolution laboratory studies discussed in Chapter 2 ensure that the first criterion is met. The most effective way to ensure that the other criteria are met is to conduct observational searches in many different frequency ranges such that a large number of

transitions are observed and a wide range of energies are probed. Aperture synthesis observations are also required such that the spatial scale of the emission can be determined and appropriate beam dilution corrections can be applied.

3.2 Observatories

The criteria outlined above require the use of several observatories for complex molecule searches in hot cores. Typical rotational temperatures in these sources are on the order of 100–300 K [28], and the Boltzmann peak for 2C and 3C species is near 230 GHz at these temperatures. The 1 mm receivers of the CSO and OVRO are therefore ideally suited for hot core observations of prebiotic species such as those studied in this thesis. Observations at lower frequencies are often more straightforward, however, because of the high line density at millimeter wavelengths, and so complimentary microwave GBT studies are also conducted. For example, the Sgr B2(N-LMH) line density is greater than 6 lines per 100 MHz at millimeter wavelengths [4], yet the line density observed in this source with the GBT is less than 3 lines per 100 MHz. GBT observations also allow for a wider range of transition energies to be probed, leading to a more complete understanding of molecular excitation mechanisms. In addition, the larger beams of the CSO and GBT are more sensitive to extended molecular emission, as the OVRO beam often resolves out extended emission. Studies combining single-dish and interferometric observations are therefore required for a complete understanding of the molecular physics in and around a hot core.

The observations conducted for this thesis involved 1 mm spectral line searches with the CSO, 3 mm and 1 mm spectral line searches and imaging with OVRO, and microwave spectral line searches with the GBT. The operating parameters of the observatories used in these studies are summarized in Table 3.1. This summary is not intended to be a complete

overview of the capabilities of these observatories, but rather a synopsis of the observing setups relevant to hot core complex molecule searches.

Table 3.1: A summary of the observatories used in these studies.

Receiver	Frequency (GHz)	T_{sys} (K)	FWHM (arcsec)	Bandwidth (MHz)	Aperture Efficiency
GBT					
K	18.0 - 26.5	30 - 40	37	50, 200	55%
K_a	26.0 - 40.0	30 - 40	30	50, 200	55%
Q	40.0 - 52.0	60 - 130	16	50, 200	40%
OVRO (combined L + E configurations)					
3 mm	86 - 116	350	7×5	1.8 - 480	65%
1 mm	210 - 270	400	5×2	1.8 - 480	40%
CSO					
1 mm	180 - 280	300	30	50, 500, 1500	70%
0.87 mm	280 - 400	300	25	50, 500, 1500	75%

3.3 Column Density Calculations

3.3.1 Rotation Diagrams

The rotation diagram approach can be used to determine the rotational temperature and column density of a species in the limit of local thermal equilibrium (LTE), optically thin emission, and negligible background radiation brightness. Under these simplest of possible conditions the integrated intensity of a transition, $\int_{-\infty}^{\infty} T_b dv$, is:

$$\int_{-\infty}^{\infty} T_b dv = \frac{hc^3}{8\pi k\nu^2} A g_u \frac{N_T}{Q(T_{rot})}\, e^{-E_u/kT_{rot}} \tag{3.1}$$

where ν is the transition frequency, N_T is the beam averaged total column density, A is the transition Einstein A-coefficient, g_u is the upper state degeneracy, $Q(T_{rot})$ is the partition

function, T_{rot} is the molecular rotational temperature, and E_u is the transition upper state energy [29]. A rotation diagram is then the plot of $ln\Big[(8\pi k\nu^2)/(hc^3 A g_u)\int_{-\infty}^{\infty} T_b dv\Big]$ versus E_u, which gives a line with slope inversely proportional to T_{rot} and with intercept equal to $ln(N_T/Q(T_{rot}))$.

The mechanisms for determining the integrated intensity ($\int_{-\infty}^{\infty} T_b dv$), the Einstein A-coefficients times the upper state degeneracy (Ag_u), and the molecular partition function ($Q(T_{rot})$) are outlined below.

3.3.2 Integrated Intensities

The integrated intensity of a transition can be calculated by:

$$\int_{-\infty}^{\infty} T_b dv = 1.064\, T_b\, \Delta v \tag{3.2}$$

where T_b is the peak brightness temperature of the line and Δv is its full width half maximum (FWHM). T_b can be approximated as T_{MB}, the peak line intensity (T_A^*) corrected to the main beam temperature scale by the relationship $T_{MB} = T_A^*/\eta$, where η is the aperture efficiency.

Beam dilution effects must be considered when the beam and source sizes are unequal. In this case, $T_b = BT_{MB}$, where the beam filling factor, B, can be calculated from the relationship between the source size, θ_s, and the beam size, θ_b, by:

$$B = \frac{\theta_s^2}{\theta_s^2 + \theta_b^2} \tag{3.3}$$

For interferometric observations, T_A^* (in K) can be determined by:

$$T_A^* = \frac{1.22 \times 10^6 Int}{\theta_A \theta_B \nu^2} \tag{3.4}$$

where θ_A and θ_B are the beam FWHMs, Int is the peak intensity in Jy/Beam, and ν is in GHz.

3.3.3 Line Strengths

The line strengths in terms of the Einstein A-coefficients times the upper state degeneracy (Ag_u) for a given transition can be calculated from the information given in the .cat files associated with the JPL CALPGM program. These files are generated by SPCAT (see Appendix C), and such files are available for a wide variety of species in the submillimeter and microwave spectral line catalog available at `http://spec.jpl.nasa.gov`. The line strengths are given here as the *log* of the intensity, I. For a given transition, then:

$$I = \sum_1^j 10^{logI_j} \tag{3.5}$$

which accounts for multiple transitions contributing to the integrated intensity of the line, and the resultant intensity is in units of nm^2MHz. The line strength, Ag_u, can then be calculated by the relationship:

$$Ag_u = \frac{2.7964 \times 10^{-16} I \nu^2 Q(T)}{e^{-E_l/kT} - e^{-E_u/kT}} \tag{3.6}$$

when ν is in MHz and I is in nm^2MHz [30].

3.3.4 Molecular Partition Functions

Neglecting centrifugal distortion, the partition function for an asymmetric rotor is given by:

$$Q(T) = \left[\prod_{i=0}^{3N-6} \left(\frac{e^{-E_i/2kT}}{1 - e^{-E_i/kT}} \right) \right] \sqrt{\frac{\pi}{ABC} \left(\frac{kT}{h} \right)^3} \tag{3.7}$$

where $\prod \left(\frac{e^{-E_i/2kT}}{1-e^{-E_i/kT}} \right)$ is the total vibrational state partition function, the E_i's are the energies of the normal modes of vibration, $\sqrt{\frac{\pi}{ABC} \left(\frac{kT}{h} \right)^3}$ is the rotational partition function, and A, B, and C are the rotational constants. The rotational constants determined for the ground state and the n vibrational states populated at T are used such that the molecular partition function is approximated as:

$$Q(T) \approx \sum_{i=0}^{n} e^{-E_i/kT} \sqrt{\frac{\pi}{A_i B_i C_i} \left(\frac{kT}{h} \right)^3} \tag{3.8}$$

Chapter 4

1,3-Dihydroxyacetone

4.1 Introduction

One of the sugars detected in carbonaceous chondrites is 1,3-dihydroxyacetone, or $CO(CH_2OH)_2$. Dihydroxyacetone is a monosaccharide commonly used as the active ingredient in sunless tanning products. Monosaccharides are polyhydroxylated aldehydes (or aldoses, whose chemical formula is H-$[CHOH]_k$-CHO) and ketones (or ketoses, whose general structure is given by H-$[CHOH]_l$-CO-$[CHOH]_m$-H) with the general formula $[C(H_2O)]_n$, where $n \geq 3$. Dihydroxyacetone and glyceraldehyde ($CH_2OHCHOHCHO$) are thus the simplest ketose and aldose monosaccharides, respectively. Dihydroxyacetone is used in numerous biological pathways, including the production of ATP, and is synthesized via glycolysis.

The 2C species glycolaldehyde is less stable than its structural isomers acetic acid (CH_3COOH) and methyl formate ($HCOOCH_3$), with methyl formate being the most stable. Similar patterns are observed with the 3C analogs, with sugars being more energetic than esters and acids (hence their biological utility), while ketoses are more stable than aldoses. The relative energies for the 2C and 3C structural isomers were calculated from Gaussian 98 MP2 6-311G++(d,p) geometry optimizations [31], and these results are discussed in

Appendix D.

The relative energies of the 3C sugars indicate that dihydroxyacetone would be more likely to survive under hot core conditions than glyceraldehyde. Indeed, in the laboratory glyceraldehyde is seen to isomerize to dihydroxyacetone [32]. Lovas et al. recently characterized the rotational spectrum of dihydroxyacetone to 40 GHz, fitting rotational and quartic centrifugal distortion constants to FTMW data [32]. We simultaneously began our study of dihydroxyacetone in a similar manner, using *ab initio* studies to guide initial FTMW experiments to 18 GHz. We then conducted millimeter and submillimeter direct absorption experiments to provide more accurate spectral predictions for observational searches.

The laboratory studies of glyceraldehyde and dihydroxyacetone provided the necessary basis for deep observational studies [32, 33]. The C_{2v} symmetry of dihydroxyacetone leads to somewhat stronger millimeter-wave emission features compared to glyceraldehyde. A glyceraldehyde K-band search with the GBT to an RMS of $\sim$5 mK revealed no transitions [17].

The *ab initio* studies of dihydroxyacetone are presented in Section 4.2, while the laboratory studies of dihydroxyacetone are presented in Section 4.3. The results of observational searches for dihydroxyacetone are given in Section 4.4.

4.2 *Ab Initio* Studies

Quantum mechanical calculations were utilized to aid in spectral predictions for dihydroxyacetone. These calculations used B3LYP Density Functional Theory (DFT) [34, 35] and were performed in two phases. The first phase used a fairly small basis set and level of theory to delineate geometries with low energies. The second phase performed

more precise quantum mechanical calculations with the best geometries from the first phase. Calculations were performed using Jaguar version 4.2, release 77 [36].

During the first phase of the calculations, the 6-31G basis set was used [37]. The four angular degrees of freedom for dihydroxyacetone were constrained to be multiples of 60 degrees while all other degrees of freedom were optimized. From these optimized geometries, the 5% with the lowest energy were used in the second phase. Here, all degrees of freedom were optimized, and the 6-31G**++ basis set was used [37–39]. Separate conformers were distinguishable by unique values for the dipole moments, and roughly ten possible geometries were optimized for each of the lowest four conformers. The rotational constants determined for each conformer were then averaged across all geometries. Relative energies, dipole moments, and rotational constants determined for the two lowest energy conformers (see Table 4.1) were then used for initial spectral predictions. The structures of these two conformers are shown in Figure 4.1. The ground state conformer optimized geometry is included in the analysis of Lovas et al. [32] and is of C_{2v} symmetry. The non-zero μ_a and μ_c values obtained in our study for this conformer are therefore unexpected and are likely artifacts of the averaging approach used for determination of each structure's parameters. Indeed, Lovas et al. report only a *b*-type dipole moment [32]. The higher energy conformer structural parameters have not been included because of the rather large inherent uncertainty due to this averaging approach as well as the unlikeliness of this conformer to exist under normal laboratory or interstellar conditions.

Table 4.1: Spectral parameters predicted for dihydroxyacetone from quantum mechanical calculations using B3LYP DFT.

Parameter	Conformer 1	Conformer 2
E	0 kcal/mol	1.9214 kcal/mol
A	9862.419 MHz	5942.059 MHz
B	2035.671 MHz	2656.905 MHz
C	1724.558 MHz	1787.788 MHz
μ_a	0.007 D	2.150 D
μ_b	1.859 D	3.601 D
μ_c	0.019 D	0.036 D

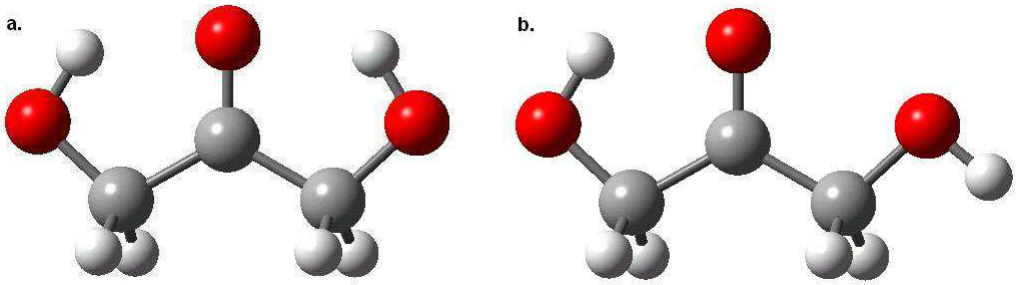


Figure 4.1: Structures of the two lowest energy dihydroxyacetone conformers: a. doubly hydrogen bonded conformer (ground state); b. singly hydrogen bonded conformer.

4.3 Spectroscopic Studies

4.3.1 Experimental

All experiments were conducted with dihydroxyacetone vapor from a sample of solid 1,3-dihydroxyacetone dimer (97% purity) purchased from Aldrich.

4.3.2 FT-Microwave Studies

The FTMW experiments were conducted with the original Balle-Flygare spectrometer. The details of the setup can be found in Chapter 2, Appendix A, and reference [20]. A

sample holder containing solid dihydroxyacetone was placed after the pulsed valve and heated sufficiently to obtain a dihydroxyacetone vapor pressure of $\sim$ 1 Torr. Argon gas was pulsed over the sample, and a molecular beam was formed by a Laval nozzle at the exit of the heated compartment (see reference [21] for further details on the heated nozzle). Predictions based on the theoretical calculations were used to guide spectral line searches. Four ^{b}R and one ^{b}Q transition were chosen for these initial searches based on their predicted line strengths. Once the $1_{0,0} \rightarrow 0_{0,0}$ transition was observed, the single-shot signal was optimized before additional spectral searches were conducted. The instrument was used in the coaxial valve configuration, resulting in classic Doppler doublets for all transitions. Linewidths were on the order of 8 kHz (see Figure 4.2). Additional searches for the singly H-bonded conformer were conducted, but no lines were observed in the supersonic expansion.

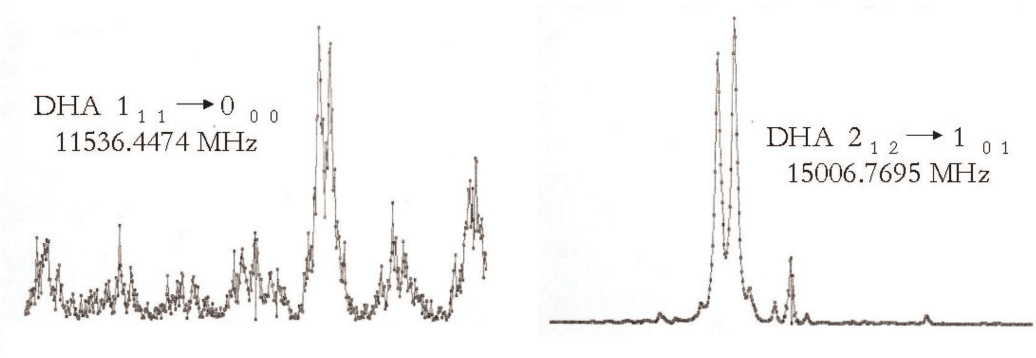


Figure 4.2: Single-shot dihydroxyacetone spectra from the FT-microwave experiments.

4.3.3 Direct Absorption Millimeter and Submillimeter Studies

Studies were conducted with the 3 mm Caltech Direct Absorption Flow Cell Spectrometer. The details of the setup can be found in Chapter 2, Appendix B, and reference [40]. Computer-automated scans of both increasing and decreasing frequency

increments were averaged in areas of low power to increase the signal-to-noise ratio. This averaging was not required for all scans as the frequency shifts due to the time constant of the lock-in amplifier were smaller than the spectral resolution. The solid dihydroxyacetone sample was placed directly in the cell, and heating tape was wrapped around this section of the cell and used to gently heat the sample to approximately 50 °C. A pressure of approximately 100 mtorr was maintained for the duration of the experiment.

An example spectrum from 112–120 GHz is shown in Figure 4.3. Strong ^{b}R branches are seen at a separation of approximately 4 GHz. Linewidths were on the order of 1 MHz.

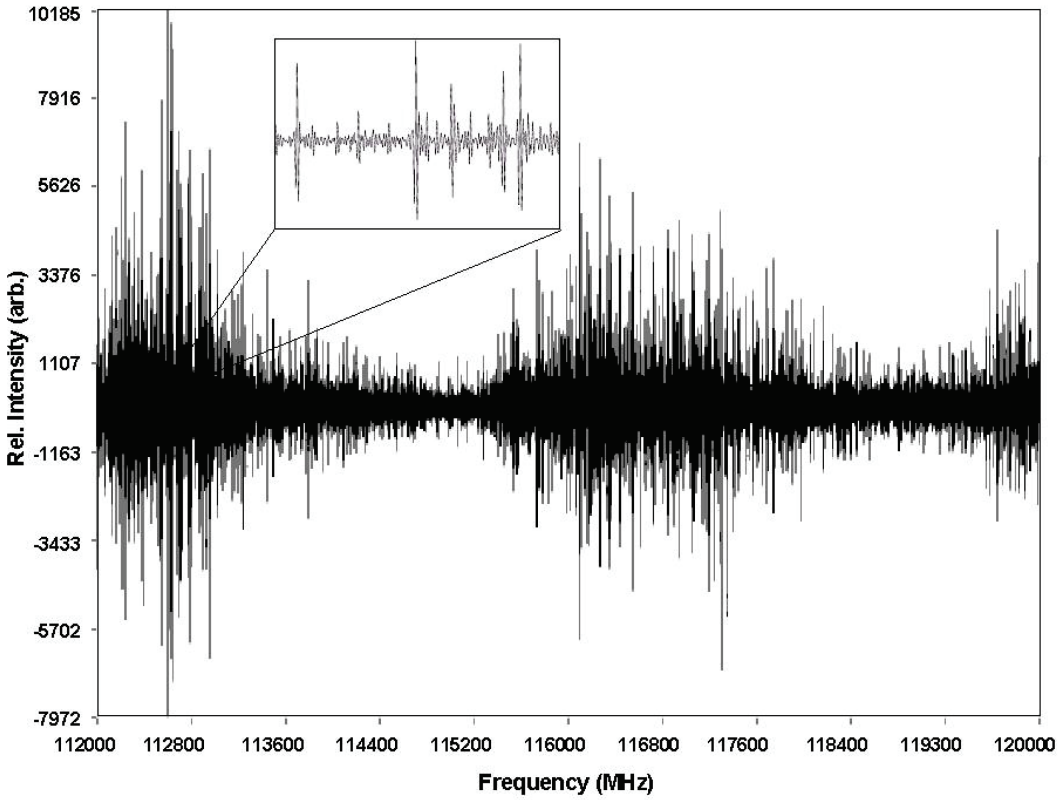


Figure 4.3: The flow cell dihydroxyacetone spectrum from 112 to 120 GHz.

The higher frequency (sub)millimeter studies were conducted with the JPL flow cell

spectrometer. The basic flow cell design and detection methods for the JPL spectrometer are outlined in reference [23]. The source frequencies were obtained using a directly synthesized beam projected from the output of a multiplier chain [41]. Second and third harmonics of this multiplier were produced on a whisker-contacted Schottky diode and detected with a helium cooled InSb bolometer. Again, averaging was not required as the errors due to the time constant of the lock-in amplifier were smaller than the spectral resolution. Linewidths were of order 1 MHz. No sample heating was required for these experiments because of the strength of the submillimeter lines. A pressure of approximately 10 mtorr was maintained for the duration of the experiment.

4.3.4 Data Analysis

The data were assigned using the SPFIT and SPCAT programs (see Appendix C, [30]). The rotational constants obtained with the *ab initio* studies, the dipole moments from reference [32], and a standard asymmetric-top Hamiltonian with the Watson A-reduction were used to generate a predicted spectrum. The initial microwave data were used to fit the rotational constants and estimate the quartic distortion constants. These constants were then used to predict the millimeter spectrum. As new data were assigned, lines were continuously added to the data set and the spectral fit further modified with the same asymmetric-top Hamiltonian. The quality of the fit to the entire data set was indicated by a microwave root mean square deviation.

A total of 2360 dihydroxyacetone lines were assigned. Significant harmonic contamination was present in the submillimeter scans, but the presence of acetonitrile as a cell contaminant led to accurate determination of the frequencies within spectral regions where acetonitrile lines were observed. However, this contaminant also led to line confusion

for weaker dihydroxyacetone lines. Therefore, while approximately 95% of the 2σ lines were assigned in the millimeter spectrum, only the strongest lines ($\sim$75% of the total lines) were assigned in the submillimeter spectra. These submillimeter assignments include almost all strong ground state transitions as well as the strongest R and Q type transitions for the other vibrational states.

Only the ground state assignments were made initially, with quartic centrifugal distortion constants determined in addition to the standard rotational constants. A total of 1284 lines have been assigned to the ground state with an RMS of 98 kHz. Additional assignments were made for four vibrational states, with RMS values ranging from 99 to 268 kHz. Although decreasing the pressure during the millimeter and submillimeter experiments could have resulted in narrower lines and therefore a lower RMS, this would have significantly decreased the observed signal and made spectral assignment quite difficult. The files associated with the analysis, including the parameters and rest frequencies, can be found in Appendix E. The output file from the spectral analysis, which includes the observed minus calculated residuals, has been included as supplementary material in the electronic version of this thesis. The assignments and other predicted rotational frequencies are accessible through the submillimeter and microwave spectral line catalog available at `http://spec.jpl.nasa.gov` [30]. The rotational and centrifugal distortion constants determined for each state are listed in Table 4.2.

As no vibrational spectral studies have been conducted for the torsional states of dihydroxyacetone, assignments of the vibrational state energies were based on the relative intensities of the observed lines to those from the ground state. Approximate relative energies were determined for each vibrational state and are included in Table 4.2. The rotational and quartic centrifugal distortion constants were determined independently for

Table 4.2: Spectral parameters determined for dihydroxyacetone.

state	ν_0	ν_1	ν_2	
E	0	∼93	∼147	cm^{-1}
A	9801.294341(269)	9764.48006(113)	9701.67778(178)	MHz
B	2051.525611(76)	2049.846696(274)	2051.55037(42)	MHz
C	1735.164871(77)	1736.322262(248)	1737.92899(33)	MHz
Δ_J	0.1823699(94)	0.183278(33)	0.185158(62)	kHz
Δ_{JK}	0.657039(88)	0.84847(40)	0.50245(102)	kHz
Δ_K	5.36670(50)	5.4775(57)	3.4799(110)	kHz
δ_J	0.02767300(181)	0.0274086(134)	0.0276239(291)	kHz
δ_K	0.569401(157)	0.64161(96)	0.35886(184)	kHz
# Lines	1284	490	312	
Fit RMS	0.098	0.099	0.142	MHz

state	ν_3	ν_4	
E	∼150	∼183	cm^{-1}
A	9662.11092(271)	10329.1(106)	MHz
B	2050.02151(45)	2065.17(41)	MHz
C	1739.41934(37)	1735.12347(60)	MHz
Δ_J	0.187123(60)		kHz
Δ_{JK}	0.60623(79)		kHz
Δ_K	7.1160(185)		kHz
δ_J	0.0265674(279)		kHz
δ_K	0.31951(205)		kHz
# Lines	241	34	
Fit RMS	0.178	0.268	

Note: One σ errors are listed in parentheses in units of last significant figure. The quartic distortion constants for the ground state were used for the fourth vibrational state.

three vibrational states. Only a partial fit has been completed for the highest energy vibrational state due to its relatively weak line strengths. In this case, the quartic distortion constants were held to the values determined for the ground state. The microwave RMS determined for this state is therefore considerably higher than those determined for the others.

4.3.5 Discussion

The millimeter and submillimeter spectra of dihydroxyacetone have been characterized up to 450 GHz. Spectral assignments include lines from the ground state and four vibrational states, and rotational and quartic centrifugal distortion constants have been determined for each of these states. Excluding the fourth vibrational state, predictions of strong submillimeter lines above 450 GHz are accurate to better than 1 MHz, and interpolations below 450 GHz are accurate to less than 100 kHz for all states based on this analysis.

The spectral parameters determined by quantum mechanical calculations were accurate to less than 1% of the experimentally determined values, indicating the value of density functional theory as a tool for the prediction of pure rotational spectra.

It was found, however, that millimeter and submillimeter predictions based on the initial FTMW work are not sufficiently accurate for observational searches in these ranges. Indeed, at 1.3 mm, near the peak of the Boltzmann distribution for dihydroxyacetone under typical hot core conditions, the microwave-based predictions for the strongest transitions differ by 10-15 MHz from the experimentally measured line positions. This corresponds to a velocity shift of >15 km/sec from the source velocity. Interstellar detection of this molecule would be quite difficult based on these parameters. Because of the relative rigidity of dihydroxyacetone in comparison to most complex organic species predicted to be present in hot cores, this study also indicates that further analysis of the rotational spectra of complex molecules beyond the microwave region is necessary to guide observational searches.

4.4 Observational Studies

The laboratory investigation of dihydroxyacetone provided the necessary information to guide observational searches using microwave through submillimeter wave telescopes. Searches for dihydroxyacetone were therefore conducted with the CSO, OVRO, and GBT observatories, and these observations are outlined below.

4.4.1 CSO Observations

4.4.1.1 Observations

A search for dihydroxyacetone emission in the 1.3 mm atmospheric window was conducted with the CSO. Initial searches were conducted toward the Sgr B2(N-LMH) hot core. The parameters for the dihydroxyacetone lines used in this search, specifically the transition quantum numbers, rest frequencies, Einstein A-coefficients times the upper state degeneracy, and upper state energies, are listed in Table 4.3. All observed lines are transitions within the ground vibrational state. Many of these lines are actually asymmetry doublets or blends of multiple transitions between similar yet distinct quantum states whose energies are nearly degenerate. These will appear in observational spectra as a single blended line because of the $\sim$10 km s^{-1} linewidths characteristic of Sgr B2. Only one frequency has been listed for asymmetry doublets occurring at the same frequency; for all others, the frequency of each individual component has been listed.

The survey was conducted using the CSO 230 GHz double sideband (DSB) heterodyne receiver on the nights of 2003 July 13–23/September 14–21 and 2004 June 30–July 7. Typical system temperatures ranged from 200–600 K, and the source position selected was $\alpha(1950)=17^h\ 44^m\ 10^s.1$, $\delta(1950)= -28^\circ\ 21'\ 17''$, which is coincident with the Sgr B2(N-LMH)

Table 4.3: A summary of dihydroxyacetone emission lines from Sgr B2(N-LMH).

$J'_{K'_a,K'_c}$–$J''_{K''_a,K''_c}$	ν_0^a (MHz)	$Ag_u\times10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	Δv^c (km s^{-1})	v_{LSR}^c (km s^{-1})
$14_{11,3} \rightarrow 13_{10,4}$	219059.1	1.23	64.98	0.14	10.60(16)	62.91(17)
$14_{11,4} \rightarrow 13_{10,3}$		1.23	64.98			
$61_{3,58} \rightarrow 60_{4,57}$	222826.4	5.17	344.98	0.48	11.50(250)	64.50(21)
$61_{4,58} \rightarrow 60_{3,57}$	222839.4	5.71	344.98	0.39	7.74(224)	65.23(26)
$15_{11,4} \rightarrow 14_{10,5}$	222847.0	1.44	67.71	0.35	8.29(252)	60.74(40)
$15_{11,5} \rightarrow 14_{10,4}$		1.44	67.71			
$60_{5,56} \rightarrow 59_{4,55}$	222861.1	4.78	341.68	0.19	10.77(132)	63.24(42)
$63_{1,62} \rightarrow 62_{2,61}$	223293.9	6.78	349.60	0.40	17.36(64)	62.38(9)
$63_{2,62} \rightarrow 62_{1,61}$		6.78	349.60			
$67_{3,64} \rightarrow 66_{4,63}$	243591.0	8.53	412.61	0.24	13.12(51)	63.78(10)
$67_{4,64} \rightarrow 66_{3,63}$	243593.0	8.53	412.61			
$72_{1,71} \rightarrow 71_{2,70}$	254459.9	11.67	453.49	0.20	8.95(140)	65.86(19)
$72_{2,71} \rightarrow 71_{1,70}$		11.67	453.49			
$75_{0,75} \rightarrow 74_{1,74}$	261654.3	14.30	479.97	0.18	9.22(46)	62.31(12)
$75_{1,75} \rightarrow 74_{0,74}$		14.30	479.97			

[a] One σ uncertainties are 0.1 MHz.
[b] One σ uncertainties are <10 mK.
[c] One σ uncertainties are listed in parentheses in units of last significant figure.

hot core. The chopping secondary with a 70″ throw was used along with chopper-wheel calibration and the facility 1.5 GHz, 500 MHz, and 50 MHz acousto-optic spectrometer (AOS) back ends to minimize the spectral baseline fluctuations. The FWHM of the CSO at these frequencies is ∼30″, and all data are placed on the T_{MB} temperature scale using a main beam efficiency of 70% determined using observations of the planets. Line confusion was a perpetual difficulty faced during the observations due to the DSB setup of the CSO and

the dense spectral line nature of the Sgr B2(N-LMH) source. Line positions were therefore verified by observing several small frequency offsets at each local oscillator (LO) setting. A v_{LSR} of 62 km/s was used for the July 2003 observations. Potential dihydroxyacetone lines were observed at 64 km/s, so this v_{LSR} was then used for the remaining observations.

Additional observations were conducted towards the Orion Compact Ridge and W51e2 hot core sources on the nights of 2003 September 14–21/December 14–16. The spectral windows centered at 222839 and 243591 MHz were observed in each source (see Table 4.3). Typical system temperatures ranged from 200-600 K, and the source positions and velocities used were $\alpha(2000)=05^h\ 35^m\ 14^s.5$, $\delta(2000)$= -05° 22′ 30″.4 and 9 km/s for the Orion Compact Ridge, and $\alpha(1950)=19^h\ 23^m\ 43^s.5$, $\delta(1950)$= 14° 30′ 34″ and 55 km/s for the W51e2 hot core. The observing parameters outlined above for the Sgr B2 search were also used for these observations.

4.4.1.2 Results

A total of nine possible dihydroxyacetone emission lines were detected in Sgr B2(N-LMH) with the CSO. The mean v_{LSR} is 63.4 ± 3.2 km/s. The observational spectra from the 500 MHz AOS in the v_{LSR} = 0 - 100 km/s window are shown in Figure 4.4. The v_{LSR} scales have been adjusted such that the LO frequency is centered at 64 km/s. Nine additional lines were either severely blended with other lines or completely obscured by stronger features in the signal or image sideband. No dihydroxyacetone lines were found to be absent in this source from any clean 1.3 mm spectral windows observable at the CSO.

Least-squares Gaussian fits to each observed line are summarized in Table 4.3 and shown in Figure 4.4. The integrated intensity was calculated by Equation 3.2, where T_{MB} = $T_A^*/0.7$ for the CSO at 230 GHz. No beam dilution corrections were applied because the

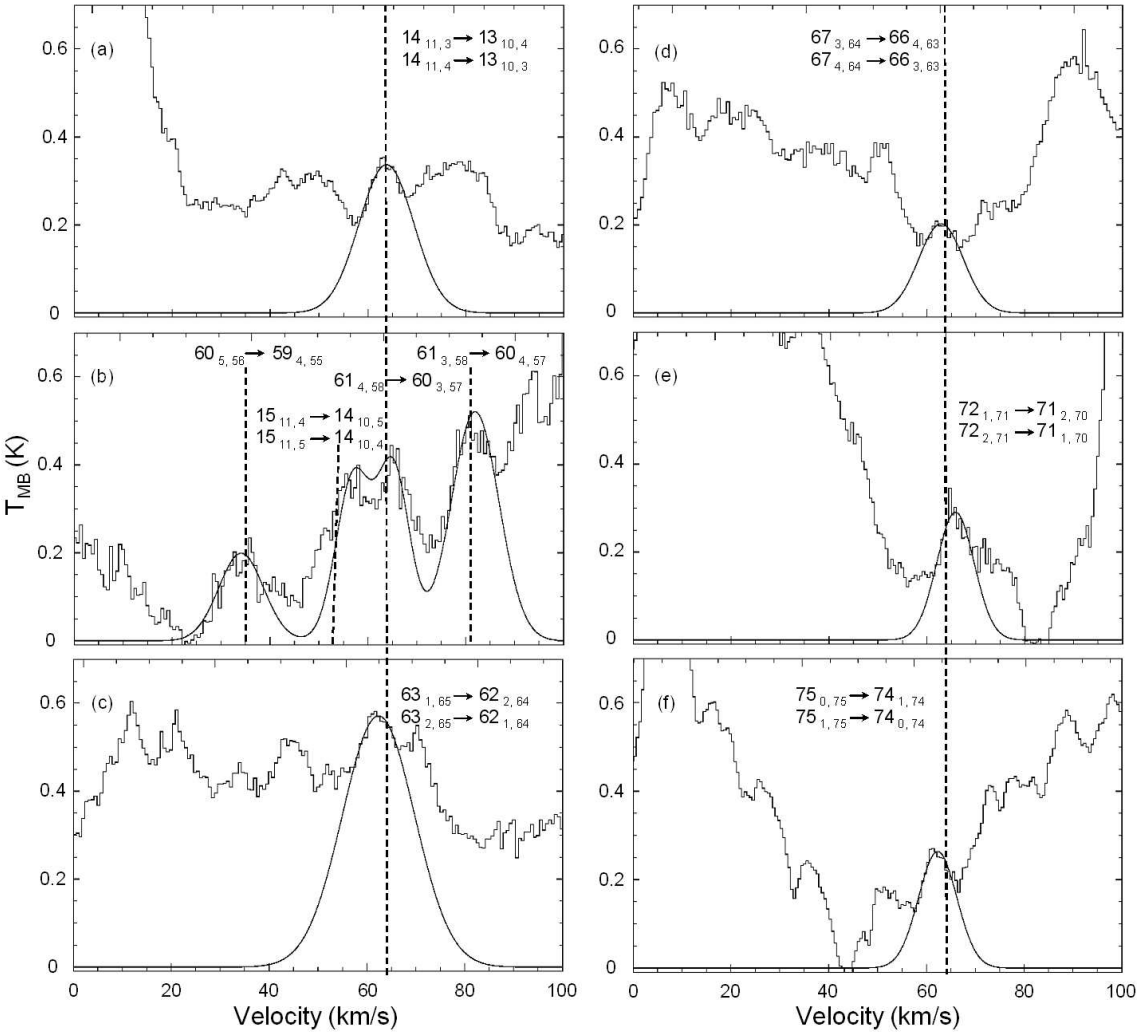


Figure 4.4: Possible dihydroxyacetone transitions observed toward Sgr B2(N-LMH) with the least-squares Gaussian fits to each line. Spectra are from the CSO 500 MHz AOS, and a linear baseline subtraction of the continuum has been performed. The vertical dotted line indicates v_{lsr} = 64 km/s. The positions of additional dihydroxyacetone lines relative to 64 km/s are indicated in spectrum (b).

spatial scale of the emission is unknown. Only single Gaussian fits are reported here since many of the potentially blended lines in Figure 4.4 are unassigned, and hence the relative contributions from individual features are poorly constrained.

A rotation diagram approach was used to determine the rotational temperature and

column density of dihydroxyacetone toward SgrB2(N-LMH) (see Section 3.3). Only the ground and first four dihydroxyacetone vibrational states are populated at T∼250 K, and a full rotational analysis has been performed for these states (see Section 4.3 and reference [33]). The rotational constants determined for each vibrational state have therefore been used such that the partition function is approximated as:

$$Q(T_{rot}) \approx \sum_{i=0}^{4} e^{-E_i/kT_{rot}} \sqrt{\frac{\pi}{A_i B_i C_i} \left(\frac{kT_{rot}}{h}\right)^3} \tag{4.1}$$

The rotation diagram for dihydroxyacetone is shown in Figure 4.5. A molecular rotational temperature of 222 ± 65 K and a column density of (4.9 ± 2.2) $\times 10^{15}$ cm^{-2} were derived, where the errors represent 95% confidence intervals.

Four lines corresponding to dihydroxyacetone transitions were observed in one window at the 222839.40 MHz LO setting (Figure 4.4b); these data are shown in Figure 4.6 along with a T_{rot}=220 K simulated spectrum. The relative intensities, line center frequencies, and linewidths of the dihydroxyacetone lines were fixed and the intensities scaled to best match the observed spectrum. The additional strong line is due to $H_2^{13}CO$ in the image sideband, and all parameters for this line were fixed to those determined in reference [24]. The simulation shows that other unidentified spectral features may be present in the DSB spectrum, and that the integrated intensity of the 222826.4 MHz dihydroxyacetone line is most affected by these features. It is therefore not included in the rotation diagram analysis.

A spectral window overlapping in frequency with two strong dihydroxyacetone lines has also been observed in this source with the Kitt Peak 12 meter telescope (J. M. Hollis 2004, private communication). There are emission features at the appropriate frequencies for these dihydroxyacetone transitions but one of the lines appears to be blended with an

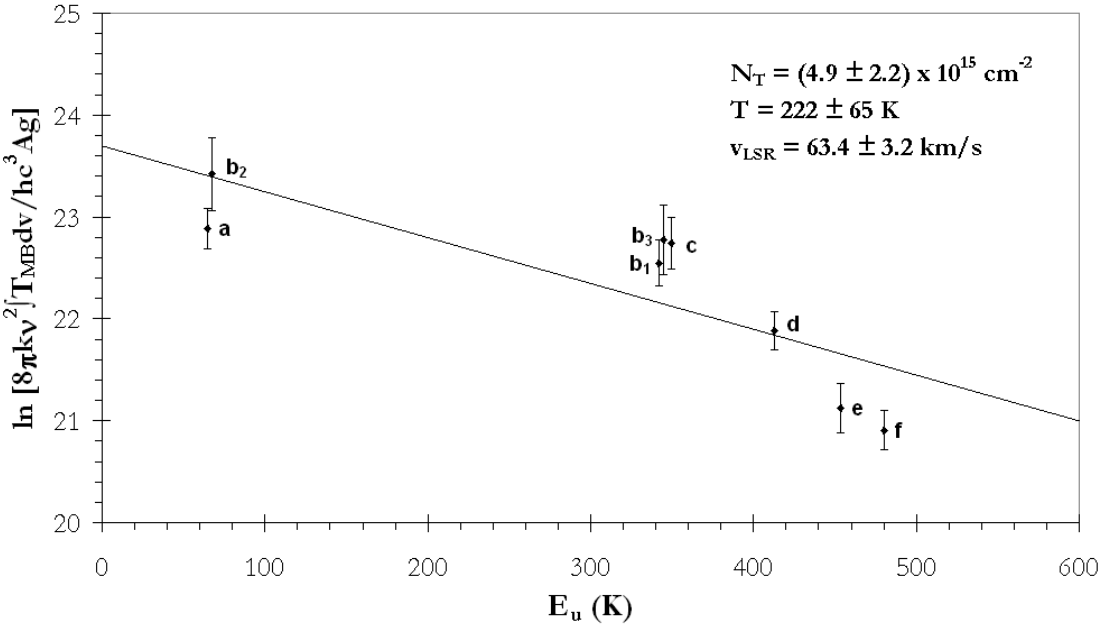


Figure 4.5: The rotation diagram for dihydroxyacetone toward SgrB2(N-LMH). The labels correspond to the panels of Figure 4.4.

unidentified line. Their inclusion in the rotation diagram analysis is quite difficult due to the lack of information regarding linewidths for dihydroxyacetone emission features in this frequency range, and therefore these data have not been included in this study.

No transitions were observed toward the Orion or W51 hot cores, and so the column density upper limit was calculated from the observed spectral intensity at the expected line position, which was placed on the T_{MB} temperature scale using a main beam efficiency of 70%. These limits are presented in Table 4.4. A linewidth of 5 km/s and a rotational temperature of 150 K, typical values observed for species in the Compact Ridge, were assumed for the Orion calculations [25]. A line width of 10 km/s and a rotational temperature of 100 K, the values found for methyl cyanide in the W51e2 source, were assumed for the W51e2 calculations [42].

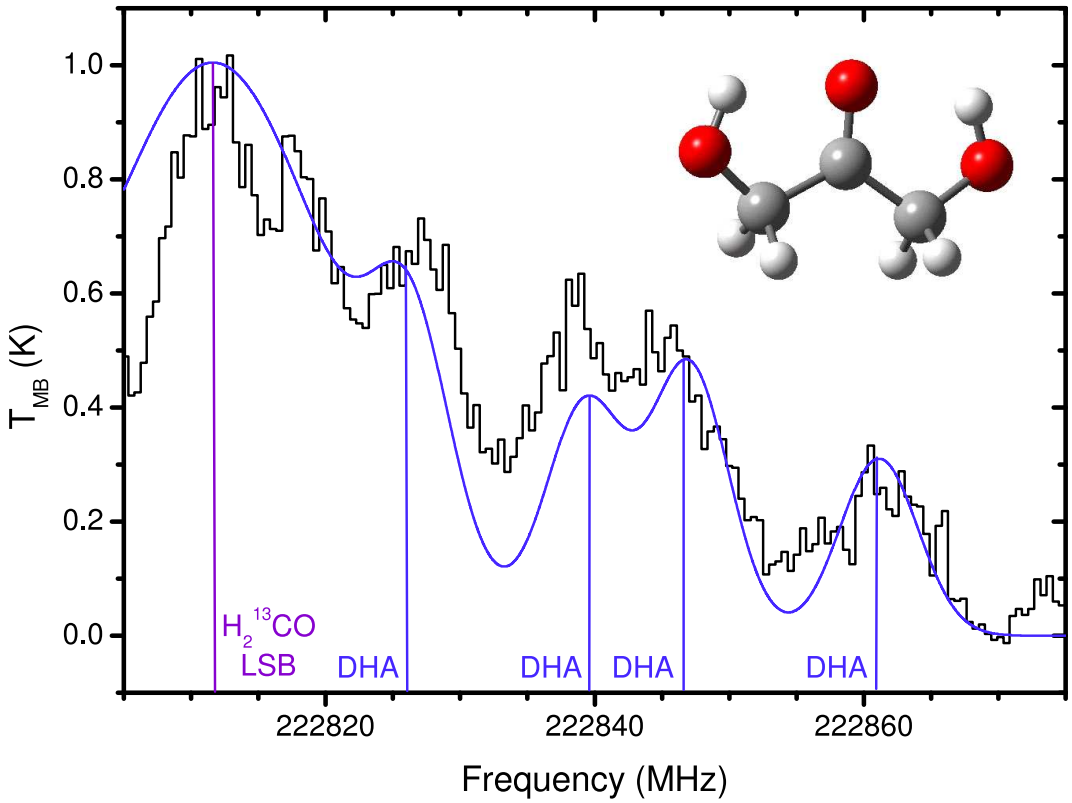


Figure 4.6: The simulated spectrum of dihydroxyacetone lines at 220 K compared to an observed Sgr B2(N-LMH) spectrum. The structure of dihydroxyacetone is shown in the inset.

4.4.2 OVRO Observations

4.4.2.1 Observations

Observations to image potential dihydroxyacetone emission in the Sgr B2(N-LMH) source were conducted with the OVRO Millimeter Array between 2003 October 13–November 18 and 2004 March 14–April 28. A source position of $\alpha(2000)=17^h\ 47^m\ 19^s.92$, $\delta(2000)$= -28° 22′ 19″.5 served as the phase center, and all correlator modules were set up using a v_{LSR} of 64 km/s. These observations were conducted in the L and E configurations, resulting in a synthesized beam of 7″.9 × 4″.0 using robust weighting. The source was observed for

Table 4.4: Dihydroxyacetone column density upper limits in Orion and W51 from CSO observations.

$J'_{K'_a,K'_c}$–$J''_{K''_a,K''_c}$	ν_0^a (MHz)	$Ag_u\times10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit [c] ($\times10^{-13}$ cm^{-2})
Orion					
$61_{4,58} \rightarrow 60_{3,57}$	222839.4	5.71	344.98	0.005(2)	0.98(14)
$67_{3,64} \rightarrow 66_{4,63}$	243591.0	8.53	412.61	0.24(2)	18.7(28)
$67_{4,64} \rightarrow 66_{3,63}$	243593.0	8.53	412.61		
W51e2					
$61_{4,58} \rightarrow 60_{3,57}$	222839.4	5.71	344.98	0.065(2)	5.25(234)
$67_{3,64} \rightarrow 66_{4,63}$	243591.0	8.53	412.61	0.12(2)	3.87(255)
$67_{4,64} \rightarrow 66_{3,63}$	243593.0	8.53	412.61		

[a] One σ uncertainties are 0.1 MHz.
[b] Assumed uncertainties are listed in parentheses in units of last significant figure.
[c] One σ uncertainties are listed in parentheses in units of last significant figure.

approximately 5 hours in each full track, and 2.5 tracks were completed in L configuration, while 4 full tracks were completed in E configuration. Four dihydroxyacetone lines were observed simultaneously, and the parameters for these lines, specifically the transition quantum numbers, rest frequencies, Einstein A-coefficients times the upper state degeneracy, and upper state energies, are listed in Table 4.5. All observed lines are transitions within the ground vibrational state.

The quasars 3C345 and 3C454.3 were observed for secondary flux and bandpass calibration, with observations of Neptune and Uranus serving to bootstrap the quasar fluxes. Observations of phase and amplitude calibrators were conducted in approximately half hour integrals throughout the tracks. Baseline-based boxcar fits to an internal noise

source modified by a second order polynomial fit to observations of the quasars were used to derive the bandpass calibration. Bandpass, phase, and flux calibrations were applied to the data with the MMA software package [43]. The MIRIAD data reduction software package [44] was used for subsequent spectral analysis.

4.4.2.2 Results

None of the transitions were detected toward Sgr B2(N-LMH), and so the column density upper limit was calculated from the observed spectral intensity at the expected line position. The transition at 112.636609 GHz is near the edge of a strong spectral line from another species. This strong feature also makes spectral baseline determination quite difficult. The combination of these two factors greatly effects the observed intensity for this transition. A linewidth of 10 km/s, roughly the average linewidth observed in the CSO observations, was assumed for the upper limit calculations. The calculated dihydroxyacetone column density upper limits are presented in Table 4.5.

4.4.3 GBT Observations

4.4.3.1 Observations

Additional observations of low energy dihydroxyacetone transitions in the Sgr B2(N-LMH) source were conducted with the GBT on the night of 2005 April 5. A source position of $\alpha(2000)=17^h\ 47^m\ 19^s.92$, $\delta(2000)=$ -28° 22′ 19″.5 and a source velocity of 64 km/s were used. These observations were conducted with the Q-band receiver, which operates over the 40–52 GHz range. The GBT spectrometer back end was used in the 4 intermediate frequency (IF), 50 MHz bandwidth, 9 level mode that allows for four 50 MHz spectral windows to be observed simultaneously in dual polarization. The observations were conducted in position

Table 4.5: Dihydroxyacetone column density upper limits in Sgr B2(N-LMH) from OVRO observations.

$J'_{K'_a,K'_c}-J''_{K''_a,K''_c}$	ν_0^a (MHz)	$Ag_u\times10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit [c] ($\times10^{-15}$ cm^{-2})
$31_{2,30} \rightarrow 30_{1,29}$	112558.8289	0.3611	89.27	0.79(10)	14.2(44)
$42_{8,35} \rightarrow 42_{7,36}$	112612.4493	0.2095	291.30	0.34(7)	10.4(33)
$32_{0,32} \rightarrow 32_{1,31}$	112630.7384	0.4622	90.28	0.15(6)	2.14(66)
$32_{1,32} \rightarrow 31_{0,31}$	112636.6087	0.4624	90.28	0.12(6)	1.71(53)

[a] One σ uncertainties are 0.1 MHz.
[b] Uncertainties are listed in parentheses in units of last significant figure and are based on an assumed flux uncertainty of ±0.02 Jy/Beam.
[c] One σ uncertainties are listed in parentheses in units of last significant figure.

switching mode, and a total of 3 hours of on-source integration was completed. The FWHM of the GBT at these frequencies is $\sim16''$, and all data are placed on the T_{MB} temperature scale using a main beam efficiency of 40%. The parameters for the dihydroxyacetone lines in these windows, specifically the transition quantum numbers, rest frequencies, Einstein A-coefficients times the upper state degeneracy, and upper state energies, are listed in Table 4.6. All observed lines are transitions within the ground vibrational state.

4.4.3.2 Results

The data from each polarization of each IF setting were calibrated and co-added independently. The two polarizations in a given IF setting were then averaged to further reduce the RMS. The column density derived from the CSO observations indicates that an RMS level of $\sim$ 5 mK (on the T_A^* scale) is required to ensure $>2\sigma$ detections for the dihydroxyacetone emission features in this spectral region. The minimum RMS level reached

Table 4.6: Dihydroxyacetone column density upper limits in Sgr B2(N-LMH) from GBT observations.

$J'_{K'_a,K'_c}-J''_{K''_a,K''_c}$	ν_0^a (MHz)	$Ag_u\times10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit [c] ($\times10^{-15}$ cm^{-2})
$30_{4,26} \rightarrow 30_{3,27}$	42007.7536	0.0071	13.79	0.025(8)	3.12(95)
$11_{1,11} \rightarrow 10_{0,10}$	41953.1665	0.0066	11.80	0.140(35)	19.1(582)
$12_{0,12} \rightarrow 11_{1,11}$	41525.1729	0.0058	20.00	0.033(10)	5.20(158)
$13_{3,11} \rightarrow 13_{2,12}$	42619.6200	0.0193	92.24	0.065(17)	3.05(94)

[a] One σ uncertainties are 0.1 MHz.
[b] Uncertainties are listed in parentheses in units of last significant figure and are based on an assumed flux uncertainty of ±0.02 Jy/Beam.
[c] One σ uncertainties are listed in parentheses in units of last significant figure.

in any of the 4 IF settings was on the order of 10 mK, and so none of the transitions were unambiguously observed. Emission is indeed seen at the dihydroxyacetone line positions, but the limited sensitivity of the observations combined with possible line confusion excludes the possibility for a definitive detection at this time. The column density upper limits were calculated from the observed spectral intensity at the expected line position. A linewidth of 10 km/s, roughly the average linewidth observed in the CSO observations, and the rotational temperature of 220 K determined from the CSO observations were assumed. The calculated dihydroxyacetone column density upper limits are presented in Table 4.6.

4.4.4 Discussion

The CSO Sgr B2 results are the first observational evidence for the presence of the 3C ketose 1,3-dihydroxyacetone in the ISM. The derived dihydroxyacetone excitation and velocity are in excellent agreement with other species detected in the Sgr B2(N-LMH) hot core, for which the most commonly quoted rotational temperature and v_{LSR} are 200 K and 64 km s^{-1}, respectively (see [28] and references therein).

The absence of dihydroxyacetone lines in the OVRO spectra does not further substantiate the CSO observations. The limits derived from these observations, however, are on the same order as or greater than the column density determined from the CSO observations and therefore do not rule out the possibility of dihydroxyacetone being present in this source if the emission is extended. The OVRO observations would be the least affected by beam dilution should the emission be compact, and so these results provide the upper limit to the column density in this case. More sensitive observations are required for determining the spatial scale of dihydroxyacetone emission in this source, and the Combined Array for Millimeter Astronomy (CARMA), which will be commissioned in 2006, will be used for this study.

Other molecules observed in Sgr B2(N-LMH) show two-component behavior in which higher energy transitions give characteristic hot core temperatures, but lower energy transitions yield much colder excitation temperatures. It is thought that these lower energy states are populated in an extended, potentially subthermally excited, source, possibly formed by shock liberated grain mantle ices [17,18]. Dihydroxyacetone should demonstrate such behavior if it is produced by grain surface chemistry. Unfortunately the sensitivity levels reached in the GBT observations remain insufficient for a definitive detection of this type of low-energy emission. The GBT and CSO observations are directly comparable for

a source size larger than 30″, and the GBT limits lie well within the margin of error for the column density derived from the CSO observations. A source size on the order of 10″, such as that observed for ethyl cyanide in this source [45], requires that these results be scaled appropriately to account for beam dilution effects. This results in a column density limit from the GBT observations of $1.09(34)\times10^{15}$ cm^{-2}, indicating that the line confusion in the CSO observations may be leading to an overestimation of the column density by approximately a factor of four if the source is on the order of 10″ in size.

The dihydroxyacetone lines observed in the Sgr B2(N-LMH) source are not present in the Orion and W51e2 spectra obtained with the CSO. The limits derived from these observations put constraints on the sugar-related chemistry in these sources. The absence of these spectral features also further strengthens the detection of dihydroxyacetone in Sgr B2(N-LMH). It is possible that weak spectral features in hot core sources may be due to unidentified vibrationally excited lines of a simpler, previously detected hot core molecule. It is clear that these emission features are not due to such a transition if they are present only in the Sgr B2(N-LMH) hot core.

The derived dihydroxyacetone column density of $(4.9 \pm 2.2) \times10^{15}$ cm^{-2} leads to interesting questions about the formation of and subsequent behavior of this molecule in the hot core. Emission from the high excitation lines of methyl formate, acetic acid, ethyl cyanide (CH_3CH_2CN), dimethyl ether (CH_3OCH_3), and acetone ($(CH_3)_2CO$) is known to be compact with respect to the CSO beam (see [46] and references therein). If similar filling factors are used for dihydroxyacetone then it would be more abundant than any of these compounds except dimethyl ether. Even if the column density derived from the CSO observations is overestimated by a factor of four, dihydroxyacetone would still be present at similar abundances to these species. Both the chopping scheme and higher frequencies of

CSO observations render them insensitive to spatial distribution for extended, low excitation emission as is seen from molecules such as acetaldehyde, ethanol, and glycolaldehyde. Direct comparisons show that these molecules are also less abundant than dihydroxyacetone.

A further complication is the inconsistent treatment of the partition functions of complex molecules. Typically only the ground vibrational state is included in partition function calculations as laboratory characterizations of excited states are often incomplete. Inclusion of vibrational state terms can greatly effect the derived total column densities of complex species under hot core conditions. For a molecule like glycolaldehyde, the inclusion of torsional states increases the partition function by ∼50% at 200 K, but they can be safely ignored below 50 K (see Chapter 6 and reference [47]). Exclusion of excited vibrational state terms in the dihydroxyacetone analysis would lower the column density by ∼60%.

Nevertheless, dihydroxyacetone would be among the most abundant complex molecules in the Sgr B2(N-LMH) hot core should the present analysis be confirmed by further observations, and so an efficient formation route must exist. No quantitative chemical scheme for the production of species such as glycolaldehyde and dihydroxyacetone has been presented. Observations of complex molecules toward low mass protostars where the dynamical time scales are short [2, 48] and careful studies of the potential reactions leading to methyl formate all seem to point toward a grain mantle synthesis [13]. In this regard it is intriguing to note that, with appropriate rearrangements, all of these species can be formed from reactions involving the abundant grain mantle constituents CO, HCOOH, and CH_3OH or their radical precursors. The importance of such reactions in interstellar grain surface chemistry is discussed in Chapter 8.

Survivability in hot cores may be another important aspect of dihydroxyacetone chemistry. As a ketose, it is both thermodynamically more stable and less reactive than

either glycolaldehyde or glyceraldehyde in hot gas. Isomerism in 3C and larger compounds is also quite extensive, and both dimethyl carbonate ($(CH_3O)_2CO$) and methyl glycolate (CH_3OCOCH_2OH) are even more stable than dihydroxyacetone. These isomers would likely be created by any surface chemistry leading to sugars. Laboratory and observational studies of these isomers are discussed in Chapter 5.

The spectral characteristics of asymmetric rotors such as dihydroxyacetone make a definitive interstellar detection quite difficult. While some spectral windows contain multiple emission lines, most contain only one strong line due to the relatively large spacing between adjacent K levels within a given J state. It can be argued that many of the isolated features presented here could arise from other unidentified species or from the excited vibrational state lines of previously detected molecules. This argument is countered by the striking similarity between the observed and simulated spectra shown in Figure 4.6. This degree of coincidental overlap with other hot core species in both rest frequency and intensity is unlikely, but additional observations are clearly warranted.

Chapter 5

Dimethyl Carbonate & Methyl Glycolate

5.1 Introduction

Structural isomerism is widespread in the ISM. The abundances of the 2C structural isomers methyl formate, acetic acid, and glycolaldehyde and the 3C structural isomers glyceraldehyde and dihydroxyacetone indicate that the relative stability of structural isomers may play a large role in their formation and/or survivability. Isomerism in 3C and larger compounds is quite extensive, and all but one of the nine 3C sugar structural isomers are lower in energy than the sugars (see Appendix D). With appropriate rearrangements, all of these 2C and 3C structural isomers can be formed from reactions involving the abundant grain mantle constituents CO, HCOOH, and CH_3OH or their radical precursors. In the case of the 3C compounds, dihydroxyacetone, dimethyl carbonate ($(CH_3O)_2CO$), and methyl glycolate (CH_3OCOCH_2OH) can be formed from simple addition of CH_3OH to CO.

Regardless of the formation pathway, dimethyl carbonate and methyl glycolate would likely be created by any chemical pathway leading to the 3C sugars. These species should therefore be present in large abundance in the Sgr B2(N-LMH) hot core. The microwave spectrum of methyl glycolate is known for the ground state [49] and several torsional

states [50, 51]. No rotational spectral studies have been conducted for dimethyl carbonate.

Dimethyl carbonate is a symmetric double internal rotor while methyl glycolate is an asymmetric single internal rotor (see Figure 5.1). The internal rotation leads to AA, AE, EA, and EE states for dimethyl carbonate and A and E states for methyl glycolate, and so their spectra are quite complex. The spectrum of methyl glycolate is much more complex than that of dimethyl carbonate due to its asymmetry. The barrier to internal rotation, V_3, has been previously measured [52], and this information coupled with the microwave spectral information eases spectral assignment at higher frequencies. Dimethyl carbonate is a much more complicated case, however, as it has a very small dipole moment ($\sim$ 0.18 D), and so its spectrum is quite weak, greatly limiting spectral assignment.

We began our study of dimethyl carbonate with FTMW studies. The microwave studies were then used to guide millimeter and submillimeter direct absorption flow cell studies. The ground state spectral analyses of these species have been completed, and this information has served as the basis for preliminary observational searches. The *ab initio* studies of dimethyl carbonate and methyl glycolate are presented in Appendix D, and the structures of their ground state conformers are shown in Figure 5.1. The laboratory studies are presented in Section 5.2. The results of the initial observational searches for these molecules are given in Section 5.3.

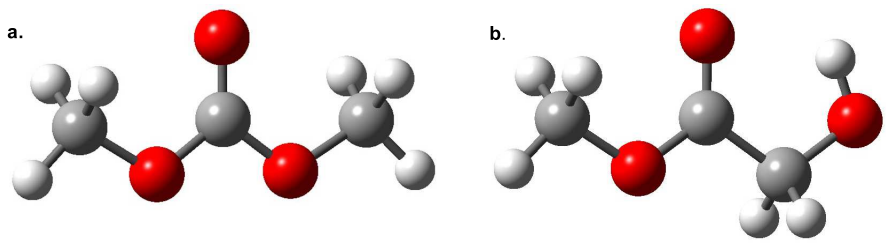


Figure 5.1: Ground state structures for a. dimethyl carbonate and b. methyl glycolate.

5.2 Spectroscopic Studies

5.2.1 Experimental

All experiments were conducted with dimethyl carbonate and methyl glycolate vapor from liquid samples (99% and 98%, respectively) purchased from Aldrich.

5.2.2 FT-Microwave Studies

The FTMW investigation of dimethyl carbonate was conducted with the original Balle-Flygare spectrometer. The details of the setup can be found in Chapter 2, Appendix A, and reference [20]. The liquid sample was placed in a bubbler and the mixing manifold was used for sample preparation and backing pressure control. First-run neon (74.9% neon in helium) from BOC Gases was used as the carrier gas. The neon flow rate was 363.5 SCCM, while the flow rate of neon through the bubbler was 4.49 SCCM.

The structural parameters from the theoretical calculations and the value of V_3 previously determined for methyl glycolate (1.177 $\pm$ 30 kcal/mol [52]) were used to generate a spectral prediction with the MOIAM and IAMCALC programs in the CALPGM suite (see Appendix C, [30]). The single-shot signal was optimized once the quadruplet corresponding to the $1_{0,0} \rightarrow 0_{0,0}$ transition was observed. The spectra for this quadruplet are shown in Figure 5.2. The optimized experimental parameters included a microwave pulse width of 1.6 μs and a backing pressure of 2.23 atm.

The spectrometer Auto Search mode was used to conduct a broadband search for all reasonably strong dimethyl carbonate lines between 12 and 18 GHz. Integrations were performed for 500 shots at each frequency setting, and a step interval of 800 kHz was used. The instrument was used in the coaxial valve configuration, resulting in classic Doppler

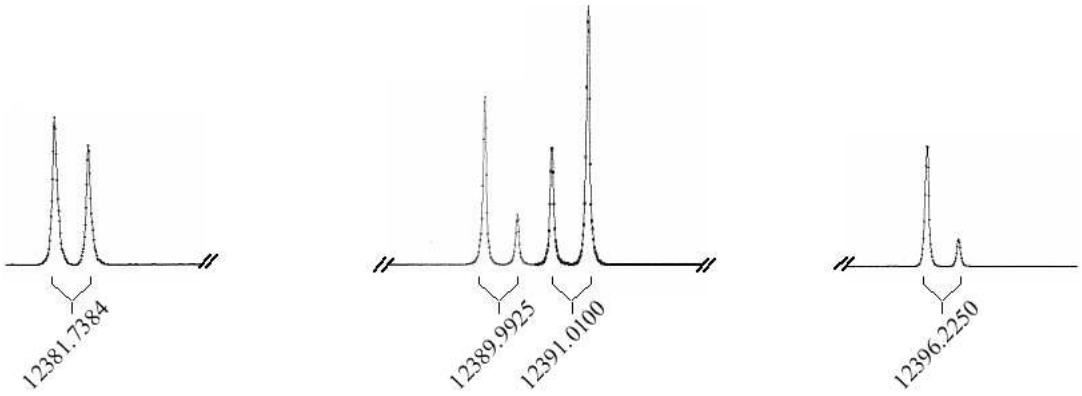


Figure 5.2: FTMW Doppler-doublet spectra of the dimethyl carbonate $1_{0,0} \rightarrow 0_{0,0}$ quartet. The frequencies are in units of MHz.

doublets for all transitions. The de-Dopplerization routine included in the spectrometer control program was used to determine the center frequencies for observed lines. This routine calculates the mean frequency, intensity, and linewidth for the two lines in a given Doppler doublet and produces a de-Dopplerized spectrum with these parameters. Line confusion limited the use of this feature within some spectral windows, and so the line center frequency was manually determined from the observed frequencies for each component of the Doppler doublet in these cases. An example of a spectrum for which this manual de-Dopplerization was performed is shown in Figure 5.3.

A total of 119 dimethyl carbonate lines were observed between 12 and 18 GHz. Linewidths were on the order of 8 kHz. Integrations of 2000 shots were performed to increase the signal-to-noise ratio for weak lines observed in the Auto Search mode spectra. A doubler was added to the frequency input of the spectrometer such that searches above 18 GHz could be conducted for specific target frequencies. The $3_{1,3} \rightarrow 2_{0,2}$ quartet near 20120 MHz was observed in this manner. The frequencies of the lines observed in the FTMW experiments are listed in Table 5.1.

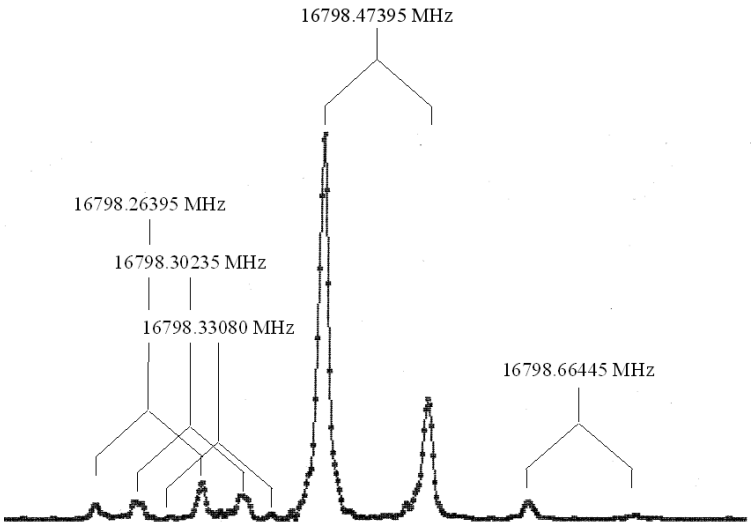


Figure 5.3: A FTMW Doppler-doublet spectrum of dimethyl carbonate for which manual de-Dopplerization was performed for line frequency determination.

Table 5.1: The frequencies (in MHz) of dimethyl carbonate lines observed in the FTMW experiments.

12225.16475	12401.58400	12897.50840	14960.80860	16600.01230	17059.85390
12225.47980	12539.98330	12898.56845	14963.76060	16600.31770	17190.50490
12225.97930	12540.32550	12898.60835	14967.10450	16601.07185	17190.60390
12226.42100	12540.37520	12899.52590	15029.10815	16601.24150	17191.05190
12226.42580	12540.56180	13066.87380	15029.26730	16613.78840	17192.72300
12340.65780	12656.06790	13067.21560	15032.15730	16798.26395	17192.82220
12349.24290	12656.25750	13070.29680	15034.60680	16798.30235	17251.37665
12350.15670	12656.39475	13073.55080	16347.09385	16798.33080	17251.58490
12350.18480	12656.62445	13092.51300	16347.92830	16798.47395	17254.91870
12355.46590	12716.15900	13094.51305	16349.88510	16798.66445	17258.35800
12381.73840	12716.67520	13094.60735	16350.73410	16842.70750	17315.21330
12382.86000	12716.97260	13095.71070	16352.29530	16872.76290	17317.68420
12389.99250	12717.52660	13121.81990	16353.13680	16874.30070	17317.97210
12391.01000	12723.31050	13121.92760	16353.61685	16875.19140	17318.94180
12392.12610	12723.53020	13122.41060	16354.69460	16984.11430	20120.24480
12395.10300	12723.63760	13526.26600	16355.46405	16984.27505	20121.57220
12396.22500	12777.98230	13526.68320	16356.93520	16984.82920	20124.21900
12397.34125	12786.25030	13739.42890	16356.94820	16985.46460	20127.68080
12401.13560	12789.24960	13741.20800	16356.96770	17058.81870	
12401.25770	12841.43130	14960.29160	16599.55755	17059.42750	
12401.39035	12859.99600	14960.54810	16599.85445	17059.48950	

5.2.3 Direct Absorption Millimeter and Submillimeter Studies

Direct absorption studies of dimethyl carbonate and methyl glycolate were conducted at 3 and 1 mm with the Caltech Direct Absorption Flow Cell Spectrometers. The details of these setups can be found in Chapter 2, Appendix B, and reference [40]. The liquid dimethyl carbonate or methyl glycolate sample was placed in a ball flask that was connected to the cell. These species are reactive with plastics and pump oil, and so a liquid nitrogen cold trap was attached to the output of the cell in order to protect the mechanical pump. Computer-automated scans of both increasing and decreasing frequency increments were averaged for all spectra.

A pressure of ∼100 mtorr was maintained for the dimethyl carbonate experiments. The dimethyl carbonate lines were particularly weak and the spectrum was very sparse, and so multiple sweeps (> 5) were averaged in small windows around each observed line. The observed lines were fairly broad with linewidths on the order of 1.5 MHz.

A pressure of ∼40 mtorr was maintained for the methyl glycolate experiments. The methyl glycolate spectrum was much stronger and also much more complex than the dimethyl carbonate spectrum. An example spectrum of methyl glycolate from 103 to 111 GHz is shown in Figure 5.4. As is shown in the inset, the spectrum is quite dense, and no clear branching pattern is observed. Methyl glycolate linewidths were on the order of 0.5 MHz.

5.2.4 Data Analysis

The internal rotation of symmetric tops within larger molecules can be treated with several different Hamiltonians that are based on the axis system chosen to define the parameters. The Principle Axis Method (PAM) utilizes parameters determined in the

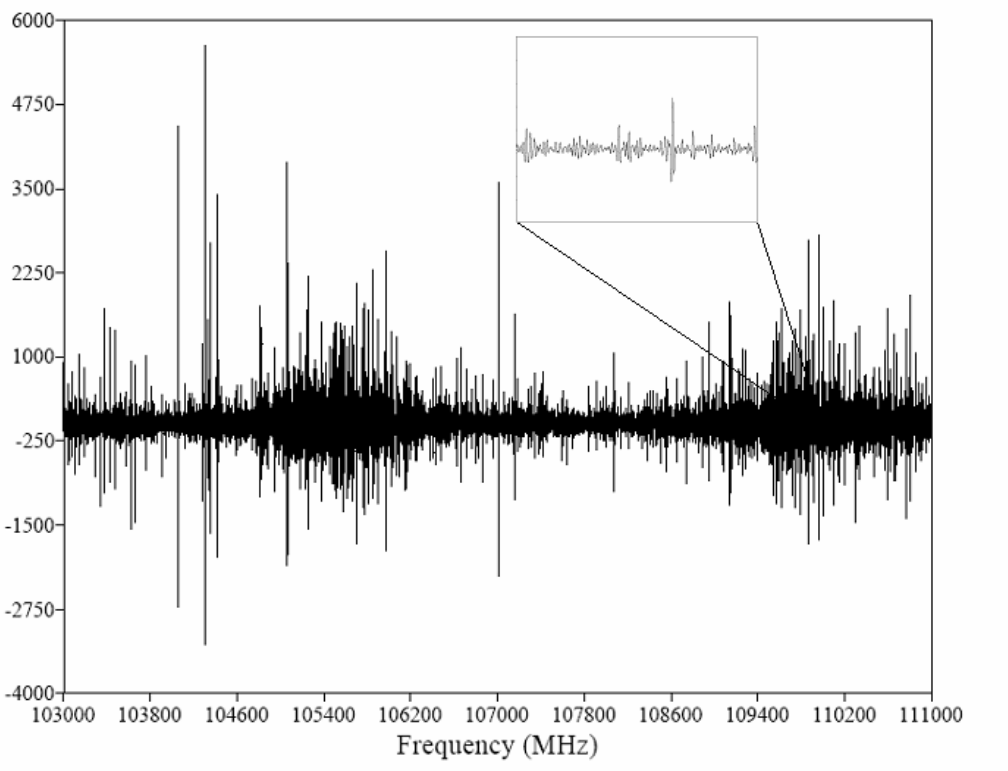


Figure 5.4: The room temperature methyl glycolate spectrum from 103 to 111 GHz.

principle axis system of the molecule. The Internal Axis Method (IAM) utilizes parameters determined in a non-diagonal inertial frame that minimizes the angular momentum of the large amplitude motion. The Rotated Axis Method (RAM) utilizes parameters determined in an arbitrary axis system chosen such that only perturbative terms that treat the large amplitude motion are included. The input to the CALPGM program suite is in the internal axis frame, but the input structure can be rotated to the appropriate axis system (i.e., the rotated axis method), and so the principle axis system can be utilized.

Both dimethyl carbonate and methyl glycolate have CH_3 groups undergoing hindered internal rotation, resulting in a threefold barrier component, V_3, to the torsional barrier potential:

$$V = \frac{V_3(1 - \cos 3\alpha)}{2} \tag{5.1}$$

where α is the angle of rotation of the group around an internal axis. For a molecule with two internal rotors, the angle of rotation of the second internal rotor group is defined as β. F is the internal rotation dynamical constant that is related to the moment of inertia, I_α, of the rotor around its internal rotation axis. The reduced barrier height, s, relates the barrier height and dynamical constant by the relationship:

$$s = \frac{4V_3}{9F} \tag{5.2}$$

The Hamiltonian used by Groner et al. for the analyses of dimethyl ether and acetone can be used for double internal rotors such as dimethyl carbonate (see [53] and references therein). This Hamiltonian contains two Fourier series "... with coefficients that can be interpreted as integrals of torsional operators." Rather than defining F and V_3 for such a molecule, then, the $\epsilon_{qq'}$ coefficients from one of these series can be used to determine the effective energy. A similar parameter, E, is used by the CALPGM programs, and E is related to ϵ by the relationship $E = -4\epsilon$.

The angle between the symmetry axis of the rotor and the a-axis of the molecule is defined by Θ. The internal rotation interaction constant, ρ_g, is defined as:

$$\rho_g = \frac{\lambda_g I_\alpha}{I_g} \tag{5.3}$$

where λ_g is the direction cosine between the symmetry axis of the rotor and the principle axis, g, of the molecule (e.g., $\lambda_a = ncos\Theta$), and I_g is the principle moment of inertia of

the molecule on the g-axis. The rotor contributes off-axis angular momentum, and the contribution of this angular momentum to the b-axis is defined as P_b.

The values of V_3, F, E ρ, and P_b can be fit to the spectral data along with the rotational and centrifugal distortion constants using the SPFIT and SPCAT programs (see Appendix C, [30]). The MOIAM and IAMCALC programs are used to generate a set of spectral parameters based on an initial approximation of the barrier height and the molecular structure. The rotational and centrifugal distortion constants, P_b, V_3, and F (or alternatively E) are expanded as Fourier series with terms of the type:

$$U_m = cos^m\left(\frac{2\pi\rho K_{av} - \sigma}{n}\right) \tag{5.4}$$

where m is a user-defined number of terms in the expansion, K_{av} is the average value of K'_a and K''_a, n is the order of the internal rotor symmetry axis (n=3 for a CH_3 group), and σ is the torsional state symmetry number ($\sigma = 0$ for A states; $\sigma = 1$, 2 for E states). The number of terms included in the expansion is determined by the magnitude of the terms, and the expansion is truncated when the contribution from additional terms becomes negligible. The ratio between the U_m terms in a given series is set by the MOIAM and IAMCALC programs. The spectroscopic parameters listed in Tables 5.2 and 5.3 are expressed as the Fourier series terms, U_m. Higher order U_m terms can be fixed relative to another term in the series or can be fit independently. Those U_m terms fit independently are listed separately, while fixed terms are listed as one value.

5.2.4.1 Dimethyl Carbonate

A simplified version of the Hamiltonian used to analyze the acetone spectrum was translated into the parameters used by the CALPGM Program Suite for the dimethyl

carbonate analysis (see Appendix C and references [30] and [53]). The microwave data were used to fit the internal axis system Hamiltonian and estimate the quartic distortion constants. These parameters were then used to predict the millimeter spectrum. As new data were assigned, lines were continuously added to the data set, and the fit was further modified with the same Hamiltonian. The quality of the fit to the entire data set was indicated by the microwave root mean square deviation. The value for ρ was held constant until the assignments were complete, and then this value was optimized to give the lowest RMS.

A total of 279 lines have been assigned to the dimethyl carbonate ground state with an RMS of 85 kHz. No vibrational state lines were observed. The spectral line density was quite low at millimeter and submillimeter frequencies. No assignable transitions were observed in the millimeter data, but $\sim$75% of the observed submillimeter lines were assignable. These assignments only include states with $K_a = 0, 1$.

Weak satellite lines were observed near many of the strongest dimethyl carbonate lines in the FTMW study. The positions of these satellites suggest that they could be isotopic variants observed in natural abundance, but no dedicated search for isotopomers was conducted. No structural information can be derived from these lines because accurate rotational constants cannot be determined with such incomplete data, and so no assignments have been made at this time. Other isotopomeric transitions might be observable with longer integration times, and this experiment should be conducted if detailed structural information is desired.

The files associated with the ground state analysis, including the parameters and rest frequencies, can be found in Appendix F. The output file from the spectral analysis, which includes the observed minus calculated residuals, has been included as supplementary

material in the electronic version of this thesis. The spectral parameters determined for the ground state are listed in Table 5.2.

Table 5.2: Spectral parameters determined for dimethyl carbonate.

ρ	0.3000	
$E(U_0 + U_1)$	-70.932(68)	MHz
$E(U_2)$	-25.5880(175)	MHz
$E(U_3)$	-7.19(42)	MHz
$E(U_4)$	-0.0236(39)	MHz
$P_b(U_1)$	-30.95(43)	MHz
$P_b(U_2)$	11.09(32)	MHz
$A - (B + C)/2$	8226.30(55)	MHz
$(B + C)/2$	2175.93622(132)	MHz
$[(B + C)/2](U_1)$	0.04096(78)	kHz
$[(B - C)/4]$	97.754285(259)	MHz
$[(B - C)/4](U_1)$	0.015282(109)	kHz
Δ_J	0.122597(129)	kHz
Δ_{JK}	11.337(219)	kHz
# Lines	279	
Fit RMS	85	kHz

Note: One σ errors are listed in parentheses in units of last significant figure.

5.2.4.2 Methyl Glycolate

The PAM internal axis system was used in the original analysis of methyl glycolate [52] and has been adopted for the methyl glycolate analysis presented here. The default axis system used in the IAM approach was rotated by an angle of 7.15° so that the PAM system could be used. The structural parameters determined in the *ab initio* study (see Appendix D) were used with the MOIAM and IAMCALC programs to generate spectral parameters. The rotational constants and quartic centrifugal distortion constants were set to the previously determined values, and the microwave data from references [49–52] were used to fit the internal axis system Hamiltonian. These parameters were then used to predict the millimeter spectrum. As new data were assigned, lines were continuously added

to the data set, and the fit was further modified with the same Hamiltonian. The quality of the fit to the entire data set was indicated by the microwave root mean square deviation. The value for F determined by the MOIAM and IAMCALC programs was held constant. Likewise, the value for ρ was held constant until the assignments were complete, and then this value was optimized to give the lowest RMS. In a generic RAM, P_b has a value on the order of 8000 MHz. None of the data were sensitive to this parameter, however, and so it was not included in this analysis.

A total of 2342 lines have been assigned to the methyl glycolate ground state with an RMS of 185 kHz. This data set represents only ∼10 - 15% of the strong lines observed in the millimeter and submillimeter data. The nine vibrational states identified in earlier work account for the large number of unassigned lines remaining in the room temperature spectrum. Assignments for the excited torsional states are planned, but these analyses have not been completed at this time. The files associated with the ground state analysis, including the parameters and rest frequencies, can be found in Appendix G. The output file from the spectral analysis, which includes the observed minus calculated residuals, has been included as supplementary material in the electronic version of this thesis. The assignments and other predicted rotational frequencies will be accessible through the submillimeter and microwave spectral line catalog available at `http://spec.jpl.nasa.gov` [30] once the torsional state assignments have been completed. The spectral parameters determined for the ground state are listed in Table 5.3.

5.2.5 Discussion

The rotational spectra of dimethyl carbonate and methyl glycolate have now been investigated up to 360 GHz. While the RMS of the dimethyl carbonate analysis is quite

Table 5.3: Spectral parameters determined for methyl glycolate.

ρ	0.05119	
$V_3(U_0+U_1+U_2)$	995.72815(28287)	kcal/mol
$F(U_0+U_1+U_2+U_3+U_4+U_5+U_6+U_7)$	168312	MHz
$A-(B+C)/2$	7974.6449(88)	MHz
$[A-(B+C)/2](U_1+U_2)$	0.2325(84)	MHz
$(B+C)/2$	2026.642270(177)	MHz
$[(B+C)/2](U_1+U_2)$	9.131(182)	kHz
$[(B-C)/4]$	88.680302(78)	MHz
$[(B-C)/4](U_1+U_2)$	4.928(57)	kHz
Δ_J	0.189728(81)	kHz
$\Delta_J(U_1+U_2)$	0.0382(222)	Hz
Δ_{JK}	1.04208(119)	kHz
$\Delta_{JK}(U_1+U_2)$	2.48(38)	Hz
Δ_K	3.255(84)	kHz
$\Delta_K(U_1+U_2)$	1.947(58)	kHz
δ_J	-0.029984(37)	kHz
δ_K	-0.4520(40)	kHz
$\delta_K(U_1+U_2)$	-0.02759(117)	kHz
Φ_J	0.0289(116)	mHz
Φ_{JJK}	4.87(87)	mHz
Φ_{JKK}	-0.0635(37)	Hz
Φ_K	-7.583(238)	Hz
ϕ_J	1.24(60)	mHz
ϕ_K	0.0349(265)	Hz
ϕ_{JK}	0.0255(57)	mHz
# Lines	2342	
Fit RMS	185	kHz

Note: One σ errors are listed in parentheses in units of last significant figure.

low, the observed minus calculated residuals on the assigned microwave spectral data are slightly higher than the experimental resolution. This indicates that the parameters used for this analysis are not fully modeling the effects of the internal rotation on the rotational spectrum of this molecule, which is not uncommon for such analyses. Also, the weak dipole moment of dimethyl carbonate limits this analysis to those states with $K_a = 0$, 1, but predictions of higher frequency lines with these K_a values should be accurate to ∼1 MHz at frequencies above 360 GHz. The analysis presented here is therefore sufficient to guide observational studies, as these states will be populated at hot core temperatures.

More sensitive millimeter and submillimeter studies are clearly required before a complete spectral analysis of this molecule can be conducted.

The ground state analysis for methyl glycolate is complete and analyses of the low-lying torsional states are planned. This information is not necessary for observational studies, however, because the vibrational contributions to the molecular partition function can be determined from the information reported in the original microwave studies. The RMS determined in the ground state analysis is approximately twice the experimental resolution, indicating that the internal rotation parameters used for this spectral analysis are not fully modeling the behavior of this species. Again, this is not uncommon for spectral analyses of internal rotors. The parameters determined here, however, are in excellent agreement with those determined in the original microwave studies [52] and provide the necessary information to guide observational studies. Based on this ground state analysis, predictions of strong submillimeter lines above 360 GHz are accurate to better than 2 MHz, and interpolations below 360 GHz are accurate to less than 200 kHz.

Partition function calculations for these two molecules must be modified from the standard asymmetric top approximation given in Equation 3.8 to include internal rotation effects. In the case of dimethyl carbonate, the situation is analogous to that of acetone [53], where the partition function can be weighted by the ratio of the total spin weight to the symmetry number. The spin weight is given by $(2I+1)^6$, which is equal to 64 in the case of a methyl top where $I = \frac{1}{2}$, while the symmetry number is 2 for a C_{2v} symmetric molecule. For dimethyl carbonate, then, the standard asymmetric top partition function should be multiplied by a factor of 32. In the case of methyl glycolate, the A and E states are singly and doubly degenerate with nuclear spin weights of 2 and 1, respectively [54]. Their contributions to the partition function are therefore equal, and so the standard asymmetric

top partition function should be multiplied by a factor of two. Rotational constants and vibrational energies have been determined for the nine vibrationally excited states of methyl glycolate reported in reference [51], and so these states can be included in the partition function analysis. For dimethyl carbonate, however, only a ground state partition function can be calculated at this time. This should be a good approximation for the total molecular partition function since no excited state lines were observed in the laboratory spectra. The partition functions for these two molecules have been calculated at a range of temperatures and are presented in Table 5.4.

Table 5.4: Dimethyl carbonate and methyl glycolate molecular partition function values at various temperatures.

Temperature (K)	Dimethyl Carbonate Q_{gs}	Methyl Glycolate Q_{total}
300	4017203	1265051
200	2186688	688606
150	1420296	447263
50	273336	86076
10	24448	7699

5.3 Observational Studies

The primary target for observational searches for dimethyl carbonate and methyl glycolate is the Sgr B2(N-LMH) hot core such that direct abundance comparisons can be made to the other 3C structural isomers. This source is only observable from the CSO during summer months, and the laboratory data had not been obtained before the summer observing season in 2004. Observational searches are scheduled for July 2005. Additional GBT observations of this source have been postponed until fall 2005.

The search for dimethyl carbonate will be greatly limited by the 0.1 D dipole moment,

as the detection limits are inversely proportional to the square of this quantity. The detection limits would therefore be a factor of 400 higher for dimethyl carbonate than dihydroxyacetone from the dipole moment ratios alone. Likewise, the dimethyl carbonate partition function is seven times that of dihydroxyacetone at 200 K. The line strengths are also quite weak for this molecule in comparison to dihydroxyacetone. Dimethyl carbonate would have to be at least five orders of magnitude more abundant than dihydroxyacetone before its emission would be detectable. This would require its abundance to be higher than nearly all organic species in the Sgr B2(N-LMH) source, which is an unlikely scenario given its level of molecular complexity.

Methyl glycolate, on the other hand, has a larger dipole moment than dihydroxyacetone (μ_a=2.68 D, μ_b=1.02 D; [51]), and the line strengths are much stronger than those for dihydroxyacetone. The partition function is three times that of dihydroxyacetone at 200 K. Detection of methyl glycolate should therefore be quite straightforward in the Sgr B2(N-LMH) source if it is present at a column density on the order of or higher than that found for dihydroxyacetone.

The first step in the search for any species in this source is to compare the spectral information to the unidentified lines in existing line surveys. A single-dish survey in the 1 mm region [24] and a combined single-dish and interferometric survey in the 3 mm region [4] are available. Unfortunately the RMS level reached in the 1 mm survey is above the level required for complex molecule identification. The 3 mm survey, however, is near the level required for such detections, and $\sim$55% of the lines observed in this survey remain unidentified [4]. No dimethyl carbonate lines match any of the unidentified lines in this survey, but several methyl glycolate line positions are covered in this survey, and emission features are indeed seen at these frequencies. The (x,y) data from this survey as well as maps

of each spectral line have been obtained (D. N. Freidel 2004, private communication). A spectral window containing many possible methyl glycolate lines is shown in Figure 5.5 along with a T_{rot}=200 K simulated spectrum. The relative intensities, line center frequencies, and linewidths of the methyl glycolate lines were fixed and the intensities scaled to best match the observed spectrum.

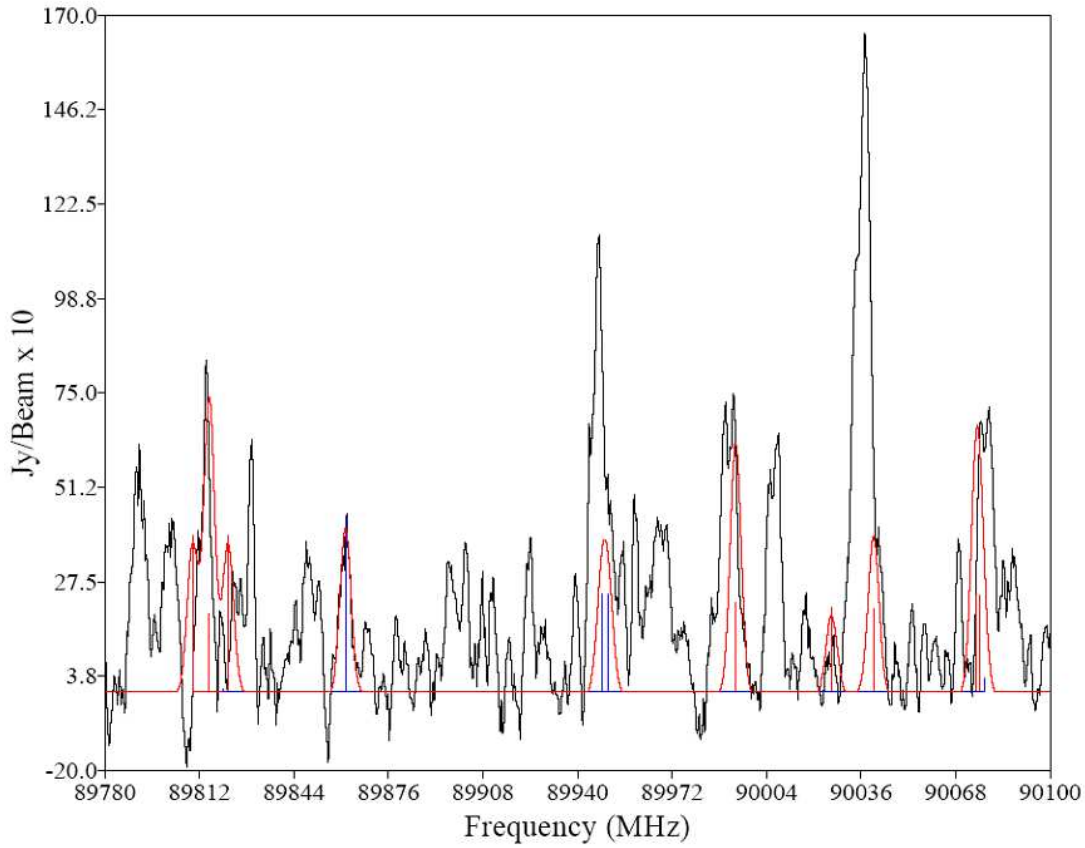


Figure 5.5: The simulated spectrum of methyl glycolate at 200 K (red) compared to a Sgr B2(N-LMH) 3 mm survey spectrum. The vertical lines correspond to line center positions, with red representing methyl glycolate lines and blue representing formic acid lines. Formic acid is the only identified species with lines in this window; all other emission features are unidentified.

The higher frequency component of the emission feature centered at 89814.7 MHz is clearly affected by the other line in the spectrum. Each of the other possible methyl glycolate lines

are in excellent agreement with the observed spectrum. Another unidentified line observed at 109960 MHz, which is not shown in Figure 5.5, also closely matches the methyl glycolate prediction.

The column density for methyl glycolate in this source can be calculated from the emission features at 89815.3, 89993.6, 90075.0, and 109960.7 MHz, and the results of this analysis are presented in Table 5.5. The parameters for these lines, specifically the transition quantum numbers, rest frequencies, Einstein A-coefficients times the upper state degeneracy, and upper state energies, are listed. All observed lines are transitions within the ground vibrational state. A rotation diagram approach cannot be used in this case because the upper state energies of these transitions are very similar, and so a rotational temperature of 200 K, the most commonly quoted rotational temperature for this source [28], was used for these calculations. These lines are asymmetry doublets and also contain both A and E state components. Only one frequency has been listed for asymmetry doublets occurring at the same frequency; for all others, the frequency of each individual component has been listed. The line strengths were calculated for the blended A/E states in the same manner as is described in Section 3.3 for asymmetry doublets. The vibrational state contributions to the partition function were included in this analysis. An average column density of $1.92(85)\times10^{16}$ cm^{-2} is determined from these data.

Each of these emission features has also been mapped, and these results further strengthen the case for a methyl glycolate detection, as all of these emission features have the same spatial distribution. The map for the emission feature at 89815 MHz is shown in Figure 5.6. The emission is on the same order as the beam size, and so beam dilution corrections are not necessary for these derived column densities.

These results indicate that methyl glycolate could indeed be present in the Sgr B2(N-

Table 5.5: Methyl glycolate column density in Sgr B2(N-LMH) determined from lines observed in the 3 mm line survey [4].

$J'_{K'_a,K'_c}$–$J''_{K''_a,K''_c}$	ν_0^a (MHz)	$Ag_u\times10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit [b] ($\times10^{-16}$ cm^{-2})
A state					
$22_{6,16} \rightarrow 21_{6,15}$	89815.3393	1.5203	63.17	0.76(19)	1.62(43)
$22_{6,17} \rightarrow 21_{6,16}$			63.17		
E state					
$22_{6,17} \rightarrow 21_{6,16}$	89815.3409		63.17		
$22_{6,16} \rightarrow 21_{6,15}$			63.17		
A state					
$22_{4,19} \rightarrow 21_{4,18}$	89993.5702	1.1979	55.64	0.76(19)	1.25(35)
E state					
$22_{4,18} \rightarrow 21_{4,17}$	89993.5702		55.64		
$22_{4,19} \rightarrow 21_{4,18}$			55.64		
A state					
$23_{2,22} \rightarrow 22_{2,21}$	90075.9787	1.2839	54.20	0.76(19)	2.88(76)
E state					
$23_{2,22} \rightarrow 22_{2,21}$	90075.0186		54.20		
$23_{2,21} \rightarrow 22_{2,20}$			54.20		
A state					
$27_{9,19} \rightarrow 26_{9,18}$	109960.6897	4.9341	104.6	2.98(35)	0.21(07)
$27_{9,18} \rightarrow 26_{9,17}$			104.6		
E state					
$27_{9,18} \rightarrow 26_{9,17}$	109960.6897		104.6		
$27_{9,19} \rightarrow 26_{9,18}$			104.6		

[a] One σ uncertainties are 0.1 MHz.
[b] Uncertainties are listed in parentheses in units of last significant figure.

LMH) hot core at a column density higher than any other complex organic yet detected. The spatial distribution is also indicative of a hot core molecule. Further observational investigation of methyl glycolate is clearly warranted before a definitive detection can be claimed, and searches with the CSO and GBT are planned. If these results are substantiated, however, the relative abundances of glyceraldehyde, dihydroxyacetone, and methyl glycolate follow similar trends to the 2C structural isomers. Their formation is governed by non-

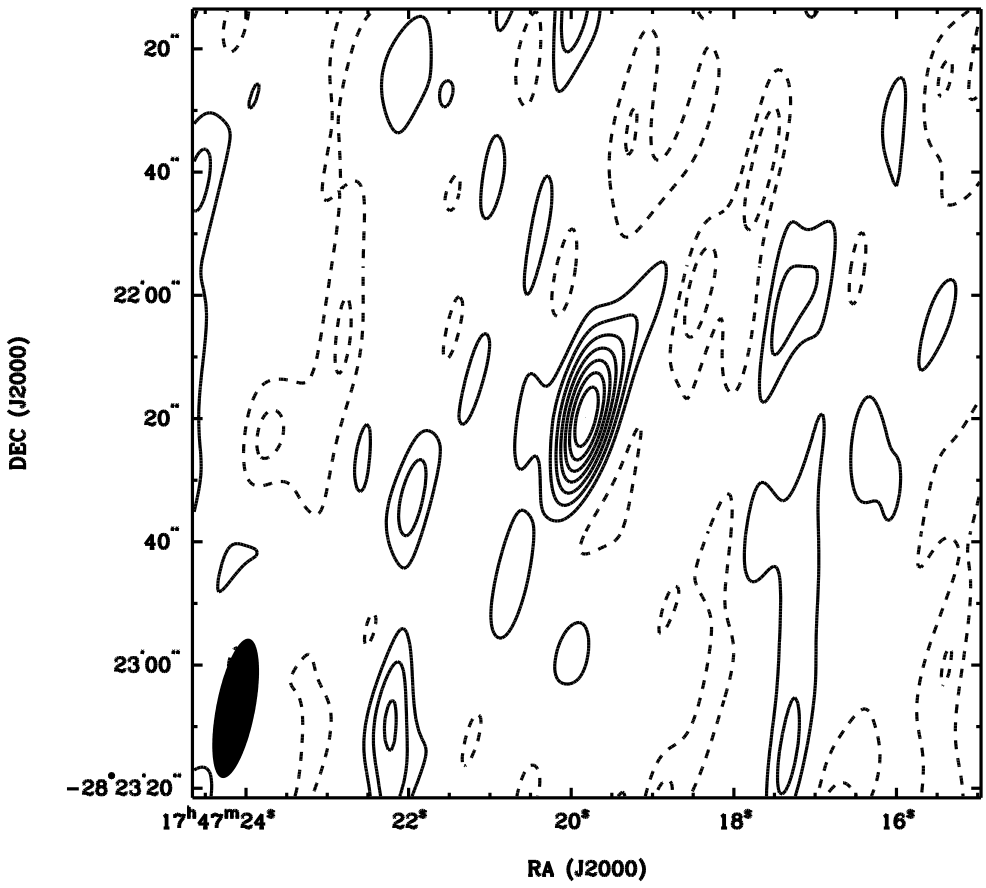


Figure 5.6: A map of the possible methyl glycolate emission feature at 89815 MHz in Sgr B2(N-LMH).

kinetic processes that are similar to the formation routes for the 2C compounds, which are thought to form on grain surfaces. The implications of these results for interstellar grain surface chemistry are discussed in Chapter 8.

Chapter 6

Glycolaldehyde

6.1 Introduction

The results of the dihydroxyacetone study have made it clear that a detailed determination of the vibrational contribution to the molecular partition function for sugar-related species is required for accurate column density determinations (see Chapter 4 and reference [55]). While the excited vibrational state partition function contribution is often negligible for small organics, this is not the case for more complex species with low energy torsional modes. Vibrational state excitation can be strongly influenced by the far-infrared radiation field in and near hot cores, and as a result low-lying states can be significantly populated, often by large factors over purely collisional excitation processes (see [56, 57]). The molecular partition function used to determine the column density of dihydroxyacetone included terms from several vibrationally excited states in addition to the ground vibrational state [55], while the glycolaldehyde column density reported by Hollis et al. was calculated using only the ground vibrational state molecular partition function [15]. A direct comparison of these two molecules therefore requires that vibrational state contributions to the glycolaldehyde molecular partition function also be determined.

The original interstellar detection of glycolaldehyde was based on an extrapolation of

earlier microwave rotational studies [58, 59], with subsequent millimeter and submillimeter measurements extending the laboratory database over the 128 - 354 GHz interval [60]. Three excited vibrational states were identified in the original microwave work, and some spectral assignments were included [58]. Gas phase infrared studies of this molecule have only been completed above 500 cm^{-1} [61], and the original microwave work included energies for only two of the three vibrational states [59]. While a rough estimate of the partition function can be made from *ab initio* predictions of vibrational state energies, the torsional energies determined in such studies often have uncertainties of >20%.

A much more precise determination of these vibrational state energies can be made from comparison of the relative intensities of the excited vibrational state lines to ground vibrational state lines. The rotational and centrifugal distortion constants derived from higher frequency spectral assignments can also be used to determine a more complete partition function. In addition, spectral lines from other low-lying torsional states not identified in the original microwave work (i.e., combination and/or overtone bands) could be present in millimeter and submillimeter spectra. If populated, these states could contribute significantly to the molecular partition function in a hot core environment. To test these possibilities, the millimeter spectrum of glycolaldehyde from 72–122.5 GHz has been obtained. The combined millimeter and submillimeter pure rotational analysis of the vibrationally excited states of glycolaldehyde has also been completed and this information used to determine a more complete molecular partition function.

6.2 Spectroscopic Studies

6.2.1 Experimental

The millimeter and submillimeter spectra of glycolaldehyde from 128–354 GHz were obtained with the Fast Scanning Submillimeter Spectroscopic Technique (FASSST) system at The Ohio State University. The spectra analyzed in this study are those obtained and analyzed in the original ground vibrational state study. Details of the experimental setup as well as a more detailed description of these data can be found in references [62] and [60], respectively.

Additional millimeter studies from 72–122.5 GHz were conducted with the JPL flow cell spectrometer. The basic flow cell design and detection methods for the JPL spectrometer are outlined in reference [23]. The source frequencies were obtained using a directly synthesized beam projected from the output of a multiplier chain [41]. The 3 mm wavelength region was readily detected with a room temperature diode detector, whereas the 1 and 2 mm regions required a helium cooled InSb bolometer. A solid sample of glycolaldehyde dimer (Aldrich 99%) was placed directly in the flow cell to ensure sufficient sample vapor pressure, which was maintained at ∼20 mtorr for the duration of the experiment. All measurements were conducted at room temperature. Measurements with a directly synthesized millimeter-wave source offer wide spectral coverage, particularly in the 100 GHz region where the final multiplier is fix-tuned (see Figure 6.1). Second and third harmonics of this multiplier were produced on a whisker-contacted Schottky diode allowing scans of up to 2 GHz per sweep. Computer-automated scans of both increasing and decreasing frequency increments were averaged to eliminate errors due to the time constant of the lock-in amplifier. The line widths were less than 1 MHz, and the spectrometer resolution is better than 100 kHz.

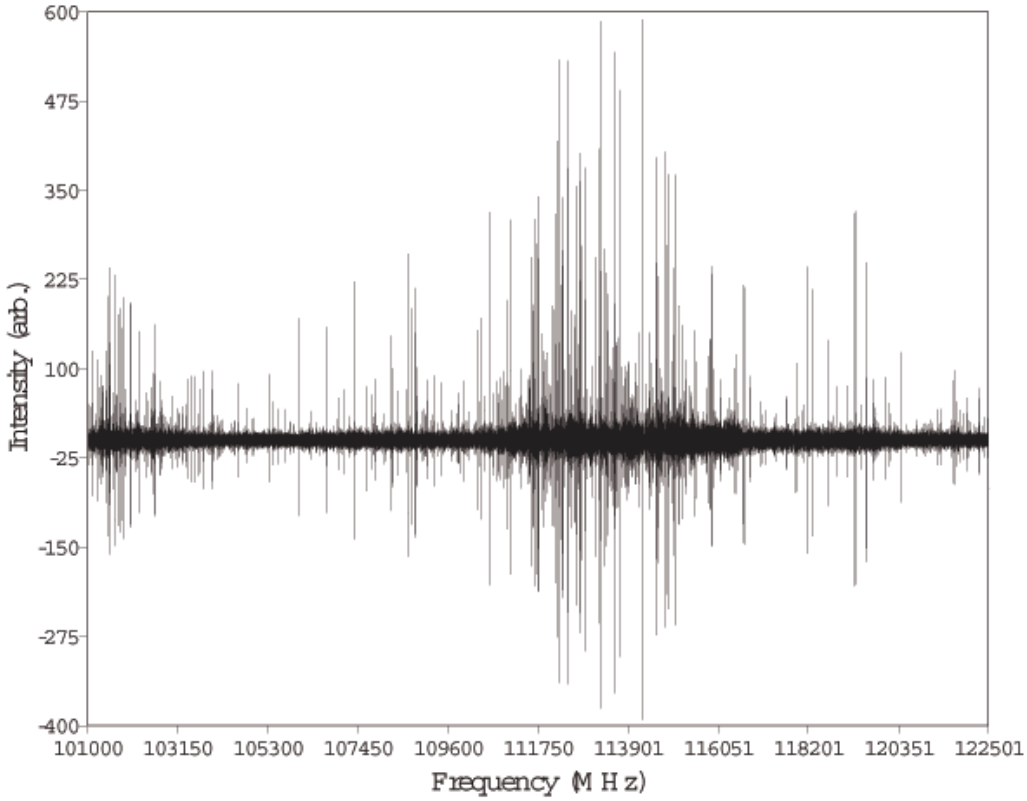


Figure 6.1: The room temperature glycolaldehyde spectrum from 101 to 122.5 GHz.

The glycolaldehyde spectrum from 101–122.5 GHz is shown in Figure 6.1. The line density is quite high in this spectrum, and strong ^{b}R branches are seen at a separation of approximately 13 GHz.

6.2.2 Data Analysis

The data were assigned using the SPFIT and SPCAT programs (see Appendix C, [30]). The rotational constants, centrifugal distortion constants, and dipole moments determined in previous spectral studies [58, 60] and a standard asymmetric-top Hamiltonian in the I^{r}-

representation were used with the Watson A-reduction to generate a predicted spectrum for the ground vibrational state and three vibrational states. These constants were then used to predict the millimeter spectrum. As new data were assigned, they were continuously added to the data set, and the fit was further modified with the same asymmetric-top Hamiltonian. The quality of the fit to the entire data set was indicated by the root mean square deviation of measured minus calculated residuals. All spectral assignments from the earlier studies were included in this fit. A total of 3160 glycolaldehyde lines, nearly all of the lines observed in the spectra, have been assigned. A total of 1657 lines have been assigned to the ground state with a RMS of 110 kHz. Additional assignments were made for three vibrational states, and these analyses have RMS values in the range of 120 to 130 kHz.

Glycolaldehyde has a strong 2.73(3) D *b*-type dipole and a weak 0.12(4) D *a*-type dipole [58]. A total of 67 *a*-type vibrational state transitions were assigned in this study. The relative intensities of the excited vibrational state lines to the ground state lines are dependent on the dipole moment and the vibrational state energy. The ground state dipole moments determined in the microwave study were used for all vibrational state predictions and assignments. Energies for the vibrational states were therefore determined by comparison of the relative intensities of these states to the ground vibrational state, and the values derived are given in Table 6.1.

The files associated with the analysis, including the parameters and rest frequencies, can be found in Appendix H. The output file from the spectral analysis, which includes the observed minus calculated residuals, has been included as supplementary material in the electronic version of this thesis. The assignments and other predicted rotational frequencies are accessible through the submillimeter and microwave spectral line catalog available at `http://spec.jpl.nasa.gov` [30]. The rotational and centrifugal distortion constants

determined for each state are listed in Table 6.1.

6.2.3 Discussion

The millimeter and submillimeter spectra of glycolaldehyde have now been fully characterized up to 354 GHz. Spectral assignments include lines from the ground state and three vibrational states, and rotational and quartic centrifugal distortion constants as well as vibrational state energies have been determined for each of these states. The RMS of the spectral analysis, $\sim$ 0.1 MHz, agrees with the resolution of both spectrometers used in this study. While the rotational constants determined from this analysis have changed only slightly from those found in the original microwave study, the centrifugal distortion constants have been significantly refined and provide an accurate submillimeter prediction for glycolaldehyde that can be used to guide future observational searches. Predictions of strong submillimeter lines above 354 GHz have similar accuracies for J-values close to the J_{max} in this analysis (see Table 4.2), while interpolations below 354 GHz are accurate to less than 100 kHz for all states based on this analysis. Uncertainties in the prediction are strongly correlated with J, but we estimate the errors are below 1 MHz for $J \sim$80.

The original microwave study derived energies of 195 $\pm$ 30 cm^{-1} and 260 $\pm$ 40 cm^{-1} for the first two excited vibrational states, which agree with those values obtained in this study [59]. A recent *ab initio* study estimates the five lowest glycolaldehyde vibrational state energies to be 213.4, 293.9, 425.7, 738.2, and 751.6 cm^{-1} [63], which also agree with the experimentally determined values within the typical uncertainties for such calculations. The experimentally determined third excited vibrational state energy, which differs the most from the *ab initio* predictions, provides the necessary information for a more complete glycolaldehyde partition function analysis.

Table 6.1: Spectral parameters determined for the ground and first three excited vibrational states of glycolaldehyde.

Parameter	Ground Vibrational State	1^{st} Excited Vibrational State	2^{nd}Excited Vibrational State	3^{rd} Excited Vibrational State	
E	0	∼195	∼260	∼313	cm^{-1}
A	18446.26074(43)	18463.55355(83)	18576.57913(104)	18524.85586(140)	MHz
B	6525.996379(161)	6482.54460(36)	6477.99471(42)	6445.62399(64)	MHz
C	4969.235801(149)	4965.052866(308)	4938.51753(40)	4933.53697(52)	MHz
Δ_J	6.222339(55)	6.280203(216)	6.196436(251)	6.35860(131)	kHz
Δ_{JK}	-20.397978(222)	-19.94946(55)	-21.59964(89)	-23.25808(149)	kHz
Δ_K	47.72338(47)	48.27689(292)	51.9581(45)	53.2488(60)	kHz
δ_J	1.8337838(135)	1.8342152(305)	1.849366(67)	1.859377(139)	kHz
δ_K	8.87889(41)	7.61421(102)	10.89546(160)	8.9558(41)	kHz
Φ_J	-6.465(42)	[a]	[a]	[a]	mHz
Φ_{JK}	0.15657(108)	[a]	[a]	[a]	Hz
Φ_{KJ}	-0.7721(34)	[a]	[a]	[a]	Hz
Φ_K	1.05703(292)	[a]	[a]	[a]	Hz
ϕ_J	2.5042(167)	[a]	[a]	[a]	mHz
ϕ_{JK}	12.98(82)	[a]	[a]	[a]	mHz
ϕ_K	0.1909(107)	[a]	[a]	[a]	Hz
J_{max}	66	61	48	39	
K_{max}	29	14	15	15	
# Lines	1657	672	491	340	
Fit RMS	0.110	0.130	0.129	0.120	MHz

Note: One σ errors are listed in parentheses in units of last significant figure.

[a]The sextic distortion constants were fit as global constants across all states.

Per the method described in Section 3.3, the rotational constants and vibrational energies determined for each vibrational state have been used such that the partition function is approximated as:

$$Q(T) \approx \sum_{i=0}^{3} e^{-E_i/kT} \sqrt{\frac{\pi}{A_i B_i C_i} \left(\frac{kT}{h}\right)^3} \tag{6.1}$$

The tabulated values for the glycolaldehyde partition function at a range of temperatures are given in Table 6.2 and compared to those tabulated for the ground vibrational state partition function. The three excited vibrational states have been included in this calculation. The absence of lines from other vibrationally excited states at room temperature indicates that overtone and combination bands of these first three states are not significantly populated at typical hot core temperatures ($\leq$300 K). These states have therefore not been included in the partition function calculation, nor have even higher energy vibrational states predicted by the *ab initio* study. Clearly, the glycolaldehyde molecular partition function increases significantly when the excited vibrational state terms are included unless the excitation temperature is very low.

Table 6.2: Glycolaldehyde molecular partition function values at various temperatures.

Temperature (K)	Q_{gs}	Q_{total}
300	35876	68405
200	19528	29435
150	12684	16331
50	2441	2452
10	218.3	218.3

The partition function values in Table 6.2 were calculated assuming that the vibrational and rotational excitation temperatures are the same, which is often the case in hot cores [56, 64]. While the rotational temperature can be derived directly from the rotational

diagram analysis, the vibrational temperature cannot. It has been found that the vibrational temperature is equal to or higher than the rotational temperature in this source due to the intense far-infrared radiation field generated by warm dust (see [56, 57]). The use of the rotational temperature in such an analysis therefore yields a lower limit for the partition function and column density and is the most accurate approximation without direct determination of the vibrational temperature.

A rotational temperature of 200 K was initially used to determine the glycolaldehyde column density in the Sgr B2(N-LMH) source [15]. The results presented here demonstrate that there is significant contribution to the molecular partition function from excited vibrational states at this temperature. As the column density is directly proportional to the partition function, the column density of glycolaldehyde in the Sgr B2(N-LMH) source is actually $\sim 2.26 \times 10^{15}$ cm^{-2} at 200 K, rather than the reported value of $\sim 1.5 \times 10^{15}$ cm^{-2} [15]. However, recent GBT observations have led to a revised theory for the behavior of glycolaldehyde in this source, and much lower rotational temperatures are now derived for beams of $\sim$10-20$''$ [17]. Nevertheless, the revised partition function values presented here should be used in future column density calculations and may be critical to future observations with arrays that are more sensitive to warm gas in the compact hot cores associated with the galactic center molecular clouds. Indeed, these results show that the excited vibrational state contribution to the partition function should be a principal consideration when determining the column density of a molecule with low lying torsional states.

Chapter 7

Aminoethanol

7.1 Introduction

Aminoalcohols are central to the gas phase formation of glycine in current hot core chemical models. The protonated forms of aminomethanol (NH_2CH_2OH) and aminoethanol ($NH_2CH_2CH_2OH$) are proposed to react with formic acid (HCOOH) to yield the protonated forms of glycine and alanine, respectively [3]. Laboratory and observational data supporting the presence of these aminoalcohols remains incomplete, however. The first step in the evaluation of these models is therefore the complete laboratory spectroscopic characterization of aminomethanol and aminoethanol.

Aminomethanol is not easily isolated under normal laboratory conditions. Aminoethanol, however, is commercially available, and gas phase spectra are easily obtained. Penn and Curl investigated the rotational spectrum of this molecule from 8–40 GHz and assigned transitions through $J = 8$. Rotational constants were determined in this work, as well as the dipole moment, r_0 structure, and the nuclear quadrupole coupling constants [65]. This data was subsequently used to determine quartic centrifugal distortion constants [66]. An internally hydrogen-bonded gauche conformer, shown in Figure 7.1, was the only conformer observed.

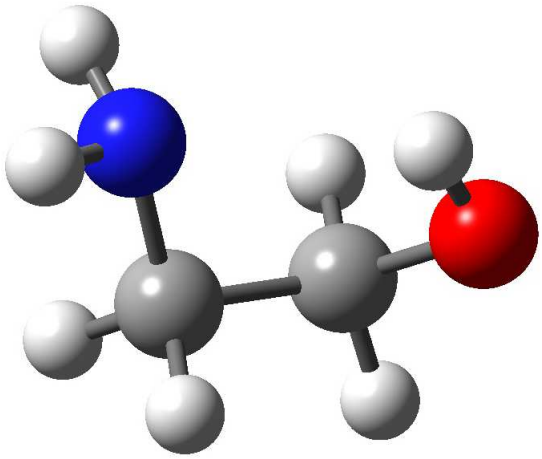


Figure 7.1: The ground state structure of 2-aminoethanol.

Although Penn and Curl made tentative assignments of transitions in excited vibrational states, the vibrational spectrum of aminoethanol had not been characterized at this time. This work was later done by Korolevich *et al.* [67], and all of the fundamental vibrational modes as well as many overtone and combination bands were identified. The work presented here therefore utilizes the nomenclature and vibrational energies determined in this study. Here, the vibrational states of interest are the highest numbered fundamental vibrational modes (i.e., ν_{25}, ν_{26}, and ν_{27}) and their respective overtones and combination bands. The assignments of Penn and Curl can be attributed to the ν_{27} and $2\nu_{27}$ states. These torsionally excited states have vibrational energies below ~ 350 cm^{-1} and are significantly populated at room temperature.

The work presented here includes measurements and analysis of the rotational spectrum of aminoethanol in selected regions from 75 to 305 GHz. Ground state transitions have been identified up to $J = 51$, and additional rotational transitions are assigned for the ν_{25}, ν_{26}, ν_{27}, $\nu_{25} + \nu_{27}$, $2\nu_{27}$, and $\nu_{26} + \nu_{27}$ vibrational states.

7.2 Spectroscopic Studies

7.2.1 Experimental

The experimental apparatus utilized is the JPL flow cell spectrometer. The flow cell and detection methods are outlined in reference [23], and the details of the frequency source and detectors are outlined in Chapter 6.

A sample of liquid aminoethanol (99%) was purchased from Acros for this study. An aminoethanol pressure of approximately 30 mtorr was maintained in the flow cell throughout the duration of the experiment, and all measurements were conducted at room temperature. Computer-automated scans of both increasing and decreasing frequency increments were averaged to eliminate errors due to the time constant of the lock-in amplifier. A sample spectrum is shown in Figure 7.2.1. Linewidths were on the order of 1 MHz. Strong ^{a}R branches are seen at a separation of approximately 11 GHz. No nitrogen hyperfine splitting patterns were observed because of the moderate- and high-J states accessed.

7.2.2 Data Analysis

The data were assigned using the SPFIT and SPCAT programs (see Appendix C, [30]). The lower frequency data of Penn and Curl [65] and a standard asymmetric-top Hamiltonian with the Watson A-reduction were used to generate a predicted spectrum for the molecule in the experimental range. As the new data were assigned, they were continuously added to the data set and processed with the same asymmetric-top Hamiltonian, further modifying the fit. A microwave root mean square deviation was used to indicate the quality of the fit to the entire data set.

A total of 2047 aminoethanol lines, approximately 85 percent of the total lines in the

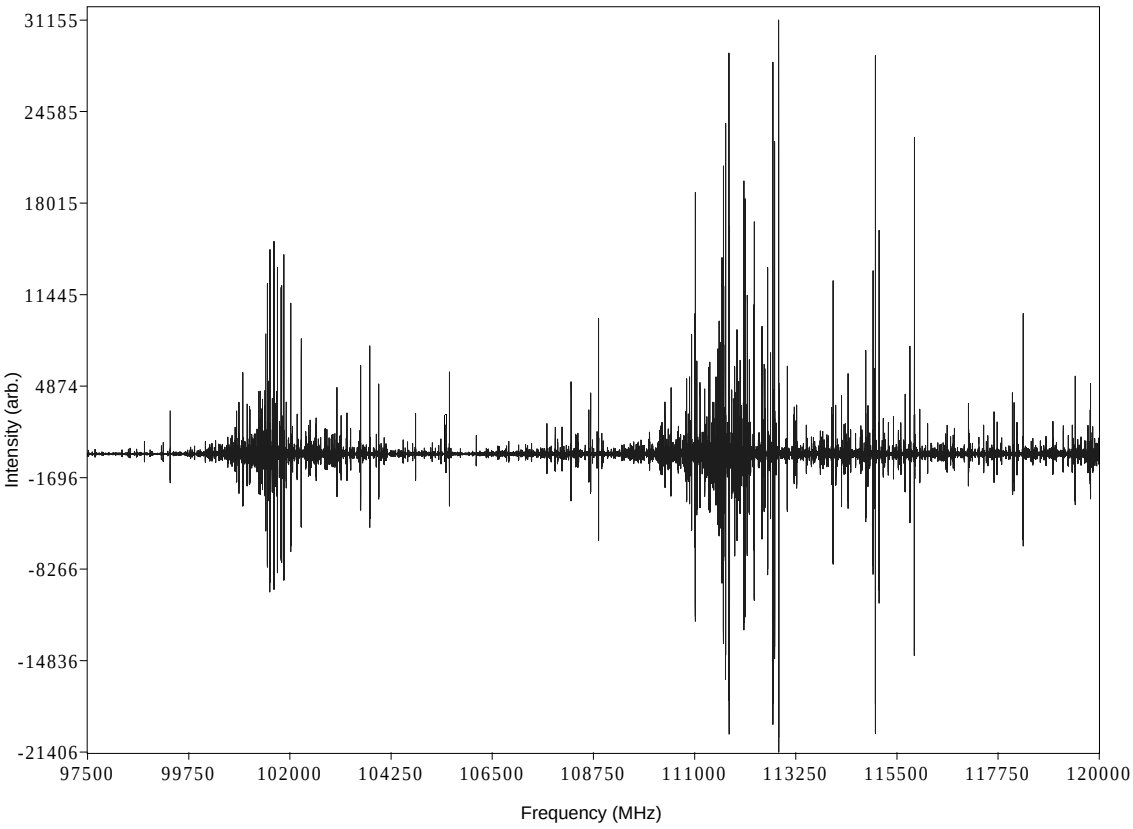


Figure 7.2: The room temperature aminoethanol spectrum from 97 to 120 GHz.

spectrum, have been assigned. The global fit microwave RMS was 113 kHz. Narrower lines could be obtained at reduced pressures of sample, resulting in center frequency accuracies of < 50 kHz, but this modest improvement in accuracy could only be obtained with a dramatic decrease in signal. The ground state assignments were made initially, and quartic and sextic centrifugal distortion constants were determined in addition to standard rotational constants. A total of 528 lines have been assigned to the ground state with a microwave RMS of 84 kHz. Assignments were made for a total of six vibrational states with microwave RMS values between 120 and 143 kHz.

Initial assignments of excited vibrational levels for the fundamental torsional modes were made by comparison of the relative intensities of the ground state to the vibrational

satellites. Subsequent assignment of overtone and combination bands were made by estimation of the rotational constants from those determined for the fundamental modes. The rotational and quartic centrifugal distortion constants were determined independently for each vibrational state, while the sextic distortion constants were determined in a global fit to all vibrational levels and the ground state. The rotational and centrifugal distortion constants determined for each state are listed in Tables 7.1 and 7.2. A separate fit of the ground state, allowing for adjustment of the sextic distortion constants, was performed and the results compared to those obtained in the global fit. Differences between the two fits were less than 3σ for each parameter, indicating that the global fit parameters are accurate values for the ground state.

The files associated with the analysis, including the parameters and rest frequencies, can be found in Appendix I. The output file from the spectral analysis, which includes the observed minus calculated residuals, has been included as supplementary material in the electronic version of this thesis. The assignments and other predicted rotational frequencies are accessible through the submillimeter and microwave spectral line catalog available at `http://spec.jpl.nasa.gov` [30].

7.2.3 Discussion

The rotational spectrum of aminoethanol has been characterized up to 305 GHz. We have extended measurements of ground state transitions and assigned transitions for the ν_{25}, ν_{26}, ν_{27}, $\nu_{25}+\nu_{27}$, $2\nu_{27}$, and $\nu_{26}+\nu_{27}$ vibrational states. Improved rotational, quartic, and sextic centrifugal distortion constants have been determined for these states. Predictions of strong spectral features in the sub-millimeter range are accurate to 1 MHz based on the current analysis. Interpolations throughout the mm-wavelength range are good to < 100

Table 7.1: Spectral parameters determined for the ground and fundamental vibrational states of aminoethanol.

state	gs	ν_{27}	ν_{26}	ν_{25}	
E	0	104	164	305	cm^{-1}
A	14508.72725(97)	14611.09449(107)	14524.58346(256)	14492.42314(117)	MHz
B	5546.49379(41)	5502.57384(43)	5537.51455(48)	5545.55220(44)	MHz
C	4570.48697(40)	4547.55919(42)	4559.95743(46)	4559.70869(43)	MHz
-Δ_J	-6.18488(67)	-6.10549(63)	-6.29271(66)	-6.29079(66)	kHz
-Δ_{JK}	0.02319299(213)	0.02413757(235)	0.02399144(268)	0.02386650(231)	MHz
-Δ_K	-0.0532367(101)	-0.0596786(112)	-0.056270(42)	-0.0541637(111)	MHz
-δ_J	-1.809587(130)	-1.784947(137)	-1.857728(194)	-1.845020(147)	kHz
-δ_K	-0.0106488(40)	-0.0111940(43)	-0.0108574(60)	-0.0104006(46)	MHz
Φ_J	-0.01392(34)				Hz
Φ_{JJK}	0.21413(78)				Hz
Φ_{JKK}	-1.1836(32)				Hz
Φ_K	1.8433(239)				Hz
ϕ_J	-5.7731(312)				mHz
ϕ_{JK}	-0.10649(140)				Hz
# Lines	573	431	254	362	
Fit RMS	0.084	0.143	0.135	0.132	

Note: One σ errors are listed in parentheses in units of last significant figure.
The sextic distortion constants for the ground state were used for all states.

Table 7.2: Spectral parameters determined for overtone and combination vibrational states of aminoethanol.

state	$2\nu_{27}$	$\nu_{26}+\nu_{27}$	$\nu_{25}+\nu_{27}$	
E	208	268	409	cm^{-1}
A	14697.53155(166)	14572.0760(128)	14631.2449(263)	MHz
B	5464.38187(50)	5503.29600(91)	5458.88835(144)	MHz
C	4527.51996(49)	4534.74149(75)	4530.87686(125)	MHz
$-\Delta_J$	-5.83239(65)	-6.29872(152)	-6.31908(179)	kHz
$-\Delta_{JK}$	0.02356607(303)	0.0250314(94)	0.0250497(129)	MHz
$-\Delta_K$	-0.0609136(146)	-0.100906(265)	-0.06804(183)	MHz
$-\delta_J$	-1.703411(210)	-1.87721(66)	-1.85843(89)	kHz
$-\delta_K$	-0.0118742(68)	-0.013395(39)	-0.012183(47)	MHz
# Lines	238	101	88	
Fit RMS	0.120	0.127	0.150	MHz

Note: One σ errors are listed in parentheses in units of last significant figure.
The sextic distortion constants for the ground state were used for all states.

kHz. The remaining unassigned transitions are all significantly weaker than the ground and lower vibrational states. Some partial assignments may be attributed to the combination $\nu_{26}+\nu_{25}$ (369 cm^{-1}) or the $3\nu_{27}$ (312 cm^{-1}) and $2\nu_{26}$ (328 cm^{-1}) overtones. It appears that these states, which lie between 300 and 400 cm^{-1}, are perturbed from the regular asymmetric top energy levels. Analysis of these states is beyond the scope of the present work.

7.3 Observational Studies

The laboratory studies of aminoethanol provided the necessary information to guide observational searches for this species. These searches were conducted with the CSO and OVRO observatories. No lines were detected for this molecule with either observatory, but upper limits for the column density have been calculated from the astronomical data. The observations and results are outlined below.

7.3.1 CSO Observations

7.3.1.1 Observations

Searches for aminoethanol in the Sgr B2(N-LMH), Orion Compact Ridge, and W51e2 sources were conducted with the CSO using the 230 GHz DSB heterodyne receiver on the nights of 2002 October 11–14 and 2004 July 3–5. Spectral windows corresponding to the frequencies of two aminoethanol lines were observed in each source, and the parameters for these lines, specifically the transition quantum numbers, rest frequencies, Einstein A-coefficients times the upper state degeneracy, and upper state energies, are listed in Table 7.3. All observed lines are asymmetry doublets whose transitions occur within the ground vibrational state. Typical system temperatures ranged from 200-600 K, and the source positions and velocities selected were $\alpha(1950)=17^h\ 44^m\ 10^s.1$, $\delta(1950)$= -28° 21′ 17″ and 64 km/s for the Sgr B2(N-LMH) hot core, $\alpha(2000)=05^h\ 35^m\ 14^s.5$, $\delta(2000)$= -05° 22′ 30″.4 and 9 km/s for the Orion Compact Ridge, and $\alpha(1950)=19^h\ 23^m\ 43^s.5$, $\delta(1950)$= 14° 30′ 34″ and 55 km/s for the W51e2 hot core. The chopping secondary with a 70″ throw was used along with chopper-wheel calibration and the facility 1.5 GHz, 500 MHz, and 50 MHz AOS back ends to minimize the spectral baseline fluctuations. The FWHM of the CSO at these frequencies is ∼30″, and all data are placed on the T_{MB} temperature scale using a main beam efficiency of 70%.

7.3.1.2 Results

No transitions were detected in any of the sources observed, and so the column density upper limit was calculated from the observed spectral intensity at the expected line position, which was placed on the T_{MB} temperature scale using a main beam efficiency of 70%. These limits are presented in Table 7.3. A linewidth of 5 km/s and a rotational temperature of 150

Table 7.3: Aminoethanol column density upper limits in Orion, W51, and Sgr B2 from CSO observations.

$J'_{K'_a,K'_c}$–$J''_{K''_a,K''_c}$	ν_0^a (MHz)	$Ag_u\times10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit [c] ($\times10^{-13}$ cm^{-2})
Orion					
$26_{1,25} \rightarrow 25_{1,24}$	246825.322	3.1364	165.04	0.05(2)	3.03(42)
$26_{2,25} \rightarrow 25_{2,24}$		3.1364	165.04		
$27_{0,27} \rightarrow 26_{0,26}$	249709.769	7.5484	169.66	0.20(2)	5.15(71)
$27_{1,27} \rightarrow 26_{1,26}$		7.5484	169.66		
W51e2					
$27_{0,27} \rightarrow 26_{0,26}$	249709.769	7.5484	169.66	0.03(2)	1.33(31)
$27_{1,27} \rightarrow 26_{1,26}$		7.5484	169.66		
$28_{0,28} \rightarrow 27_{0,27}$	258826.376	8.7195	182.08	0.08(2)	7.34(74)
$28_{1,28} \rightarrow 27_{1,27}$		8.7195	182.08		
Sgr B2(N-LMH)					
$27_{0,27} \rightarrow 26_{0,26}$	249709.769	7.5484	169.66	0.063(5)	2.96(30)
$27_{1,27} \rightarrow 26_{1,26}$		7.5484	169.66		
$28_{0,28} \rightarrow 27_{0,27}$	258826.376	8.7195	182.08	0.030(5)	5.90(14)
$28_{1,28} \rightarrow 27_{1,27}$		8.7195	182.08		

[a] One σ uncertainties are 0.1 MHz.
[b] Assumed uncertainties are listed in parentheses in units of last significant figure.
[c] One σ uncertainties are listed in parentheses in units of last significant figure.

K, typical values observed for species in the Compact Ridge, were assumed for the Orion calculations [25]. A line width of 10 km/s and a rotational temperature of 100 K, the values found for methyl cyanide in the W51e2 source, were assumed for the W51e2 calculations [42]. A line width of 10 km/s, the approximate linewidth observed for dihydroxyacetone in the Sgr B2(N-LMH) source (see Section 4.4), and a rotational temperature of 200 K, the most

commonly quoted temperature for this source [28], were assumed for the Sgr calculations. The vibrational state contributions to the partition function were included in this analysis.

7.3.2 OVRO Observations

7.3.2.1 Observations

Searches for aminoethanol in the Orion and W51e2 sources were conducted with the OVRO Millimeter Array between 2001 October 1–November 4. The source positions used were $\alpha(2000)=05^h\ 35^m\ 14^s.5$, $\delta(2000)=$ -05° 22′ 30″.4 for Orion, which is coincident with the Orion Compact Ridge source, and $\alpha(2000)=19^h\ 23^m\ 43^s.9$, $\delta(2000)=$ 14° 30′ 34″.0 for W51e2. The source velocities used were 9 and 55 km/s, respectively. These observations were conducted in the L and C configurations. Each source was observed for approximately 8 hours in each full track, and one track in each configuration was completed for Orion, while two half tracks in each configuration were completed for W51e2. Two aminoethanol lines were observed simultaneously, and the parameters for these lines, specifically the vibrational ground state transition quantum numbers, rest frequencies, Einstein A-coefficients times the upper state degeneracy, and upper state energies, are listed in Table 7.4. The beam sizes for these observations were 6″.8×4″.8 and 5.″6×4″.5 for Orion and W51e2, respectively. The quasars 3C84, 3C345, and 3C454.3 were observed for flux and bandpass calibration, and observations of Uranus were conducted for bootstrapping the quasar fluxes. Observations of phase and amplitude calibrators were conducted in approximately half hour intervals throughout the tracks.

Table 7.4: Aminoethanol column density upper limits in Orion and W51 from OVRO observations.

$J'_{K'_a,K'_c}$–$J''_{K''_a,K''_c}$	ν_0^a (MHz)	$Ag_u\times10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit [c] ($\times10^{-13}$ cm^{-2})
Orion					
$12_{1,12} \rightarrow 11_{1,11}$	112742.2238	0.1386	35.94	0.27(9)	5.05(68)
$11_{4,7} \rightarrow 10_{4,6}$	112779.8117	0.1118	39.52	0.45(9)	10.4(14)
W51e2					
$12_{1,12} \rightarrow 11_{1,11}$	112742.2238	0.1386	35.94	0.59(13)	89.5(185)
$11_{4,7} \rightarrow 10_{4,6}$	112779.8117	0.1118	39.52	0.52(13)	99.8(206)

[a] One σ uncertainties are 0.1 MHz.
[b] Uncertainties are listed in parentheses in units of last significant figure and are based on an assumed flux uncertainty of ±0.02 Jy/Beam.
[c] One σ uncertainties are listed in parentheses in units of last significant figure.

7.3.2.2 Results

Boxcar fits to an internal noise source modified by second order polynomial fits to observations of the quasars were used for bandpass calibration. The quasars were also used to establish the flux density scale, with fluxes bootstrapped from observations of Uranus. Bandpass, phase, and flux calibrations were applied to the data with the MMA software package [43]. The MIRIAD data reduction software package [44] was used for subsequent spectral analysis. Neither transition was observed in either source, and so the column density upper limits were calculated as described for the CSO observations. The calculated aminoethanol column density upper limits are presented in Table 7.4.

7.3.3 Discussion

The upper limit for the aminoethanol column density in the Orion Compact Ridge, W51e2, and Sgr B2(N-LMH) hot core sources is on the order of $\sim 3\times10^{13}$ cm^{-2} for an extended source and $\sim 9\times10^{14}$ cm^{-2} for a compact source. Aminoethanol is expected to be present in amounts similar to those observed for ethanol if it is formed by the simple grain surface mechanisms proposed in reference [3]. Ethanol column densities in these sources are on the order of $\sim 10^{15}$ cm^{-2} [24, 68]. Emission from ethanol is extended in the Orion and Sgr clouds, and similar behavior would be expected for aminoethanol if it was formed by a similar process [18, 68]. Grain surface formation pathways should therefore be reinvestigated, as the aminoethanol upper limits found here are two orders of magnitude below the expected levels. The only mechanism that has been proposed for the interstellar formation of amino acids involves gas phase ion-molecule reactions of aminoalcohols [3], and so these results call into question the viability of amino acid formation in hot cores.

Chapter 8

Conclusions and Implications for Interstellar Chemistry

The studies presented in this thesis involve the rotational spectroscopic characterization of and observational searches for several key prebiotic molecules. A summary of the results of these studies and a discussion of their implications and future applications are presented below.

8.1 Laboratory Rotational Spectroscopy

Combined studies using the original Fourier Transform Microwave Spectrometer and the Caltech and JPL Direct Absorption Flow Dell Spectrometers were conducted to obtain the microwave, millimeter, and submillimeter spectra of several key prebiotic species. The CALPGM program suite and the SMAP spectral analysis program were then used to assign these data and determine the spectroscopic parameters for each species.

The ground and first four vibrational states of the 3C ketose, dihydroxyacetone, are now characterized up to 450 GHz. The spectral analysis of its 3C structural isomer, dimethyl carbonate, was quite limited because of the weak nature of the spectrum, but the K_a=0, 1 lines of this species have been assigned up to 360 GHz. In the case of another 3C structural

isomer, methyl glycolate, full characterization of the ground state up to 360 GHz has been completed. The analyses of dimethyl carbonate and methyl glycolate present challenges to current internal rotation models. Additional higher sensitivity laboratory investigation of dimethyl carbonate is required, and the results of such a study might enable a more complete model to be developed. In addition, assignments of the pure rotational lines in the many torsional states of methyl glycolate should be completed.

The pure rotational analysis of the ground and first three vibrational states of the 2C α-hydroxy aldehyde, glycolaldehyde, has also been completed for frequencies up to 354 GHz. A similar analysis to 305 GHz has been completed for the second most complex aminoalcohol, aminoethanol, which is a predicted interstellar grain surface product and the suspected precursor to the amino acid alanine.

The information gained in these studies was used to guide subsequent observational searches, the results of which are discussed in the next section. The vibrational state analyses also provided the necessary information to determine accurate partition functions for these molecules. It is clear from the dihydroxyacetone and glycolaldehyde studies that the vibrational state contribution to the partition functions of such complex molecules is significant, and these results will influence future such calculations in observational astronomy.

The results of the microwave/millimeter-wave studies will be used as a starting point for further characterization of these types of molecules in the THz spectral range as appropriate laboratory techniques are developed. THz laboratory work will provide the necessary information to guide searches with the CASIMIR instrument on the SOFIA observatory and the HIFI instrument on the Herschel Observatory. Species such as those studied here often have much stronger torsional bands than rotational bands, and so observational searches

for molecules such as dimethyl carbonate may indeed become possible with these new high frequency instruments if the appropriate spectral information is available.

8.2 Observational Astronomy

The results of the laboratory studies were used to guide observational searches for these species with the CSO, OVRO, and GBT observatories. Glycolaldehyde was previously detected in the Sgr B2(N-LMH) hot core, and so no searches for this species were conducted.

The key result of the CSO searches in particular is the first observational evidence for an interstellar ketose, dihydroxyacetone, which was detected at a higher column density than any other similarly complex species previously observed in the Sgr B2(N-LMH) hot core. The rotational temperature and line center velocities imply that this emission arises from the hot core rather than from the cooler extended envelope. Attempts at imaging this emission were unsuccessful, but more sensitive studies will be conducted after commissioning of the CARMA observatory. The sensitivity level required for confirming GBT observations of low-energy transitions was not reached. The nine lines observed with the CSO make a strong case for the presence of this species, but these results must be confirmed before a definitive detection can be claimed.

The more stable 3C structural isomers are expected to be formed by any process leading to dihydroxyacetone. Searches are planned for dimethyl carbonate and methyl glycolate, but no observations have been completed at this time. Lines that could be attributed to methyl glycolate were observed in a 3 mm survey of the Sgr B2(N-LMH) source, however, and a preliminary analysis places this species at an even higher column density than that determined for dihydroxyacetone. The CSO/BIMA results and earlier studies of 2C compounds make it clear that structural isomerism plays an important role in interstellar

chemistry.

Aminoethanol was not detected in any hot core source, and the limits derived for its column density call into question the proposed grain surface pathways leading to its formation. If aminoalcohols are not produced by single-atom addition reactions on grain surfaces, then new interstellar formation pathways for amino acids may be required.

The combined results of the laboratory and observational studies indicate that prebiotic chemistry does indeed achieve high levels of complexity well before incorporation into a parent body. These results raise serious questions about the validity of current interstellar chemical models and imply that complex interstellar chemistry is very poorly understood. The extremely large abundances of the 3C species relative to much simpler species coupled with the lack of observational evidence for one of the simplest predicted grain surface species indicates that current interstellar chemistry models require extensive revision. Chemical pathways that may explain these results do exist, but have not yet been considered for complex interstellar chemistry. These pathways are compared to existing chemical models below, and their implications in light of the conclusions drawn from the work presented here are discussed.

8.3 Implications for Interstellar Chemistry

Early interstellar chemical models considered complex molecule formation on grains [12], but current models for interstellar chemistry rely on both solid and gas phase reactions for the formation of the most complex interstellar organic molecules, which tend to be the simplest examples of various compounds (alcohols, ethers, esters, etc.). There are two main grain surface chemistry mechanisms used in these models, namely radical-radical reactions and single-atom addition reactions. Both classes of models rely on initial single-

atom addition reactions to form simple radicals. The subsequent processing of these radicals is treated quite differently, however, in these two classes of models.

In the first approach, the radicals formed from single-atom addition reactions undergo radical-radical combination to form more complex species (see [69–72]). Many of these higher order reactions are those included in the model by Allen and Robinson [12], but only a subset of the complex reactions included in this earlier work are considered in more recent models. These models assume that these species are in constant flux with the gas phase, where they can undergo ion-molecule reactions to form even more complex species. The most recent of these models has also considered photolysis effects on the grain surface chemistry [72], though very little information is provided as to the molecules undergoing photolysis or the branching ratios for the photolysis pathways. Likewise, some of the reactions involving major photolysis products that are included in the earlier grain surface model [12] are not considered in this work.

The second approach for grain surface chemical models involves only single-atom addition reactions. Gas phase reactions in interstellar clouds can efficiently form CO, N_2, O_2, C_2H_2, and C_2H_4, and these species are thought to accrete onto grain surfaces and undergo single-atom addition reactions [3, 73, 74]. Four basic principles developed from the conditions and limitations of grain surface chemistry guide this class of models. Due to the overwhelming abundance of hydrogen in the interstellar medium, it is assumed that the great majority of grain chemistry is driven by the reaction of hydrogen atoms with multiply-bonded molecules and surface radicals. It is also assumed that multiple bonds in any single molecule are broken in order of hydrogen-tunnelling energy barriers, beginning with the lowest barrier. Radical stability is imposed on all intermediates predicted by these reactions, eliminating all reactions with unstable intermediates from appearing in

the model. Also, pathways involving migration or reaction between two radicals are not permitted. Many potential grain surface reaction pathways are eliminated by the conditions imposed, greatly simplifying the possible products of grain synthesis. The simplest case for such a reaction network, as is shown in Figure 8.1, predicts that such a system will not extend in molecular complexity beyond alcohols and aminoalcohols without subsequent gas phase ion-molecule reactions.

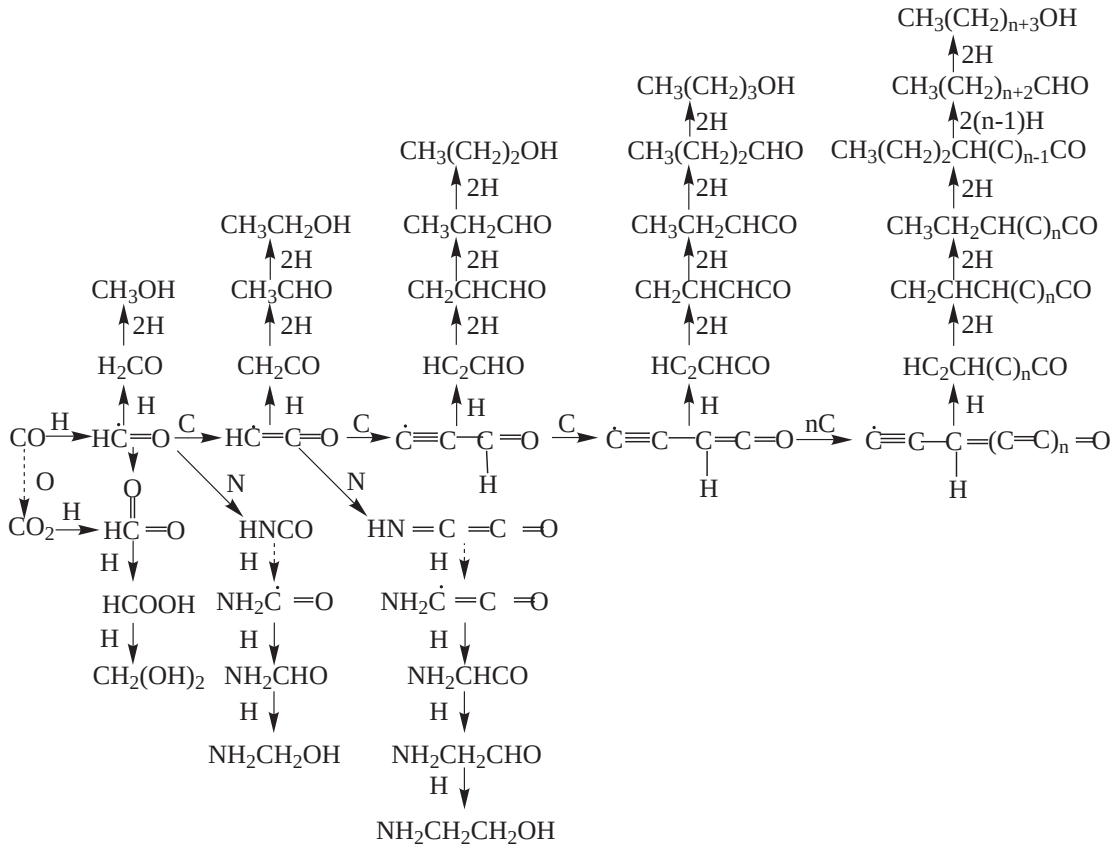


Figure 8.1: The simplest chemical model of grain surface reactions driven by single-atom addition to CO [3].

Both classes of models predict the formation of more complex species by gas phase ion-molecule reactions. It has been shown, however, that such processes are insufficient for the production of such complex organic species as ethanol (CH_3CH_2OH) and methyl formate (CH_3OCHO) [13]. Organics such as acetaldehyde (CH_3CHO), ethanol, methyl formate,

acetic acid (CH_3COOH), and glycolaldehyde (CH_2OHCHO) have also been detected in high abundance in regions of grain mantle disruption and evaporation, suggesting that these species are formed on grain surfaces [15, 18, 19, 75]. The mechanisms for complex molecule production on grains are clearly much more important, and much more complex, than has been recognized.

Recent observational studies, including those presented in Chapters 4 and 5, have offered insight into the mechanisms for grain surface synthesis. The relative hot core abundances of the 2C structural isomers methyl formate, acetic acid, and glycolaldehyde (52:2:1, respectively [16]) indicate that if they form on grains it is not from kinetically-controlled single-atom addition reactions. Likewise, the 3C aldose sugar, glyceraldehyde ($CH_2OHCHOHCHO$), was not detected in Sgr B2(N-LMH) [76] while the 3C ketose sugar, dihydroxyacetone ($CO(CH_2OH)_2$), was detected in this source (see Chapter 4). Another 3C structural isomer, methyl glycolate ($HOCH_2COOCH_3$), has also been tentatively detected in the Sgr B2(N-LMH) source at twice the abundance of dihydroxyacetone (see Chapter 5). These observed abundances follow the pattern of the relative thermodynamic stability (see Appendix D), with the more stable structural isomers being more abundant. The notable exception to this trend is acetic acid, which is much less abundant than methyl formate but is the most thermodynamically stable of the 2C isomers. Acids undergo esterification reactions in the presence of alcohols, which comprise a large fraction of ice grain surface material. Relative reactivity should therefore also be considered, as the observed abundance of any highly reactive species should be lower than predicted by any simple reaction network.

These results require that new chemical processes be incorporated into existing grain surface chemical models, and the first step toward more accurate models is to consider complex molecule formation. Reactions of the type originally proposed by Allen and

Robinson [12] can lead to the complex organics being sought, but expansion of this original network is required to explain the 3C compounds. Ice grain mantles in dense clouds are known to be comprised primarily of H_2O, CH_3OH, CO, and NH_3, and varying ratios of these species are used in laboratory studies of grain surface chemistry [10]. All of the 2C and 3C species, as well as many others observed in hot cores, can be formed from reactions involving these species and their radical precursors through addition of radicals to carbonyl functional groups. These types of reactions have not been considered in previous grain surface models. *Ab initio* studies have shown that the barriers to radical abstraction of an aldehyde proton are much lower than the barriers to radical addition to the aldehyde group [77]. The aldehyde radicals produced by these abstractions could then undergo further radical-radical combination reactions with other more mobile surface species. It is possible that these types of abstraction and aldehyde radical reactions could lead to a wide array of organics on grain surfaces. A chemical network involving these reactions and its implications for grain surface chemistry are outlined below.

8.3.1 Proposed Grain Surface Chemical Network

The chemical network presented here is based on the photolysis products of the major grain mantle species H_2O, CH_3OH, CO, and NH_3. The photolysis pathways and rates for these species in dense clouds are presented in Table 8.1 [78] and [79]. The photolysis rates for each pathway are determined by the product of the branching ratio and this overall rate. Water photolysis is dominated by the OH pathway, which has branching ratios ranging from 0.9 to 0.99 [80]. Investigation of methanol photolysis branching ratios has only been conducted at a few wavelengths, and only gas phase experiments were conducted in the most quantitative study [81]. The branching ratio for the CH_3O pathway was determined

to be 0.86, but it is not clear if this is applicable for the solid state. *Ab initio* studies indicate that the CH_2OH pathway is the most energetically favored, and so it is possible that it is the secondary photolysis product, but there are no laboratory results to support this hypothesis [82]. Clearly these branching ratios will drastically affect the grain surface chemistry, and laboratory experiments should be conducted to examine methanol photolysis in ices.

Table 8.1: Photolysis pathways and rates for major grain mantle components in dense interstellar clouds at A_v=6.

							Γ_{total} (s^{-1})
NH_3	+	hν	→	NH_2	+	H	3.43×10^{-15}
CH_3OH	+	hν	→	CH_3	+	OH	3.09×10^{-15}
			→	CH_3O	+	H	
			→	CH_2OH	+	H	
H_2O	+	hν	→	H	+	OH	1.22×10^{-14}
			→	O	+	H_2	
CO	+	hν	→	C	+	O	7.61×10^{-20}

While most of the photolysis products listed in Table 8.1 have been included in previous models, reactions involving CH_3O have not been considered in any but the original model by Allen and Robinson [12], and in this case only the simplest reactions were considered. Many higher order reactions involving CH_2OH were also excluded from this and subsequent models. These radicals will play critical roles in grain surface chemistry if they are indeed the primary methanol photolysis products.

Dense clouds are typically at 10 K, and the photolysis products listed in Table 8.1 are mobile on grain surfaces at this temperature. Periodic warm-up events to as high as 50 K are also possible, especially in star forming regions, and the heavier species will become much more mobile at these temperatures. CO reactions are important on grain surfaces,

and these are outlined in Table 8.2. The mobile radical species can also form more complex species through activationless radical-radical reactions such as those outlined in Table 8.3. Aldehydes formed by these reactions could then undergo proton abstraction reactions such as those summarized in Table 8.4. The resultant radicals would not be very mobile on grain surfaces, but the more mobile photolysis products could certainly recombine with these species to produce highly complex products through the reactions shown in Table 8.5. The rate constants for these reactions have been determined by the method outlined in the next section.

Table 8.2: Reactions of CO with surface radicals.

							E_a	k (cm^3/s)	
							(K)	10 K	50 K
OH	+	CO	→	CO_2	+	H	300	1.07×10^{-12}	$6.33\times10^{+00}$
H	+	CO	→	HCO			1000	$6.03\times10^{+06}$	$4.30\times10^{+07}$
O	+	CO	→	CO_2			0	$1.58\times10^{+03}$	$3.75\times10^{+11}$

Table 8.3: Radical-radical reactions between photolysis products and secondary radicals.

					k (cm^3/s)	
					10 K	50 K
H	+	H	→	H_2	$3.83\times10^{+12}$	$2.73\times10^{+13}$
H	+	NH_2	→	NH_3	$1.92\times10^{+12}$	$1.39\times10^{+13}$
H	+	CH_3	→	CH_4	$1.92\times10^{+12}$	$1.37\times10^{+13}$
H	+	OH	→	H_2O	$1.92\times10^{+12}$	$1.37\times10^{+13}$
H	+	CH_3O	→	CH_3OH	$1.92\times10^{+12}$	$1.36\times10^{+13}$
H	+	CH_2OH	→	CH_3OH	$1.92\times10^{+12}$	$1.36\times10^{+13}$
H	+	O	→	OH	$1.92\times10^{+12}$	$1.40\times10^{+13}$
C	+	O	→	CO	$3.41\times10^{+03}$	$7.48\times10^{+11}$
H	+	C	→	CH	$1.92\times10^{+12}$	$1.40\times10^{+13}$
NH_2	+	NH_2	→	NH_2NH_2	$6.24\times10^{+02}$	$5.15\times10^{+11}$
NH_2	+	CH_3	→	NH_2CH_3	$3.12\times10^{+02}$	$3.08\times10^{+11}$
NH_2	+	OH	→	NH_2OH	$3.12\times10^{+02}$	$3.08\times10^{+11}$
NH_2	+	CH_3O	→	NH_2OCH_3	$3.12\times10^{+02}$	$2.59\times10^{+11}$
NH_2	+	CH_2OH	→	NH_2CH_2OH	$3.12\times10^{+02}$	$2.58\times10^{+11}$
CH_3	+	CH_3	→	CH_3CH_3	8.73×10^{-02}	$1.01\times10^{+11}$
CH_3	+	OH	→	CH_3OH	4.57×10^{-02}	$7.76\times10^{+10}$
CH_3	+	CH_3O	→	CH_3OCH_3	4.36×10^{-02}	$5.21\times10^{+10}$
CH_3	+	CH_2OH	→	CH_3CH_2OH	4.36×10^{-02}	$5.07\times10^{+10}$
OH	+	OH	→	HOOH	4.18×10^{-03}	$5.42\times10^{+10}$
OH	+	CH_3O	→	$HOOCH_3$	2.09×10^{-03}	$2.86\times10^{+10}$
OH	+	CH_2OH	→	$HOCH_2OH$	2.09×10^{-03}	$2.72\times10^{+10}$
CH_3O	+	CH_3O	→	CH_3OOCH_3	4.53×10^{-09}	$3.09\times10^{+09}$
CH_3O	+	CH_2OH	→	CH_3OCH_2OH	2.27×10^{-09}	$1.66\times10^{+09}$
CH_2OH	+	CH_2OH	→	$HOCH_2CH_2OH$	6.41×10^{-15}	$2.29\times10^{+08}$
H	+	HCO	→	H_2CO	$1.92\times10^{+12}$	$1.36\times10^{+13}$
NH_2	+	HCO	→	NH_2CHO	$5.14\times10^{+05}$	$1.02\times10^{+12}$
CH_3	+	HCO	→	H_3CCHO	4.36×10^{-02}	$5.56\times10^{+10}$
OH	+	HCO	→	HOCHO	2.09×10^{-03}	$3.21\times10^{+10}$
CH_3O	+	HCO	→	CH_3OCHO	9.26×10^{-07}	$6.56\times10^{+09}$
CH_2OH	+	HCO	→	$HOCH_2CHO$	9.23×10^{-07}	$5.13\times10^{+09}$
HCO	+	HCO	→	OHCCHO	1.85×10^{-06}	$1.00\times10^{+10}$
CH	+	H	→	CH_2	$1.92\times10^{+12}$	$1.45\times10^{+13}$
CH_2	+	H	→	CH_3	$1.92\times10^{+12}$	$1.38\times10^{+13}$

Table 8.4: Aldehyde proton abstraction reactions.

							k (cm^3/s)	
							10 K	50 K
H	+	HCOOH	→	H_2	+	COOH	7.20×10^{-01}	$5.12\times10^{+00}$
NH_2	+	HCOOH	→	NH_3	+	COOH	2.30×10^{-41}	1.90×10^{-32}
CH_3	+	HCOOH	→	CH_4	+	COOH	3.33×10^{-44}	3.86×10^{-32}
OH	+	HCOOH	→	H_2O	+	COOH	1.70×10^{-47}	2.21×10^{-34}
CH_3O	+	HCOOH	→	CH_3OH	+	COOH	3.10×10^{-63}	2.12×10^{-45}
CH_2OH	+	HCOOH	→	CH_3OH	+	COOH	4.38×10^{-69}	1.69×10^{-46}
HCO	+	HCOOH	→	H_2CO	+	COOH	1.53×10^{-59}	8.33×10^{-44}
H	+	H_2CO	→	H_2	+	HCO	8.46×10^{-01}	$6.02\times10^{+00}$
NH_2	+	H_2CO	→	NH_3	+	HCO	1.13×10^{-38}	9.41×10^{-30}
CH_3	+	H_2CO	→	CH_4	+	HCO	1.10×10^{-41}	1.30×10^{-29}
OH	+	H_2CO	→	H_2O	+	HCO	1.24×10^{-44}	1.68×10^{-31}
CH_3O	+	H_2CO	→	CH_3OH	+	HCO	3.71×10^{-58}	3.63×10^{-40}
CH_2OH	+	H_2CO	→	CH_3OH	+	HCO	6.89×10^{-59}	1.72×10^{-40}
H	+	NH_2CHO	→	H_2	+	NH_2CO	7.25×10^{-01}	$5.15\times10^{+00}$
NH_2	+	NH_2CHO	→	NH_3	+	NH_2CO	3.04×10^{-41}	2.51×10^{-32}
CH_3	+	NH_2CHO	→	CH_4	+	NH_2CO	4.32×10^{-44}	5.00×10^{-32}
OH	+	NH_2CHO	→	H_2O	+	NH_2CO	2.29×10^{-47}	2.97×10^{-34}
CH_3O	+	NH_2CHO	→	CH_3OH	+	NH_2CO	5.33×10^{-63}	3.70×10^{-45}
CH_2OH	+	NH_2CHO	→	CH_3OH	+	NH_2CO	7.54×10^{-69}	3.39×10^{-46}
HCO	+	NH_2CHO	→	H_2CO	+	NH_2CO	2.55×10^{-59}	1.39×10^{-43}
H	+	H_3CCHO	→	H_2	+	CH_3CO	7.30×10^{-01}	$5.19\times10^{+00}$
NH_2	+	H_3CCHO	→	NH_3	+	CH_3CO	4.07×10^{-41}	3.36×10^{-32}
CH_3	+	H_3CCHO	→	CH_4	+	CH_3CO	5.66×10^{-44}	6.55×10^{-32}
OH	+	H_3CCHO	→	H_2O	+	CH_3CO	3.12×10^{-47}	4.05×10^{-34}
CH_3O	+	H_3CCHO	→	CH_3OH	+	CH_3CO	9.33×10^{-63}	6.37×10^{-45}
CH_2OH	+	H_3CCHO	→	CH_3OH	+	CH_3CO	1.32×10^{-68}	4.88×10^{-46}
HCO	+	H_3CCHO	→	H_2CO	+	CH_3CO	4.32×10^{-59}	2.35×10^{-43}
H	+	CH_3OCHO	→	H_2	+	CH_3OCO	7.30×10^{-01}	$5.19\times10^{+00}$
NH_2	+	CH_3OCHO	→	NH_3	+	CH_3OCO	9.99×10^{-43}	8.24×10^{-34}
CH_3	+	CH_3OCHO	→	CH_4	+	CH_3OCO	1.80×10^{-45}	2.09×10^{-33}
OH	+	CH_3OCHO	→	H_2O	+	CH_3OCO	5.92×10^{-49}	7.67×10^{-36}
CH_3O	+	CH_3OCHO	→	CH_3OH	+	CH_3OCO	5.80×10^{-66}	3.95×10^{-48}
CH_2OH	+	CH_3OCHO	→	CH_3OH	+	CH_3OCO	8.20×10^{-72}	2.94×10^{-49}
HCO	+	CH_3OCHO	→	H_2CO	+	CH_3OCO	4.23×10^{-62}	2.30×10^{-46}
H	+	$HOCH_2CHO$	→	H_2	+	$HOCH_2CO$	6.73×10^{-01}	$4.78\times10^{+00}$
NH_2	+	$HOCH_2CHO$	→	NH_3	+	$HOCH_2CO$	1.20×10^{-42}	9.91×10^{-34}
CH_3	+	$HOCH_2CHO$	→	CH_4	+	$HOCH_2CO$	2.14×10^{-45}	2.48×10^{-33}
OH	+	$HOCH_2CHO$	→	H_2O	+	$HOCH_2CO$	7.21×10^{-49}	9.34×10^{-36}
CH_3O	+	$HOCH_2CHO$	→	CH_3OH	+	$HOCH_2CO$	8.46×10^{-66}	5.76×10^{-48}
CH_2OH	+	$HOCH_2CHO$	→	CH_3OH	+	$HOCH_2CO$	1.20×10^{-71}	4.28×10^{-49}
HCO	+	$HOCH_2CHO$	→	H_2CO	+	$HOCH_2CO$	6.02×10^{-62}	3.27×10^{-46}

Table 8.5: Aldehyde radical recombination reactions.

					k (cm^3/s)	
					10 K	50 K
H	+	NH_2CO	→	NH_2CHO	$1.92\times10^{+12}$	$1.36\times10^{+13}$
NH_2	+	NH_2CO	→	NH_2CONH_2	$3.12\times10^{+02}$	$2.58\times10^{+11}$
CH_3	+	NH_2CO	→	NH_2COCH_3	4.36×10^{-02}	$5.08\times10^{+10}$
OH	+	NH_2CO	→	NH_2COOH	2.09×10^{-03}	$2.74\times10^{+10}$
CH_3O	+	NH_2CO	→	NH_2COOCH_3	2.27×10^{-09}	$1.85\times10^{+09}$
CH_2OH	+	NH_2CO	→	NH_2COCH_2OH	1.08×10^{-12}	$4.22\times10^{+08}$
HCO	+	NH_2CO	→	NH_2COCHO	9.23×10^{-07}	$5.33\times10^{+09}$
H	+	CH_3CO	→	CH_3CHO	$1.92\times10^{+12}$	$1.36\times10^{+13}$
NH_2	+	CH_3CO	→	CH_3CONH_2	$3.12\times10^{+02}$	$2.58\times10^{+11}$
CH_3	+	CH_3CO	→	CH_3COCH_3	4.36×10^{-02}	$5.06\times10^{+10}$
OH	+	CH_3CO	→	CH_3COOH	2.09×10^{-03}	$2.71\times10^{+10}$
CH_3O	+	CH_3CO	→	CH_3COOCH_3	2.27×10^{-09}	$1.57\times10^{+09}$
CH_2OH	+	CH_3CO	→	CH_3COCH_2OH	3.21×10^{-15}	$1.45\times10^{+08}$
HCO	+	CH_3CO	→	CH_3COCHO	9.23×10^{-07}	$5.05\times10^{+09}$
H	+	CH_3OCO	→	CH_3OCHO	$1.92\times10^{+12}$	$1.36\times10^{+13}$
NH_2	+	CH_3OCO	→	CH_3OCONH_2	$3.12\times10^{+02}$	$2.58\times10^{+11}$
CH_3	+	CH_3OCO	→	CH_3OCOCH_3	4.36×10^{-02}	$5.05\times10^{+10}$
OH	+	CH_3OCO	→	CH_3OCOOH	2.09×10^{-03}	$2.71\times10^{+10}$
CH_3O	+	CH_3OCO	→	$CH_3OCOOCH_3$	2.27×10^{-09}	$1.54\times10^{+09}$
CH_2OH	+	CH_3OCO	→	CH_3OCOCH_2OH	3.20×10^{-15}	$1.15\times10^{+08}$
HCO	+	CH_3OCO	→	$CH_3OCOCHO$	9.23×10^{-07}	$5.02\times10^{+09}$
H	+	$HOCH_2CO$	→	$HOCH_2CHO$	$1.92\times10^{+12}$	$1.36\times10^{+13}$
NH_2	+	$HOCH_2CO$	→	$HOCH_2CONH_2$	$3.12\times10^{+02}$	$2.58\times10^{+11}$
CH_3	+	$HOCH_2CO$	→	$HOCH_2COCH_3$	4.36×10^{-02}	$5.05\times10^{+10}$
OH	+	$HOCH_2CO$	→	$HOCH_2COOH$	2.09×10^{-03}	$2.71\times10^{+10}$
CH_3O	+	$HOCH_2CO$	→	$HOCH_2COOCH_3$	2.27×10^{-09}	$1.54\times10^{+09}$
CH_2OH	+	$HOCH_2CO$	→	$HOCH_2COCH_2OH$	3.20×10^{-15}	$1.15\times10^{+08}$
HCO	+	$HOCH_2CO$	→	$HOCH_2COCHO$	9.23×10^{-07}	$5.02\times10^{+09}$
H	+	COOH	→	HCOOH	$1.92\times10^{+12}$	$1.36\times10^{+13}$
NH_2	+	COOH	→	NH_2COOH	$3.12\times10^{+02}$	$2.58\times10^{+11}$
CH_3	+	COOH	→	CH_3COOH	4.36×10^{-02}	$5.08\times10^{+10}$
OH	+	COOH	→	HOCOOH	2.09×10^{-03}	$2.73\times10^{+10}$
CH_3O	+	COOH	→	CH_3OCOOH	2.27×10^{-09}	$1.77\times10^{+09}$
CH_2OH	+	COOH	→	$HOCH_2COOH$	2.41×10^{-13}	$3.42\times10^{+08}$
HCO	+	COOH	→	OHCCOOH	9.23×10^{-07}	$5.25\times10^{+09}$

8.3.2 Determination of the Rate Constants

The rate constants for these reactions were derived in the manner outlined in reference [69] and depend on the diffusion rates, R_{diff}, of the two species involved. R_{diff} is the inverse of the diffusion time, t_{diff}, which is equal to the product of the hopping time, t_{hop}, and the density of surface sites on the grain, N_s ($\sim 10^6$). The hopping time can be determined by the relationship

$$t_{hop} = \nu_0^{-1} e^{E_b/kT} \tag{8.1}$$

where ν_0 is the characteristic vibrational frequency for the adsorbed species, E_b is the potential energy barrier between adjacent surface potential energy wells, k is the Boltzmann constant, and T is the temperature of the grain. E_b is approximated as $0.3E_D$, the barrier to diffusion, and ν_0 is also related to this quantity by the equation:

$$\nu_0 = (2n_s E_D/\pi^2 m)^{1/2} \tag{8.2}$$

where m is the mass of the species, and n_s is the surface density of sites ($\sim 1.5\times 10^{15}$ cm^{-2}). R_{diff} can therefore be determined by the relationship:

$$R_{diff} = \frac{(2n_s E_D/\pi^2 m)^{1/2} e^{-0.3E_D/kT}}{N_s} \tag{8.3}$$

The rate coefficient for the reaction between two species, k_{ij}, can be determined by the relationship:

$$k_{ij} = \kappa_{ij} \frac{R_{diff,i} + R_{diff,j}}{n_d} \tag{8.4}$$

where n_d is the number density of grains ($\sim 2.66 \times 10^{-7}$ cm^{-3}) and κ_{ij} is the probability for the reaction to occur. This probability is unity for a reaction with no activation barrier, such as radical-radical combination reactions. For a reaction with activation energy E_a, κ_{ij} is expressed as:

$$\kappa_{ij} = e^{-2a/\hbar(2\mu E_a)^{1/2}} \tag{8.5}$$

which is the exponential portion of the probability for quantum mechanical tunneling through a barrier of thickness a (1 Å).

Higher temperatures may be required to initiate more complex reactions on the grain surface since the heavier radicals will become more mobile at these temperatures. The diffusion barriers from references [12] and [69] were used to determine the diffusion rates at 10 and 50 K for the photolysis radicals as well as aldehyde radicals, and these values are presented in Table 8.6. All aldehyde proton abstraction barriers are estimated to be 5030 K (10 kcal/mol), which is the upper threshold for the barriers determined in the *ab initio* studies [77].

The reaction rates at 10 and 50 K were calculated from this information and are presented in Tables 8.2–8.5.

8.3.3 Discussion

The diffusion rates shown in Table 8.6 indicate that the simpler photolysis products will dominate grain surface chemistry at low temperatures. H will clearly be the most mobile species on grain surfaces, and so it is likely to immediately react with any radical produced during photolysis at 10 K. This mechanism indicates a buildup of simple species such as CH_3OH, H_2O, CH_4, NH_3, and H_2CO on cold grain surfaces, a conclusion

Table 8.6: Diffusion barriers and rates for reactive surface species.

	E_D (kcal/mol)	E_D (K)	R_{diff} (s^{-1}) 10 K	50 K
H	0.7	350	$5.100\times10^{+04}$	$3.62\times10^{+05}$
C	1.6	800	4.855×10^{-05}	$1.07\times10^{+04}$
O	1.6	800	4.207×10^{-05}	$9.24\times10^{+03}$
CH	1.3	654	3.377×10^{-03}	$2.22\times10^{+04}$
CH_2	1.9	956	4.581×10^{-07}	$4.23\times10^{+03}$
CO	2.4	1207	1.920×10^{-10}	$7.44\times10^{+02}$
OH	2.5	1258	5.557×10^{-11}	$7.20\times10^{+02}$
HCO	3.0	1509	2.456×10^{-14}	$1.34\times10^{+02}$
NH_2	1.7	855	8.302×10^{-06}	$6.85\times10^{+03}$
CH_3	2.3	1157	1.161×10^{-09}	$1.34\times10^{+03}$
CH_3O	3.4	1710	6.030×10^{-17}	$4.11\times10^{+01}$
CH_2OH	4.3	2163	8.523×10^{-23}	$3.05\times10^{+00}$
COOH	4.0	2012	6.324×10^{-21}	$6.04\times10^{+00}$
HCOOH	5.1	2565	4.335×10^{-28}	2.44×10^{-01}
H_2CO	3.5	1761	1.375×10^{-17}	$3.13\times10^{+01}$
NH_2CO	3.9	1962	2.857×10^{-20}	$8.16\times10^{+00}$
CH_3CO	4.7	2364	1.804×10^{-25}	8.10×10^{-01}
CH_3OCO	6.2	3119	2.590×10^{-35}	8.57×10^{-03}
$HOCH_2CO$	6.9	3471	7.032×10^{-40}	1.09×10^{-03}
NH_2CHO	4.7	2364	1.764×10^{-25}	7.91×10^{-01}
CH_3CHO	5.4	2716	4.920×10^{-30}	1.04×10^{-01}
CH_3OCHO	6.5	3270	2.838×10^{-37}	3.52×10^{-03}
$HOCH_2CHO$	7.4	3722	3.838×10^{-43}	2.50×10^{-04}

Note: Quantum tunneling dominates over diffusion for H at 10 K, and so the H tunneling rate is given at this temperature.

reinforced by recent observational studies of interstellar ices, which have abundance ratios of H_2O:CO_2:H_2CO:CO:CH_3OH:NH_3 of 100:18:12:10:8:7 [83].

At 50 K, however, the diffusion rates of the other radicals increase significantly, and so more complex species could form in this type of environment if the diffusion rates are comparable to the arrival rate of H from the gas phase. The hydrogen accretion rate from the gas phase can be calculated by the following equation:

$$dn_{H,grain}/dt = \pi r^2 (2kT/m)^{1/2} n_{H,gas} m \zeta n_g \tag{8.6}$$

The gas phase hydrogen density, $n_{H,gas}$, can be approximated as 2×10^{-4} $n_{T,gas}$, and $n_{T,gas}$ is on the order of $\sim 10^4$ cm^{-3}. A sticking coefficient, ζ, of unity, an average grain radius, r, of 1×10^{-7} m, and a grain density, n_g, of 10^{-12} $n_{T,gas}$ can also be assumed. The flux of H from the gas phase is therefore on the order of 2×10^{-7} s^{-1} at both 10 and 50 K. The 50 K diffusion rates in Table 8.6 of the more complex radicals are indeed higher than this arrival rate, and so complex chemistry involving these species is certainly possible. Indeed, recent observations of UV-processed interstellar ices with the *Spitzer Space Telescope* reveal that HCOOH is enhanced in such regions [84].

The photolysis products presented in Table 8.1 are clearly important in the formation of compounds such as methyl formate and glycolaldehyde as well as all of the 3C compounds, and so their reactions should certainly be included in grain surface models. The 2C structural isomers methyl formate, acetic acid, and glycolaldehyde could indeed form in significant quantities from these processes. Direct comparisons can be made for these simpler species formed from radical-radical combinations using the information derived above and the observed interstellar ratios for the starting material. An analysis of the relative reaction rates of the HCO + radical combination reactions results in the abundance ratios shown in Table 8.7. The branching ratios discussed above were combined with a CH_3 production pathway branching ratio of 0.1 for the purposes of this calculation. The assumption was made here that the available H on the grain surface would be determined by its production from photolysis processes. H will be in steady flux between the grain surface and gas phase, and so this number is an underestimate of the total amount of H on the grain surface. This estimation, however, provides an upper limit for the amount of more complex species that could form in such environments.

This comparison shows that the calculated reaction rate coefficients may in fact be

Table 8.7: Observed and calculated abundance ratios for the products of HCO+radical combination reactions relative to formaldehyde at 50 K. The observed column densities are those determined for Sgr B2(N-LMH).

		$N_T/N_{T,formaldehyde}$	
Formula	Species	Observed	Predicted at 50 K
H_2CO	formaldehyde	1	1
NH_2CHO	formamide	6	1.6×10^{-03}
CH_3CHO	acetaldehyde	21	8.8×10^{-06}
HCOOH	formic acid	0.3	2.3×10^{-03}
CH_3OCHO	methyl formate	4	8.9×10^{-06}
$HOCH_2CHO$	glycolaldehyde	0.1	3.3×10^{-07}

underestimated if the abundance ratios in hot cores are truly linked to grain surface mechanisms. It is likely, however, that the simpler, more reactive species such as formic acid and glycolaldehyde may undergo more complex reactions either on the grain or in the gas phase in the hot core, and so these observed abundances may not truly reflect grain surface composition. Regardless, abstraction pathways are clearly competitive on grain surfaces in warm regions, and these types of reactions should be integrated into current astrochemical models.

It is also likely that the 3C species discussed in this thesis could be formed on grains if abstraction reactions can compete with radical-radical combination reactions and single-atom addition reactions. It is clear from the rates presented in Table 8.4 that hydrogen will dominate both formation and abstraction reactions at both temperatures, so formaldehyde will likely be the dominant product of such channels at 10 K. As is demonstrated by the analysis presented in Table 8.7, however, the other radical reaction channels with HCO are also possible at 50 K, and so other complex aldehydes will likely be present in warmer regions.

The *ab initio* studies of radical-aldehyde interactions indicate that hydrogen abstraction

reactions have much lower barriers than do addition reactions involving the carbonyl group [77]. The hydrogen abstraction routes alone are therefore enough to compete with the single-atom addition reactions considered in other models. Once the aldehyde radicals are formed, these species could recombine with any of the mobile radicals. The products of recombination with hydrogen will be the primary products of these reactions, but the more complex pathways involving heavier radicals are also possible at 50 K. Species such as dihydroxyacetone, dimethyl carbonate, and methyl glycolate may well form from such mechanisms, and an analysis similar to that conducted for the simpler species in Table 8.7 can be used to investigate the predicted relative ratios of these isomers. Such an analysis reveals that the relative ratios of these species should be roughly 1:8300:8000, respectively. These results follow the trend reflected by the observational results, and once again demonstrate the need for aldehyde proton abstraction reactions to be incorporated into grain surface models.

It is clear from these preliminary analyses that grain surface chemistry has the potential to achieve considerable complexity. H addition reactions dominate the grain surface chemistry at low temperature, forming simple species such as water, methanol, and formaldehyde. Photolysis of simple grain mantle constituents leads to the production of surface radicals that can efficiently compete with H addition reactions at warmer temperatures, and so periodic thermal processing of grain mantles will lead to the buildup of more complex species such as formic acid, methyl formate, formamide, acetaldehyde, and glycolaldehyde. Aldehyde proton abstraction reactions can efficiently compete with single-atom addition reactions at both low and high temperatures, and so the mobile radicals can then react with the resultant aldehyde radicals to form more complex species such as those investigated in this thesis. Simpler species will be favored at low temperature, but

these radicals may also be stored in the grain mantle at low temperature and undergo more complex reactions upon grain mantle heating in hot core regions.

8.4 Future Work

The chemical network presented above indicates that complex molecule formation on grains should be reincorporated into interstellar chemistry models. Additional observational studies are required to investigate these revised chemical models once predictions for other complex species are obtained. Definitive observational tests of grain surface chemistry are quite limited, however. Observational searches for complex molecules in interstellar ices are difficult because individual spectral features are unresolvable. In addition, accretion disk regions with high gas phase abundances of complex species are smaller than the spatial resolution of current observatories. This limitation will be overcome upon the commissioning of the Combined Array for Millimeter Astronomy (CARMA) and Atacama Large Millimeter Array (ALMA) observatories over the next several years.

In the meantime, more sensitive studies of hot core sources combined with the direct study of grain mantle species in regions of grain mantle disruption are required. The first investigations of hot corinos, where the dynamical timescales are short and gas phase material remains primarily unprocessed, show a similar level of molecular complexity to high mass hot cores (see references [75] and [2]). Likewise, investigation of shocked regions in the Galactic Center also indicates large column densities of grain mantle material (see reference [18]).

Deep, broadband surveys of the Orion Compact Ridge and Sgr B2(N-LMH) sources are underway with a new 4 GHz IF bandwidth 1.3 mm SIS receiver at the CSO, and such studies should provide the spectral information necessary to identify previously undetected

complex species. A double sideband spectrum of the Orion Compact Ridge, the first result of this survey, is shown in Figure 8.2. It must be stressed that this spectrum is preliminary, as it has not been fully temperature or frequency calibrated. An RMS level on the order of 20 mK was reached with these observations, however, and the spectral line density at this sensitivity level is clearly quite high.

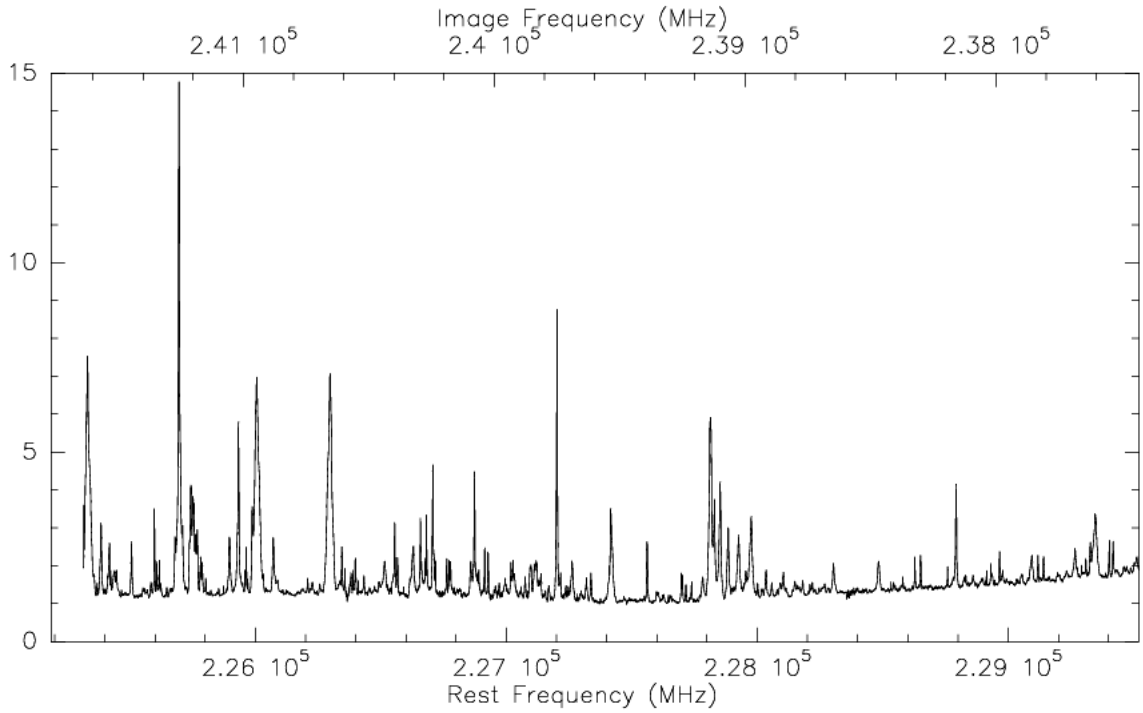


Figure 8.2: Initial results from a deep broadband line survey of the Orion Compact Ridge. The temperature and frequency calibrations are preliminary, but the RMS level is ∼20 mK.

Similar, if not more complicated, spectra are expected from the CASIMIR instrument on SOFIA and the HIFI instrument on the Herschel Observatory. Laboratory investigations to support these observations are also extremely important, and so experiments such as those detailed in this work should be continued for other complex molecules of interest. The laboratory spectral information available in the frequency ranges of these instruments is also quite limited, and so further THz studies are required to support these observations.

Appendix A

Flygare Operation

A.1 Instrumentation

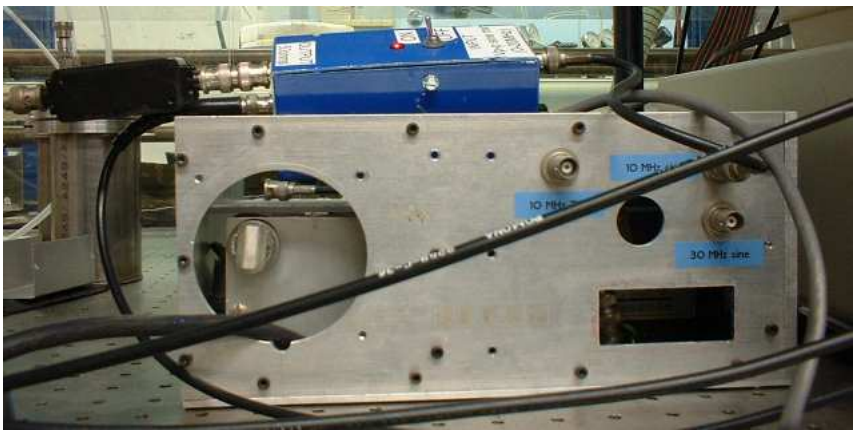
The original FTMW instrument was moved to the Blake labs at Caltech in September 2000. Most of the instrumentation is that from the most recent upgrade of the spectrometer, which was performed by Dr. Tryggvi Emilsson and colleagues at the University of Illinois [21]. While much of the original instrumentation is still in use, some components have been upgraded, and more upgrades are planned for the near future. While many previous publications have described the specific instrumentation used with this instrument, none have presented the general operating procedures. This appendix is therefore a detailed outline for general use of this specific instrument and assumes a general knowledge of FTMW principles. Reference [21] should be consulted for more detailed information on the instrumentation, and the general FTMW principles are outlined in reference [20].

An FTMW instrument involves a pulsed molecular source and a pulsed microwave source. When an experiment begins, a valve is triggered, expanding a pulse of gas into the cavity. This expansion can occur either transversely or coaxially to the incident radiation (there are gate valves that act as pulsed valve feedthroughs at both the top and side of the instrument). A train of 16 microwave pulses is fired for each gas shot. The sample

resides in the cavity for a finite amount of time, and the length of and spacing between the microwave pulses determines the extent to which each sample pulse is probed. The switch to the detector is closed when a microwave pulse is fired, and this switch remains closed until the majority of the radiation in the cavity has rung down. The molecules are excited by the radiation pulse, and the molecules de-excite to the ground state and emit radiation at their resonant frequencies. This emission occurs after the cavity has rung down, and the free induction decay is monitored by the detector.

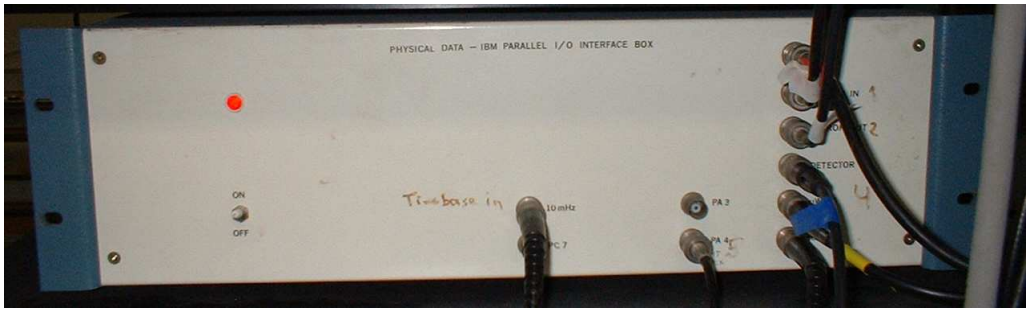
A.1.1 Instrument Control System

A very precise time base is required for control of each of the experimental aspects. This time base is provided by a rubidium clock that is housed in the metal box shown in the bottom of the picture below. This clock produces a 10 MHz sine wave signal that is then converted to two output signals by the blue filter box that is located on the top of the rubidium clock housing. The signals produced are a 30 MHz sine wave and a 10 MHz TTL pulse.



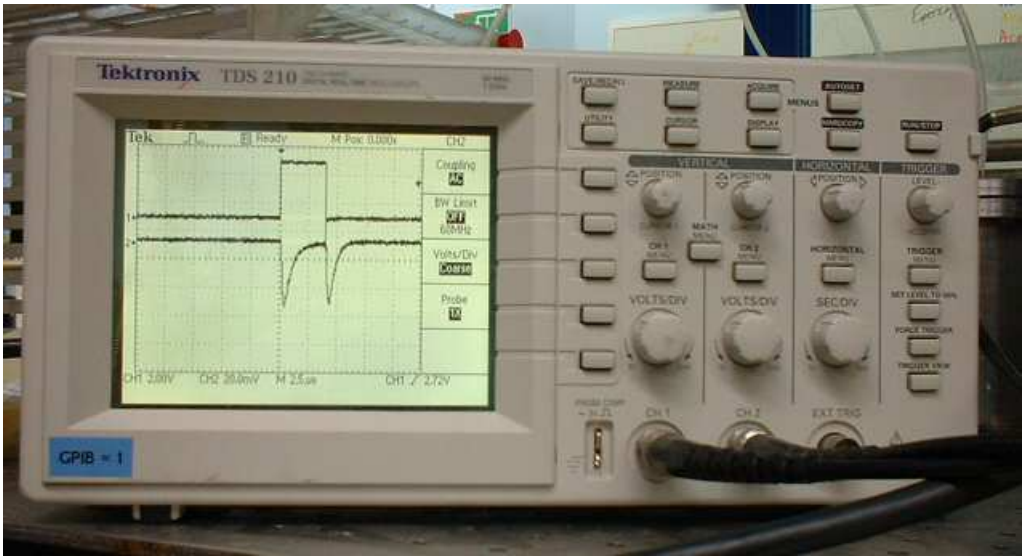
The 10 MHz TTL pulse is the timing signal for the instrument. This signal is the input to the "Physical Data–IBM Parallel I/O Interface Box," which communicates with

the computer and issues all of the control signals for the valve, mirrors, and microwave switches:



The 'detector' and 'μwave' output signals from the interface box control the switches for the detector and the microwave input into the cavity, respectively.

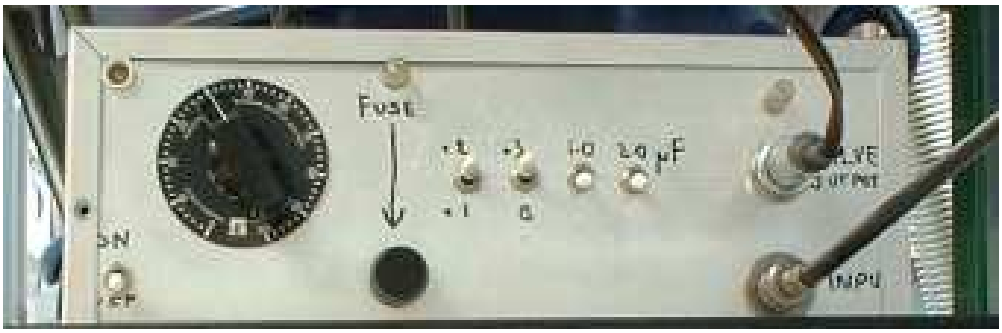
The 'scope' output signal from the interface box is identical to the microwave output signal and is the trigger used by the oscilloscope to monitor the cavity tuning. There are two channels displayed on this oscilloscope, the top signal being the trigger, and the bottom signal being the signal from the cavity:



The signal shape shown here is that observed when the cavity is properly tuned to the MO frequency. The first peak is due to the radiation that is backscattered from the waveguide

and the mirror, while the second peak is due to the cavity ringdown. This wide microwave pulse is not one of the segments of the microwave pulse train, but rather is a signal produced by the spectrometer for the purposes of tuning. The train of microwave pulses can be observed on the oscilloscope if the scaling is changed appropriately.

The 'valve' output signal from the interface box drives the voltage supply for the valve. The rep rate of the valve can be controlled by varying the voltage and capacitance:

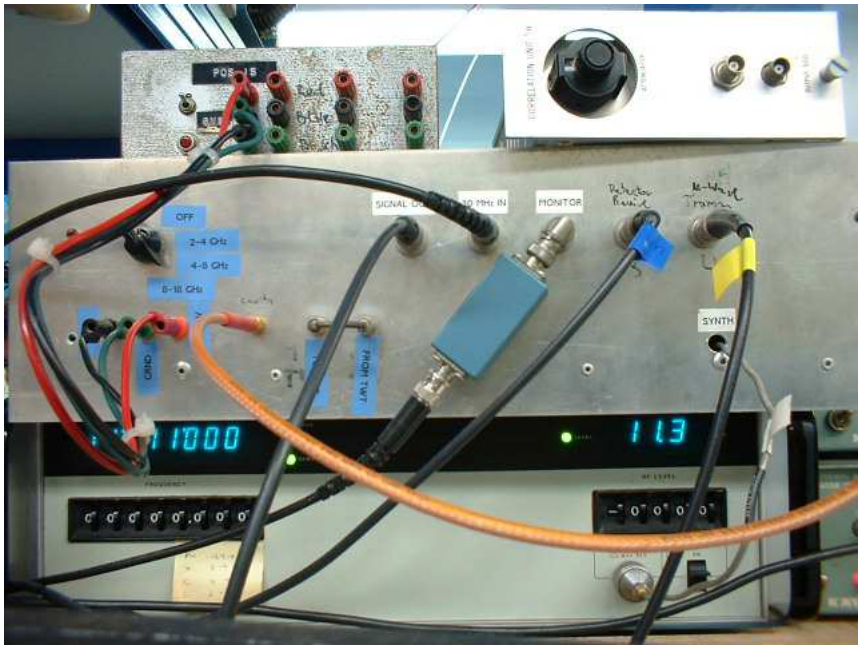


The 'mirror in' and 'mirror out' output signals from the interface box drive the control for the step motor. One of the mirrors can be moved such that the cavity is tuned to the MO frequency. The step motor can also be controlled manually by the switches on the front of this control box:

Amplifiers are used to amplify the 30 MHz sine wave output of the timing circuit and

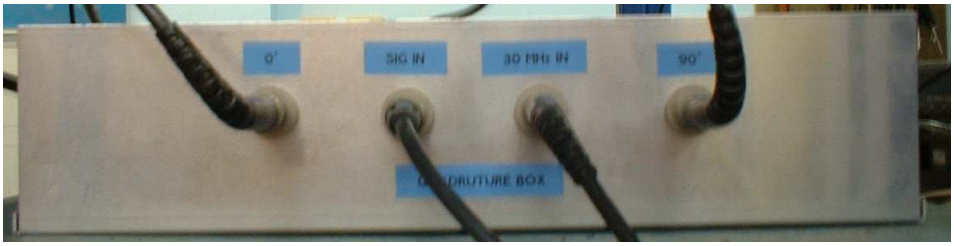
the output signal from the cavity:

The MO signal is produced by the frequency synthesizer, which is the bottom instrument in the picture below. The metal box located on top of the frequency synthesizer contains the switches, detectors, and other microwave components. The power supply for this microwave box is the small box at the top of the equipment rack:



The output signal from the detectors is then routed to the "Quadruture Box," which is

the metal box located at the top of the interface box equipment rack. The quadruture box downconverts the detected signal and sends it to the computer:



A.1.2 Gas Handling and Sample Delivery

The gas handling system is based on the design developed in Illinois [21]. A picture of the mixing manifold is shown below, and a schematic diagram is shown in Figure A.1:

This system involves four mass flow controllers, two of which are high-throughput for carrier gas delivery. The low-throughput flow meters can be used for gas samples or to

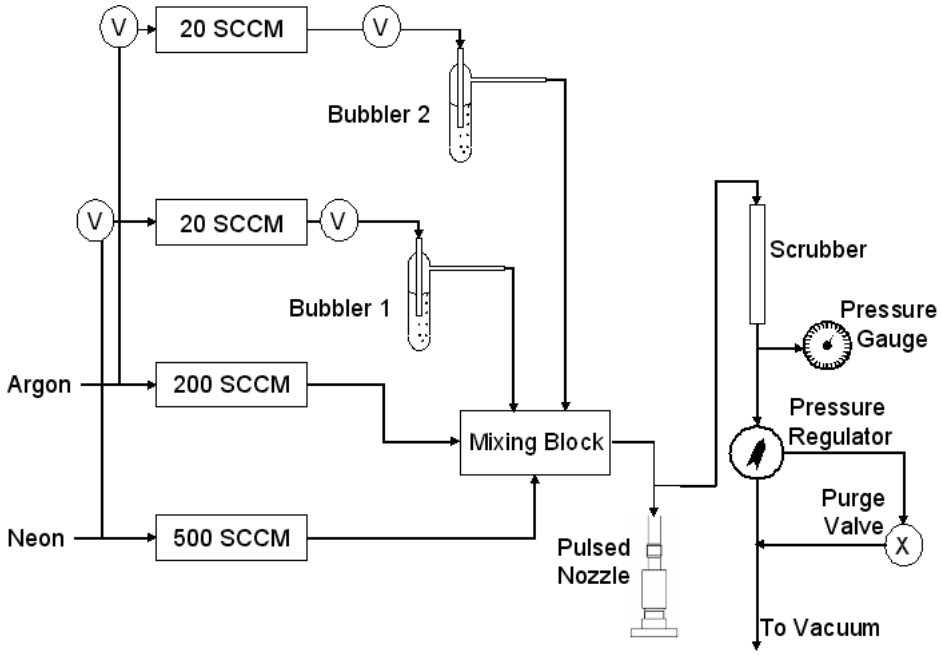


Figure A.1: A schematic diagram of the FTMW mixing manifold.

control the gas delivery to the bubblers for liquid samples. Experiments are typically conducted with flow rates of a few hundred SCCM of carrier gas and less than 10 SCCM of gas through the bubbler. The mass flow meters are controlled by a flow controller:

The valves (V) used in the mixing manifold are Hamilton HV plug valves. The two valves at the input of the flow controllers are four-port flow valves, while the two valves between the flow meters and bubblers are four-port loop valves. Details of the valve design and operation can be found at `http://www.hamiltoncompany.com/product/valve/valves.html`.

Teflon tubing connects the output of the mixing block with the valve. A tee-fitting is connected to the end of the metal valve assembly (described in detail below) with an O-ring fitting. Another O-ring fitting on this tee couples the tubing into the valve assembly. The tubing is inserted such that it is as close to the valve as possible without forming a complete seal. This allows the gas to flow through the tubing and up to the valve. The valve consumes gas when it is running; the excess gas flows around the end of the tubing and back through the valve assembly. The output goes through the scrubber and into the pressure regulator. This regulator is a diaphragm that has a control valve that can be used to adjust the pressure in the line and thus regulate the valve backing pressure. Turning the control valve on the pressure regulator clockwise will increase the backing pressure, turning it counter-clockwise will decrease the pressure, and turning it to a vertical position will hold the backing pressure at the current value. Backing pressures are typically on the order of 1–10 in. Hg above atmospheric pressure (1 in. Hg = 0.0334 atm).

A.1.3 Valve Assemblies

There are currently two valve assemblies that can be used with the instrument, one with six electrical feedthroughs and one with eight electrical feedthroughs. These valve assemblies utilize pulsed General Valves (see `http://www.parker.com/pneutron` for more information). The feedthroughs consist of a 1/4 inch metal tube inside of a 1/2 inch metal tube. Electrical leads for the valve and any accessories run through the space between these two tubes and are held in place with heat shrink. These leads are soldered to electrical feedthroughs that are on a circular metal disk that is welded to the inner tube and sealed to the outer tube by an UltraTorr fitting near the base of the valve. A circular piece of plexiglass with an O-ring groove is connected to the outside of the 1/2 inch tube with an

UltraTorr fitting. This component is free to slide over the length of the tube until the UltraTorr fitting is tightened. A plexiglass tube forms an O-ring seal with the chamber on one end and with this circular component on the other. The valve assembly is placed against this plexiglass tube and positioned at one of the gate valves. This forms a vacuum interlock for insertion and removal of the valve.

A.1.4 Heated Sample Holder

Studies of solid samples often require that the sample be heated such that a sufficient vapor pressure can be maintained. A heated sample holder was developed at Illinois for such studies [21], and a similar sample holder has been constructed at Caltech. A schematic diagram of this sample holder is shown in Figure A.2. This sample holder can be attached to the valve face plate. A carrier gas is pulsed over the sample, and a molecular beam is formed by a Laval nozzle at the exit of the heated compartment. Stainless steel poppets have been constructed for use with this sample holder. A valve face plate press-fit with a Kevlar insert should be used with these poppets. Poppet lifetimes are generally on the order of several weeks with this setup.

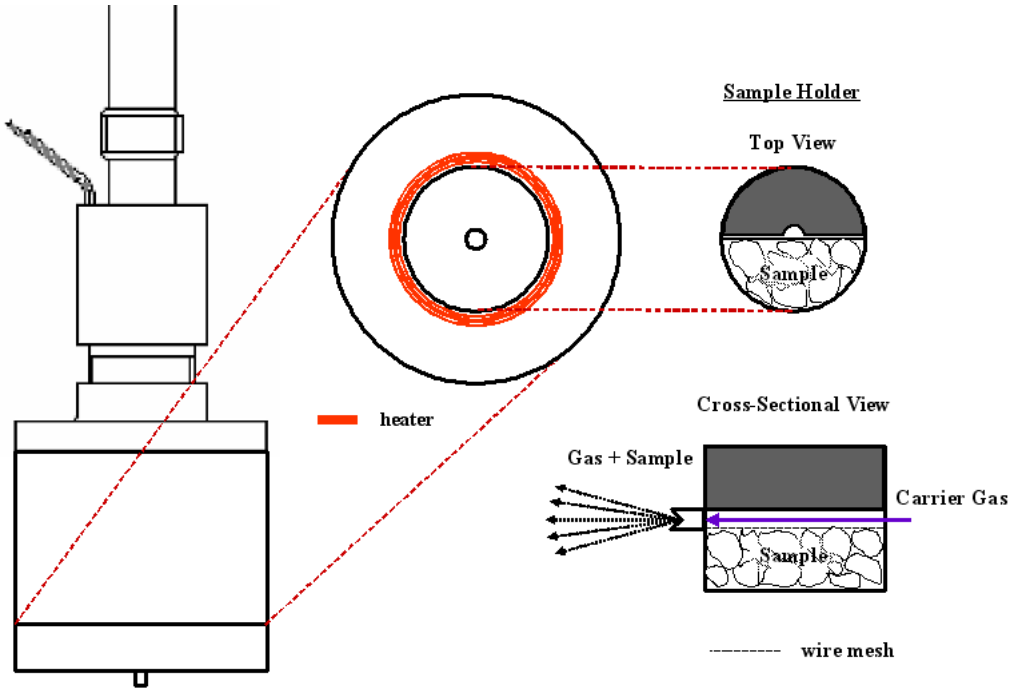


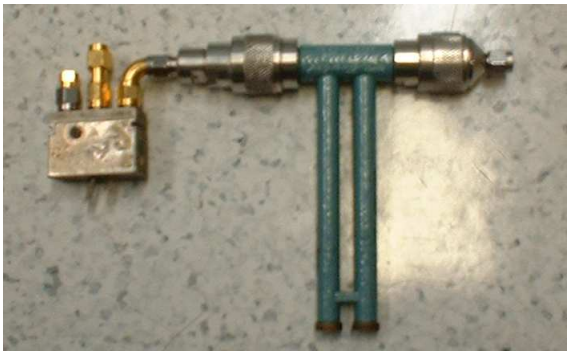
Figure A.2: A schematic diagram of the FTMW heated nozzle.

A.2 Spectrometer Startup Procedure

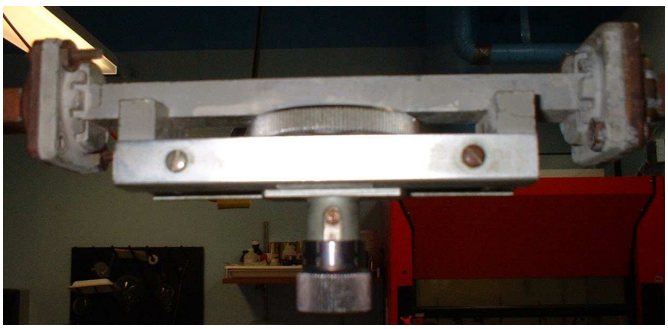
1. Insert the correct waveguide and tuner assembly. The instrument has two frequency ranges, 2–8 GHz and 8–18 GHz, and an SMA assembly is used for low frequency applications while a waveguide assembly is used for high frequency applications. The high frequency assembly is simply a waveguide that should be bolted to the instrument at the O-ring seal. The low frequency assembly is an SMA throughput that slides through the waveguide and then seals to the outside of the waveguide at the same O-ring seal:

For low frequency experiments, insert the SMA until the connector passes through the mirror iris. A dipole antenna can be found in the box labelled “dipole,” and this antenna

should be connected to the SMA connector in the chamber (remove the gate valve flange at the top of the instrument to do this). The entire SMA assembly should then be pushed back through the iris such that the antenna is positioned against the face of the mirror. The low frequency tuner is connected to the SMA at the input of the assembly and has two rods that slide up and down to adjust the tuning:



At high frequency the tuner is a slide tuner directly attached to the waveguide. This tuner has a coarse and fine adjustment:



Cavity coupling is quite bad at frequencies between 8 and 10.5 GHz, and a teflon dielectric waveguide should be inserted into the mirror iris for this frequency range. This waveguide is also located in the "dipole" box.

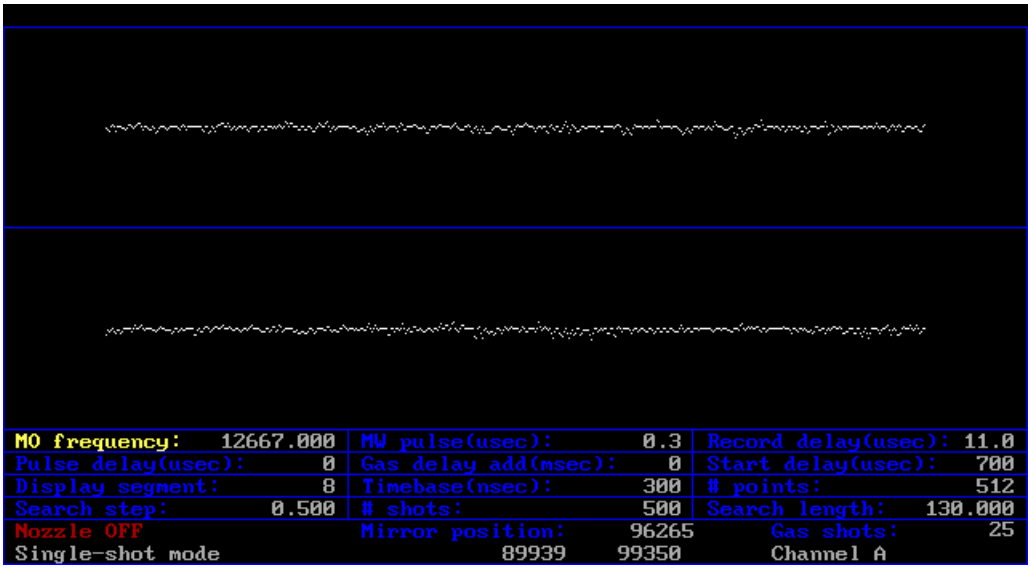
2. Turn on both water recirculators in the pump room. The diffusion pump flow meter readout next to the chamber should be reading a flow rate of ∼5 GPM. Close the gate valve

between the cold trap and the pump line and turn on the two mechanical pumps. Slowly open the gate valve and pump down the chamber. Turn on the Roots blower once the line pressure reaches ∼1 Torr. Turn on the diffusion pump once the chamber pressure is <10 mtorr. It will take approximately 30 minutes for the chamber to pump down to $\sim 10^{-6}$ Torr. The diffusion pump cooling water output temperature should be ∼70 degrees when the pump is warmed up completely.

3. Turn on the filter box, the interface box, the oscilloscope, the microwave box power supply, the frequency synthesizer, and the amplifiers. Be sure to do this before starting the operating program. (Note: The rubidium clock should remain plugged in at all times.)

4. Select the desired detector with the switch on the front of the microwave box.

5. Turn on the computer. Change to the directory where data should be saved (normally the C:\MWDATA directory). Type "v15" at the command prompt and press enter to load the operating program. The main control screen for the operating program should appear:



6. Confirm that the frequency synthesizer output is equal to the MO frequency minus 30 MHz.

7. The top window in the main control screen displays the signal, while the bottom window displays the noise in single-shot mode and the average of all 16 FIDs in averaging mode. Some noise should appear in both windows. The figure above shows a typical noise level. Check the amplifiers if no noise is observed.

The digitizer board in the computer may also not always work properly. If the signal is completely static, exit the v15 program, change directories to C:\DIGI, type "WAAG2," and press enter. This loads a diagnostic program for the digitizer card. The card should begin working properly again if a command is issued from this program. Exit the program, change directories to C:\MWDATA, and start the v15 program.

8. The experimental parameters are entered in the bottom of the main control window and are defined as follows:

- MO frequency: The experimental frequency
- Pulse delay: The delay in the train of microwave pulses
- Display segment: The segment of the pulse train displayed in the top two windows
- Search step: The increment by which the frequency is changed during an autosearch
- MW pulse: The length of the microwave pulses
- Gas delay add: The delay in the gas pulses
- Timebase: The sampling time (the inverse of the sampling rate)
- # shots: The number of shots to be averaged in averaging mode
- Record delay: The delay before digitization
- Start delay: The delay between the gas pulse and the beginning of the pulse train
- # points: The number of points recorded
- Search length: The amount of frequency to be covered in autosearch mode
- Nozzle: 'ON' or 'OFF' gives the status of the nozzle
- Mirror position: The current position of the mirror, in steps
- Gas shots: A counter for the number of gas shots
- Mode: The mode of data acquisition: 'single-shot,' 'averaging,' or 'autosearch'
- The numbers below the mirror position are the nearest resonant mirror positions.
- Channel: Channel being viewed (B = A + 90°)

Enter the desired experimental settings in the main control screen. The timing settings shown above are those used in standard experiments. The pulse width should be increased to 1 μsec for species with small dipole moments (< 0.5 D).

The commands for the main control screen are as follows:

a: Averaging mode
b: Toggle between Auto Search display and Single-Shot display during Auto Search mode
c: Toggle view of channels
d: Averaging mode (until certain number of shots)
f: new frequency
i: search increment (advance frequency by search step, move mirrors)
k: search decrement (decrease frequency by search step, move mirrors)
m: New mirror position (used to correct mirror calibration)
n: Nozzle on/off
s: Single-shot mode
t: Stop averaging and go to Pre-FFT screen
v: Auto Search mode
x: Exit program and save startup information
z: Averaging mode (reset on overflow)
‘: Turbo mode toggle
F1: Microwave power level decrement
F2: Microwave power level increment
F3: Mirror in continuously slow
Shift-F3: Mirror in continuously fast
F4: Mirror out continuously slow
Shift-F4: Mirror out continuously fast
F5: Mirror in 1 step
F6: Mirror out 1 step
F7: Mirror in 5 steps
F8: Mirror out 5 steps
F9: Mirror in 20 steps
F10: Mirror out 20 steps
Home: Large increment of value highlighted by cursor (if applicable)
End: Large decrement of the value highlighted by the cursor (if applicable)
Page up: Small increment of value highlighted by cursor
Page down: Small decrement of the value highlighted by cursor
Right arrow: Move cursor right
Left arrow: Move cursor left
Up arrow: Move cursor up
Down arrow: Move cursor down

9. Load the sample. Liquid samples should be placed in a bubbler and solid samples should be placed in the heated sample holder. If using the heated sample holder, be sure to secure the lid with the small set screw on the side or the lid could fall off in the chamber. Attach the sample holder to the valve face plate. The sample holder is not C_{2v} symmetric, so confirm that it is aligned appropriately or the valve will not completely insert in the coaxial setup.

10. Optimize the valve, set the tensioning with the set screw, and use electrical tape to secure the leads so that they do not get caught in the chamber.

11. Turn on the carrier gas and set the flow controller rates and the backing pressure.

12. Insert the valve assembly into the chamber by placing it against the plexiglass tube, positioning this tube at one of the gate valves, and opening the gate valve. Warning: Firm O-ring seals should be established before and maintained while the gate valve is open! If the seal is broken, quickly pull the valve assembly out of the chamber and immediately shut the gate valve. Wait at least 10 minutes before reinserting the valve assembly so that the diffusion pump is not overloaded.

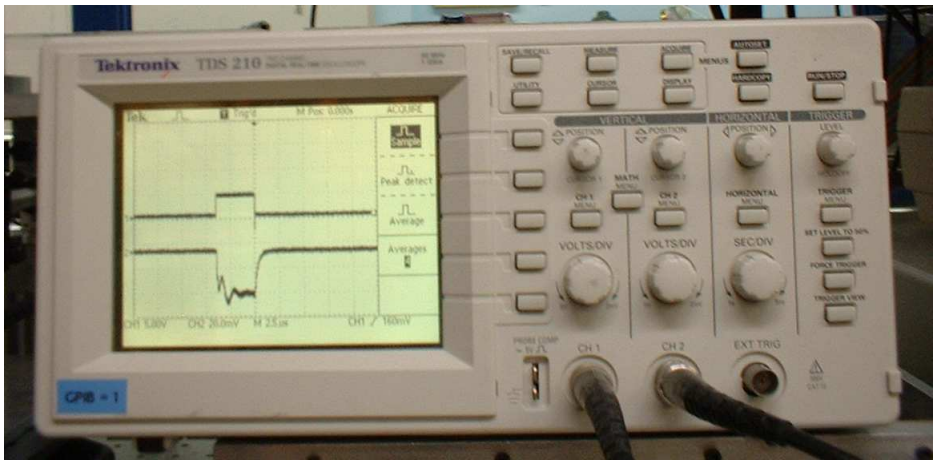
13. Slowly insert the feedthrough until it is at the position marked on the outer tube. The valve should be gently resting against the mirror when using the coaxial setup. Some rotation of the assembly may be required for the last few inches of insertion, as the valve face plate is matched to the size of the chamber to ensure alignment with the mirror iris. Warning: There is a plug in the mirror that can be knocked into the chamber when the valve is inserted coaxially! Be gentle! The UltraTorr fitting should be tightened once the valve is inserted completely. The chamber pressure should quickly decrease to a value only

slightly higher than that observed with the static system. If a drastic change in pressure occurs, there is likely a leak in the valve assembly.

14. Set the MO frequency to the desired value.

15. The cavity now requires tuning. Begin moving the mirror out in the 'mirror out continuously slow' mode. Watch the oscilloscope signal, as the tuning signal will 'wiggle' when close to a cavity mode. Find the mode farthest **out** in mirror position and stop the mirror by pressing any of the mirror control hot keys. Warning: Caution should be taken to ensure that the mirror is not driven too far to either end of its track, as it will become stuck. The current outer limit for the mirror position is ∼110,000. If the mirror does become stuck, loosen the bolts on the step motor and manually move the mirror in the appropriate direction with the step motor control box.

16. Move the mirror (out) just past the cavity mode (where the signal stops wiggling). Move the mirror inward stepwise until it is at the outermost edge of the mode. The signal on the oscilloscope should be similar to that shown below:



17. Iteratively adjust the two settings of the tuner and the mirror position until a tun-

ing signal such as the one shown in Section A.1.1 is achieved. In the low frequency setup the SMA and dipole can also be rotated and adjusted in horizontal position to aid in tuning.

18. It is often the case that, despite the appearance of excellent tuning with the oscilloscope signal, some modes will produce ringing that is observable on the main control screen. This ringing can be mistaken for signal and should be avoided. If slight adjustments in tuning do not eliminate the ringing, move the mirror inward until the next cavity mode is reached and retune.

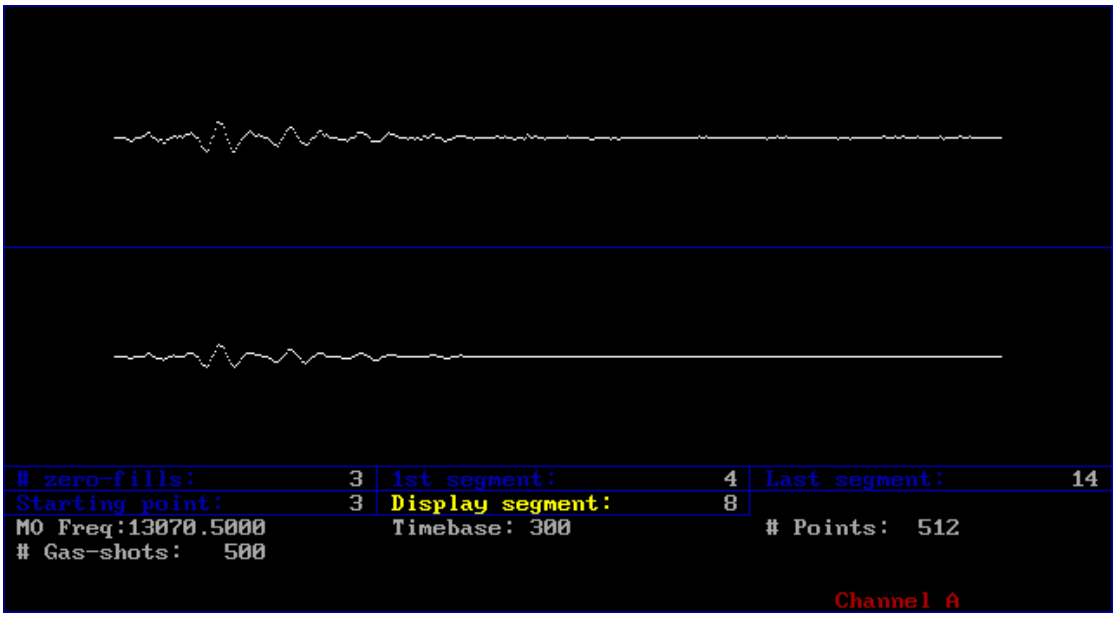
19. Once the cavity is tuned, set the desired experimental parameters. Turn on the nozzle and ensure that the chamber pressure does not rise above 4×10^{-4} Torr.

20. Select the desired data acquisition mode and begin collecting data. Single-shot mode displays the instantaneous FID. Averaging mode averages the FIDs for all shots. Auto Search can be used with predefined parameters to do fast line searches over a large frequency range. Retuning will be required after each manual change in frequency unless the search increment and decrement options are used. These functions step the frequency by the search step increment and appropriately adjust the mirror position. Slight retuning may be required, but these options do keep the spectrometer very close to optimum tuning.

21. Before selecting Auto Search mode, set the number of shots, search step, and search length to the desired values. Turn on the printer and add paper. Once Auto Search mode begins, the computer will automatically step the frequency, move the mirror, integrate, take a transform internally, and record the information on the printout. Be prepared for on-the-fly tuning while in autosearch mode, as the instrument tends to detune slightly with each frequency step. The program will prompt for a threshold when autosearch mode is selected.

This is the cutoff intensity for saved files, and so if there is a spectral feature with intensity higher than this threshold the data will be saved. A threshold of 10–20 is generally used.

22. The spectrum can be viewed during single-shot mode and general averaging mode by pressing 't,' which loads the Pre-FFT screen. Another version of averaging mode can be used in which the program automatically goes to the Pre-FFT screen after the defined number of shots. The Pre-FFT screen displays the obtained FIDs and allows the user to choose the parameters for the transform:



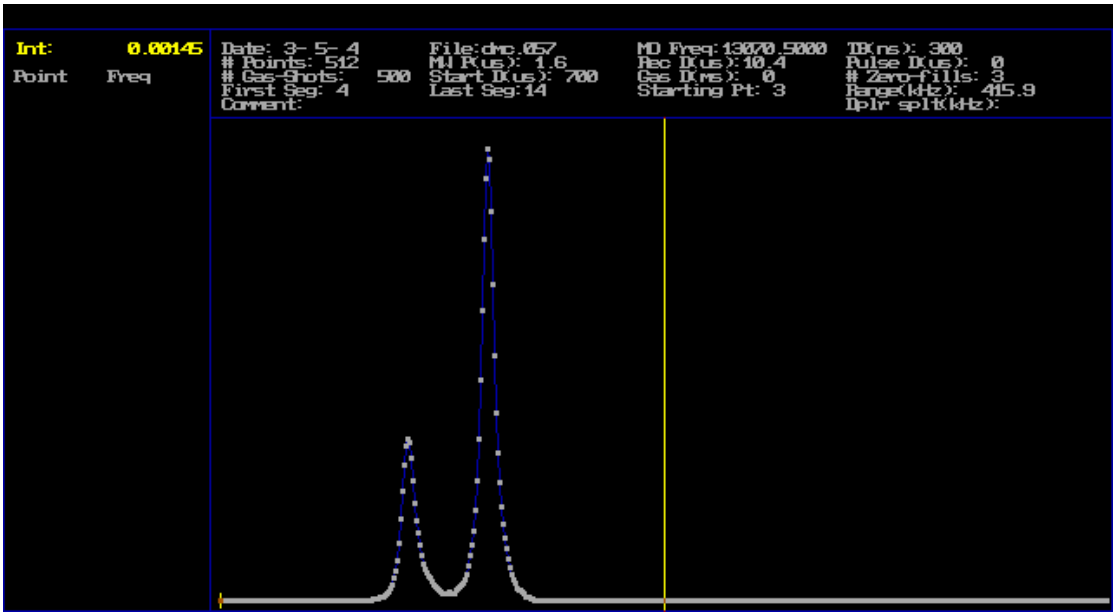
The FID is displayed on this screen in the same manner as it is displayed in the main control screen. The data to be included in the analysis can be selected with the parameters at the bottom of this screen, which are defined as follows:

- # zero fills: The number of times to double the length of the FID by adding zeroes
- 1st segment: The first FID segment to be included in the transform
- Last segment: The last FID segment to be included in the transform
- Starting Point: The first point in the FID that is to be transformed
- Display segment: The screen segment shown above

The commands for the Pre-FFT screen are as follows:

b: FFT of channel B
c: Toggle view of channels
e: Return to main screen without zeroing data array (nondestructive return)
n: Complex FFT (power spectrum)
r: Return to main screen
v: FFT of Channel A
F3: 0 order phased real FFT
Shift-F3: 0 & 1st order phased real FFT
F4: 0 order phased imaginary FFT
Shift-F4: 0 & 1st order phased imaginary FFT
F5: Real FFT
F6: Imaginary FFT
Page up: Small increment of value highlighted by cursor
Page down: Small decrement of the value highlighted by cursor
Right arrow: Move cursor right
Left arrow: Move cursor left

23. The FFT of the FID can now be taken. The real FFT of the FID gives a spectrum with the upper and lower sidebands superimposed, and so the frequencies are ambiguous. The complex FFT, however, gives the power spectrum, and so the sidebands are separated:



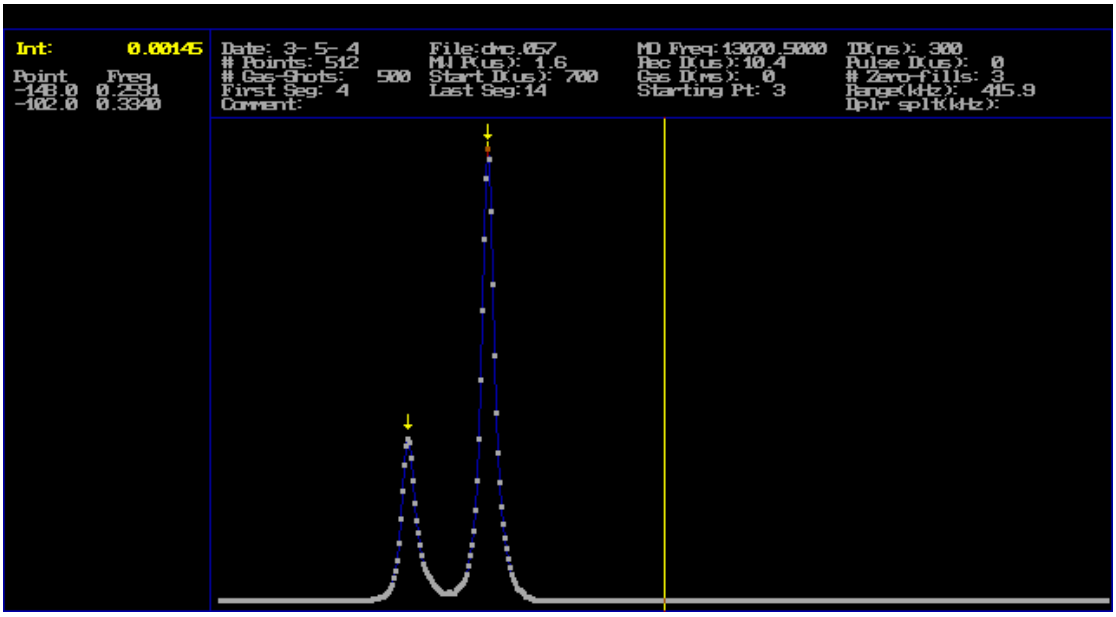
It is common for the program to prompt for a scaling factor when averaging mode is in use. Enter any number and press enter. The screen will then slowly go entirely blue. This is due to a program overload, and although it is irritating, it does not have any bearing on the spectral information. Simply press 'r' to enter the complex FFT screen. The position of the MO frequency is indicated in the complex FFT screen by the yellow line.

The commands for the complex FFT screen are as follows:

a: Mark point
A: Pseudo amplitude scale [sqrt(power spectrum)]
b: FFT of channel B
c: Clear marked points
d: Mark point + 1/2
f: New filename
l: Logarithmic scale y $\rightarrow$ log(y)
L: Loglog scale y $\rightarrow$ log(log(y))
m: Input comment
o: Save transform in Auto LISP format for Auto CAD in file called ft.tsp
p: Print transform
r: Return from current level to next valid level
s: Save transform
v: FFT of channel A
F1: auto peak picking
Shift-F1: auto peak picking with user defined threshold
F2: De-dopplerize
Shift-F2: De-Dopplerize with user defined range in pts
F3: 0 order phased real FFT
Shift-F3: 0 & 1st order phased real FFT
F4: 0 order phased imaginary FFT
Shift-F4: 0 & 1st order phased imaginary FFT
F5: Real FFT
F6: Imaginary FFT
Home: Move cursor +8
End: Move cursor -8
Page up: Move cursor +1
Page down: Move cursor -1
Right arrow: Scroll transform right
Left arrow: Scroll transform left
Up arrow: Increase magnification on transform
Down arrow: Decrease magnification on transforms

The spectrum can be saved at this point. The filename should be changed before saving. Three-digit numerical extensions are required. It is advisable to begin a search for a molecule with the extension .001, and any further spectra will automatically be assigned the subsequent numbered filename (i.e., if the first spectrum is saved as dha.001, the next spectrum will automatically be named dha.002).

The peaks can be chosen by either moving the cursor and manually marking the point or by auto peak picking. The frequencies are displayed to the right of the screen, and only the MHz place and decimal places are shown:



Any additional adjustments to the spectrum can be made at this point, but the raw data (before transform) rather than the FFT will be written to the file when saved. Doppler split lines will be observed in the coaxial setup, and the program can perform de-Dopplerization of the data in the FFT screen.

24. The saved files can be viewed at a later time by running the plot15 program. This program can be loaded similarly to the v15 program, by typing ‘plot15’ at the command

prompt in the directory where the files are saved. The program will prompt for "Input filename [path]cccccc.nnn>." The filename should be entered here (i.e., 'dha.001'). The program will then prompt "Read file dha.001 to dha." Enter the appropriate numbered extension for the last file to be viewed (i.e., '005' will allow files dha.001 - dha.005 to be viewed). The Pre-FFT screen for each file will load in sequence. All commands for the Pre-FFT screen and the complex FFT screen are the same as those used in v15. To close the first file and move to the next, press 'r' in the Pre-FFT screen. Pressing 'x' will close the program.

25. The best way to transfer the data to another computer is by printing a hardcopy of the spectrum and subsequently scanning this hardcopy to obtain a digital version. The other option is saving the transform in Auto LISP format for Auto CAD in a file called 'ft.tsp.' It has been found, however, that the intensities are often written incorrectly in this format. This is a major programming flaw that should be corrected.

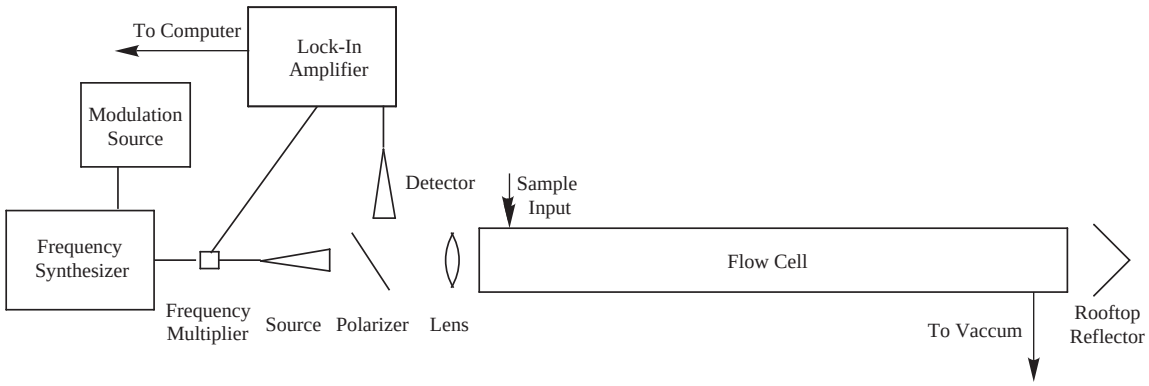
A screen capture program has also been loaded on this computer. Change to the C:\SCRAP directory, type SCRCAP, and press enter to load the program. Load the image to be captured (a change in directory may be required). Press 'ALT' and 'c' at the same time to capture the screen image. This saves the file with the name 'CAP-xxx.SCR', where xxx is a three-digit number. Transfer the file to the SCRAP directory and then type 'SCR2GIF' at the prompt to convert the .SCR file to a .GIF file. The computer's floppy drive (A:\) can be used to transfer the files to another computer.

Appendix B

Flow Cell Operation

B.1 Instrumentation

The Caltech Direct Absorption Flow Cell Spectrometer is controlled by the Submillimeter Spectroscopy Scanning Program software developed by the Microwave, Millimeter, and Submillimeter Spectroscopy Laboratory at JPL. A general schematic diagram of the experimental setup and detailed information on the instrumentation are shown below:



B.2 Spectrometer Startup Procedure

1. Turn on the frequency synthesizer and the lock-in amplifier.

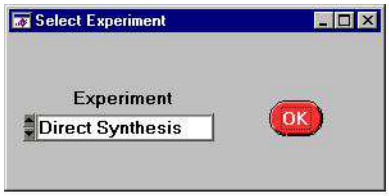
2. Confirm that none of the power supply connections are connected to the multiplier chain

Table B.1: Caltech Direct Absorption Flow Cell Spectrometer Instrumentation

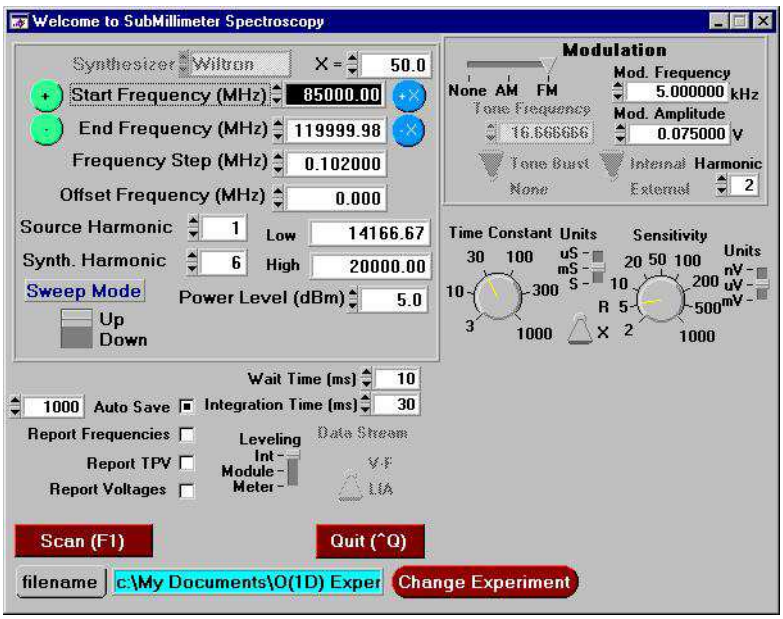
Equipment	Specifications
Frequency Synthesizer	Wiltron 6747A-20 Swept Frequency Synthesizer
Modulation Source	lock-in amplifier internal modulation source
Lock-In Amplifier	Stanford Research Systems SR830 DSP Lock-In Amplifier
Multiplier Chain	Miteq MAX2M2040 Active Frequency Doubler
	Miteq JP2-26004000-110-20SP Power Amplifier
	Virginia Diodes WR-9.3x3 Frequency Tripler
	Spacek SPW-18-14 Power Amplifier
	Virginia Diodes WR-3.4x3 Frequency Tripler (1 mm)
Power Supplies	Harrison dual power supply (± 8 V for Miteq Amplifier)
	HP dual output power supply (± 15 V for Miteq Doubler; ± 12 V for Spacek Amplifier)
Source	waveguide horn matched to multiplier chain output flange
Polarizer	wire grid
Lens	teflon
Cell	d = 0.05 m, l = 2.44 m (3 mm)
	d = 0.035 m, l = 2.56 m (1 mm)
Rooftop Reflector	gold coating
Detector	Pacific Millimeter WD GaAs Schottky diode (3 mm)
	4 K InSb hot electron bolometer (1 mm)
Computer	930 MHz Pentium III; National Instruments GPIB card

components. Turn on the power supplies and then connect the leads to the appropriate multiplier chain components, attaching the negative leads first, followed by the positive leads. Care should be taken, as connecting the leads in the opposite order could short the multipliers and amplifiers.

3. Double click on the "JPL Scanning Program" icon on the desktop to start the Submillimeter Spectroscopy Scanning Program. Click 'ok' to select a Direct Synthesis experiment:



The next window is the main control window for the scanning program. The experimental parameters for the spectrometer are entered here:



4. One of the lock-in amplifier settings must be changed before beginning an experiment so as to establish communication between the computer and the lock-in.

B.3 Spectrometer Parameters

• The frequency range to be covered by the experiment is set with the start and end frequency options by either typing the desired frequencies in the boxes, or by clicking on the blue '+X' and '-X' buttons to change the start and end frequencies, respectively, by the increment entered in the 'X=' box.

• The frequency step can be changed to the desired experimental resolution.

• The source harmonic setting should always remain as 1, while the synthesizer harmonic should be changed to the harmonic of the multiplier chain in use (in this example, the 3

mm multiplier chain is in use, so the output frequency is the 6th harmonic of the synthesizer frequency; for the 1 mm multiplier chain, the synthesizer harmonic should be set to 18).

• The power level option controls the output power level of the frequency synthesizer and should be optimized experimentally such that the multiplier chain is driven with the optimum input power.

• The scanning program will save the spectrum in a temporary file if the 'Auto Save' option is selected. The number of points to be taken between each auto save should be entered in the box next to this option.

• The wait time is the amount of time that the program waits after the frequency is stepped before beginning to integrate the lock-in signal. The integration time is the amount of time over which the program integrates the lock-in signal before stepping the frequency.

• The modulation settings control the internal modulation of the lock-in amplifier. These parameters should be optimized to give the best signal-to-noise ratio without significantly broadening the linewidths. AM modulation and a harmonic setting of '1' should be used when monitoring the power, while FM modulation and a harmonic setting of '2' should be used when recording spectral data.

• The lock-in amplifier phase setting should be set manually on the front panel of the instrument. This parameter is not included in the control software so that it can be changed during an experiment without stopping the scan.

• The time constant and sensitivity settings for the lock-in can also be controlled from the main window. The optimum time constant for all flow cell experiments is 30 ms. The

sensitivity should be set to the dynamic range of the spectrometer, which is often governed by the strength of the observed lines. The lock-in signal is set to either 'R' (for power scans) or 'X' (for spectral scans).

• The file in which the spectral data is recorded is set by clicking on the 'filename' button and choosing the desired directory and filename.

B.4 Spectrometer Alignment Procedure

1. Set the start frequency to the frequency in the middle of your desired scanning range.

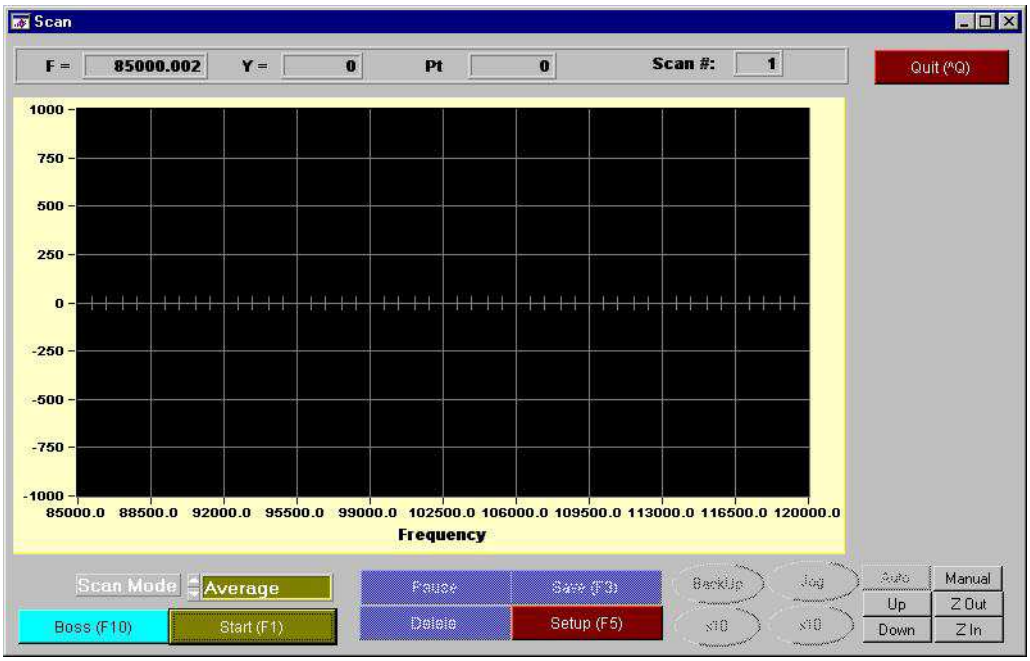
2. Switch to AM modulation and decrease the harmonic number to 1. Switch to R (rather than X) for the lock-in setting. Generally the sensitivity should be set to 1000 mV, but this setting should be adjusted to the appropriate value to give a fluctuating lock-in signal (i.e., such that the spectrometer is sensitive to noise). An attenuator may be required if the power is overloading the lock-in when it is on the least sensitive setting.

3. Note the modulation setting (in volts). Unhook the BNC cable that connects the lock-in to the 'Ext FM' input on the synthesizer. Attach the BNC cable from the 'Ext. AM' input on the synthesizer to the lock-in. Press the 'return to local' button on the Wiltron. Then press the 'measure FM from dev/ measure AM depth' button on the synthesizer until 'measure AM depth' is selected. Set the modulation setting to 0.775 V (or an appropriate voltage resulting in a 'modulation time' readout on the Wiltron close to 99%).

4. Place all optical components in the appropriate positions and roughly align them. At this point some signal should be registering on the 'Channel One' readout on the lock-in. Adjust

the x, y, and z positions of each component to maximize the power by either adjusting the positions of the mounts or by adjusting the micrometers on the translation stages. It is best to begin with the lens and polarizer, followed by the source and detector. Iteratively align each component until all are optimized. If the rooftop is in use, monitor the output of 'Channel One' on the lock-in with a voltmeter and carefully align the rooftop (the tilt stage is the most important adjustment here). The voltmeter will also be required if it is a 1 mm experiment, as only single-pass experiments are possible when the InSb bolometer detector is in use, and so the detector will be on the opposite end of the cell from the instrumentation.

5. Set the scanning increment to a large value (generally between 10 and 50 MHz). Change the filename to the appropriate file. Change the range to the desired frequency range. Click on the 'scan' button to go to the scanning window:



Click the 'start' button to begin a scan. Click the 'Auto' button to auto scale the window. After one scan across the full range, click 'Save,' enter any comments, and click 'save' again.

Note the regions in which there was sufficient power. Click 'Setup' to return to the main screen.

B.5 Spectral Acquisition Procedure

1. Change the sensitivity to 5 μV, the lock-in setting to X (rather than R), the modulation to FM, the harmonic number to 2, and the frequency step to 0.1 MHz. Set the frequency range to that which had sufficient power. Reconnect the FM BNC cable to the frequency synthesizer. Press the "return to local" button on the synthesizer and then change the option to 'measure FM from DEV.' Adjust the modulation amplitude to the previous setting. Regulate the sample pressure (see below).

2. Press 'scan.' Press 'start' on the scanning window to begin the scan. Once the scan reaches the upper frequency limit, the scanning direction will reverse and the scan will continue back to the start frequency. The forward and reverse scans will be averaged. This averaging will continue until the scan is saved or stopped. The current scan is displayed in yellow or magenta, depending on whether the scaling is changed after the scan begins. The averaged scan is offset above the current scan and is displayed in white. Clicking on the 'Boss' option loads the most recently saved scan onto the screen; this scan is displayed in green. There is a 'save and continue' option that allows the current state of the scan to be saved without stopping the scan.

3. Spectral lines are typically $\sim$1 MHz FWHM and should have the characteristic second derivative shape. They should be well above noise level and should retrace on the reverse scan. Wide frequency coverage is often required before a line is observed, especially for

molecules with weak spectra. Once a line is observed, return to the main screen after saving the scan.

4. Set the start frequency to the exact center frequency of the line. Adjust the phase option on the lock-in until the signal in the 'Channel One' readout is maximized. Once the maximum is found, pressing the +/- 90 degrees buttons should reduce the signal to the noise level. Changing the phase by 180 degrees should result in the negative of the optimized signal.

5. Narrow the scanning range to a 5–10 MHz range around the line. Record a spectrum of the line at these instrument settings, and then adjust the modulation amplitude, modulation frequency, power level, and sample pressure, monitoring the change in the line intensity after each adjustment. Optimized values for the 3 mm and 1 mm experimental setups are shown in Table B.2. Once optimum parameters are found for a given experiment, return to the main screen and begin a large scan.

Table B.2: Optimized parameters for flow cell experiments.

Parameter	3 mm	1 mm
Phase	80 degrees	-80 degrees
Mod. Amplitude (V)	0.05 V	0.05 V
Mod. Frequency (kHz)	6 kHz	4 kHz
Power level	12 dBm	5 dBm

B.6 Sample Pressure and Temperature Regulation

The sample cell pressure should be optimized to give maximum signal strength without significant line broadening. Pressures on the order of ∼30 mtorr are typical for such

experiments. The cell pressure is regulated by adjusting the valve between the cell and the pump. A needle valve can also be placed at the sample input port to further regulate the pressure. Gas sample lines should be directly attached to the input of the cell.

Liquid samples should be placed in either a ball flask (high vapor pressure) or a sparger (low vapor pressure). A ball flask can be attached directly to the cell input through use of an UltraTorr fitting, and direct pumping on the sample will set up ample pressure in the cell. For lower vapor pressure samples, however, a carrier gas should be bubbled through the sample to increase the amount of sample vapor in the cell. A sparger is used for this purpose. The carrier gas line should be attached to the sparger input, and the sparger output should be connected to the cell.

Solid samples should be placed directly in the cell by removing the endcap near the source (be cautious of the polarizer while doing this). Use of a sample boat often significantly reduces the transmitted power, and so aluminum foil should be used as a sample holder, as it can be formed to the shape of the cell. Be VERY cautious when first evacuating or venting the cell, as powdered samples are likely to scatter. If this does occur, the "flow cell squeegee" that is located in the lab (next to the vacuum cleaner) can be used to clean the sample from the cell walls.

Reduction of the cell temperature is often used to depopulate higher energy states for molecules with large partition functions. Baking out the cell is also sometimes necessary to remove adsorbed contaminants from the cell walls. The cell used in the 1 mm studies has a jacket around the inner cell that can be filled with liquid and appropriately cooled or heated. Water is most often used for this purpose, and a water recirculator is located under the cell, beneath the optics table. Fill the water reservoir before using the recirculator. Turn on the recirculator and monitor the water level, refilling when necessary until the

level does not change. Adjust the temperature to desired value. The heating system will run automatically, but the cooling system must be turned on separately if the desired temperature is below room temperature.

B.7 Spectral File Format

The spectral information saved during scanning is saved in the file designated in the filename box in the main control window. The file extension should be set to the '.lwa' option. The file is a simple ASCII text file, with a format as follows:

DATE MM-DD-YYYY TIME hh:mm:ss
comment
start frequency step frequency number of points 1 1 1 START
Y_1 Y_2 Y_3 Y_4 ... Y_n

The header information is that which is recorded from the scanning program, and the Y_n's are the signal intensities read from the lock-in amplifier at each frequency step. The information for each scan is appended to the end of a given file upon saving until the filename is changed in the scanning program.

Appendix C

Spectral Assignment

C.1 The CALPGM Suite

The CALPGM suite, developed by Pickett et al. (1998) at JPL, was designed to fit spectral information to quantum mechanical models to both obtain information about the structure of the molecule and to enable predictions in other spectral regions. Detailed information for the files associated with the CALPGM programs is available at `http://spec.jpl.nasa.gov`. The programs included in this suite can process the ground state and up to 99 vibrationally excited states, and can be used in conjunction with the Submillimeter Analysis Program (SMAP, described below) to assign spectral data.

The SPCAT program performs spectral predictions from a set of user-defined parameters that are defined in two input files, namely the .var file and the .int file. These parameters include molecule-specific information such as the dipole moment, rotational constants, distortion constants, and partition function. Other parameters include temperature, frequency range, and quantum number range as well as the type of reduction to be used for the Hamiltonian. Line positions and strengths are then calculated based on these user-defined parameters. Initial predictions are written to a .cat file.

The .cat file can be merged with spectral assignments with the CALMRG program.

This program produces a .mrg file that is formatted similarly to the .cat file, but markers distinguish between transitions that have been assigned and those that are predictions.

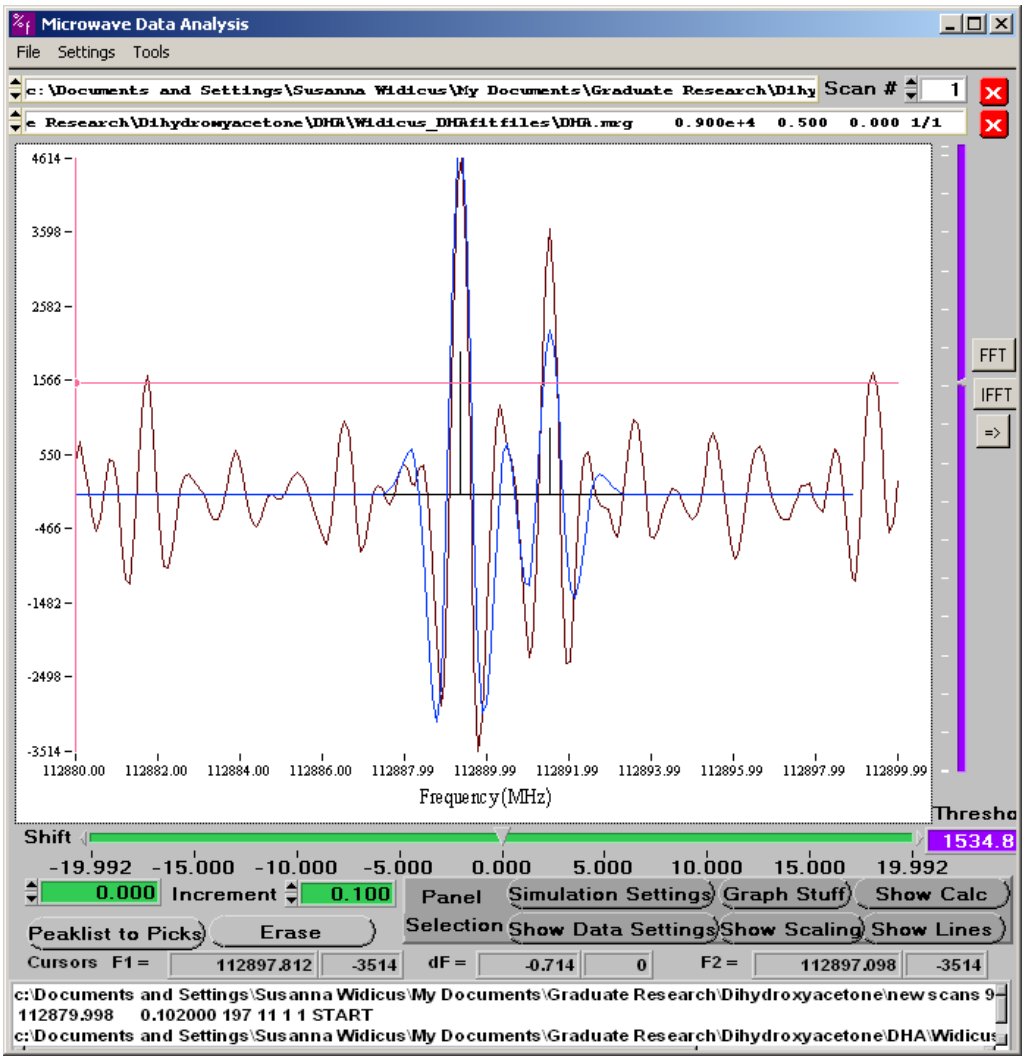
The SPFIT program utilizes files containing the frequency, intensity, and quantum numbers (J, K_a, K_c, ν) assigned for transitions to fit such spectroscopic information by a least squares analysis using a user-defined reduction of the Hamiltonian to a user-defined set of rotational and centrifugal distortion constants. The output of the SMAP program is formatted appropriately for a .lin file, which is the input file for SPFIT and contains the quantum numbers and frequencies for each of the assigned spectral lines. The initial spectral parameters are read from a .par file, which is identical to the .var file used by SPCAT. Both of these files are overwritten with the new spectral parameters each time the SPFIT program is run.

The MOIAM and IAMCALC programs can be used to generate spectral parameters for molecules with internal rotation groups. The Z-Matrix for the molecule and an initial estimate of the barrier to internal rotation are entered into a .inp file. An internal rotation group has n equivalent structures, and the MOIAM program generates coordinates for each of the atoms in the molecule for each structure. This information is then used to generate a set of parameters for an internal axis system Hamiltonian with the IAMCALC program. These parameters are written to a .par file, and these parameters can be used as the input to SPCAT in a .var file.

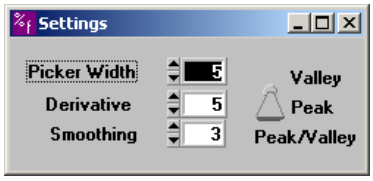
An iterative process is used to analyze spectral data. Literature or *ab initio* information is used to generate a predicted spectrum with the SPCAT program. The SMAP program is then used to compare the experimental spectrum to this prediction and to assign lines accordingly. The SPFIT program is then used to calculate a new set of parameters after spectral assignments are made.

C.2 The Submillimeter Analysis Program

The graphical interface used for spectral analysis is the Submillimeter Analysis Program (SMAP) developed by Brian Drouin from the Microwave, Millimeter, and Submillimeter Spectroscopy Laboratory at JPL. The .lwa files saved during scanning can be loaded into this program, which plots the xy data as either a line or a stick spectrum. Line spectra are most commonly used for line assignment purposes. The buttons in the main window for the SMAP program can be selected to bring up popup control windows for different aspects of the program:

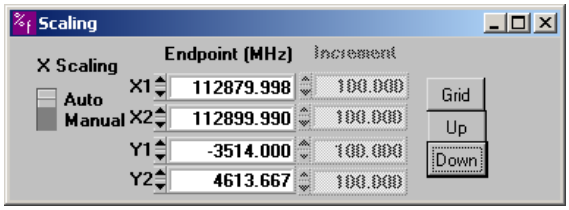


Spectral data files and spectral prediction catalog files can be loaded with the 'Open Data File' and 'Open Catalog' commands at the top of the screen. In the example shown above, the experimental spectrum is shown in black while the prediction is shown in blue. Each saved scan in a given file can be loaded by selecting the appropriate scan number at the top of the screen. The spectral data settings can be selected in the 'Show Data Settings' popup window:



The fifth derivative of the spectrum with a boxcar smoothing of n=3 is commonly used to remove the sinusoidal background from the spectral data. The 'FFT' and 'IFFT' options to the side of the spectral display window can also be used for this purpose.

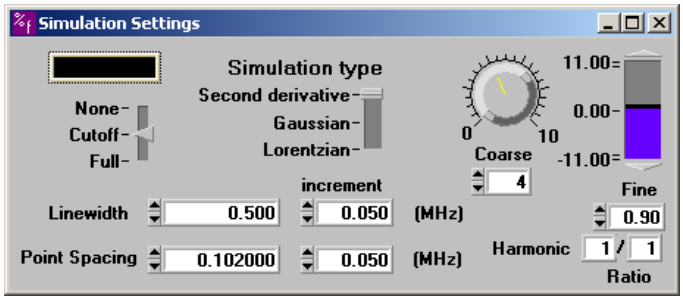
The xy scaling for the displayed spectrum can be adjusted in the 'Show Scaling' popup window:



The 'Up' and 'Down' buttons will shift to a new frequency window by an increment equal to the width of the current view. One can therefore scroll through the spectrum one window at a time, which is quite useful for line assignment. In addition, left-clicking in the spectral display window and dragging the mouse creates a selection box that can be used for changing the spectral scale. Right-clicking will zoom in on the boxed area of the spectrum once the

desired spectral window is selected. Double-clicking will then set the scaling back to the previous setting.

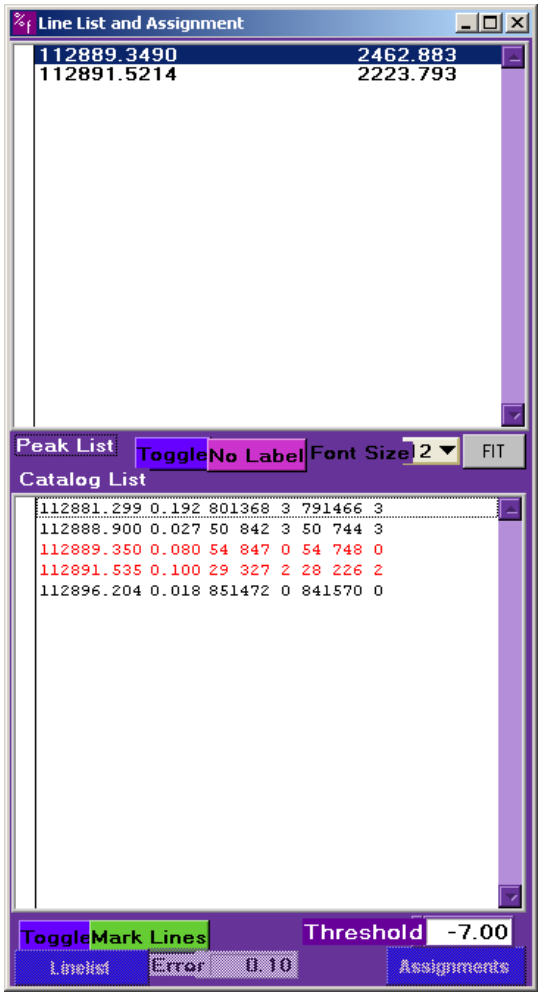
A total of eight different catalogs can be loaded with the current version of the program. The parameters of the predicted spectrum are controlled by the 'Simulation Settings' popup window:



Changes implemented in this window only change the settings for the catalog that is selected at that time, and so different settings can be used for different catalogs. The course and fine adjustments can be used to scale the intensity of the prediction relative to the spectral data. The simulation type can be chosen to match the spectral data line shape (flow cell spectra are second derivative spectra). The linewidth and point spacing can also be adjusted to match the spectral data. The prediction appears as a stick spectrum until the toggle is changed from 'None' to either 'Cutoff' or 'Full.' The cutoff option loads only the predicted spectral features in the window displayed on the screen, while the full option loads the entire prediction. The harmonic option can be used to select a different harmonic of the observed frequency, which is particularly useful when tunable frequency sources are used.

Spectral assignment is performed by comparing the simulated spectrum to the laboratory spectral data. The simulation can be shifted in frequency by using the green control boxes in the lower left corner of the main window. Once the simulation is shifted to match the observed spectral lines, the threshold option to the right of the display window should be

adjusted such that the desired spectral line is selected by the peak picker. The 'Show Lines' popup window shows the selected lines from the experimental data in the top window, and the predicted lines and their respective quantum numbers in the bottom window:

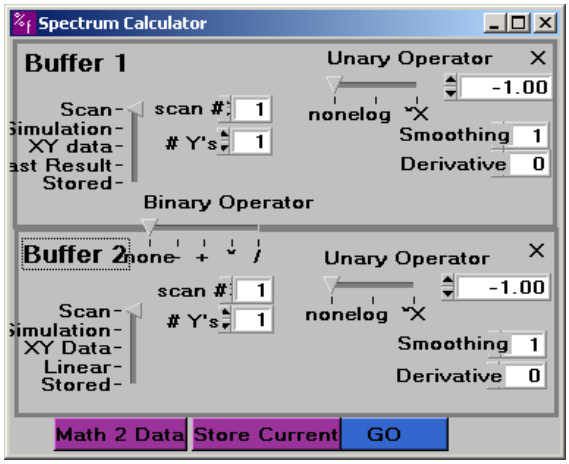


Clicking the 'Toggle' button in the bottom window will select all of the lines from the simulation, making them eligible for assignment. Clicking the 'Mark Lines' button will select the experimental lines that match these predictions to within the error value set at the bottom of the window (this value is usually set to the experimental resolution, 0.1 MHz). Clicking the 'Assignments' button at this point will write the quantum numbers from the prediction and the frequency of the observed line to the selected .lin file. The threshold

option in the lower right corner of this window can be used to set a minimum intensity threshold for assigned lines. No lines weaker than this threshold value will be included in the written assignments.

While the initial prediction is a .cat file, subsequent predictions are loaded in .mrg files. The lines that have been experimentally assigned are displayed in red font in the 'Show Lines' popup window and are not eligible for assignment. This ensures that the same set of quantum numbers is not assigned to multiple frequencies in a given spectral line file.

The SMAP program also includes a calculator option that can be accessed in the 'Show Calc' popup window. Mathematical manipulation of spectral data (i.e., the current scan, other scans, simulations, etc.) can be performed, and the results can be loaded over the displayed spectral data:



Appendix D

Geometry Optimizations of the $C_2H_4O_2$ & $C_3H_6O_3$ Structural Isomers

D.1 Introduction

Gaussian 98 MP2 6-311G++(d,p) geometry optimizations were performed for each of the 2C and 3C structural isomers [31]. The rotational constants, dipole moments, and absolute energies determined for the 2C and 3C species are given in Tables D.1 and D.2, respectively, and the resultant relative energy diagrams are shown in Figure D.1. The Gaussian Z-Matrices for each species are presented below.

Table D.1: The 2C structural isomer parameters determined by Gaussian 98 MP2 6-311G++(d,p) geometry optimizations.

Molecule	Energy (hartree)	A (GHz)	B (GHz)	C (GHz)	μ_a	μ_b	μ_c
trans-Acetic Acid	-227.8804311	11.2468400	9.4827443	5.3147628	1.5425	0.0003	-1.2339
cis-Acetic Acid	-227.8697261	10.9315932	9.5932037	5.2786903	2.7307	0.0000	-4.2473
Methyl Formate	-227.8532323	19.8277665	6.9450273	5.3160885	-1.9831	0.0000	-0.1656
Glycolaldehyde	-227.8355319	18.4048626	6.5032670	4.9540965	-1.6280	-0.0572	2.6078

Table D.2: The 3C structural isomer parameters determined by Gaussian 98 MP2 6-311G++(d,p) geometry optimizations.

Molecule	Energy (hartree)	A (GHz)	B (GHz)	C (GHz)	μ_a	μ_b	μ_c
Methylene Glycol Monoformate	-341.8040962	7.60414370	2.3977662	1.9750716	-0.7189	-1.6788	2.1665
Lactic Acid	-341.8035662	5.13517570	3.3496150	2.2075216	-2.4423	0.1351	0.5798
Dimethyl Carbonate	-341.7934922	10.3609486	2.3813303	1.9849098	0.1465	0.0000	0.1066
Methyl Glycolate	-341.7859758	9.95904630	2.2064690	1.8483288	1.3939	2.2628	-1.7720
Methoxy Acetic Acid	-341.7817050	7.56583090	2.3822053	2.0314708	1.9062	1.3609	-0.3790
Glycol Monoformate	-341.7794099	11.2177614	1.8101431	1.6839068	-0.6154	1.6346	0.7070
1,3-Dihydroxyacetone	-341.7676901	9.65454720	2.0397462	1.7323502	0.5000	-1.7533	1.0791
Glyceraldehyde	-341.7634662	5.48513980	2.7894964	2.4086035	1.0842	-2.5990	0.3055
Trioxane	-341.7493150	5.29309690	5.2925296	2.9496941	2.4597	-0.0015	-0.8622

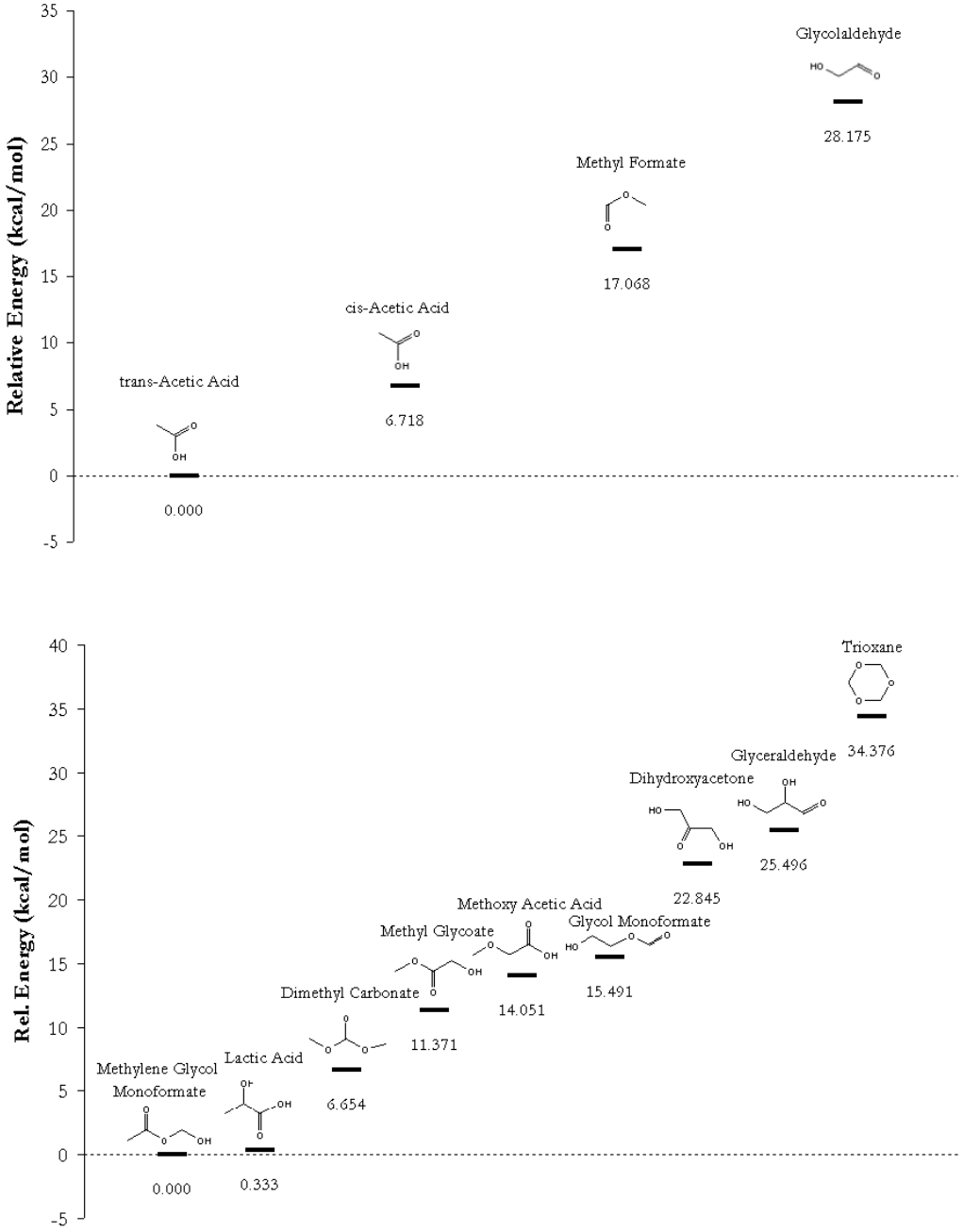


Figure D.1: The relative energies of the $C_2H_4O_2$ (top panel) and $C_3H_6O_3$ (bottom panel) structural isomers.

D.2 Z-Matrices

Table D.3: trans-Acetic Acid Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
C	1	1.503700				
O	2	1.358950	1	111.059625		
H	1	1.088360	2	109.499963	3	179.954742
H	1	1.092271	2	109.523526	3	-59.067658
H	1	1.092264	2	109.529672	3	58.968175
O	2	1.210396	1	126.239110	3	-179.988613
H	3	0.968019	2	105.880805	1	-179.999002

Table D.4: cis-Acetic Acid Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
C	1	1.514811				
O	2	1.365307	1	115.038831		
H	1	1.088383	2	109.211593	3	-179.999852
H	1	1.093990	2	110.171725	3	-59.755578
H	1	1.093990	2	110.171713	3	59.755879
O	2	1.203462	1	124.979429	3	179.999715
H	3	0.963129	2	109.216503	1	-0.000120

Table D.5: Methyl Formate Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
O	1	1.439039				
C	2	1.342820	1	114.123223		
O	3	1.207677	2	125.731253	1	0.000000
H	3	1.097084	2	109.030435	1	-180.000000
H	1	1.087577	2	105.347611	3	-180.000000
H	1	1.091003	2	110.297528	3	60.397010
H	1	1.091003	2	110.297528	3	-60.397010

Table D.6: Glycolaldehyde Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
O						
C	1	1.216358				
C	2	1.509742	1	121.952987		
O	3	1.402974	2	112.266930	1	0.000170
H	4	0.966960	3	105.487287	2	0.011002
H	2	1.105956	1	121.622223	3	-179.995669
H	3	1.099382	2	107.637875	1	122.356765
H	3	1.099397	2	107.631456	1	-122.343986

Table D.7: Methylene Glycol Monoformate Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
C	1	1.525309				
C	2	1.506987	1	111.672591		
O	3	1.215286	2	125.206497	1	8.910305
H	1	1.097583	2	109.626362	3	59.787453
H	1	1.091852	2	109.260546	3	178.184188
O	3	1.351351	2	112.059797	1	-171.585792
H	7	0.968893	3	106.169777	2	-178.343340
H	2	1.095301	1	111.384635	3	-121.586169
H	2	1.095538	1	109.954184	3	119.537879
O	1	1.417311	2	112.140281	3	-64.025342
H	11	0.963865	1	105.429147	2	65.311785

Table D.8: Lactic Acid Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
O						
H	1	0.968758				
C	1	1.348129	2	106.356517		
O	3	1.212801	1	123.875337	2	0.702006
C	3	1.517941	1	112.346787	2	-177.944873
H	5	1.100231	3	106.071131	1	65.847372
C	5	1.523316	3	112.075702	1	-53.644315
H	7	1.091857	5	110.974153	3	63.282595
H	7	1.092065	5	108.681597	3	-176.439566
H	7	1.093130	5	109.916409	3	-57.931883
O	5	1.411925	3	109.827967	1	-175.123445
H	11	0.965841	5	106.474398	3	-15.961845

Table D.9: Dimethyl Carbonate Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
O	1	1.338797				
O	1	1.338797	2	107.820415		
C	2	1.435114	1	113.502682	3	179.999999
H	4	1.091117	2	110.509182	1	60.607259
H	4	1.091117	2	110.509182	1	-60.607259
H	4	1.087999	2	105.142494	1	180.000000
C	3	1.435114	1	113.502682	2	-180.000000
H	8	1.091117	3	110.509182	1	-60.607259
H	8	1.091117	3	110.509182	1	60.607259
H	8	1.087999	3	105.142495	1	180.000000
O	1	1.210758	2	126.089792	4	0.000000

Table D.10: Methyl Glycolate Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
C	1	1.515309				
H	2	1.095651	1	108.205654		
H	2	1.095618	1	108.217122	3	116.773821
O	1	1.338913	2	111.747328	4	58.316900
O	1	1.214318	2	123.352467	5	-179.992768
O	2	1.407602	1	111.096393	6	-0.067947
H	7	0.965986	2	105.821878	1	0.134171
C	5	1.439953	1	114.560283	2	179.987660
H	9	1.087693	5	105.250932	1	-179.999743
H	9	1.090889	5	110.213053	1	-60.468310
H	9	1.090887	5	110.213301	1	60.468843

Table D.11: Methoxy Acetic Acid Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
O	1	1.420513				
C	2	1.396539	1	112.311695		
C	3	1.522851	2	113.504856	1	-74.996247
O	4	1.206939	3	126.557079	2	-0.069676
O	4	1.357945	3	109.623802	2	-179.576155
H	6	0.968236	4	106.261800	3	178.980760
H	3	1.093625	2	107.673258	1	166.083302
H	3	1.100786	2	112.134344	1	47.772178
H	1	1.098690	2	110.522883	3	-58.480384
H	1	1.094190	2	111.496974	3	63.843977
H	1	1.089885	2	106.539316	3	-177.024465

Table D.12: Glycol Monoformate Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
C	1	1.528415				
O	2	1.412307	1	114.347702		
O	1	1.453147	2	114.056725	3	97.769306
C	4	1.333737	1	116.631752	2	-68.334659
O	5	1.212591	4	126.243317	1	3.172829
H	5	1.096436	4	109.414019	1	-176.883010
H	1	1.093622	2	110.171399	3	-25.408419
H	1	1.090205	2	110.732082	3	-147.052458
H	2	1.099672	1	108.445413	4	-28.041192
H	2	1.093073	1	108.114766	4	-144.662847
H	3	0.965246	2	106.211583	1	-51.688895

Table D.13: 1,3-Dihydroxyacetone Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
C	1	1.514665				
H	2	1.101962	1	106.409456		
H	2	1.095236	1	109.780776	3	-116.049712
C	1	1.514675	2	118.405260	4	-42.162081
H	5	1.095158	1	109.801311	2	-42.045849
H	5	1.101966	1	106.406408	2	74.025658
O	1	1.221370	2	120.796268	5	179.983688
O	5	1.404249	1	112.130211	2	-163.446551
H	9	0.966185	5	105.762029	1	-25.060504
O	2	1.404121	1	112.136696	8	16.399881
H	11	0.966200	2	105.767937	1	-24.788882

Table D.14: Glyceraldehyde Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
C	1	1.523478				
H	2	1.096842	1	108.597282		
H	2	1.093765	1	110.256321	3	-118.906916
C	1	1.516183	2	110.674020	4	59.015863
H	5	1.105654	1	116.435269	2	-53.308715
O	1	1.410485	2	108.592495	5	121.450366
H	7	0.968698	1	105.546873	2	-134.748948
O	5	1.215756	1	121.710439	2	127.677466
O	2	1.415281	1	110.684405	7	62.245137
H	10	0.964149	2	105.704544	1	-56.062409
H	1	1.103124	2	109.028659	10	-176.653874

Table D.15: Trioxane Z-Matrix.

Atom 1	Atom 2	Bond (Å)	Atom 3	Angle (°)	Atom 4	Dihedral Angle (°)
C						
H	1	1.087341				
H	1	1.103708	2	111.408314		
O	1	1.408253	2	107.615748	3	-119.919101
O	1	1.408837	2	107.584294	4	-120.237198
C	4	1.408777	1	108.644724	2	-176.275190
H	6	1.087343	4	107.585058	1	176.325387
H	6	1.103731	4	109.354212	1	-62.538123
C	5	1.407974	1	108.649293	2	176.311887
H	9	1.103746	5	109.418694	1	62.517471
H	9	1.087351	5	107.624267	1	-176.292182
O	6	1.408328	4	111.471551	1	58.553254

Appendix E

1,3-Dihydroxyacetone Spectral Analysis

E.1 1,3-Dihydroxyacetone .int File

```
dihydroxyacetone !!
 0001 710xx  149018,  0, 110, -9.9,-9.9, 600. 300
 001  0.00
 002  1.77
 003  0.00
 111  0.00
 112  1.77
 113  0.00
 221  0.00
 222  1.77
 223  0.00
 331  0.00
 332  1.77
 333  0.00
 441  0.00
 442  1.77
 443  0.00
```

E.2 1,3-Dihydroxyacetone .par File

```
   dihydroxyacetone                                  20-FETue Mar 08 17:38:25 2005
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a   1   5   0    80   0
              0 -3.077843878215719E-054 1.00000000E-030
             11  2.800000000000000E+006 1.00000000E-020
             22  4.400000000000000E+006 1.00000000E-020
             33  4.500000000000000E+006 1.00000000E-020
             44  5.500000000000000E+006 1.00000000E-020
          10000  9.801294319558918E+003 5.53870991E+020 /A0
          20000  2.051525618181228E+003 1.05923781E+020 /B0
          30000  1.735164875163197E+003 1.15205066E+020 /C0
            200 -1.823673048868642E-004 2.54257079E+020 /-D_J0
           1100 -6.570554374745859E-004 3.64239903E+020 /-D_JK0
           2000 -5.366574855355530E-003 2.05182933E+020 /-D_K0
          40100 -2.767395760072777E-005 1.09377716E+020 /-d_1 0
          41000 -5.692623750760164E-004 9.70460529E+020 /-d_2 0
          10011  9.764480575891592E+003 5.53870991E+020 /A1
          20011  2.049846713320285E+003 1.05923781E+020 /B1
          30011  1.736322273353199E+003 1.15205066E+020 /C1
            211 -1.832943431901232E-004 2.54257079E+020 /-D_J1
           1111 -8.486092640387109E-004 3.64239903E+020 /-D_JK1
           2011 -5.479072811759285E-003 2.05182933E+020 /-D_K1
          40111 -2.741193228166894E-005 1.09377716E+020 /-d_1 1
          41011 -6.416701923482689E-004 9.70460529E+020 /-d_2 1
          10022  9.701677625461267E+003 5.53870991E+020 /A2
          20022  2.051549856707002E+003 1.05923781E+020 /B2
          30022  1.737929258700044E+003 1.15205066E+020 /C2
            222 -1.850708256907718E-004 2.54257079E+020 /-D_J2
           1122 -5.030694682634194E-004 3.64239903E+020 /-D_JK2
           2022 -3.476139815329533E-003 2.05182933E+020 /-D_K2
          40122 -2.755822936763215E-005 1.09377716E+020 /-d_1 2
          41022 -3.586944284235681E-004 9.70460529E+020 /-d_2 2
          10033  9.662111202535310E+003 5.53870991E+020 /A3
          20033  2.050021645635964E+003 1.05923781E+020 /B3
          30033  1.739419282882642E+003 1.15205066E+020 /C3
            233 -1.871573555017875E-004 2.54257079E+020 /-D_J3
           1133 -6.065320805558970E-004 3.64239903E+020 /-D_JK3
           2033 -7.117704538112456E-003 2.05182933E+020 /-D_K3
          40133 -2.659488373510768E-005 1.09377716E+020 /-d_1 3
          41033 -3.173100906087768E-004 9.70460529E+020 /-d_2 3
          10044  1.032831972121139E+004 5.53870991E+020 /A4
          20044  2.065184247922443E+003 1.05923781E+020 /B4
          30044  1.735124047466261E+003 1.15205066E+020 /C4
            244 -1.823705977705431E-004 2.54257079E-020 /-D_J4
           1144 -6.570441988138593E-004 3.64239903E-020 /-D_JK4
           2044 -5.366717861588423E-003 2.05182933E-020 /-D_K4
          40144 -2.767291508665058E-005 1.09377716E-020 /-d_1 4
          41044 -5.694116911197475E-004 9.70460529E-020 /-d_2 4
```

E.3 1,3-Dihydroxyacetone .lin File

3	2	1	0	4	1	4	0	10230.5000	0.0040
5	1	4	0	5	0	5	0	10540.6400	0.0020
2	2	1	0	3	1	2	0	11420.6455	0.0040
1	1	1	0	0	0	0	0	11536.4474	0.0020
6	1	5	0	6	0	6	0	11731.7598	0.0040
5	0	5	0	4	1	4	0	12302.5023	0.0020
7	1	6	0	7	0	7	0	13208.4570	0.0040
8	1	7	0	8	0	8	0	14995.2940	0.0040
2	1	2	0	1	0	1	0	15006.7695	0.0020
6	0	6	0	5	1	5	0	16596.6445	0.0020
3	1	3	0	2	0	2	0	18322.5566	0.0040
10	1	9	0	10	0	10	0	19546.4736	0.0040
9	2	7	0	9	1	8	0	19882.2109	0.0040
8	2	6	0	8	1	7	0	20157.6729	0.0040
4	3	2	0	5	2	3	0	20329.7578	0.0040
7	2	5	0	7	1	6	0	20592.8721	0.0040
7	0	7	0	6	1	6	0	20897.9053	0.0040
6	2	4	0	6	1	5	0	21132.7061	0.0040
4	1	4	0	3	0	3	0	21495.9492	0.0040
5	2	3	0	5	1	4	0	21720.5107	0.0040
4	2	2	0	4	1	3	0	22301.8613	0.0040
3	2	1	0	3	1	2	0	22828.0713	0.0040
2	2	0	0	2	1	1	0	23258.6963	0.0040
2	2	1	0	2	1	2	0	24198.2861	0.0040
5	1	5	0	4	0	4	0	24546.4023	0.0040
3	2	2	0	3	1	3	0	24678.6514	0.0040
26	13	14	0	27	12	15	0	94930.2947	0.0800
26	13	13	0	27	12	16	0	94930.2947	0.0800
26	13	14	0	27	12	16	0	94930.2947	0.0800
26	13	13	0	27	12	15	0	94930.2947	0.0800
44	6	39	0	44	5	40	0	95063.4624	0.0800
55	6	49	0	55	5	50	0	95118.3010	0.0800
27	1	27	2	26	0	26	2	95438.5796	0.1000
67	8	59	0	67	7	60	0	95462.9407	0.0800
61	7	54	0	61	6	55	0	95463.8262	0.0800
27	1	26	0	26	2	25	0	97995.6541	0.0800
71	10	61	0	71	9	62	0	98007.2266	0.0800
50	5	45	0	50	4	46	0	98532.6447	0.0800
32	7	25	0	32	6	26	0	98540.2046	0.0800
34	7	28	0	34	6	29	0	98954.2080	0.0800
48	8	40	0	48	7	41	0	99051.4985	0.0800
31	7	25	0	31	6	26	0	99910.4932	0.0800
46	7	40	0	46	6	41	0	99943.0951	0.0800
68	8	60	0	68	7	61	0	100458.7032	0.0800
29	7	23	0	29	6	24	0	100508.3201	0.0800
47	8	39	0	47	7	40	0	101408.7858	0.0800
25	7	18	0	25	6	19	0	101414.8335	0.0800
25	7	19	0	25	6	20	0	101479.2105	0.0800
22	7	16	1	22	6	17	1	101522.7244	0.1000
28	1	27	0	27	2	26	0	101595.8837	0.1000
18	7	12	1	18	6	12	1	101946.7563	0.1000
18	7	11	1	18	6	12	1	101946.7563	0.1000

18	7	11	1	18	6	13	1	101947.9732	0.1000
18	7	12	1	18	6	13	1	101947.9732	0.1000
22	7	15	0	22	6	16	0	101974.0933	0.0800
48	7	42	0	48	6	43	0	101975.8019	0.0800
85	11	74	0	85	10	75	0	101987.2679	0.0800
22	7	16	0	22	6	17	0	101988.6939	0.0800
29	1	29	2	28	0	28	2	102378.9548	0.1000
28	2	27	0	27	1	26	0	102406.5625	0.0800
35	4	31	0	34	5	30	0	102415.1598	0.0800
18	7	11	0	18	6	12	0	102417.9074	0.0800
18	7	12	0	18	6	12	0	102417.9074	0.0800
18	7	11	0	18	6	13	0	102419.2240	0.0800
18	7	12	0	18	6	13	0	102419.2240	0.0800
29	0	29	3	28	1	28	3	102436.6732	0.1000
24	3	22	0	23	2	21	0	102439.4472	0.0800
28	2	27	1	27	1	26	1	102443.8660	0.1000
29	1	29	3	28	0	28	3	102453.3801	0.1000
31	3	28	0	30	4	27	0	102463.5445	0.0800
24	3	22	1	23	2	21	1	102479.8305	0.1000
17	7	11	0	17	6	11	0	102490.8095	0.0800
17	7	10	0	17	6	11	0	102490.8095	0.0800
17	7	11	0	17	6	12	0	102491.6719	0.0800
17	7	10	0	17	6	12	0	102491.6719	0.0800
28	2	27	2	27	1	26	2	102497.0673	0.1000
28	2	27	3	27	1	26	3	102550.3978	0.1000
16	7	10	0	16	6	10	0	102552.2285	0.1000
16	7	10	0	16	6	11	0	102552.2285	0.1000
16	7	9	0	16	6	11	0	102552.2285	0.1000
16	7	9	0	16	6	10	0	102552.2285	0.1000
86	11	75	1	86	10	76	1	102969.5556	0.1000
41	4	38	0	41	3	39	0	102987.0737	0.0800
42	3	39	3	42	2	40	3	102991.2322	0.1000
61	22	39	0	62	21	42	0	102995.3407	0.0800
61	22	40	0	62	21	42	0	102995.3407	0.0800
61	22	40	0	62	21	41	0	102995.3407	0.0800
61	22	39	0	62	21	41	0	102995.3407	0.0800
38	2	36	1	38	1	37	1	103015.9025	0.1000
51	5	46	0	51	4	47	0	103256.7906	0.0800
46	8	38	1	46	7	39	1	103259.9847	0.1000
49	7	43	0	49	6	44	0	103274.6085	0.0800
62	8	55	0	61	9	52	0	103311.8037	0.0800
38	3	36	1	38	2	37	1	103336.5340	0.1000
64	8	57	0	63	9	54	0	103390.4872	0.0800
83	14	70	0	82	15	67	0	103403.3863	0.0800
48	6	43	1	48	5	44	1	103449.7507	0.1000
15	3	12	0	14	2	13	0	103493.6929	0.0800
57	6	51	3	57	5	52	3	103506.0791	0.1000
46	4	42	0	46	3	43	0	103529.4090	0.0800
13	4	10	1	12	3	9	1	103540.6286	0.1000
46	8	38	0	46	7	39	0	103544.3024	0.0800
50	7	44	2	50	6	45	2	103598.0896	0.1000
69	10	59	1	69	9	60	1	103762.2218	0.1000
38	2	36	0	38	1	37	0	103776.6834	0.0800

69	10	59	0	69	9	60	0	103784.5425	0.0800
58	9	49	1	58	8	50	1	103841.5408	0.1000
86	11	75	0	86	10	76	0	103870.8442	0.0800
45	8	37	2	45	7	38	2	103944.1769	0.1000
45	5	41	1	45	4	42	1	103946.5543	0.1000
58	9	49	0	58	8	50	0	103947.4843	0.0800
80	11	69	1	80	10	70	1	104015.4249	0.1000
63	9	55	0	62	10	52	0	104039.1734	0.0800
42	3	39	1	42	2	40	1	104070.3964	0.1000
38	3	36	0	38	2	37	0	104091.1918	0.0800
50	7	44	1	50	6	45	1	104104.2477	0.1000
45	6	39	0	44	7	38	0	104194.8618	0.0800
48	6	43	0	48	5	44	0	104205.9662	0.0800
25	3	23	0	24	2	22	0	104208.5475	0.0800
25	3	23	1	24	2	22	1	104255.2878	0.1000
35	1	34	0	35	0	35	0	104319.3707	0.0800
9	5	4	2	8	4	4	2	104364.8013	0.1000
9	5	5	2	8	4	4	2	104364.8013	0.1000
9	5	5	2	8	4	5	2	104366.1663	0.1000
9	5	4	2	8	4	5	2	104366.1663	0.1000
51	7	45	3	51	6	46	3	104539.8733	0.1000
40	5	35	0	39	6	34	0	104661.4230	0.0800
66	5	61	0	65	6	59	0	104730.0515	0.0800
45	5	41	0	45	4	42	0	104735.5097	0.0800
50	7	44	0	50	6	45	0	104765.4990	0.0800
29	2	27	0	28	3	26	0	104792.8553	0.0800
42	3	39	0	42	2	40	0	104887.2340	0.0800
9	5	4	1	8	4	4	1	104914.1060	0.1000
9	5	5	1	8	4	4	1	104914.1060	0.1000
9	5	4	1	8	4	5	1	104915.5177	0.1000
9	5	5	1	8	4	5	1	104915.5177	0.1000
29	2	27	2	28	3	26	2	104970.4187	0.1000
81	10	71	0	81	9	72	0	105086.8266	0.0800
75	9	66	0	75	8	67	0	105129.9498	0.0800
45	8	37	1	45	7	38	1	105130.9364	0.1000
29	1	28	0	28	2	27	0	105163.7291	0.0800
29	1	28	1	28	2	27	1	105193.6027	0.0800
9	5	4	0	8	4	4	0	105248.1483	0.0800
9	5	5	0	8	4	4	0	105248.1483	0.0800
9	5	5	0	8	4	5	0	105249.4403	0.0800
9	5	4	0	8	4	5	0	105249.4403	0.0800
29	1	28	2	28	2	27	2	105280.8300	0.1000
29	1	28	3	28	2	27	3	105327.1149	0.1000
42	4	39	1	42	3	40	1	105417.8104	0.1000
57	6	51	0	57	5	52	0	105431.2338	0.0800
45	8	37	0	45	7	38	0	105450.4529	0.0800
44	8	36	2	44	7	37	2	105627.4002	0.1000
30	0	30	0	29	1	29	0	105690.6158	0.0800
30	1	30	0	29	0	29	0	105702.5003	0.0800
30	0	30	1	29	1	29	1	105748.9102	0.0800
51	7	45	1	51	6	46	1	105754.1440	0.1000
30	1	30	1	29	0	29	1	105760.9618	0.0800
29	2	28	0	28	1	27	0	105766.4223	0.0800

69	8	61	0	69	7	62	0	105767.4664	0.0800
29	2	28	1	28	1	27	1	105804.9196	0.1000
30	0	30	2	29	1	29	2	105839.2366	0.1000
30	1	30	2	29	0	29	2	105850.7508	0.1000
29	2	28	2	28	1	27	2	105865.3089	0.1000
30	0	30	3	29	1	29	3	105916.0218	0.1000
29	2	28	3	28	1	27	3	105920.6938	0.1000
30	1	30	3	29	0	29	3	105928.3053	0.1000
49	6	44	1	49	5	45	1	106075.1901	0.1000
63	7	56	0	63	6	57	0	106111.1739	0.0800
26	3	24	0	25	2	23	0	106129.1949	0.0800
26	3	24	1	25	2	23	1	106179.8048	0.1000
42	4	39	0	42	3	40	0	106209.5632	0.0800
39	2	37	1	39	1	38	1	106312.0284	0.1000
52	7	46	3	52	6	47	3	106374.9916	0.1000
23	13	10	0	24	12	13	0	106435.2662	0.0800
23	13	11	0	24	12	13	0	106435.2662	0.0800
23	13	11	0	24	12	12	0	106435.2662	0.0800
23	13	10	0	24	12	12	0	106435.2662	0.0800
51	7	45	0	51	6	46	0	106447.7113	0.0800
56	21	36	0	57	20	37	0	106456.4488	0.0800
56	21	35	0	57	20	37	0	106456.4488	0.0800
56	21	36	0	57	20	38	0	106456.4488	0.0800
56	21	35	0	57	20	38	0	106456.4488	0.0800
87	11	76	0	87	10	77	0	106543.7657	0.0800
79	11	68	0	79	10	69	0	106562.0598	0.0800
47	4	43	2	47	3	44	2	106563.9201	0.1000
47	4	43	1	47	3	44	1	106641.4085	0.1000
44	8	36	1	44	7	37	1	106780.0590	0.1000
67	10	58	0	66	11	56	0	106804.2308	0.1000
57	9	48	1	57	8	49	1	106834.3939	0.1000
52	5	47	1	52	4	48	1	106841.1512	0.1000
49	6	44	0	49	5	45	0	106863.5286	0.0800
14	4	11	1	13	3	10	1	106914.5244	0.1000
27	14	14	0	28	13	16	0	106973.0740	0.0800
27	14	13	0	28	13	16	0	106973.0740	0.0800
27	14	14	0	28	13	15	0	106973.0740	0.0800
27	14	13	0	28	13	15	0	106973.0740	0.0800
57	9	48	0	57	8	49	0	106976.0623	0.0800
46	5	42	1	46	4	43	1	107019.3214	0.1000
68	10	58	1	68	9	59	1	107039.3114	0.1000
68	10	58	0	68	9	59	0	107060.3421	0.0800
39	2	37	0	39	1	38	0	107093.9807	0.0800
43	8	35	2	43	7	36	2	107099.5068	0.1000
44	8	36	0	44	7	37	0	107131.7415	0.0800
52	7	46	2	52	6	47	2	107152.9421	0.1000
14	4	11	0	13	3	10	0	107159.0173	0.0800
39	3	37	0	39	2	38	0	107329.5280	0.0800
36	1	35	0	36	0	36	0	107541.1450	0.0800
47	4	43	0	47	3	44	0	107549.2908	0.0800
36	2	35	0	36	1	36	0	107569.1269	0.0800
64	9	56	0	63	10	53	0	107575.4722	0.0800
52	7	46	1	52	6	47	1	107591.1566	0.1000

50	6	45	3	50	5	46	3	107669.4531	0.1000
46	5	42	0	46	4	43	0	107835.8356	0.0800
52	5	47	0	52	4	48	0	107857.0541	0.0800
56	9	47	3	56	8	48	3	107926.2775	0.1000
42	8	34	3	42	7	35	3	107933.6251	0.1000
14	4	10	2	13	3	11	2	107940.7740	0.1000
35	16	20	0	36	15	21	0	107998.7791	0.0800
35	16	19	0	36	15	21	0	107998.7791	0.0800
35	16	19	0	36	15	22	0	107998.7791	0.0800
35	16	20	0	36	15	22	0	107998.7791	0.0800
84	14	71	0	83	15	68	0	108119.0679	0.0800
27	3	25	2	26	2	24	2	108128.8643	0.1000
27	3	25	0	26	2	24	0	108218.9226	0.0800
43	8	35	1	43	7	36	1	108221.2557	0.1000
27	3	25	1	26	2	24	1	108271.1659	0.1000
52	7	46	0	52	6	47	0	108318.4624	0.0800
32	3	29	1	31	4	28	1	108337.0681	0.1000
14	4	10	1	13	3	11	1	108337.0681	0.1000
42	8	34	2	42	7	35	2	108379.0866	0.1000
43	3	40	0	43	2	41	0	108432.0406	0.0800
32	3	29	0	31	4	28	0	108442.1016	0.0800
56	8	48	0	55	9	47	0	108592.3490	0.0800
43	8	35	0	43	7	36	0	108601.6167	0.0800
6	6	0	2	5	5	0	2	108611.7042	0.1000
6	6	0	2	5	5	1	2	108611.7042	0.1000
6	6	1	2	5	5	0	2	108611.7042	0.1000
6	6	1	2	5	5	1	2	108611.7042	0.1000
10	5	5	1	9	4	5	1	108689.5113	0.1000
10	5	6	1	9	4	5	1	108689.5113	0.1000
10	5	6	1	9	4	6	1	108692.9418	0.1000
10	5	5	1	9	4	6	1	108692.9418	0.1000
30	1	29	0	29	2	28	0	108706.4295	0.0800
30	1	29	1	29	2	28	1	108739.5372	0.0800
37	2	36	3	37	1	37	3	108782.6925	0.1000
91	12	79	0	91	11	80	0	108803.8851	0.0800
50	6	45	1	50	5	46	1	108824.8376	0.1000
30	1	29	2	29	2	28	2	108826.9500	0.1000
32	3	29	2	31	4	28	2	108830.5319	0.1000
30	1	29	3	29	2	28	3	108877.1174	0.1000
49	8	42	3	49	7	43	3	108920.8110	0.1000
48	8	41	3	48	7	42	3	108938.3413	0.1000
43	18	26	0	44	17	28	0	108968.9741	0.0800
43	18	25	0	44	17	27	0	108968.9741	0.0800
43	18	25	0	44	17	28	0	108968.9741	0.0800
43	18	26	0	44	17	27	0	108968.9741	0.0800
41	8	33	3	41	7	34	3	109018.8410	0.1000
50	8	43	3	50	7	44	3	109019.7644	0.1000
10	5	6	0	9	4	5	0	109023.8208	0.0800
10	5	5	0	9	4	6	0	109027.5413	0.0800
47	8	40	3	47	7	41	3	109056.4572	0.1000
30	2	28	1	29	3	27	1	109072.5110	0.1000
30	2	28	0	29	3	27	0	109093.2937	0.0800
92	12	80	0	92	11	81	0	109131.1303	0.0800

30	2	29	0	29	1	28	0	109152.5290	0.0800
31	0	31	0	30	1	30	0	109161.0061	0.0800
31	1	31	0	30	0	30	0	109169.3633	0.0800
80	13	68	0	79	14	65	0	109191.4160	0.0800
31	0	31	1	30	1	30	1	109221.5402	0.0800
31	1	31	1	30	0	30	1	109230.0515	0.0800
30	2	28	3	29	3	27	3	109252.6792	0.1000
30	2	28	2	29	3	27	2	109257.4160	0.1000
30	2	29	2	29	1	28	2	109259.2233	0.1000
46	8	39	3	46	7	40	3	109259.2233	0.1000
90	12	78	0	90	11	79	0	109282.4395	0.0800
6	6	1	1	5	5	1	1	109299.3320	0.1000
6	6	0	1	5	5	1	1	109299.3320	0.1000
6	6	0	1	5	5	0	1	109299.3320	0.1000
6	6	1	1	5	5	0	1	109299.3320	0.1000
31	0	31	2	30	1	30	2	109315.0289	0.1000
30	2	29	3	29	1	28	3	109316.6586	0.1000
31	1	31	2	30	0	30	2	109323.1362	0.1000
31	0	31	3	30	1	30	3	109394.7109	0.1000
48	4	44	3	48	3	45	3	109444.8272	0.1000
43	4	40	0	43	3	41	0	109453.0920	0.0800
78	11	67	0	78	10	68	0	109453.0920	0.0800
42	8	34	1	42	7	35	1	109473.6398	0.1000
41	8	33	2	41	7	34	2	109487.1889	0.1000
49	8	42	2	49	7	43	2	109488.4459	0.1000
48	8	41	2	48	7	42	2	109493.9375	0.1000
16	3	13	0	15	2	14	0	109534.2864	0.0800
53	7	47	1	53	6	48	1	109610.1206	0.1000
82	10	72	0	82	9	73	0	109627.1895	0.0800
36	4	32	0	35	5	31	0	109628.2380	0.0800
50	6	45	0	50	5	46	0	109645.0153	0.0800
56	9	47	1	56	8	48	1	109669.8995	0.1000
71	11	60	0	70	12	59	0	109698.9648	0.0800
6	6	1	0	5	5	0	0	109704.8610	0.0800
6	6	1	0	5	5	1	0	109704.8610	0.0800
6	6	0	0	5	5	0	0	109704.8610	0.0800
6	6	0	0	5	5	1	0	109704.8610	0.0800
46	8	39	2	46	7	40	2	109798.7498	0.1000
51	8	44	2	51	7	45	2	109851.5551	0.1000
56	9	47	0	56	8	48	0	109852.6352	0.0800
42	8	34	0	42	7	35	0	109879.0087	0.0800
51	20	31	0	52	19	34	0	109894.7953	0.0800
51	20	32	0	52	19	33	0	109894.7953	0.0800
51	20	32	0	52	19	34	0	109894.7953	0.0800
51	20	31	0	52	19	33	0	109894.7953	0.0800
40	8	32	3	40	7	33	3	109957.8022	0.1000
88	11	77	0	88	10	78	0	109972.4415	0.0800
45	8	38	2	45	7	39	2	110065.8008	0.1000
47	5	43	1	47	4	44	1	110149.4909	0.1000
76	12	65	0	75	13	62	0	110180.0884	0.0800
43	8	36	3	43	7	37	3	110220.8502	0.1000
52	8	45	2	52	7	46	2	110250.4951	0.1000
22	13	9	0	23	12	12	0	110261.2999	0.0800

22	13	10	0	23	12	11	0	110261.2999	0.0800
22	13	9	0	23	12	11	0	110261.2999	0.0800
22	13	10	0	23	12	12	0	110261.2999	0.0800
64	7	57	1	64	6	58	1	110267.6371	0.1000
93	12	81	0	93	11	82	0	110290.8251	0.0800
68	10	59	0	67	11	56	0	110312.4757	0.0800
49	8	42	1	49	7	43	1	110368.9755	0.0800
53	7	47	0	53	6	48	0	110371.9050	0.0800
15	4	12	0	14	3	11	0	110372.9974	0.0800
76	9	67	0	76	8	68	0	110376.2147	0.0800
44	8	37	2	44	7	38	2	110388.5693	0.1000
40	2	38	0	40	1	39	0	110395.0178	0.0800
48	8	41	1	48	7	42	1	110397.7551	0.0800
40	8	32	2	40	7	33	2	110445.4930	0.1000
67	10	57	0	67	9	58	0	110450.5266	0.0800
50	8	43	1	50	7	44	1	110456.2313	0.0800
28	3	26	0	27	2	25	0	110485.2888	0.0800
58	6	52	0	58	5	53	0	110502.9030	0.0800
89	12	77	0	89	11	78	0	110519.6863	0.1000
51	7	44	0	50	8	43	0	110526.5014	0.0800
47	8	40	1	47	7	41	1	110526.5014	0.0800
28	3	26	1	27	2	25	1	110537.5056	0.1000
48	4	44	1	48	3	45	1	110538.8776	0.1000
41	8	33	1	41	7	34	1	110558.4193	0.1000
40	3	38	0	40	2	39	0	110570.7664	0.0800
42	8	35	3	42	7	36	3	110612.9178	0.1000
51	8	44	1	51	7	45	1	110675.5910	0.1000
46	8	39	1	46	7	40	1	110739.0933	0.0800
43	8	36	2	43	7	37	2	110752.8432	0.1000
37	1	36	0	37	0	37	0	110759.8314	0.0800
39	8	31	3	39	7	32	3	110770.6226	0.1000
72	11	62	0	71	12	59	0	110774.8458	0.0800
37	2	36	0	37	1	37	0	110780.0562	0.0800
59	22	38	0	60	21	40	0	110785.1089	0.0800
59	22	38	0	60	21	39	0	110785.1089	0.0800
59	22	37	0	60	21	39	0	110785.1089	0.0800
59	22	37	0	60	21	40	0	110785.1089	0.0800
26	14	12	0	27	13	14	0	110807.6471	0.0800
26	14	12	0	27	13	15	0	110807.6471	0.0800
26	14	13	0	27	13	15	0	110807.6471	0.0800
26	14	13	0	27	13	14	0	110807.6471	0.0800
65	9	57	0	64	10	54	0	110809.0195	0.0800
54	8	47	3	54	7	48	3	110876.4015	0.1000
49	8	42	0	49	7	43	0	110891.8595	0.0800
48	8	41	0	48	7	42	0	110909.0025	0.0800
41	8	33	0	41	7	34	0	110985.4503	0.0800
50	8	43	0	50	7	44	0	110993.7202	0.0800
75	11	65	0	75	10	65	0	110994.6557	0.0800
45	8	38	1	45	7	39	1	111019.6730	0.0800
41	8	34	3	41	7	35	3	111020.7562	0.1000
47	8	40	0	47	7	41	0	111028.7432	0.0800
52	8	45	1	52	7	46	1	111041.5453	0.1000
44	3	41	1	44	2	42	1	111071.9769	0.1000

42	8	35	2	42	7	36	2	111145.6724	0.1000
63	23	41	0	64	22	42	0	111219.3475	0.0800
63	23	40	0	64	22	42	0	111219.3475	0.0800
63	23	40	0	64	22	43	0	111219.3475	0.0800
63	23	41	0	64	22	43	0	111219.3475	0.0800
51	8	44	0	51	7	45	0	111230.2445	0.0800
46	8	39	0	46	7	40	0	111234.6558	0.0800
39	8	31	2	39	7	32	2	111274.8072	0.1000
70	8	62	0	70	7	63	0	111291.7046	0.0800
44	8	37	1	44	7	38	1	111353.1745	0.0800
51	6	46	2	51	5	47	2	111415.6661	0.1000
54	7	48	2	54	6	49	2	111427.3088	0.1000
40	8	33	3	40	7	34	3	111434.7568	0.1000
48	4	44	0	48	3	45	0	111463.2121	0.0800
38	8	30	3	38	7	31	3	111475.8073	0.1000
40	8	32	1	40	7	33	1	111497.2375	0.0800
45	8	38	0	45	7	39	0	111510.7596	0.0800
64	7	57	0	64	6	58	0	111538.1369	0.0800
54	8	47	2	54	7	48	2	111548.5476	0.1000
41	8	34	2	41	7	35	2	111555.4265	0.1000
53	8	46	1	53	7	47	1	111567.5672	0.1000
52	8	45	0	52	7	46	0	111616.2954	0.0800
41	2	39	3	41	1	40	3	111631.3047	0.1000
51	6	46	1	51	5	47	1	111685.5041	0.1000
43	8	36	1	43	7	37	1	111725.5225	0.0800
54	7	48	1	54	6	49	1	111803.3091	0.1000
44	8	37	0	44	7	38	0	111841.7349	0.0800
39	8	32	3	39	7	33	3	111846.6377	0.1000
66	10	56	3	66	9	57	3	111865.2303	0.1000
44	4	41	1	44	3	42	1	111872.7823	0.1000
44	3	41	0	44	2	42	0	111927.8880	0.0800
40	8	32	0	40	7	33	0	111942.5770	0.0800
40	8	33	2	40	7	34	2	111972.1630	0.1000
38	8	30	2	38	7	31	2	111993.9235	0.1000
37	8	29	3	37	7	30	3	112089.5656	0.1000
42	8	35	1	42	7	36	1	112124.2061	0.0800
53	8	46	0	53	7	47	0	112165.5318	0.0800
46	6	40	1	45	7	39	1	112197.2476	0.1000
43	8	36	0	43	7	37	0	112213.3027	0.0800
31	1	30	0	30	2	29	0	112229.9812	0.0800
38	8	31	3	38	7	32	3	112249.9463	0.1000
54	8	47	1	54	7	48	1	112265.4162	0.0800
31	1	30	1	30	2	29	1	112266.1883	0.0800
94	12	82	0	94	11	83	0	112288.1782	0.0800
15	4	11	1	14	3	12	1	112306.1263	0.1000
39	8	31	1	39	7	32	1	112310.4037	0.0800
53	5	48	0	53	4	49	0	112322.1053	0.0800
31	1	30	2	30	2	29	2	112354.3904	0.1000
39	8	32	2	39	7	33	2	112387.4635	0.1000
46	6	40	0	45	7	39	0	112387.4635	0.0800
41	5	36	1	40	6	35	1	112392.3698	0.1000
31	1	30	3	30	2	29	3	112408.0912	0.1000
88	12	76	0	88	11	77	0	112449.5793	0.1000

11	5	7	1	10	4	6	1	112456.5332	0.1000
11	5	6	1	10	4	7	1	112465.0818	0.1000
55	8	48	2	55	7	49	2	112468.2677	0.1000
19	3	16	3	19	0	19	3	112514.2450	0.1000
55	9	46	0	55	8	47	0	112529.9507	0.0800
51	6	46	0	51	5	47	0	112536.9515	0.0800
41	8	34	1	41	7	35	1	112537.9499	0.0800
31	2	30	0	30	1	29	0	112558.8289	0.0800
15	4	11	0	14	3	12	0	112580.2057	0.0800
41	5	36	0	40	6	35	0	112590.8853	0.0800
31	2	30	1	30	1	29	1	112600.2144	0.1000
54	7	48	0	54	6	49	0	112600.2144	0.0800
42	8	35	0	42	7	36	0	112612.5095	0.0800
37	8	29	2	37	7	30	2	112619.2757	0.1000
36	8	28	3	36	7	29	3	112625.5634	0.1000
32	0	32	0	31	1	31	0	112630.7384	0.0800
32	1	32	0	31	0	31	0	112636.6087	0.0800
37	8	30	3	37	7	31	3	112639.3241	0.1000
31	2	30	2	30	1	29	2	112672.6882	0.1000
32	0	32	1	31	1	31	1	112693.6258	0.0800
32	1	32	1	31	0	31	1	112699.6354	0.0800
77	11	66	0	77	10	67	0	112708.7000	0.0800
44	4	41	0	44	3	42	0	112712.2287	0.0800
32	0	32	4	31	1	31	4	112714.7459	0.1000
32	1	32	4	31	0	31	4	112721.8748	0.1000
31	2	30	3	30	1	29	3	112732.4683	0.1000
39	8	31	0	39	7	32	0	112771.2248	0.0800
38	2	37	2	38	1	38	2	112790.2753	0.1000
32	0	32	2	31	1	31	2	112790.2753	0.1000
11	5	7	0	10	4	6	0	112791.2219	0.0800
38	8	31	2	38	7	32	2	112794.7279	0.1000
32	1	32	2	31	0	31	2	112795.9529	0.1000
11	5	7	0	10	4	7	0	112799.8826	0.0800
11	5	6	0	10	4	7	0	112799.8826	0.0800
42	18	24	0	43	17	27	0	112833.6413	0.0800
42	18	25	0	43	17	26	0	112833.6413	0.0800
42	18	24	0	43	17	26	0	112833.6413	0.0800
42	18	25	0	43	17	27	0	112833.6413	0.0800
41	2	39	1	41	1	40	1	112857.9304	0.1000
85	14	72	0	84	15	69	0	112870.5585	0.0800
32	0	32	3	31	1	31	3	112873.7792	0.1000
32	1	32	3	31	0	31	3	112878.8709	0.1000
54	8	47	0	54	7	48	0	112889.3502	0.0800
29	3	27	2	28	2	26	2	112891.5350	0.1000
55	7	49	3	55	6	50	3	112925.6808	0.1000
29	3	27	0	28	2	26	0	112926.7823	0.0800
54	9	45	3	54	8	46	3	112956.1886	0.1000
40	8	33	1	40	7	34	1	112957.0893	0.0800
29	3	27	3	28	2	26	3	112958.0278	0.1000
29	3	27	1	28	2	26	1	112977.8139	0.0800
41	3	39	1	41	2	40	1	112991.5300	0.1000
36	8	29	3	36	7	30	3	113011.0329	0.1000
38	8	30	1	38	7	31	1	113016.2340	0.0800

41	8	34	0	41	7	35	0	113027.9092	0.0800
7	6	1	1	6	5	2	1	113088.1075	0.0800
7	6	2	1	6	5	1	1	113088.1075	0.0800
7	6	1	1	6	5	1	1	113088.1075	0.0800
7	6	2	1	6	5	2	1	113088.1075	0.0800
35	8	27	3	35	7	28	3	113095.5447	0.1000
55	8	48	1	55	7	49	1	113145.1115	0.0800
36	8	28	2	36	7	29	2	113165.1247	0.1000
37	8	30	2	37	7	31	2	113188.2169	0.1000
31	2	29	1	30	3	28	1	113224.1284	0.0800
31	2	29	0	30	3	28	0	113237.6665	0.0800
45	3	42	3	45	2	43	3	113298.6000	0.1000
46	19	28	0	47	18	30	0	113307.9443	0.0800
46	19	27	0	47	18	30	0	113307.9443	0.0800
46	19	28	0	47	18	29	0	113307.9443	0.0800
46	19	27	0	47	18	29	0	113307.9443	0.0800
48	5	44	1	48	4	45	1	113326.7832	0.0800
35	8	28	3	35	7	29	3	113362.1272	0.1000
39	8	32	1	39	7	33	1	113373.5909	0.0800
31	2	29	2	30	3	28	2	113391.6454	0.1000
31	2	29	3	30	3	28	3	113393.8739	0.1000
16	4	13	0	15	3	12	0	113401.4761	0.0800
41	5	36	3	40	6	35	3	113426.1874	0.1000
40	8	33	0	40	7	34	0	113449.5383	0.0800
38	8	30	0	38	7	31	0	113490.0856	0.0800
7	6	2	0	6	5	1	0	113494.1617	0.0800
7	6	2	0	6	5	2	0	113494.1617	0.0800
7	6	1	0	6	5	1	0	113494.1617	0.0800
7	6	1	0	6	5	2	0	113494.1617	0.0800
34	8	26	3	34	7	27	3	113509.2268	0.1000
36	8	29	2	36	7	30	2	113564.1275	0.1000
56	8	49	2	56	7	50	2	113578.3510	0.1000
37	8	29	1	37	7	30	1	113630.7860	0.0800
35	8	27	2	35	7	28	2	113643.4962	0.1000
41	2	39	0	41	1	40	0	113682.7960	0.0800
34	8	27	3	34	7	28	3	113691.2067	0.1000
50	20	30	0	51	19	33	0	113771.8986	0.0800
50	20	31	0	51	19	33	0	113771.8986	0.0800
50	20	30	0	51	19	32	0	113771.8986	0.0800
50	20	31	0	51	19	32	0	113771.8986	0.0800
38	8	31	1	38	7	32	1	113780.7729	0.1000
66	10	56	1	66	9	57	1	113790.7150	0.1000
55	8	48	0	55	7	49	0	113797.3494	0.0800
41	3	39	0	41	2	40	0	113813.2687	0.0800
66	10	56	0	66	9	57	0	113854.6292	0.0800
39	8	32	0	39	7	33	0	113869.1185	0.0800
33	8	25	3	33	7	26	3	113874.4926	0.1000
35	8	28	2	35	7	29	2	113919.5685	0.1000
38	2	37	0	38	1	38	0	113990.3945	0.0800
33	8	26	3	33	7	27	3	113996.9942	0.1000
34	8	26	2	34	7	27	2	114064.2945	0.1000
33	3	30	1	32	4	29	1	114080.4326	0.0800
21	13	8	0	22	12	11	0	114083.5484	0.0800

21	13	9	0	22	12	10	0	114083.5484	0.0800
21	13	8	0	22	12	10	0	114083.5484	0.0800
21	13	9	0	22	12	11	0	114083.5484	0.0800
89	11	78	0	89	10	79	0	114102.9565	0.0800
57	8	50	3	57	7	51	3	114114.3395	0.1000
37	8	29	0	37	7	30	0	114115.6965	0.0800
55	7	49	1	55	6	50	1	114161.4071	0.1000
36	8	28	1	36	7	29	1	114167.9589	0.0800
37	8	30	1	37	7	31	1	114173.7341	0.0800
33	3	30	0	32	4	29	0	114181.2702	0.0800
48	5	44	0	48	4	45	0	114196.6409	0.0800
32	8	24	3	32	7	25	3	114198.0883	0.1000
56	8	49	1	56	7	50	1	114213.5437	0.0800
54	21	33	0	55	20	36	0	114226.7115	0.0800
54	21	34	0	55	20	35	0	114226.7115	0.0800
54	21	33	0	55	20	35	0	114226.7115	0.0800
54	21	34	0	55	20	36	0	114226.7115	0.0800
34	8	27	2	34	7	28	2	114252.6501	0.1000
32	8	25	3	32	7	26	3	114279.1499	0.1000
38	8	31	0	38	7	32	0	114279.9980	0.0800
49	4	45	1	49	3	46	1	114341.1185	0.1000
52	6	47	2	52	5	48	2	114381.8962	0.1000
69	10	60	0	68	11	57	0	114477.0586	0.0800
31	8	23	3	31	7	24	3	114485.2441	0.1000
45	3	42	1	45	2	43	1	114506.7632	0.1000
54	5	49	3	54	4	50	3	114533.1737	0.1000
33	3	30	2	32	4	29	2	114534.3383	0.1000
31	8	24	3	31	7	25	3	114538.2221	0.1000
36	8	29	1	36	7	30	1	114548.4758	0.0800
33	8	26	2	33	7	27	2	114562.4142	0.1000
25	14	11	0	26	13	13	0	114638.0305	0.0800
25	14	12	0	26	13	14	0	114638.0305	0.0800
25	14	12	0	26	13	13	0	114638.0305	0.0800
25	14	11	0	26	13	14	0	114638.0305	0.0800
35	8	27	1	35	7	28	1	114639.1806	0.0800
52	6	47	1	52	5	48	1	114643.7548	0.1000
62	9	53	0	61	10	52	0	114653.5373	0.0800
36	8	28	0	36	7	29	0	114662.0548	0.0800
37	8	30	0	37	7	31	0	114676.6808	0.0800
83	10	73	0	83	9	74	0	114691.7533	0.0800
30	8	22	3	30	7	23	3	114740.5418	0.1000
32	8	24	2	32	7	25	2	114764.4041	0.1000
30	8	23	3	30	7	24	3	114774.5132	0.1000
32	8	25	2	32	7	26	2	114848.5214	0.1000
57	8	50	2	57	7	51	2	114882.9413	0.1000
56	8	49	0	56	7	50	0	114896.6865	0.0800
35	8	28	1	35	7	29	1	114902.4990	0.0800
81	13	68	0	80	14	67	0	114974.0568	0.0800
54	9	45	0	54	8	46	0	114979.0531	0.0800
55	7	49	0	55	6	50	0	114993.5482	0.0800
34	8	26	1	34	7	27	1	115054.2913	0.0800
36	8	29	0	36	7	30	0	115055.3545	0.0800
95	12	83	0	95	11	84	0	115106.7099	0.0800

31	8	24	2	31	7	25	2	115110.9406	0.1000
45	4	42	1	45	3	43	1	115119.7334	0.1000
35	8	27	0	35	7	28	0	115141.0997	0.0800
28	8	21	3	28	7	22	3	115182.9611	0.1000
34	8	27	1	34	7	28	1	115233.7838	0.0800
49	4	45	0	49	3	46	0	115282.4255	0.0800
30	8	22	2	30	7	23	2	115315.3449	0.1000
27	8	19	3	27	7	20	3	115349.4334	0.1000
30	8	23	2	30	7	24	2	115350.4675	0.1000
27	8	20	3	27	7	21	3	115357.2618	0.1000
45	3	42	0	45	2	43	0	115382.8118	0.0800
35	8	28	0	35	7	29	0	115413.2507	0.0800
33	8	25	1	33	7	26	1	115420.9458	0.0800
59	6	53	0	59	5	54	0	115460.1903	0.0800
57	8	50	1	57	7	51	1	115475.8705	0.0800
26	8	19	3	26	7	19	3	115508.4445	0.1000
26	8	18	3	26	7	19	3	115508.4445	0.1000
26	8	18	3	26	7	20	3	115513.2928	0.1000
26	8	19	3	26	7	20	3	115513.2928	0.1000
71	8	63	1	71	7	64	1	115522.8779	0.1000
30	3	28	2	29	2	27	2	115522.8779	0.1000
52	6	47	0	52	5	48	0	115525.8473	0.0800
30	3	28	0	29	2	27	0	115533.9023	0.0800
33	8	26	1	33	7	27	1	115541.7394	0.0800
29	8	21	2	29	7	22	2	115545.7869	0.1000
34	8	26	0	34	7	27	0	115562.7691	0.0800
29	8	22	2	29	7	23	2	115567.9798	0.1000
29	8	21	2	29	7	23	2	115568.8517	0.1000
58	8	51	3	58	7	52	3	115578.4282	0.1000
30	3	28	1	29	2	27	1	115582.9847	0.0800
25	8	17	3	25	7	19	3	115652.0017	0.1000
25	8	18	3	25	7	19	3	115652.0017	0.1000
32	1	31	0	31	2	30	0	115738.9829	0.0800
32	8	24	1	32	7	25	1	115745.8871	0.0800
34	8	27	0	34	7	28	0	115748.4132	0.0800
28	8	20	2	28	7	21	2	115750.7212	0.1000
42	2	40	2	42	1	41	2	115753.5077	0.1000
28	8	21	2	28	7	22	2	115764.4739	0.1000
33	4	29	2	33	3	31	2	115764.4739	0.1000
24	8	16	3	24	7	17	3	115774.2072	0.1000
24	8	17	3	24	7	17	3	115774.2072	0.1000
24	8	16	3	24	7	18	3	115775.5825	0.1000
24	8	17	3	24	7	18	3	115775.5825	0.1000
32	1	31	1	31	2	30	1	115778.0154	0.0800
32	8	25	1	32	7	26	1	115825.9005	0.0800
32	1	31	2	31	2	30	2	115867.5817	0.1000
23	8	16	3	23	7	16	3	115883.6715	0.1000
23	8	15	3	23	7	16	3	115883.6715	0.1000
23	8	16	3	23	7	17	3	115884.5534	0.1000
23	8	15	3	23	7	17	3	115884.5534	0.1000
32	1	31	3	31	2	30	3	115924.7242	0.1000
27	8	19	2	27	7	20	2	115932.8844	0.1000
33	8	25	0	33	7	26	0	115935.0942	0.0800

77	9	68	0	77	8	69	0	115940.1390	0.0800
27	8	20	2	27	7	21	2	115941.2584	0.1000
32	2	31	0	31	1	30	0	115980.5024	0.0800
22	8	15	3	22	7	16	3	115980.5024	0.1000
22	8	14	3	22	7	16	3	115980.5024	0.1000
45	4	42	0	45	3	43	0	115982.4501	0.0800
32	2	31	1	31	1	30	1	116023.6046	0.0800
31	8	23	1	31	7	24	1	116034.4090	0.0800
33	8	26	0	33	7	27	0	116060.0137	0.0800
21	8	14	3	21	7	14	3	116063.5763	0.1000
21	8	13	3	21	7	15	3	116063.5763	0.1000
21	8	14	3	21	7	15	3	116063.5763	0.1000
21	8	13	3	21	7	14	3	116063.5763	0.1000
31	8	24	1	31	7	25	1	116086.5828	0.0800
26	8	18	2	26	7	19	2	116094.4980	0.1000
33	0	33	0	32	1	32	0	116100.0946	0.0800
32	2	31	2	31	1	30	2	116101.1456	0.1000
33	1	33	0	32	0	32	0	116104.2457	0.0800
42	2	40	1	42	1	41	1	116113.2965	0.1000
67	9	59	0	66	10	56	0	116127.2771	0.0800
20	8	12	3	20	7	13	3	116136.1797	0.1000
20	8	13	3	20	7	13	3	116136.1797	0.1000
20	8	13	3	20	7	14	3	116136.1797	0.1000
20	8	12	3	20	7	14	3	116136.1797	0.1000
33	0	33	1	32	1	32	1	116165.2792	0.0800
33	1	33	1	32	0	32	1	116169.5216	0.0800
33	1	33	4	32	0	32	4	116188.2625	0.1000
57	8	50	0	57	7	51	0	116191.9354	0.0800
8	6	2	2	7	5	3	2	116195.2232	0.1000
8	6	3	2	7	5	3	2	116195.2232	0.1000
8	6	2	2	7	5	2	2	116195.2232	0.1000
8	6	3	2	7	5	2	2	116195.2232	0.1000
19	8	12	3	19	7	13	3	116198.6810	0.1000
19	8	11	3	19	7	13	3	116198.6810	0.1000
19	8	12	3	19	7	12	3	116198.6810	0.1000
19	8	11	3	19	7	12	3	116198.6810	0.1000
12	5	8	1	11	4	7	1	116212.3995	0.1000
42	3	40	1	42	2	41	1	116212.3995	0.1000
17	4	14	0	16	3	13	0	116215.9296	0.0800
76	11	65	0	76	10	66	0	116215.9296	0.1000
12	5	7	1	11	4	8	1	116230.6324	0.1000
25	8	18	2	25	7	18	2	116237.5673	0.1000
25	8	17	2	25	7	18	2	116237.5673	0.1000
25	8	17	2	25	7	19	2	116240.4555	0.1000
25	8	18	2	25	7	19	2	116240.4555	0.1000
18	8	11	3	18	7	11	3	116252.2800	0.1000
18	8	11	3	18	7	12	3	116252.2800	0.1000
18	8	10	3	18	7	11	3	116252.2800	0.1000
18	8	10	3	18	7	12	3	116252.2800	0.1000
32	8	24	0	32	7	25	0	116264.9621	0.0800
33	1	33	2	32	0	32	2	116269.0624	0.1000
30	8	22	1	30	7	23	1	116290.9215	0.0800
17	8	9	3	17	7	11	3	116297.7943	0.1000

17	8	10	3	17	7	11	3	116297.7943	0.1000
17	8	9	3	17	7	10	3	116297.7943	0.1000
17	8	10	3	17	7	10	3	116297.7943	0.1000
57	8	49	0	56	9	48	0	116319.7987	0.0800
30	8	23	1	30	7	24	1	116324.5286	0.0800
16	8	9	3	16	7	9	3	116336.0800	0.1000
16	8	9	3	16	7	10	3	116336.0800	0.1000
16	8	8	3	16	7	10	3	116336.0800	0.1000
16	8	8	3	16	7	9	3	116336.0800	0.1000
32	8	25	0	32	7	26	0	116347.6046	0.0800
33	0	33	3	32	1	32	3	116351.0754	0.1000
33	1	33	3	32	0	32	3	116354.9579	0.1000
24	8	16	2	24	7	17	2	116363.8480	0.1000
24	8	17	2	24	7	17	2	116363.8480	0.1000
15	8	8	3	15	7	9	3	116367.9519	0.1000
15	8	7	3	15	7	8	3	116367.9519	0.1000
15	8	8	3	15	7	8	3	116367.9519	0.1000
15	8	7	3	15	7	9	3	116367.9519	0.1000
58	8	51	2	58	7	52	2	116383.6280	0.1000
14	8	7	3	14	7	7	3	116394.3978	0.1000
14	8	6	3	14	7	8	3	116394.3978	0.1000
14	8	7	3	14	7	8	3	116394.3978	0.1000
14	8	6	3	14	7	7	3	116394.3978	0.1000
13	8	6	3	13	7	6	3	116415.8306	0.1000
13	8	5	3	13	7	6	3	116415.8306	0.1000
13	8	5	3	13	7	7	3	116415.8306	0.1000
13	8	6	3	13	7	7	3	116415.8306	0.1000
12	8	4	3	12	7	5	3	116433.0014	0.1000
12	8	4	3	12	7	6	3	116433.0014	0.1000
12	8	5	3	12	7	6	3	116433.0014	0.1000
12	8	5	3	12	7	5	3	116433.0014	0.1000
11	8	3	3	11	7	5	3	116446.6021	0.1000
11	8	3	3	11	7	4	3	116446.6021	0.1000
11	8	4	3	11	7	5	3	116446.6021	0.1000
11	8	4	3	11	7	4	3	116446.6021	0.1000
23	8	15	2	23	7	16	2	116475.0451	0.1000
23	8	16	2	23	7	16	2	116475.0451	0.1000
23	8	15	2	23	7	17	2	116475.9492	0.1000
23	8	16	2	23	7	17	2	116475.9492	0.1000
29	8	21	1	29	7	22	1	116519.2790	0.0800
37	4	33	1	36	5	32	1	116536.7032	0.1000
29	8	22	1	29	7	23	1	116540.3922	0.0800
49	5	45	1	49	4	46	1	116541.9243	0.0800
12	5	8	0	11	4	7	0	116547.2453	0.0800
100	13	87	1	100	12	88	1	116556.6797	0.1000
31	8	23	0	31	7	24	0	116557.5986	0.0800
12	5	7	0	11	4	8	0	116565.6077	0.0800
22	8	14	2	22	7	15	2	116572.3471	0.1000
22	8	15	2	22	7	15	2	116572.3471	0.1000
31	8	24	0	31	7	25	0	116611.6135	0.0800
54	5	49	0	54	4	50	0	116650.1529	0.0800
16	4	12	0	15	3	13	0	116652.1651	0.0800
21	8	13	2	21	7	14	2	116657.3492	0.1000

21	8	13	2	21	7	15	2	116657.3492	0.1000
21	8	14	2	21	7	14	2	116657.3492	0.1000
21	8	14	2	21	7	15	2	116657.3492	0.1000
37	4	33	0	36	5	32	0	116710.8925	0.0800
28	8	20	1	28	7	21	1	116722.4382	0.0800
20	8	12	2	20	7	14	2	116730.9422	0.1000
20	8	13	2	20	7	13	2	116730.9422	0.1000
20	8	13	2	20	7	14	2	116730.9422	0.1000
20	8	12	2	20	7	13	2	116730.9422	0.1000
28	8	21	1	28	7	22	1	116735.5148	0.0800
19	8	11	2	19	7	13	2	116794.3426	0.1000
19	8	12	2	19	7	13	2	116794.3426	0.1000
19	8	11	2	19	7	12	2	116794.3426	0.1000
19	8	12	2	19	7	12	2	116794.3426	0.1000
30	8	22	0	30	7	23	0	116817.7547	0.0800
18	8	10	2	18	7	11	2	116848.6708	0.1000
18	8	11	2	18	7	11	2	116848.6708	0.1000
18	8	10	2	18	7	12	2	116848.6708	0.1000
18	8	11	2	18	7	12	2	116848.6708	0.1000
30	8	23	0	30	7	24	0	116852.4018	0.0800
8	6	3	1	7	5	3	1	116875.9648	0.0800
8	6	3	1	7	5	2	1	116875.9648	0.0800
8	6	2	1	7	5	2	1	116875.9648	0.0800
8	6	2	1	7	5	3	1	116875.9648	0.0800
17	8	10	2	17	7	11	2	116894.7798	0.1000
17	8	9	2	17	7	11	2	116894.7798	0.1000
17	8	10	2	17	7	10	2	116894.7798	0.1000
17	8	9	2	17	7	10	2	116894.7798	0.1000
27	8	19	1	27	7	20	1	116903.0184	0.0800
27	8	20	1	27	7	21	1	116911.0048	0.0800
16	8	8	2	16	7	9	2	116933.6041	0.1000
16	8	9	2	16	7	9	2	116933.6041	0.1000
16	8	9	2	16	7	10	2	116933.6041	0.1000
16	8	8	2	16	7	10	2	116933.6041	0.1000
58	8	51	1	58	7	52	1	116933.6041	0.0800
65	7	58	0	65	6	59	0	116934.5666	0.0800
71	8	63	0	71	7	64	0	116935.9636	0.0800
42	2	40	0	42	1	41	0	116959.5701	0.0800
15	8	8	2	15	7	9	2	116965.9581	0.1000
15	8	7	2	15	7	9	2	116965.9581	0.1000
15	8	8	2	15	7	8	2	116965.9581	0.1000
15	8	7	2	15	7	8	2	116965.9581	0.1000
14	8	6	2	14	7	7	2	116992.6696	0.1000
14	8	7	2	14	7	8	2	116992.6696	0.1000
14	8	6	2	14	7	8	2	116992.6696	0.1000
14	8	7	2	14	7	7	2	116992.6696	0.1000
13	8	6	2	13	7	7	2	117014.3379	0.1000
13	8	5	2	13	7	6	2	117014.3379	0.1000
13	8	6	2	13	7	6	2	117014.3379	0.1000
13	8	5	2	13	7	7	2	117014.3379	0.1000
12	8	4	2	12	7	6	2	117031.6157	0.1000
12	8	4	2	12	7	5	2	117031.6157	0.1000
12	8	5	2	12	7	6	2	117031.6157	0.1000

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11	8	4	2	11	7	4	2	117045.5473	0.1000
11	8	3	2	11	7	5	2	117045.5473	0.1000
11	8	3	2	11	7	4	2	117045.5473	0.1000
11	8	4	2	11	7	5	2	117045.5473	0.1000
29	8	21	0	29	7	22	0	117049.2611	0.0800
42	3	40	0	42	2	41	0	117056.3560	0.0800
10	8	2	2	10	7	3	2	117056.3560	0.1000
10	8	2	2	10	7	4	2	117056.3560	0.1000
10	8	3	2	10	7	4	2	117056.3560	0.1000
10	8	3	2	10	7	3	2	117056.3560	0.1000
26	8	18	1	26	7	19	1	117063.3038	0.0800
26	8	19	1	26	7	20	1	117067.9936	0.0800
29	8	22	0	29	7	23	0	117070.9995	0.0800
65	10	55	1	65	9	56	1	117081.9674	0.1000
65	10	55	0	65	9	56	0	117184.5191	0.0800
53	9	44	0	53	8	45	0	117187.6068	0.0800
39	1	38	0	39	0	39	0	117189.3728	0.0800
25	8	17	1	25	7	18	1	117205.3799	0.0800
25	8	18	1	25	7	19	1	117208.0623	0.0800
25	8	17	1	25	7	19	1	117208.0623	0.0800
32	2	30	1	31	3	29	1	117241.6343	0.0800
32	2	30	0	31	3	29	0	117248.1155	0.0800
28	8	20	0	28	7	21	0	117255.0594	0.0800
28	8	21	0	28	7	22	0	117268.6608	0.0800
100	13	87	0	100	12	88	0	117279.2930	0.0800
8	6	2	0	7	5	3	0	117282.6484	0.0800
8	6	3	0	7	5	2	0	117282.6484	0.0800
8	6	2	0	7	5	2	0	117282.6484	0.0800
8	6	3	0	7	5	3	0	117282.6484	0.0800
24	8	17	1	24	7	17	1	117330.7175	0.0800
24	8	16	1	24	7	17	1	117330.7175	0.0800
24	8	16	1	24	7	18	1	117332.2829	0.0800
24	8	17	1	24	7	18	1	117332.2829	0.0800
32	2	30	2	31	3	29	2	117393.2883	0.1000
32	2	30	3	31	3	29	3	117403.5069	0.1000
53	6	48	2	53	5	49	2	117429.9021	0.1000
27	8	19	0	27	7	20	0	117437.9408	0.0800
27	8	20	0	27	7	20	0	117437.9408	0.0800
23	8	16	1	23	7	16	1	117440.9892	0.0800
23	8	15	1	23	7	16	1	117440.9892	0.0800
23	8	16	1	23	7	17	1	117441.9300	0.0800
23	8	15	1	23	7	17	1	117441.9300	0.0800
27	8	20	0	27	7	21	0	117446.3608	0.0800
27	8	19	0	27	7	21	0	117446.3608	0.0800
52	9	43	2	52	8	44	2	117446.3608	0.1000
22	8	14	1	22	7	15	1	117537.8328	0.0800
22	8	15	1	22	7	15	1	117537.8328	0.0800
56	7	50	0	56	6	51	0	117540.6595	0.0800
26	8	18	0	26	7	19	0	117600.3936	0.0800
26	8	19	0	26	7	20	0	117605.3217	0.0800
21	8	14	1	21	7	14	1	117622.2392	0.0800
21	8	13	1	21	7	14	1	117622.2392	0.0800

49	20	30	0	50	19	31	0	117644.5581	0.0800
49	20	29	0	50	19	31	0	117644.5581	0.0800
49	20	29	0	50	19	32	0	117644.5581	0.0800
49	20	30	0	50	19	32	0	117644.5581	0.0800
58	8	51	0	58	7	52	0	117684.9510	0.0800
20	8	13	1	20	7	13	1	117695.3512	0.0800
20	8	13	1	20	7	14	1	117695.3512	0.0800
20	8	12	1	20	7	13	1	117695.3512	0.0800
25	8	18	0	25	7	18	0	117744.1638	0.0800
25	8	17	0	25	7	18	0	117744.1638	0.0800
25	8	17	0	25	7	19	0	117747.0452	0.0800
25	8	18	0	25	7	19	0	117747.0452	0.0800
19	8	11	1	19	7	13	1	117758.4221	0.0800
19	8	12	1	19	7	13	1	117758.4221	0.0800
19	8	12	1	19	7	12	1	117758.4221	0.0800
19	8	11	1	19	7	12	1	117758.4221	0.0800
18	8	10	1	18	7	11	1	117812.4697	0.0800
18	8	11	1	18	7	12	1	117812.4697	0.0800
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17	8	9	1	17	7	10	1	117858.3537	0.0800
17	8	10	1	17	7	11	1	117858.3537	0.0800
17	8	9	1	17	7	11	1	117858.3537	0.0800
17	8	10	1	17	7	10	1	117858.3537	0.0800
24	8	16	0	24	7	17	0	117871.1431	0.0800
24	8	17	0	24	7	17	0	117871.1431	0.0800
24	8	17	0	24	7	18	0	117872.7475	0.0800
24	8	16	0	24	7	18	0	117872.7475	0.0800
16	8	9	1	16	7	10	1	117897.0318	0.0800
16	8	9	1	16	7	9	1	117897.0318	0.0800
16	8	8	1	16	7	10	1	117897.0318	0.0800
16	8	8	1	16	7	9	1	117897.0318	0.0800
20	13	8	0	21	12	10	0	117901.9096	0.0800
20	13	7	0	21	12	9	0	117901.9096	0.0800
20	13	8	0	21	12	9	0	117901.9096	0.0800
20	13	7	0	21	12	10	0	117901.9096	0.0800
46	3	43	1	46	2	44	1	117907.2630	0.0800
15	8	7	1	15	7	9	1	117929.3133	0.0800
15	8	8	1	15	7	9	1	117929.3133	0.0800
15	8	8	1	15	7	8	1	117929.3133	0.0800
15	8	7	1	15	7	8	1	117929.3133	0.0800
14	8	6	1	14	7	8	1	117955.8981	0.0800
14	8	6	1	14	7	7	1	117955.8981	0.0800
14	8	7	1	14	7	7	1	117955.8981	0.0800
14	8	7	1	14	7	8	1	117955.8981	0.0800
13	8	6	1	13	7	7	1	117977.5334	0.0800
13	8	6	1	13	7	6	1	117977.5334	0.0800
13	8	5	1	13	7	6	1	117977.5334	0.0800
13	8	5	1	13	7	7	1	117977.5334	0.0800
23	8	16	0	23	7	16	0	117982.8190	0.0800
23	8	15	0	23	7	16	0	117982.8190	0.0800
23	8	15	0	23	7	17	0	117983.7559	0.0800
23	8	16	0	23	7	17	0	117983.7559	0.0800

12	8	4	1	12	7	6	1	117994.8543	0.0800
12	8	5	1	12	7	5	1	117994.8543	0.0800
12	8	4	1	12	7	5	1	117994.8543	0.0800
12	8	5	1	12	7	6	1	117994.8543	0.0800
11	8	4	1	11	7	4	1	118008.6506	0.0800
11	8	3	1	11	7	4	1	118008.6506	0.0800
11	8	4	1	11	7	5	1	118008.6506	0.0800
11	8	3	1	11	7	5	1	118008.6506	0.0800
10	8	2	1	10	7	3	1	118019.1914	0.0800
10	8	2	1	10	7	4	1	118019.1914	0.0800
10	8	3	1	10	7	4	1	118019.1914	0.0800
10	8	3	1	10	7	3	1	118019.1914	0.0800
9	8	2	1	9	7	2	1	118027.2568	0.0800
9	8	1	1	9	7	2	1	118027.2568	0.0800
9	8	1	1	9	7	3	1	118027.2568	0.0800
9	8	2	1	9	7	3	1	118027.2568	0.0800
86	12	74	0	86	11	75	0	118034.5684	0.0800
50	4	46	1	50	3	47	1	118060.0610	0.1000
59	8	52	2	59	7	53	2	118079.2251	0.1000
22	8	14	0	22	7	16	0	118081.1948	0.0800
22	8	15	0	22	7	16	0	118081.1948	0.0800
68	9	60	0	67	10	57	0	118082.1756	0.0800
21	8	14	0	21	7	14	0	118166.2023	0.0800
21	8	13	0	21	7	14	0	118166.2023	0.0800
20	8	13	0	20	7	14	0	118240.2003	0.0800
20	8	12	0	20	7	13	0	118240.2003	0.0800
20	8	13	0	20	7	13	0	118240.2003	0.0800
20	8	12	0	20	7	14	0	118240.2003	0.0800
31	3	29	0	30	2	28	0	118291.6195	0.0800
19	8	11	0	19	7	12	0	118303.9961	0.0800
19	8	12	0	19	7	13	0	118303.9961	0.0800
19	8	11	0	19	7	13	0	118303.9961	0.0800
19	8	12	0	19	7	12	0	118303.9961	0.0800
31	3	29	1	30	2	28	1	118338.4947	0.0800
18	8	11	0	18	7	11	0	118358.6416	0.0800
18	8	10	0	18	7	12	0	118358.6416	0.0800
18	8	10	0	18	7	11	0	118358.6416	0.0800
18	8	11	0	18	7	12	0	118358.6416	0.0800
31	3	29	3	30	2	28	3	118365.7880	0.1000
46	4	43	1	46	3	44	1	118374.5701	0.1000
17	8	9	0	17	7	10	0	118404.9895	0.0800
17	8	10	0	17	7	11	0	118404.9895	0.0800
17	8	9	0	17	7	11	0	118404.9895	0.0800
17	8	10	0	17	7	10	0	118404.9895	0.0800
16	8	9	0	16	7	10	0	118444.1569	0.0800
16	8	8	0	16	7	10	0	118444.1569	0.0800
16	8	9	0	16	7	9	0	118444.1569	0.0800
16	8	8	0	16	7	9	0	118444.1569	0.0800
24	14	11	0	25	13	13	0	118464.2613	0.0800
24	14	10	0	25	13	12	0	118464.2613	0.0800
24	14	11	0	25	13	12	0	118464.2613	0.0800
24	14	10	0	25	13	13	0	118464.2613	0.0800
15	8	7	0	15	7	8	0	118476.7264	0.0800

15	8	8	0	15	7	8	0	118476.7264	0.0800
15	8	7	0	15	7	9	0	118476.7264	0.0800
15	8	8	0	15	7	9	0	118476.7264	0.0800
14	8	7	0	14	7	7	0	118503.5840	0.0800
14	8	6	0	14	7	7	0	118503.5840	0.0800
14	8	7	0	14	7	8	0	118503.5840	0.0800
14	8	6	0	14	7	8	0	118503.5840	0.0800
101	13	88	0	101	12	89	0	118519.3255	0.0800
13	8	6	0	13	7	7	0	118525.4360	0.0800
13	8	5	0	13	7	7	0	118525.4360	0.0800
13	8	6	0	13	7	6	0	118525.4360	0.0800
13	8	5	0	13	7	6	0	118525.4360	0.0800
12	8	5	0	12	7	6	0	118542.9460	0.0800
12	8	4	0	12	7	5	0	118542.9460	0.0800
12	8	5	0	12	7	5	0	118542.9460	0.0800
12	8	4	0	12	7	6	0	118542.9460	0.0800
57	22	36	0	58	21	38	0	118556.8321	0.0800
57	22	35	0	58	21	37	0	118556.8321	0.0800
11	8	4	0	11	7	5	0	118556.8321	0.0800
11	8	3	0	11	7	4	0	118556.8321	0.0800
11	8	3	0	11	7	5	0	118556.8321	0.0800
57	22	35	0	58	21	38	0	118556.8321	0.0800
11	8	4	0	11	7	4	0	118556.8321	0.0800
57	22	36	0	58	21	37	0	118556.8321	0.0800
10	8	2	0	10	7	3	0	118567.5403	0.0800
10	8	3	0	10	7	4	0	118567.5403	0.0800
10	8	3	0	10	7	3	0	118567.5403	0.0800
10	8	2	0	10	7	4	0	118567.5403	0.0800
9	8	2	0	9	7	2	0	118575.6106	0.0800
9	8	2	0	9	7	3	0	118575.6106	0.0800
9	8	1	0	9	7	2	0	118575.6106	0.0800
9	8	1	0	9	7	3	0	118575.6106	0.0800
53	6	48	0	53	5	49	0	118598.6464	0.0800
18	4	15	0	17	3	14	0	118794.2042	0.0800
52	7	45	0	51	8	44	0	118796.3356	0.0800
46	3	43	0	46	2	44	0	118803.7460	0.0800
90	11	79	0	90	10	80	0	118860.8026	0.0800
50	4	46	0	50	3	47	0	119018.6894	0.0800
57	7	51	2	57	6	52	2	119025.2281	0.1000
52	9	43	0	52	8	44	0	119156.8273	0.0800
33	1	32	0	32	2	31	0	119237.0126	0.0800
46	4	43	0	46	3	44	0	119260.2615	0.0800
33	1	32	1	32	2	31	1	119278.7710	0.0800
33	2	32	0	32	2	31	0	119311.8013	0.0800
43	2	41	1	43	1	42	1	119359.2630	0.1000
33	1	32	2	32	2	31	2	119370.1430	0.1000
59	8	52	0	59	7	53	0	119374.8132	0.0800
33	2	32	0	32	1	31	0	119413.7594	0.0800
33	2	32	1	32	1	31	1	119458.6647	0.0800
33	2	32	2	32	1	31	2	119540.9452	0.1000
54	6	49	3	54	5	50	3	119545.9835	0.1000
34	0	34	0	33	1	33	0	119569.0876	0.0800
34	1	34	0	33	0	33	0	119572.0390	0.0800

33	2	32	3	32	1	31	3	119605.2038	0.1000
34	0	34	1	33	1	33	1	119636.6032	0.0800
34	1	34	1	33	0	33	1	119639.5472	0.0800
34	0	34	4	33	1	33	4	119653.1131	0.1000
34	1	34	4	33	0	33	4	119657.0793	0.1000
34	3	31	0	33	4	30	0	119665.9505	0.0800
78	12	67	0	77	13	64	0	119720.4111	0.0800
34	0	34	2	33	1	33	2	119739.5536	0.1000
34	1	34	2	33	0	33	2	119742.3737	0.1000
50	5	46	1	50	4	47	1	119786.8638	0.1000
34	0	34	3	33	1	33	3	119828.3706	0.1000
34	1	34	3	33	0	33	3	119831.1168	0.1000
75	11	64	0	75	10	65	0	119861.9917	0.0800
74	11	64	0	73	12	61	0	119930.2595	0.0800
13	5	9	1	12	4	8	1	119952.9388	0.1000
60	8	53	2	60	7	54	2	119966.0400	0.1000
34	3	31	2	33	4	30	2	119985.3085	0.1000
9	6	3	2	8	5	4	2	119985.3085	0.1000
9	6	4	2	8	5	3	2	119985.3085	0.1000
9	6	3	2	8	5	3	2	119985.3085	0.1000
9	6	4	2	8	5	4	2	119985.3085	0.1000
13	5	8	1	12	4	9	1	119988.8789	0.1000
22	8	14	0	21	7	14	0	201766.9971	0.0800
57	2	56	0	56	1	55	0	202508.3540	0.0800
57	2	56	0	56	2	55	0	202508.3540	0.0800
57	1	56	0	56	1	55	0	202508.3540	0.0800
57	1	56	0	56	2	55	0	202508.3540	0.0800
58	0	58	0	57	0	57	0	202776.3617	0.1000
58	0	58	0	57	1	57	0	202776.3617	0.1000
58	1	58	0	57	0	57	0	202776.3617	0.1000
58	1	58	0	57	1	57	0	202776.3617	0.1000
14	10	4	0	13	9	5	0	203251.9767	0.0800
14	10	5	0	13	9	4	0	203251.9767	0.0800
14	10	4	0	13	9	4	0	203251.9767	0.0800
14	10	5	0	13	9	5	0	203251.9767	0.0800
83	6	77	0	83	5	78	0	206559.1204	0.0800
13	11	3	0	12	10	3	0	215270.8908	0.0800
13	11	2	0	12	10	3	0	215270.8908	0.0800
13	11	3	0	12	10	2	0	215270.8908	0.0800
13	11	2	0	12	10	2	0	215270.8908	0.0800
58	4	54	0	57	5	53	0	215565.4756	0.0800
59	4	56	0	58	3	55	0	215925.9069	0.0800
61	2	60	0	60	2	59	0	216365.9975	0.0800
61	2	60	0	60	1	59	0	216365.9975	0.0800
61	1	60	0	60	1	59	0	216365.9975	0.0800
61	1	60	0	60	2	59	0	216365.9975	0.0800
62	1	62	0	61	0	61	0	216634.7011	0.0800
62	1	62	0	61	1	61	0	216634.7011	0.0800
62	0	62	0	61	1	61	0	216634.7011	0.0800
62	0	62	0	61	0	61	0	216634.7011	0.0800
62	0	62	1	61	0	61	1	216766.0045	0.0800
62	1	62	1	61	1	61	1	216766.0045	0.0800
62	1	62	1	61	0	61	1	216766.0045	0.0800

62	0	62	1	61	1	61	1	216766.0045	0.0800
22	9	13	0	21	8	14	0	217653.5742	0.0800
22	9	14	0	21	8	13	0	217653.5742	0.0800
22	9	13	0	21	8	13	0	217653.5742	0.0800
22	9	14	0	21	8	14	0	217653.5742	0.0800
53	11	42	0	54	8	47	0	218387.8448	0.0800
31	7	24	0	30	6	25	0	218684.9315	0.0800
14	11	4	0	13	10	4	0	219059.0642	0.1000
14	11	3	0	13	10	3	0	219059.0642	0.1000
14	11	3	0	13	10	4	0	219059.0642	0.1000
14	11	4	0	13	10	3	0	219059.0642	0.1000
59	4	55	0	58	5	54	0	219075.9990	0.0800
43	10	33	0	44	7	38	0	219092.1224	0.0800
60	3	57	0	59	4	56	0	219364.2496	0.0800
60	4	57	0	59	3	56	0	219382.1310	0.0800
60	4	57	1	59	3	56	1	219443.1443	0.0800
59	5	55	0	58	4	54	0	219458.2949	0.0800
19	10	10	3	18	9	10	3	219550.0551	0.1000
19	10	10	3	18	9	9	3	219550.0551	0.1000
19	10	9	3	18	9	9	3	219550.0551	0.1000
19	10	9	3	18	9	10	3	219550.0551	0.1000
61	2	59	0	60	2	58	0	219579.4799	0.0800
61	3	59	0	60	3	58	0	219579.4799	0.0800
61	2	59	1	60	3	58	1	219664.2624	0.1000
41	6	35	3	40	5	35	3	219664.2624	0.1000
23	9	14	2	22	8	15	2	219766.6641	0.1000
23	9	14	2	22	8	14	2	219766.6641	0.1000
23	9	15	2	22	8	14	2	219766.6641	0.1000
23	9	15	2	22	8	15	2	219766.6641	0.1000
27	8	19	1	26	7	20	1	219811.1162	0.1000
62	2	61	0	61	2	60	0	219830.1288	0.0800
62	2	61	0	61	1	60	0	219830.1288	0.0800
62	1	61	0	61	1	60	0	219830.1288	0.0800
62	1	61	0	61	2	60	0	219830.1288	0.0800
62	2	61	1	61	2	60	1	219939.3897	0.0800
62	1	61	1	61	1	60	1	219939.3897	0.0800
62	1	61	1	61	2	60	1	219939.3897	0.0800
62	2	61	1	61	1	60	1	219939.3897	0.0800
87	6	81	0	87	5	82	0	219985.2209	0.0800
77	3	74	0	77	2	75	0	220073.8050	0.0800
77	4	74	0	77	3	75	0	220073.8050	0.0800
62	1	61	4	61	2	60	4	220085.4503	0.1000
62	2	61	4	61	2	60	4	220085.4503	0.1000
62	2	61	4	61	1	60	4	220085.4503	0.1000
62	1	61	4	61	1	60	4	220085.4503	0.1000
63	1	63	0	62	1	62	0	220099.0005	0.0800
63	1	63	0	62	0	62	0	220099.0005	0.0800
63	0	63	0	62	1	62	0	220099.0005	0.0800
63	0	63	0	62	0	62	0	220099.0005	0.0800
62	1	61	2	61	2	60	2	220117.9998	0.1000
62	2	61	2	61	2	60	2	220117.9998	0.1000
62	2	61	2	61	1	60	2	220117.9998	0.1000
62	1	61	2	61	1	60	2	220117.9998	0.1000

63	1	63	4	62	1	62	4	220180.5332	0.1000
63	0	63	4	62	1	62	4	220180.5332	0.1000
63	0	63	4	62	0	62	4	220180.5332	0.1000
63	1	63	4	62	0	62	4	220180.5332	0.1000
63	0	63	1	62	0	62	1	220232.4883	0.0800
63	1	63	1	62	1	62	1	220232.4883	0.0800
63	0	63	1	62	1	62	1	220232.4883	0.0800
63	1	63	1	62	0	62	1	220232.4883	0.0800
62	1	61	3	61	2	60	3	220263.8363	0.1000
62	2	61	3	61	1	60	3	220263.8363	0.1000
62	1	61	3	61	1	60	3	220263.8363	0.1000
62	2	61	3	61	2	60	3	220263.8363	0.1000
27	8	19	0	26	7	20	0	220370.4404	0.0800
63	1	63	2	62	1	62	2	220427.1677	0.1000
63	0	63	2	62	1	62	2	220427.1677	0.1000
63	0	63	2	62	0	62	2	220427.1677	0.1000
63	1	63	2	62	0	62	2	220427.1677	0.1000
63	0	63	3	62	0	62	3	220598.5813	0.1000
63	0	63	3	62	1	62	3	220598.5813	0.1000
63	1	63	3	62	1	62	3	220598.5813	0.1000
63	1	63	3	62	0	62	3	220598.5813	0.1000
23	9	15	1	22	8	14	1	220778.1008	0.1000
23	9	14	1	22	8	15	1	220778.1008	0.1000
23	9	15	1	22	8	15	1	220778.1008	0.1000
23	9	14	1	22	8	14	1	220778.1008	0.1000
59	5	54	0	58	6	53	0	220807.7646	0.0800
91	8	84	0	91	7	85	0	220916.2474	0.0800
32	7	26	0	31	6	25	0	221407.4956	0.0800
23	9	14	0	22	8	15	0	221413.0336	0.0800
23	9	15	0	22	8	14	0	221413.0336	0.0800
23	9	15	0	22	8	15	0	221413.0336	0.0800
23	9	14	0	22	8	14	0	221413.0336	0.0800
19	10	9	1	18	9	10	1	221467.1532	0.1000
19	10	10	1	18	9	10	1	221467.1532	0.1000
19	10	9	1	18	9	9	1	221467.1532	0.1000
19	10	10	1	18	9	9	1	221467.1532	0.1000
84	5	79	0	84	4	80	0	221723.7113	0.0800
84	6	79	0	84	5	80	0	221725.2190	0.0800
35	6	29	0	34	5	30	0	221790.2800	0.0800
58	12	47	0	57	12	46	0	221798.7686	0.0800
15	11	5	1	14	10	5	1	222069.3606	0.1000
15	11	4	1	14	10	5	1	222069.3606	0.1000
15	11	4	1	14	10	4	1	222069.3606	0.1000
15	11	5	1	14	10	4	1	222069.3606	0.1000
58	6	53	3	57	5	52	3	222113.3928	0.1000
19	10	9	0	18	9	10	0	222173.8489	0.0800
19	10	10	0	18	9	10	0	222173.8489	0.0800
19	10	9	0	18	9	9	0	222173.8489	0.0800
19	10	10	0	18	9	9	0	222173.8489	0.0800
60	4	56	0	59	5	55	0	222573.0614	0.0800
72	1	71	0	72	0	72	0	222760.2406	0.0800
72	2	71	0	72	1	72	0	222760.2406	0.0800
81	5	77	0	81	4	78	0	222799.1508	0.0800

61	3	58	0	60	4	57	0	222826.3943	0.0800
61	3	58	0	60	3	57	0	222833.8050	0.0800
61	4	58	0	60	3	57	0	222839.4007	0.0800
15	11	5	0	14	10	5	0	222847.0288	0.0800
15	11	4	0	14	10	4	0	222847.0288	0.0800
15	11	4	0	14	10	5	0	222847.0288	0.0800
15	11	5	0	14	10	4	0	222847.0288	0.0800
60	5	56	0	59	4	55	0	222861.1306	0.0800
61	4	58	1	60	3	57	1	222902.6686	0.0800
58	10	48	2	57	10	47	2	223192.3801	0.1000
63	2	62	0	62	2	61	0	223293.8964	0.0800
63	2	62	0	62	1	61	0	223293.8964	0.0800
63	1	62	0	62	2	61	0	223293.8964	0.0800
63	1	62	0	62	1	61	0	223293.8964	0.0800
63	2	62	1	62	1	61	1	223405.5514	0.0800
63	1	62	1	62	2	61	1	223405.5514	0.0800
63	1	62	1	62	1	61	1	223405.5514	0.0800
63	2	62	1	62	2	61	1	223405.5514	0.0800
63	1	62	4	62	1	61	4	223549.3752	0.1000
63	2	62	4	62	1	61	4	223549.3752	0.1000
63	1	62	4	62	2	61	4	223549.3752	0.1000
63	2	62	4	62	2	61	4	223549.3752	0.1000
64	0	64	0	63	1	63	0	223563.0883	0.0800
64	0	64	0	63	0	63	0	223563.0883	0.0800
64	1	64	0	63	0	63	0	223563.0883	0.0800
64	1	64	0	63	1	63	0	223563.0883	0.0800
63	2	62	2	62	2	61	2	223587.2535	0.1000
63	1	62	2	62	2	61	2	223587.2535	0.1000
63	2	62	2	62	1	61	2	223587.2535	0.1000
63	1	62	2	62	1	61	2	223587.2535	0.1000
64	1	64	1	63	0	63	1	223698.7881	0.1000
64	0	64	1	63	1	63	1	223698.7881	0.1000
64	1	64	1	63	1	63	1	223698.7881	0.1000
64	0	64	1	63	0	63	1	223698.7881	0.1000
42	6	36	0	41	5	36	0	223718.1740	0.0800
63	2	62	3	62	1	61	3	223735.7910	0.1000
63	2	62	3	62	2	61	3	223735.7910	0.1000
63	1	62	3	62	1	61	3	223735.7910	0.1000
63	1	62	3	62	2	61	3	223735.7910	0.1000
64	1	64	2	63	1	63	2	223896.4289	0.1000
64	0	64	2	63	0	63	2	223896.4289	0.1000
64	1	64	2	63	0	63	2	223896.4289	0.1000
64	0	64	2	63	1	63	2	223896.4289	0.1000
28	8	21	0	27	7	20	0	224047.3992	0.0800
28	8	20	0	27	7	21	0	224056.1545	0.0800
64	0	64	3	63	0	63	3	224071.1227	0.1000
64	1	64	3	63	1	63	3	224071.1227	0.1000
64	1	64	3	63	0	63	3	224071.1227	0.1000
64	0	64	3	63	1	63	3	224071.1227	0.1000
20	10	10	2	19	9	10	2	224097.7112	0.1000
20	10	11	2	19	9	10	2	224097.7112	0.1000
20	10	10	2	19	9	11	2	224097.7112	0.1000
20	10	11	2	19	9	11	2	224097.7112	0.1000

61	6	55	0	60	7	54	0	224393.1129	0.0800
64	15	49	0	64	14	51	0	224443.0552	0.0800
64	15	50	0	64	14	51	0	224443.0552	0.0800
96	8	88	0	96	7	89	0	224530.1399	0.0800
24	9	16	1	23	8	15	1	224531.5663	0.1000
24	9	15	1	23	8	15	1	224531.5663	0.1000
24	9	15	1	23	8	16	1	224531.5663	0.1000
24	9	16	1	23	8	16	1	224531.5663	0.1000
33	7	27	0	32	6	26	0	224642.5077	0.0800
60	5	55	0	59	6	54	0	224674.1493	0.0800
63	15	48	0	63	14	50	0	224741.0666	0.0800
63	15	49	0	63	14	49	0	224741.0666	0.0800
63	15	48	0	63	14	49	0	224741.0666	0.0800
63	15	49	0	63	14	50	0	224741.0666	0.0800
59	6	54	0	58	5	53	0	224856.7663	0.0800
62	15	48	0	62	14	48	0	225024.1354	0.0800
62	15	47	0	62	14	49	0	225024.1354	0.0800
62	15	48	0	62	14	49	0	225024.1354	0.0800
62	15	47	0	62	14	48	0	225024.1354	0.0800
45	15	30	2	45	14	31	2	225165.4471	0.1000
45	15	31	2	45	14	31	2	225165.4471	0.1000
45	15	30	2	45	14	32	2	225165.4471	0.1000
45	15	31	2	45	14	32	2	225165.4471	0.1000
24	9	16	0	23	8	15	0	225166.8551	0.0800
24	9	16	0	23	8	16	0	225166.8551	0.0800
24	9	15	0	23	8	16	0	225166.8551	0.0800
24	9	15	0	23	8	15	0	225166.8551	0.0800
20	10	11	1	19	9	10	1	225245.4331	0.1000
20	10	11	1	19	9	11	1	225245.4331	0.1000
20	10	10	1	19	9	10	1	225245.4331	0.1000
20	10	10	1	19	9	11	1	225245.4331	0.1000
61	15	47	0	61	14	47	0	225292.8991	0.1000
61	15	46	0	61	14	48	0	225292.8991	0.0800
61	15	46	0	61	14	47	0	225292.8991	0.1000
61	15	47	0	61	14	48	0	225292.8991	0.0800
60	15	45	0	60	14	46	0	225547.8224	0.0800
60	15	46	0	60	14	47	0	225547.8224	0.0800
60	15	45	0	60	14	47	0	225547.8224	0.0800
60	15	46	0	60	14	46	0	225547.8224	0.0800
16	11	5	1	15	10	6	1	225855.9898	0.1000
16	11	6	1	15	10	6	1	225855.9898	0.1000
16	11	6	1	15	10	5	1	225855.9898	0.1000
16	11	5	1	15	10	5	1	225855.9898	0.1000
33	7	26	0	32	6	27	0	225915.7211	0.0800
20	10	10	0	19	9	11	0	225952.9598	0.0800
20	10	11	0	19	9	11	0	225952.9598	0.0800
20	10	10	0	19	9	10	0	225952.9598	0.0800
20	10	11	0	19	9	10	0	225952.9598	0.0800
58	15	44	0	58	14	45	0	226018.3586	0.0800
58	15	43	0	58	14	45	0	226018.3586	0.0800
58	15	43	0	58	14	44	0	226018.3586	0.0800
58	15	44	0	58	14	44	0	226018.3586	0.0800
61	4	57	0	60	5	56	0	226059.9570	0.0800

57	15	43	0	57	14	43	0	226235.1717	0.0800
57	15	42	0	57	14	44	0	226235.1717	0.0800
57	15	42	0	57	14	43	0	226235.1717	0.0800
57	15	43	0	57	14	44	0	226235.1717	0.0800
61	4	57	2	60	5	56	2	226240.7997	0.1000
61	5	57	0	60	4	56	0	226276.1190	0.0800
62	3	59	0	61	4	58	0	226288.0223	0.0800
62	4	59	0	61	3	58	0	226297.2991	0.0800
61	5	57	1	60	4	56	1	226320.7473	0.1000
62	4	59	1	61	3	58	1	226362.7731	0.1000
12	12	1	1	11	11	1	1	226437.6314	0.1000
12	12	0	1	11	11	0	1	226437.6314	0.1000
12	12	0	1	11	11	1	1	226437.6314	0.1000
12	12	1	1	11	11	0	1	226437.6314	0.1000
63	2	61	0	62	2	60	0	226505.1056	0.0800
63	3	61	0	62	3	60	0	226505.1056	0.0800
49	15	34	1	49	14	36	1	226535.7389	0.1000
49	15	34	1	49	14	35	1	226535.7389	0.1000
49	15	35	1	49	14	36	1	226535.7389	0.1000
49	15	35	1	49	14	35	1	226535.7389	0.1000
63	2	61	1	62	3	60	1	226594.5208	0.1000
63	3	61	1	62	3	60	1	226594.5208	0.0800
63	2	61	1	62	2	60	1	226594.5208	0.0800
63	3	61	1	62	2	60	1	226594.5208	0.1000
16	11	6	0	15	10	5	0	226634.3521	0.0800
16	11	5	0	15	10	6	0	226634.3521	0.0800
16	11	5	0	15	10	5	0	226634.3521	0.0800
16	11	6	0	15	10	6	0	226634.3521	0.0800
64	2	63	0	63	1	62	0	226757.6057	0.0800
64	2	63	0	63	2	62	0	226757.6057	0.0800
64	1	63	0	63	1	62	0	226757.6057	0.0800
64	1	63	0	63	2	62	0	226757.6057	0.0800
63	2	61	2	62	2	60	2	226764.0861	0.1000
63	3	61	2	62	3	60	2	226764.0861	0.1000
63	2	61	2	62	3	60	2	226764.0861	0.1000
54	15	39	0	54	14	41	0	226817.8564	0.0800
54	15	39	0	54	14	40	0	226817.8564	0.0800
54	15	40	0	54	14	41	0	226817.8564	0.0800
54	15	40	0	54	14	40	0	226817.8564	0.0800
64	2	63	1	63	2	62	1	226871.3599	0.0800
64	1	63	1	63	2	62	1	226871.3599	0.0800
64	1	63	1	63	1	62	1	226871.3599	0.0800
64	2	63	1	63	1	62	1	226871.3599	0.0800
53	15	38	0	53	14	39	0	226990.8408	0.0800
53	15	39	0	53	14	39	0	226990.8408	0.0800
53	15	39	0	53	14	40	0	226990.8408	0.0800
53	15	38	0	53	14	40	0	226990.8408	0.0800
65	1	65	0	64	0	64	0	227026.9903	0.0800
65	0	65	0	64	0	64	0	227026.9903	0.0800
65	0	65	0	64	1	64	0	227026.9903	0.0800
65	1	65	0	64	1	64	0	227026.9903	0.0800
64	2	63	2	63	1	62	2	227056.3737	0.1000
64	1	63	2	63	2	62	2	227056.3737	0.1000

64	1	63	2	63	1	62	2	227056.3737	0.1000
64	2	63	2	63	2	62	2	227056.3737	0.1000
65	0	65	4	64	1	64	4	227108.2477	0.1000
65	0	65	4	64	0	64	4	227108.2477	0.1000
65	1	65	4	64	0	64	4	227108.2477	0.1000
65	1	65	4	64	1	64	4	227108.2477	0.1000
52	15	38	0	52	14	39	0	227154.2096	0.0800
52	15	37	0	52	14	39	0	227154.2096	0.0800
52	15	38	0	52	14	38	0	227154.2096	0.0800
52	15	37	0	52	14	38	0	227154.2096	0.0800
65	1	65	1	64	0	64	1	227164.9766	0.0800
65	0	65	1	64	1	64	1	227164.9766	0.0800
65	0	65	1	64	0	64	1	227164.9766	0.0800
65	1	65	1	64	1	64	1	227164.9766	0.0800
64	1	63	3	63	2	62	3	227207.6130	0.1000
64	2	63	3	63	1	62	3	227207.6130	0.1000
64	1	63	3	63	1	62	3	227207.6130	0.1000
64	2	63	3	63	2	62	3	227207.6130	0.1000
12	12	1	0	11	11	1	0	227286.4556	0.0800
12	12	1	0	11	11	0	0	227286.4556	0.0800
12	12	0	0	11	11	0	0	227286.4556	0.0800
12	12	0	0	11	11	1	0	227286.4556	0.0800
65	1	65	2	64	1	64	2	227365.8527	0.1000
65	0	65	2	64	0	64	2	227365.8527	0.1000
65	1	65	2	64	0	64	2	227365.8527	0.1000
65	0	65	2	64	1	64	2	227365.8527	0.1000
50	15	35	0	50	14	37	0	227453.1676	0.0800
50	15	36	0	50	14	36	0	227453.1676	0.0800
50	15	36	0	50	14	37	0	227453.1676	0.0800
50	15	35	0	50	14	36	0	227453.1676	0.0800
65	1	65	3	64	0	64	3	227543.2015	0.1000
65	0	65	3	64	1	64	3	227543.2015	0.1000
65	1	65	3	64	1	64	3	227543.2015	0.1000
65	0	65	3	64	0	64	3	227543.2015	0.1000
38	15	24	1	38	14	25	1	227560.9986	0.1000
38	15	23	1	38	14	25	1	227560.9986	0.1000
38	15	24	1	38	14	24	1	227560.9986	0.1000
38	15	23	1	38	14	24	1	227560.9986	0.1000
49	15	34	0	49	14	36	0	227589.4308	0.0800
49	15	35	0	49	14	36	0	227589.4308	0.0800
49	15	35	0	49	14	35	0	227589.4308	0.0800
49	15	34	0	49	14	35	0	227589.4308	0.0800
29	8	22	0	28	7	21	0	227712.9600	0.0800
48	15	33	0	48	14	35	0	227717.6393	0.0800
48	15	33	0	48	14	34	0	227717.6393	0.0800
48	15	34	0	48	14	34	0	227717.6393	0.0800
48	15	34	0	48	14	35	0	227717.6393	0.0800
29	8	21	0	28	7	22	0	227728.0850	0.0800
34	7	28	0	33	6	27	0	227758.1092	0.0800
47	15	33	0	47	14	33	0	227838.0440	0.0800
47	15	33	0	47	14	34	0	227838.0440	0.0800
47	15	32	0	47	14	33	0	227838.0440	0.0800
47	15	32	0	47	14	34	0	227838.0440	0.0800

46	15	31	0	46	14	33	0	227950.8044	0.0800
46	15	31	0	46	14	32	0	227950.8044	0.0800
46	15	32	0	46	14	32	0	227950.8044	0.0800
46	15	32	0	46	14	33	0	227950.8044	0.0800
45	15	31	0	45	14	31	0	228056.7729	0.0800
45	15	30	0	45	14	32	0	228056.7729	0.0800
45	15	30	0	45	14	31	0	228056.7729	0.0800
45	15	31	0	45	14	32	0	228056.7729	0.0800
43	15	28	0	43	14	29	0	228247.9485	0.0800
43	15	29	0	43	14	30	0	228247.9485	0.0800
43	15	28	0	43	14	30	0	228247.9485	0.0800
43	15	29	0	43	14	29	0	228247.9485	0.0800
41	15	26	0	41	14	28	0	228414.6505	0.0800
41	15	27	0	41	14	28	0	228414.6505	0.0800
41	15	27	0	41	14	27	0	228414.6505	0.0800
41	15	26	0	41	14	27	0	228414.6505	0.0800
61	5	56	0	60	6	55	0	228452.2293	0.0800
40	15	25	0	40	14	26	0	228489.3196	0.0800
40	15	26	0	40	14	26	0	228489.3196	0.0800
40	15	26	0	40	14	27	0	228489.3196	0.0800
40	15	25	0	40	14	27	0	228489.3196	0.0800
39	15	24	0	39	14	25	0	228558.5224	0.0800
39	15	25	0	39	14	26	0	228558.5224	0.0800
39	15	25	0	39	14	25	0	228558.5224	0.0800
39	15	24	0	39	14	26	0	228558.5224	0.0800
38	15	24	0	38	14	24	0	228623.0823	0.0800
38	15	24	0	38	14	25	0	228623.0823	0.0800
38	15	23	0	38	14	25	0	228623.0823	0.0800
38	15	23	0	38	14	24	0	228623.0823	0.0800
37	15	23	0	37	14	24	0	228682.4554	0.0800
37	15	23	0	37	14	23	0	228682.4554	0.0800
37	15	22	0	37	14	23	0	228682.4554	0.0800
37	15	22	0	37	14	24	0	228682.4554	0.0800
35	15	20	0	35	14	22	0	228788.1524	0.0800
35	15	21	0	35	14	22	0	228788.1524	0.0800
35	15	21	0	35	14	21	0	228788.1524	0.0800
35	15	20	0	35	14	21	0	228788.1524	0.0800
30	15	16	0	30	14	17	0	228985.2218	0.0800
30	15	15	0	30	14	17	0	228985.2218	0.0800
30	15	15	0	30	14	16	0	228985.2218	0.0800
30	15	16	0	30	14	16	0	228985.2218	0.0800
21	10	11	1	20	9	12	1	229020.9669	0.1000
21	10	12	1	20	9	11	1	229020.9669	0.1000
21	10	12	1	20	9	12	1	229020.9669	0.1000
21	10	11	1	20	9	11	1	229020.9669	0.1000
62	4	58	0	61	5	57	0	229538.6687	0.0800
34	7	27	0	33	6	28	0	229557.4766	0.0800
62	5	58	0	61	4	57	0	229700.8108	0.0800
21	10	11	0	20	9	11	0	229729.4141	0.0800
21	10	12	0	20	9	11	0	229729.4141	0.0800
21	10	12	0	20	9	12	0	229729.4141	0.0800
21	10	11	0	20	9	12	0	229729.4141	0.0800
63	4	60	0	62	3	59	0	229755.8372	0.0800

63	4	60	1	62	4	59	1	229819.3921	0.0800
63	4	60	1	62	3	59	1	229823.5232	0.0800
64	2	62	0	63	2	61	0	229967.7288	0.0800
64	2	62	0	63	3	61	0	229967.7288	0.0800
64	3	62	0	63	3	61	0	229967.7288	0.0800
64	3	62	0	63	2	61	0	229967.7288	0.0800
64	2	62	1	63	3	61	1	230059.4383	0.0800
64	3	62	1	63	2	61	1	230059.4383	0.1000
64	3	62	1	63	3	61	1	230059.4383	0.0800
64	2	62	1	63	2	61	1	230059.4383	0.0800
65	1	64	0	64	2	63	0	230221.0508	0.0800
65	2	64	0	64	2	63	0	230221.0508	0.0800
65	1	64	0	64	1	63	0	230221.0508	0.0800
65	2	64	0	64	1	63	0	230221.0508	0.0800
13	12	1	1	12	11	2	1	230225.7767	0.1000
13	12	1	1	12	11	1	1	230225.7767	0.1000
13	12	2	1	12	11	2	1	230225.7767	0.1000
13	12	2	1	12	11	1	1	230225.7767	0.1000
64	3	62	2	63	2	61	2	230231.8343	0.1000
64	2	62	2	63	3	61	2	230231.8343	0.1000
64	2	62	2	63	2	61	2	230231.8343	0.1000
64	3	62	2	63	3	61	2	230231.8343	0.1000
65	1	64	1	64	2	63	1	230337.0450	0.0800
65	1	64	1	64	1	63	1	230337.0450	0.0800
65	2	64	1	64	2	63	1	230337.0450	0.0800
65	2	64	1	64	1	63	1	230337.0450	0.0800
17	11	7	0	16	10	6	0	230420.6251	0.0800
17	11	6	0	16	10	7	0	230420.6251	0.0800
17	11	6	0	16	10	6	0	230420.6251	0.0800
17	11	7	0	16	10	7	0	230420.6251	0.0800
66	0	66	0	65	1	65	0	230490.6689	0.0800
66	1	66	0	65	0	65	0	230490.6689	0.0800
66	0	66	0	65	0	65	0	230490.6689	0.0800
66	1	66	0	65	1	65	0	230490.6689	0.0800
65	1	64	2	64	1	63	2	230525.0755	0.1000
65	1	64	2	64	2	63	2	230525.0755	0.1000
65	2	64	2	64	1	63	2	230525.0755	0.1000
65	2	64	2	64	2	63	2	230525.0755	0.1000
66	1	66	1	65	1	65	1	230630.8379	0.0800
66	0	66	1	65	1	65	1	230630.8379	0.0800
66	0	66	1	65	0	65	1	230630.8379	0.0800
66	1	66	1	65	0	65	1	230630.8379	0.0800
65	2	64	3	64	2	63	3	230679.1794	0.1000
65	1	64	3	64	2	63	3	230679.1794	0.1000
65	2	64	3	64	1	63	3	230679.1794	0.1000
65	1	64	3	64	1	63	3	230679.1794	0.1000
35	7	29	0	34	6	28	0	230728.2832	0.0800
66	0	66	2	65	0	65	2	230834.7528	0.1000
66	1	66	2	65	0	65	2	230834.7528	0.1000
66	1	66	2	65	1	65	2	230834.7528	0.1000
66	0	66	2	65	1	65	2	230834.7528	0.1000
61	6	56	0	60	5	55	0	230909.6927	0.0800
61	6	56	1	60	5	55	1	230965.2542	0.1000

66	1	66	3	65	1	65	3	231015.0384	0.1000
66	0	66	3	65	0	65	3	231015.0384	0.1000
66	0	66	3	65	1	65	3	231015.0384	0.1000
66	1	66	3	65	0	65	3	231015.0384	0.1000
13	12	2	0	12	11	2	0	231075.2408	0.0800
13	12	1	0	12	11	1	0	231075.2408	0.0800
13	12	2	0	12	11	1	0	231075.2408	0.0800
13	12	1	0	12	11	2	0	231075.2408	0.0800
30	8	23	0	29	7	22	0	231360.3587	0.0800
30	8	22	0	29	7	23	0	231384.8057	0.0800
26	9	18	1	25	8	18	1	232019.3270	0.1000
26	9	17	1	25	8	17	1	232019.3270	0.1000
26	9	18	1	25	8	17	1	232019.3270	0.1000
26	9	17	1	25	8	18	1	232019.3270	0.1000
62	5	57	0	61	6	56	0	232159.2122	0.0800
26	9	18	0	25	8	18	0	232654.9173	0.0800
26	9	17	0	25	8	18	0	232654.9173	0.0800
26	9	18	0	25	8	17	0	232654.9173	0.0800
26	9	17	0	25	8	17	0	232654.9173	0.0800
31	8	24	3	30	7	23	3	232979.0550	0.1000
64	4	61	0	63	3	60	0	233214.7671	0.0800
65	3	63	0	64	3	62	0	233430.1067	0.0800
65	2	63	0	64	2	62	0	233430.1067	0.0800
65	2	63	0	64	3	62	0	233430.1067	0.0800
65	3	63	0	64	2	62	0	233430.1067	0.0800
22	10	12	0	21	9	13	0	233502.9007	0.0800
22	10	13	0	21	9	13	0	233502.9007	0.0800
22	10	13	0	21	9	12	0	233502.9007	0.0800
22	10	12	0	21	9	12	0	233502.9007	0.0800
65	2	63	1	64	3	62	1	233524.0473	0.1000
65	2	63	1	64	2	62	1	233524.0473	0.1000
65	3	63	1	64	2	62	1	233524.0473	0.1000
65	3	63	1	64	3	62	1	233524.0473	0.1000
66	1	65	0	65	1	64	0	233684.3797	0.0800
66	2	65	0	65	1	64	0	233684.3797	0.0800
66	1	65	0	65	2	64	0	233684.3797	0.0800
66	2	65	0	65	2	64	0	233684.3797	0.0800
65	3	63	2	64	2	62	2	233699.5675	0.1000
65	3	63	2	64	3	62	2	233699.5675	0.1000
65	2	63	2	64	2	62	2	233699.5675	0.1000
65	2	63	2	64	3	62	2	233699.5675	0.1000
66	2	65	1	65	1	64	1	233802.6063	0.0800
66	1	65	1	65	2	64	1	233802.6063	0.0800
66	2	65	1	65	2	64	1	233802.6063	0.0800
66	1	65	1	65	1	64	1	233802.6063	0.0800
66	2	65	4	65	2	64	4	233939.4151	0.1000
66	2	65	4	65	1	64	4	233939.4151	0.1000
66	1	65	4	65	2	64	4	233939.4151	0.1000
66	1	65	4	65	1	64	4	233939.4151	0.1000
67	1	67	0	66	0	66	0	233954.1095	0.0800
67	1	67	0	66	1	66	0	233954.1095	0.0800
67	0	67	0	66	1	66	0	233954.1095	0.0800
67	0	67	0	66	0	66	0	233954.1095	0.0800

66	2	65	2	65	1	64	2	233993.7522	0.1000
66	2	65	2	65	2	64	2	233993.7522	0.1000
66	1	65	2	65	1	64	2	233993.7522	0.1000
66	1	65	2	65	2	64	2	233993.7522	0.1000
62	6	57	0	61	5	56	0	234061.6198	0.0800
67	0	67	1	66	0	66	1	234096.4702	0.0800
67	1	67	1	66	0	66	1	234096.4702	0.0800
67	1	67	1	66	1	66	1	234096.4702	0.0800
67	0	67	1	66	1	66	1	234096.4702	0.0800
66	2	65	3	65	1	64	3	234150.5399	0.1000
66	2	65	3	65	2	64	3	234150.5399	0.1000
66	1	65	3	65	2	64	3	234150.5399	0.1000
66	1	65	3	65	1	64	3	234150.5399	0.1000
18	11	7	0	17	10	8	0	234205.9664	0.0800
18	11	8	0	17	10	7	0	234205.9664	0.0800
18	11	8	0	17	10	8	0	234205.9664	0.0800
18	11	7	0	17	10	7	0	234205.9664	0.0800
67	0	67	2	66	0	66	2	234303.6465	0.1000
67	1	67	2	66	0	66	2	234303.6465	0.1000
67	1	67	2	66	1	66	2	234303.6465	0.1000
67	0	67	2	66	1	66	2	234303.6465	0.1000
63	6	57	0	62	7	56	0	234325.7022	0.0800
67	1	67	3	66	0	66	3	234486.5297	0.1000
67	0	67	3	66	0	66	3	234486.5297	0.1000
67	0	67	3	66	1	66	3	234486.5297	0.1000
67	1	67	3	66	1	66	3	234486.5297	0.1000
75	9	66	0	74	10	65	0	234822.7807	0.0800
14	12	2	0	13	11	2	0	234863.9340	0.0800
14	12	2	0	13	11	3	0	234863.9340	0.0800
14	12	3	0	13	11	2	0	234863.9340	0.0800
14	12	3	0	13	11	3	0	234863.9340	0.0800
70	8	62	0	69	9	61	0	234953.5112	0.0800
31	8	24	0	30	7	23	0	234986.6193	0.0800
41	4	37	0	40	3	37	0	235734.9757	0.0800
85	5	81	0	85	4	82	0	235760.3826	0.0800
85	4	81	0	85	3	82	0	235760.3826	0.0800
63	5	58	0	62	6	57	0	235809.1689	0.0800
27	9	18	0	26	8	18	0	236387.6259	0.0800
27	9	19	0	26	8	18	0	236387.6259	0.0800
64	4	60	0	63	5	59	0	236480.0225	0.0800
64	5	60	0	63	4	59	0	236570.3805	0.0800
65	3	62	0	64	4	61	0	236670.3810	0.0800
65	4	62	0	64	3	61	0	236673.9755	0.0800
65	3	62	1	64	4	61	1	236742.1267	0.1000
66	3	64	0	65	3	63	0	236892.4813	0.0800
66	2	64	0	65	2	63	0	236892.4813	0.0800
66	2	64	0	65	3	63	0	236892.4813	0.0800
66	3	64	0	65	2	63	0	236892.4813	0.0800
36	7	29	0	35	6	30	0	236968.5874	0.0800
66	2	64	1	65	3	63	1	236988.6568	0.0800
66	3	64	1	65	2	63	1	236988.6568	0.0800
66	3	64	1	65	3	63	1	236988.6568	0.0800
66	2	64	1	65	2	63	1	236988.6568	0.0800

67	1	66	0	66	2	65	0	237147.4498	0.0800
67	2	66	0	66	1	65	0	237147.4498	0.0800
67	2	66	0	66	2	65	0	237147.4498	0.0800
67	1	66	0	66	1	65	0	237147.4498	0.0800
66	2	64	2	65	2	63	2	237167.1305	0.1000
66	3	64	2	65	3	63	2	237167.1305	0.1000
66	3	64	2	65	2	63	2	237167.1305	0.1000
66	2	64	2	65	3	63	2	237167.1305	0.1000
19	11	8	1	18	10	9	1	237209.6545	0.1000
19	11	9	1	18	10	9	1	237209.6545	0.1000
19	11	8	1	18	10	8	1	237209.6545	0.1000
19	11	9	1	18	10	8	1	237209.6545	0.1000
67	1	66	1	66	2	65	1	237267.9629	0.0800
67	2	66	1	66	1	65	1	237267.9629	0.0800
67	2	66	1	66	2	65	1	237267.9629	0.0800
67	1	66	1	66	1	65	1	237267.9629	0.0800
23	10	14	0	22	9	13	0	237273.0907	0.0800
23	10	14	0	22	9	14	0	237273.0907	0.0800
23	10	13	0	22	9	14	0	237273.0907	0.0800
23	10	13	0	22	9	13	0	237273.0907	0.0800
63	6	58	0	62	5	57	0	237276.4990	0.0800
68	0	68	0	67	1	67	0	237417.4300	0.0800
68	1	68	0	67	0	67	0	237417.4300	0.0800
68	1	68	0	67	1	67	0	237417.4300	0.0800
68	0	68	0	67	0	67	0	237417.4300	0.0800
67	1	66	2	66	2	65	2	237462.2389	0.1000
67	2	66	2	66	1	65	2	237462.2389	0.1000
67	1	66	2	66	1	65	2	237462.2389	0.1000
67	2	66	2	66	2	65	2	237462.2389	0.1000
68	1	68	1	67	1	67	1	237562.0770	0.0800
68	0	68	1	67	0	67	1	237562.0770	0.0800
68	1	68	1	67	0	67	1	237562.0770	0.0800
68	0	68	1	67	1	67	1	237562.0770	0.0800
67	1	66	3	66	2	65	3	237621.6930	0.1000
67	1	66	3	66	1	65	3	237621.6930	0.1000
67	2	66	3	66	2	65	3	237621.6930	0.1000
67	2	66	3	66	1	65	3	237621.6930	0.1000
68	1	68	2	67	0	67	2	237772.2469	0.1000
68	1	68	2	67	1	67	2	237772.2469	0.1000
68	0	68	2	67	1	67	2	237772.2469	0.1000
68	0	68	2	67	0	67	2	237772.2469	0.1000
15	12	4	1	14	11	4	1	237801.2575	0.1000
15	12	4	1	14	11	3	1	237801.2575	0.1000
15	12	3	1	14	11	3	1	237801.2575	0.1000
15	12	3	1	14	11	4	1	237801.2575	0.1000
19	11	9	0	18	10	9	0	237990.0977	0.0800
19	11	8	0	18	10	8	0	237990.0977	0.0800
19	11	8	0	18	10	9	0	237990.0977	0.0800
19	11	9	0	18	10	8	0	237990.0977	0.0800
104	10	95	0	104	9	96	0	238367.9143	0.0800
32	8	24	0	31	7	25	0	238649.8034	0.0800
15	12	4	0	14	11	4	0	238652.2858	0.0800
15	12	3	0	14	11	3	0	238652.2858	0.0800

15	12	3	0	14	11	4	0	238652.2858	0.0800
15	12	4	0	14	11	3	0	238652.2858	0.0800
72	16	56	0	72	15	57	0	238728.3870	0.0800
72	16	56	0	72	15	58	0	238728.3870	0.0800
72	16	57	0	72	15	57	0	238728.3870	0.0800
72	16	57	0	72	15	58	0	238728.3870	0.0800
55	7	49	0	54	6	48	0	239345.8081	0.0800
64	5	59	0	63	6	58	0	239414.0319	0.0800
70	16	54	0	70	15	55	0	239417.9218	0.0800
70	16	55	0	70	15	55	0	239417.9218	0.0800
70	16	55	0	70	15	56	0	239417.9218	0.0800
70	16	54	0	70	15	56	0	239417.9218	0.0800
69	16	53	0	69	15	55	0	239739.2520	0.0800
69	16	54	0	69	15	55	0	239739.2520	0.0800
69	16	53	0	69	15	54	0	239739.2520	0.0800
69	16	54	0	69	15	54	0	239739.2520	0.0800
65	5	61	0	64	5	60	0	239973.8759	0.0800
65	5	61	0	64	4	60	0	240012.3069	0.0800
68	16	53	0	68	15	54	0	240045.5086	0.0800
68	16	53	0	68	15	53	0	240045.5086	0.0800
68	16	52	0	68	15	54	0	240045.5086	0.0800
68	16	52	0	68	15	53	0	240045.5086	0.0800
64	5	59	0	63	5	58	0	240052.2428	0.0800
28	9	20	0	27	8	19	0	240112.1151	0.0800
28	9	20	0	27	8	20	0	240112.1151	0.0800
28	9	19	0	27	8	20	0	240112.1151	0.0800
28	9	19	0	27	8	19	0	240112.1151	0.0800
66	3	63	0	65	4	62	0	240130.7686	0.0800
66	4	63	0	65	3	62	0	240133.3525	0.0800
66	3	63	1	65	4	62	1	240204.7006	0.0800
66	4	63	1	65	4	62	1	240205.9558	0.0800
66	4	63	1	65	3	62	1	240207.4441	0.0800
59	7	53	0	58	6	52	0	240328.6410	0.0800
24	10	15	1	23	9	15	1	240329.8746	0.1000
24	10	15	1	23	9	14	1	240329.8746	0.1000
24	10	14	1	23	9	15	1	240329.8746	0.1000
24	10	14	1	23	9	14	1	240329.8746	0.1000
67	16	51	0	67	15	53	0	240337.1223	0.0800
67	16	52	0	67	15	52	0	240337.1223	0.0800
67	16	51	0	67	15	52	0	240337.1223	0.0800
67	16	52	0	67	15	53	0	240337.1223	0.0800
67	3	65	0	66	2	64	0	240354.6507	0.0800
67	2	65	0	66	3	64	0	240354.6507	0.0800
67	2	65	0	66	2	64	0	240354.6507	0.0800
67	3	65	0	66	3	64	0	240354.6507	0.0800
67	3	65	1	66	3	64	1	240453.1436	0.0800
67	2	65	1	66	3	64	1	240453.1436	0.0800
67	2	65	1	66	2	64	1	240453.1436	0.0800
67	3	65	1	66	2	64	1	240453.1436	0.0800
39	7	33	0	38	6	32	0	240529.7965	0.0800
68	1	67	0	67	1	66	0	240610.2995	0.0800
68	1	67	0	67	2	66	0	240610.2995	0.0800
68	2	67	0	67	1	66	0	240610.2995	0.0800

68	2	67	0	67	2	66	0	240610.2995	0.0800
66	16	51	0	66	15	52	0	240615.2189	0.0800
66	16	50	0	66	15	52	0	240615.2189	0.0800
66	16	50	0	66	15	51	0	240615.2189	0.0800
66	16	51	0	66	15	51	0	240615.2189	0.0800
67	2	65	2	66	2	64	2	240634.7560	0.1000
67	3	65	2	66	3	64	2	240634.7560	0.1000
67	3	65	2	66	2	64	2	240634.7560	0.1000
67	2	65	2	66	3	64	2	240634.7560	0.1000
68	2	67	1	67	2	66	1	240733.1513	0.0800
68	1	67	1	67	2	66	1	240733.1513	0.0800
68	1	67	1	67	1	66	1	240733.1513	0.0800
68	2	67	1	67	1	66	1	240733.1513	0.0800
67	2	65	3	66	2	64	3	240770.8261	0.1000
67	2	65	3	66	3	64	3	240770.8261	0.1000
67	3	65	3	66	2	64	3	240770.8261	0.1000
67	3	65	3	66	3	64	3	240770.8261	0.1000
68	2	67	4	67	1	66	4	240864.9991	0.1000
68	1	67	4	67	2	66	4	240864.9991	0.1000
68	1	67	4	67	1	66	4	240864.9991	0.1000
68	2	67	4	67	2	66	4	240864.9991	0.1000
69	1	69	0	68	1	68	0	240880.4158	0.0800
69	1	69	0	68	0	68	0	240880.4158	0.0800
69	0	69	0	68	0	68	0	240880.4158	0.0800
69	0	69	0	68	1	68	0	240880.4158	0.0800
68	2	67	2	67	1	66	2	240930.4956	0.1000
68	2	67	2	67	2	66	2	240930.4956	0.1000
68	1	67	2	67	1	66	2	240930.4956	0.1000
68	1	67	2	67	2	66	2	240930.4956	0.1000
69	1	69	1	68	1	68	1	241027.3431	0.0800
69	1	69	1	68	0	68	1	241027.3431	0.0800
69	0	69	1	68	1	68	1	241027.3431	0.0800
69	0	69	1	68	0	68	1	241027.3431	0.0800
24	10	15	0	23	9	15	0	241039.5674	0.0800
24	10	14	0	23	9	14	0	241039.5674	0.0800
24	10	15	0	23	9	14	0	241039.5674	0.0800
24	10	14	0	23	9	15	0	241039.5674	0.0800
68	2	67	3	67	1	66	3	241092.5899	0.1000
68	1	67	3	67	2	66	3	241092.5899	0.1000
68	1	67	3	67	1	66	3	241092.5899	0.1000
68	2	67	3	67	2	66	3	241092.5899	0.1000
64	16	49	0	64	15	49	0	241132.0923	0.0800
64	16	49	0	64	15	50	0	241132.0923	0.0800
64	16	48	0	64	15	50	0	241132.0923	0.0800
64	16	48	0	64	15	49	0	241132.0923	0.0800
69	0	69	2	68	0	68	2	241240.7648	0.1000
69	0	69	2	68	1	68	2	241240.7648	0.1000
69	1	69	2	68	1	68	2	241240.7648	0.1000
69	1	69	2	68	0	68	2	241240.7648	0.1000
63	16	47	0	63	15	48	0	241371.7087	0.0800
63	16	48	0	63	15	48	0	241371.7087	0.0800
63	16	48	0	63	15	49	0	241371.7087	0.0800
63	16	47	0	63	15	49	0	241371.7087	0.0800

60	7	54	0	59	6	53	0	241380.1600	0.0800
69	0	69	3	68	1	68	3	241429.1322	0.1000
69	0	69	3	68	0	68	3	241429.1322	0.1000
69	1	69	3	68	1	68	3	241429.1322	0.1000
69	1	69	3	68	0	68	3	241429.1322	0.1000
16	12	5	1	15	11	5	1	241588.4123	0.1000
16	12	4	1	15	11	4	1	241588.4123	0.1000
16	12	5	1	15	11	4	1	241588.4123	0.1000
16	12	4	1	15	11	5	1	241588.4123	0.1000
62	16	46	0	62	15	48	0	241599.7578	0.0800
62	16	47	0	62	15	47	0	241599.7578	0.0800
62	16	46	0	62	15	47	0	241599.7578	0.0800
62	16	47	0	62	15	48	0	241599.7578	0.0800
20	11	10	0	19	10	9	0	241772.6816	0.0800
20	11	9	0	19	10	9	0	241772.6816	0.0800
20	11	10	0	19	10	10	0	241772.6816	0.0800
20	11	9	0	19	10	10	0	241772.6816	0.0800
61	16	46	0	61	15	47	0	241816.3730	0.0800
61	16	45	0	61	15	47	0	241816.3730	0.0800
61	16	46	0	61	15	46	0	241816.3730	0.0800
61	16	45	0	61	15	46	0	241816.3730	0.0800
60	16	44	0	60	15	46	0	242022.1793	0.0800
60	16	45	0	60	15	45	0	242022.1793	0.0800
60	16	44	0	60	15	45	0	242022.1793	0.0800
60	16	45	0	60	15	46	0	242022.1793	0.0800
59	16	43	0	59	15	44	0	242217.5168	0.0800
59	16	44	0	59	15	45	0	242217.5168	0.0800
59	16	43	0	59	15	45	0	242217.5168	0.0800
59	16	44	0	59	15	44	0	242217.5168	0.0800
87	4	83	0	87	3	84	0	242228.7992	0.0800
87	5	83	0	87	4	84	0	242228.7992	0.0800
33	8	25	0	32	7	26	0	242257.2376	0.0800
40	7	34	0	39	6	33	0	242295.6185	0.0800
58	16	42	0	58	15	44	0	242402.7659	0.0800
58	16	43	0	58	15	44	0	242402.7659	0.0800
58	16	43	0	58	15	43	0	242402.7659	0.0800
58	16	42	0	58	15	43	0	242402.7659	0.0800
16	12	4	0	15	11	5	0	242440.2523	0.0800
16	12	4	0	15	11	4	0	242440.2523	0.0800
16	12	5	0	15	11	5	0	242440.2523	0.0800
16	12	5	0	15	11	4	0	242440.2523	0.0800
57	16	41	0	57	15	43	0	242578.4711	0.0800
57	16	42	0	57	15	43	0	242578.4711	0.0800
57	16	41	0	57	15	42	0	242578.4711	0.0800
57	16	42	0	57	15	42	0	242578.4711	0.0800
56	16	41	0	56	15	41	0	242744.7601	0.0800
56	16	40	0	56	15	41	0	242744.7601	0.0800
56	16	40	0	56	15	42	0	242744.7601	0.0800
56	16	41	0	56	15	42	0	242744.7601	0.0800
67	7	60	0	66	8	59	0	242807.7345	0.0800
55	16	40	0	55	15	40	0	242902.3885	0.0800
55	16	39	0	55	15	40	0	242902.3885	0.0800
55	16	39	0	55	15	41	0	242902.3885	0.0800

55	16	40	0	55	15	41	0	242902.3885	0.0800
65	5	60	0	64	6	59	0	242983.2559	0.0800
54	16	39	0	54	15	40	0	243051.2989	0.0800
54	16	38	0	54	15	39	0	243051.2989	0.0800
54	16	39	0	54	15	39	0	243051.2989	0.0800
54	16	38	0	54	15	40	0	243051.2989	0.0800
52	16	36	0	52	15	37	0	243325.1716	0.0800
52	16	37	0	52	15	37	0	243325.1716	0.0800
52	16	36	0	52	15	38	0	243325.1716	0.0800
52	16	37	0	52	15	38	0	243325.1716	0.0800
66	4	62	0	65	5	61	0	243407.7912	0.0800
51	16	36	0	51	15	36	0	243450.4009	0.0800
51	16	36	0	51	15	37	0	243450.4009	0.0800
51	16	35	0	51	15	36	0	243450.4009	0.0800
51	16	35	0	51	15	37	0	243450.4009	0.0800
66	5	62	0	65	4	61	0	243457.7615	0.0800
50	16	35	0	50	15	36	0	243568.6070	0.0800
50	16	34	0	50	15	35	0	243568.6070	0.0800
50	16	34	0	50	15	36	0	243568.6070	0.0800
50	16	35	0	50	15	35	0	243568.6070	0.0800
67	3	64	0	66	4	63	0	243590.9943	0.0800
67	4	64	0	66	3	63	0	243592.9935	0.0800
49	16	33	0	49	15	35	0	243679.9928	0.0800
49	16	34	0	49	15	34	0	243679.9928	0.0800
49	16	34	0	49	15	35	0	243679.9928	0.0800
49	16	33	0	49	15	34	0	243679.9928	0.0800
48	16	33	0	48	15	33	0	243784.7276	0.0800
48	16	32	0	48	15	34	0	243784.7276	0.0800
48	16	32	0	48	15	33	0	243784.7276	0.0800
48	16	33	0	48	15	34	0	243784.7276	0.0800
68	3	66	0	67	2	65	0	243816.7327	0.0800
68	2	66	0	67	2	65	0	243816.7327	0.0800
29	9	20	0	28	8	21	0	243826.9729	0.0800
65	6	60	0	64	5	59	0	243847.2691	0.0800
47	16	31	0	47	15	32	0	243882.9486	0.0800
47	16	32	0	47	15	32	0	243882.9486	0.0800
47	16	32	0	47	15	33	0	243882.9486	0.0800
47	16	31	0	47	15	33	0	243882.9486	0.0800
68	3	66	1	67	3	65	1	243917.2472	0.0800
68	3	66	1	67	2	65	1	243917.2472	0.0800
68	2	66	1	67	3	65	1	243917.2472	0.0800
68	2	66	1	67	2	65	1	243917.2472	0.0800
46	16	30	0	46	15	31	0	243975.1729	0.0800
46	16	31	0	46	15	32	0	243975.1729	0.0800
46	16	30	0	46	15	32	0	243975.1729	0.0800
46	16	31	0	46	15	31	0	243975.1729	0.0800
45	16	30	0	45	15	31	0	244061.6538	0.0800
45	16	29	0	45	15	30	0	244061.6538	0.0800
45	16	29	0	45	15	31	0	244061.6538	0.0800
45	16	30	0	45	15	30	0	244061.6538	0.0800
69	2	68	0	68	2	67	0	244072.9969	0.0800
69	1	68	0	68	2	67	0	244072.9969	0.0800
69	1	68	0	68	1	67	0	244072.9969	0.0800

69	2	68	0	68	1	67	0	244072.9969	0.0800
25	10	16	1	24	9	16	1	244091.7515	0.1000
25	10	15	1	24	9	16	1	244091.7515	0.1000
25	10	16	1	24	9	15	1	244091.7515	0.1000
25	10	15	1	24	9	15	1	244091.7515	0.1000
68	3	66	2	67	2	65	2	244101.9855	0.1000
68	2	66	2	67	3	65	2	244101.9855	0.1000
68	2	66	2	67	2	65	2	244101.9855	0.1000
68	3	66	2	67	3	65	2	244101.9855	0.1000
44	16	28	0	44	15	30	0	244142.7613	0.0800
44	16	28	0	44	15	29	0	244142.7613	0.0800
44	16	29	0	44	15	30	0	244142.7613	0.0800
44	16	29	0	44	15	29	0	244142.7613	0.0800
69	1	68	1	68	2	67	1	244197.9991	0.0800
69	2	68	1	68	2	67	1	244197.9991	0.0800
69	1	68	1	68	1	67	1	244197.9991	0.0800
69	2	68	1	68	1	67	1	244197.9991	0.0800
42	16	26	0	42	15	28	0	244289.0411	0.0800
42	16	26	0	42	15	27	0	244289.0411	0.0800
42	16	27	0	42	15	28	0	244289.0411	0.0800
42	16	27	0	42	15	27	0	244289.0411	0.0800
70	1	70	0	69	1	69	0	244343.4571	0.0800
70	1	70	0	69	0	69	0	244343.4571	0.0800
70	0	70	0	69	0	69	0	244343.4571	0.0800
70	0	70	0	69	1	69	0	244343.4571	0.0800
41	16	26	0	41	15	26	0	244354.9603	0.0800
41	16	25	0	41	15	26	0	244354.9603	0.0800
41	16	26	0	41	15	27	0	244354.9603	0.0800
41	16	25	0	41	15	27	0	244354.9603	0.0800
69	2	68	2	68	1	67	2	244398.5427	0.1000
69	1	68	2	68	2	67	2	244398.5427	0.1000
69	2	68	2	68	2	67	2	244398.5427	0.1000
69	1	68	2	68	1	67	2	244398.5427	0.1000
40	16	24	0	40	15	25	0	244416.2251	0.0800
40	16	25	0	40	15	25	0	244416.2251	0.0800
40	16	25	0	40	15	26	0	244416.2251	0.0800
40	16	24	0	40	15	26	0	244416.2251	0.0800
70	0	70	1	69	0	69	1	244492.4341	0.0800
70	1	70	1	69	1	69	1	244492.4341	0.0800
70	1	70	1	69	0	69	1	244492.4341	0.0800
70	0	70	1	69	1	69	1	244492.4341	0.0800
38	16	22	0	38	15	24	0	244526.1263	0.0800
38	16	23	0	38	15	24	0	244526.1263	0.0800
38	16	22	0	38	15	23	0	244526.1263	0.0800
38	16	23	0	38	15	23	0	244526.1263	0.0800
37	16	21	0	37	15	23	0	244575.0725	0.0800
37	16	22	0	37	15	23	0	244575.0725	0.0800
37	16	21	0	37	15	22	0	244575.0725	0.0800
37	16	22	0	37	15	22	0	244575.0725	0.0800
36	16	21	0	36	15	21	0	244620.3966	0.0800
36	16	20	0	36	15	22	0	244620.3966	0.0800
36	16	21	0	36	15	22	0	244620.3966	0.0800
36	16	20	0	36	15	21	0	244620.3966	0.0800

35	16	20	0	35	15	20	0	244661.9822	0.0800
35	16	19	0	35	15	20	0	244661.9822	0.0800
35	16	19	0	35	15	21	0	244661.9822	0.0800
35	16	20	0	35	15	21	0	244661.9822	0.0800
70	0	70	2	69	1	69	2	244708.9310	0.1000
70	1	70	2	69	1	69	2	244708.9310	0.1000
70	0	70	2	69	0	69	2	244708.9310	0.1000
70	1	70	2	69	0	69	2	244708.9310	0.1000
33	16	18	0	33	15	18	0	244735.7428	0.0800
33	16	17	0	33	15	18	0	244735.7428	0.0800
33	16	18	0	33	15	19	0	244735.7428	0.0800
33	16	17	0	33	15	19	0	244735.7428	0.0800
32	16	16	0	32	15	18	0	244768.0183	0.0800
32	16	17	0	32	15	18	0	244768.0183	0.0800
32	16	16	0	32	15	17	0	244768.0183	0.0800
32	16	17	0	32	15	17	0	244768.0183	0.0800
21	11	11	1	20	10	10	1	244771.6587	0.1000
21	11	10	1	20	10	11	1	244771.6587	0.1000
21	11	10	1	20	10	10	1	244771.6587	0.1000
21	11	11	1	20	10	11	1	244771.6587	0.1000
31	16	16	0	31	15	16	0	244797.4041	0.0800
31	16	16	0	31	15	17	0	244797.4041	0.0800
31	16	15	0	31	15	16	0	244797.4041	0.0800
31	16	15	0	31	15	17	0	244797.4041	0.0800
25	10	15	0	24	9	16	0	244801.8769	0.0800
25	10	15	0	24	9	15	0	244801.8769	0.0800
25	10	16	0	24	9	16	0	244801.8769	0.0800
25	10	16	0	24	9	15	0	244801.8769	0.0800
30	16	15	0	30	15	15	0	244824.5161	0.0800
30	16	14	0	30	15	15	0	244824.5161	0.0800
30	16	15	0	30	15	16	0	244824.5161	0.0800
30	16	14	0	30	15	16	0	244824.5161	0.0800
29	16	13	0	29	15	14	0	244848.9653	0.0800
29	16	14	0	29	15	14	0	244848.9653	0.0800
29	16	13	0	29	15	15	0	244848.9653	0.0800
29	16	14	0	29	15	15	0	244848.9653	0.0800
28	16	13	0	28	15	13	0	244871.1886	0.0800
28	16	12	0	28	15	13	0	244871.1886	0.0800
28	16	12	0	28	15	14	0	244871.1886	0.0800
28	16	13	0	28	15	14	0	244871.1886	0.0800
27	16	12	0	27	15	12	0	244891.1711	0.0800
27	16	12	0	27	15	13	0	244891.1711	0.0800
27	16	11	0	27	15	13	0	244891.1711	0.0800
27	16	11	0	27	15	12	0	244891.1711	0.0800
70	1	70	3	69	0	69	3	244900.0428	0.1000
70	0	70	3	69	1	69	3	244900.0428	0.1000
70	0	70	3	69	0	69	3	244900.0428	0.1000
70	1	70	3	69	1	69	3	244900.0428	0.1000
24	16	8	0	24	15	10	0	244940.1285	0.0800
24	16	8	0	24	15	9	0	244940.1285	0.0800
24	16	9	0	24	15	10	0	244940.1285	0.0800
24	16	9	0	24	15	9	0	244940.1285	0.0800
17	12	6	1	16	11	5	1	245374.9777	0.1000

17	12	5	1	16	11	6	1	245374.9777	0.1000
17	12	6	1	16	11	6	1	245374.9777	0.1000
17	12	5	1	16	11	5	1	245374.9777	0.1000
21	11	10	0	20	10	10	0	245553.4891	0.0800
21	11	11	0	20	10	10	0	245553.4891	0.0800
21	11	11	0	20	10	11	0	245553.4891	0.0800
21	11	10	0	20	10	11	0	245553.4891	0.0800
13	13	1	1	12	12	1	1	245955.3012	0.1000
13	13	0	1	12	12	1	1	245955.3012	0.1000
13	13	0	1	12	12	0	1	245955.3012	0.1000
13	13	1	1	12	12	0	1	245955.3012	0.1000
17	12	6	0	16	11	5	0	246227.7811	0.0800
17	12	5	0	16	11	6	0	246227.7811	0.0800
17	12	6	0	16	11	6	0	246227.7811	0.0800
17	12	5	0	16	11	5	0	246227.7811	0.0800
66	5	61	0	65	6	60	0	246524.8018	0.0800
13	13	1	0	12	12	1	0	246878.2038	0.0800
13	13	1	0	12	12	0	0	246878.2038	0.0800
13	13	0	0	12	12	1	0	246878.2038	0.0800
13	13	0	0	12	12	0	0	246878.2038	0.0800
68	3	65	0	67	4	64	0	247051.0957	0.0800
68	4	65	0	67	3	64	0	247052.4484	0.0800
68	3	65	1	67	4	64	1	247129.6467	0.0800
68	4	65	1	67	3	64	1	247131.0039	0.0800
66	6	61	0	65	5	60	0	247184.2832	0.0800
69	2	67	0	68	2	66	0	247278.4396	0.0800
69	2	67	0	68	3	66	0	247278.4396	0.0800
69	3	67	0	68	2	66	0	247278.4396	0.0800
69	3	67	0	68	3	66	0	247278.4396	0.0800
69	2	67	1	68	3	66	1	247381.3405	0.0800
69	2	67	1	68	2	66	1	247381.3405	0.0800
69	3	67	1	68	3	66	1	247381.3405	0.0800
69	3	67	1	68	2	66	1	247381.3405	0.0800
70	1	69	0	69	2	68	0	247535.5636	0.0800
70	2	69	0	69	1	68	0	247535.5636	0.0800
70	2	69	0	69	2	68	0	247535.5636	0.0800
70	1	69	0	69	1	68	0	247535.5636	0.0800
69	2	67	2	68	2	66	2	247569.2136	0.1000
69	3	67	2	68	3	66	2	247569.2136	0.1000
69	3	67	2	68	2	66	2	247569.2136	0.1000
69	2	67	2	68	3	66	2	247569.2136	0.1000
70	2	69	1	69	1	68	1	247662.7044	0.0800
70	2	69	1	69	2	68	1	247662.7044	0.0800
70	1	69	1	69	1	68	1	247662.7044	0.0800
70	1	69	1	69	2	68	1	247662.7044	0.0800
71	1	71	0	70	1	70	0	247806.0358	0.0800
71	1	71	0	70	0	70	0	247806.0358	0.0800
71	0	71	0	70	1	70	0	247806.0358	0.0800
71	0	71	0	70	0	70	0	247806.0358	0.0800
70	1	69	2	69	1	68	2	247866.2958	0.1000
70	2	69	2	69	1	68	2	247866.2958	0.1000
70	1	69	2	69	2	68	2	247866.2958	0.1000
70	2	69	2	69	2	68	2	247866.2958	0.1000

71	1	71	1	70	1	70	1	247957.2193	0.0800
71	1	71	1	70	0	70	1	247957.2193	0.0800
71	0	71	1	70	1	70	1	247957.2193	0.0800
71	0	71	1	70	0	70	1	247957.2193	0.0800
70	1	69	3	69	2	68	3	248034.0348	0.1000
70	2	69	3	69	2	68	3	248034.0348	0.1000
70	2	69	3	69	1	68	3	248034.0348	0.1000
70	1	69	3	69	1	68	3	248034.0348	0.1000
71	0	71	2	70	1	70	2	248176.9228	0.1000
71	1	71	2	70	0	70	2	248176.9228	0.1000
71	0	71	2	70	0	70	2	248176.9228	0.1000
71	1	71	2	70	1	70	2	248176.9228	0.1000
71	1	71	3	70	0	70	3	248370.8077	0.1000
71	0	71	3	70	0	70	3	248370.8077	0.1000
71	1	71	3	70	1	70	3	248370.8077	0.1000
71	0	71	3	70	1	70	3	248370.8077	0.1000
22	11	12	1	21	10	11	1	248549.8743	0.1000
22	11	11	1	21	10	12	1	248549.8743	0.1000
22	11	11	1	21	10	11	1	248549.8743	0.1000
22	11	12	1	21	10	12	1	248549.8743	0.1000
26	10	16	0	25	9	17	0	248559.5856	0.0800
26	10	17	0	25	9	17	0	248559.5856	0.0800
26	10	17	0	25	9	16	0	248559.5856	0.0800
26	10	16	0	25	9	16	0	248559.5856	0.0800
64	7	58	0	63	6	57	0	248580.0250	0.0800
18	12	6	1	17	11	7	1	249160.8736	0.1000
18	12	6	1	17	11	6	1	249160.8736	0.1000
18	12	7	1	17	11	7	1	249160.8736	0.1000
18	12	7	1	17	11	6	1	249160.8736	0.1000
35	8	28	0	34	7	27	0	249205.6773	0.0800
35	8	27	0	34	7	28	0	249422.5084	0.0800
14	13	1	1	13	12	2	1	249743.3321	0.1000
14	13	2	1	13	12	1	1	249743.3321	0.1000
14	13	1	1	13	12	1	1	249743.3321	0.1000
14	13	2	1	13	12	2	1	249743.3321	0.1000
18	12	7	0	17	11	6	0	250014.2178	0.0800
18	12	6	0	17	11	6	0	250014.2178	0.0800
18	12	6	0	17	11	7	0	250014.2178	0.0800
18	12	7	0	17	11	7	0	250014.2178	0.0800
68	4	64	0	67	5	63	0	250328.3453	0.0800
67	5	62	0	66	5	61	0	250329.7587	0.0800
68	4	64	0	67	4	63	0	250344.1283	0.0800
68	5	64	0	67	4	63	0	250355.7105	0.0800
69	3	66	0	68	4	65	0	250510.9544	0.0800
69	4	66	0	68	3	65	0	250512.0836	0.0800
67	6	62	0	66	5	61	0	250546.6436	0.0800
69	4	66	1	68	3	65	1	250592.8267	0.0800
14	13	2	0	13	12	1	0	250666.9249	0.0800
14	13	1	0	13	12	2	0	250666.9249	0.0800
14	13	1	0	13	12	1	0	250666.9249	0.0800
14	13	2	0	13	12	2	0	250666.9249	0.0800
70	3	68	0	69	3	67	0	250740.1395	0.0800
70	2	68	0	69	2	67	0	250740.1395	0.0800

70	3	68	0	69	2	67	0	250740.1395	0.0800
70	2	68	0	69	3	67	0	250740.1395	0.0800
70	3	68	1	69	3	67	1	250845.2454	0.0800
70	2	68	1	69	3	67	1	250845.2454	0.0800
70	2	68	1	69	2	67	1	250845.2454	0.0800
70	3	68	1	69	2	67	1	250845.2454	0.0800
69	3	66	3	68	4	65	3	250884.2615	0.1000
69	4	66	3	68	3	65	3	250885.3596	0.1000
15	13	3	3	14	12	3	3	250969.3375	0.1000
15	13	2	3	14	12	2	3	250969.3375	0.1000
15	13	3	3	14	12	2	3	250969.3375	0.1000
15	13	2	3	14	12	3	3	250969.3375	0.1000
71	1	70	0	70	1	69	0	250997.6866	0.0800
71	1	70	0	70	2	69	0	250997.6866	0.0800
71	2	70	0	70	1	69	0	250997.6866	0.0800
71	2	70	0	70	2	69	0	250997.6866	0.0800
70	3	68	2	69	2	67	2	251036.1204	0.1000
70	2	68	2	69	2	67	2	251036.1204	0.1000
70	2	68	2	69	3	67	2	251036.1204	0.1000
70	3	68	2	69	3	67	2	251036.1204	0.1000
23	11	13	2	22	10	12	2	251063.2389	0.1000
23	11	12	2	22	10	12	2	251063.2389	0.1000
23	11	13	2	22	10	13	2	251063.2389	0.1000
23	11	12	2	22	10	13	2	251063.2389	0.1000
71	1	70	1	70	2	69	1	251127.3101	0.0800
71	2	70	1	70	2	69	1	251127.3101	0.0800
71	1	70	1	70	1	69	1	251127.3101	0.0800
71	2	70	1	70	1	69	1	251127.3101	0.0800
70	3	68	3	69	3	67	3	251180.1207	0.1000
70	2	68	3	69	2	67	3	251180.1207	0.1000
70	2	68	3	69	3	67	3	251180.1207	0.1000
70	3	68	3	69	2	67	3	251180.1207	0.1000
31	9	23	0	30	8	22	0	251223.2147	0.0800
31	9	22	0	30	8	22	0	251223.2196	0.0800
31	9	23	0	30	8	23	0	251224.9276	0.0800
31	9	22	0	30	8	23	0	251224.9281	0.0800
72	8	64	0	71	9	63	0	251238.4789	0.0800
72	1	72	0	71	0	71	0	251268.3537	0.0800
72	1	72	0	71	1	71	0	251268.3537	0.0800
72	0	72	0	71	1	71	0	251268.3537	0.0800
72	0	72	0	71	0	71	0	251268.3537	0.0800
71	2	70	2	70	1	69	2	251333.9397	0.1000
71	1	70	2	70	2	69	2	251333.9397	0.1000
71	1	70	2	70	1	69	2	251333.9397	0.1000
71	2	70	2	70	2	69	2	251333.9397	0.1000
72	1	72	1	71	1	71	1	251421.9704	0.0800
72	1	72	1	71	0	71	1	251421.9704	0.0800
72	0	72	1	71	1	71	1	251421.9704	0.0800
72	0	72	1	71	0	71	1	251421.9704	0.0800
71	2	70	3	70	2	69	3	251504.2128	0.1000
71	1	70	3	70	1	69	3	251504.2128	0.1000
71	2	70	3	70	1	69	3	251504.2128	0.1000
71	1	70	3	70	2	69	3	251504.2128	0.1000

67	6	61	0	66	7	60	0	251534.4562	0.0800
27	10	17	1	26	9	17	1	251601.0161	0.1000
27	10	18	1	26	9	17	1	251601.0161	0.1000
27	10	18	1	26	9	18	1	251601.0161	0.1000
27	10	17	1	26	9	18	1	251601.0161	0.1000
72	1	72	2	71	1	71	2	251644.7297	0.1000
72	0	72	2	71	0	71	2	251644.7297	0.1000
72	1	72	2	71	0	71	2	251644.7297	0.1000
72	0	72	2	71	1	71	2	251644.7297	0.1000
72	0	72	3	71	1	71	3	251841.2626	0.1000
72	1	72	3	71	1	71	3	251841.2626	0.1000
72	0	72	3	71	0	71	3	251841.2626	0.1000
72	1	72	3	71	0	71	3	251841.2626	0.1000
27	10	18	0	26	9	17	0	252311.9900	0.0800
27	10	18	0	26	9	18	0	252311.9900	0.0800
27	10	17	0	26	9	18	0	252311.9900	0.0800
27	10	17	0	26	9	17	0	252311.9900	0.0800
23	11	13	1	22	10	13	1	252325.5990	0.1000
23	11	12	1	22	10	13	1	252325.5990	0.1000
23	11	13	1	22	10	12	1	252325.5990	0.1000
23	11	12	1	22	10	12	1	252325.5990	0.1000
22	22	0	0	23	21	3	0	252591.6403	0.0800
22	22	1	0	23	21	2	0	252591.6403	0.0800
40	7	33	0	39	6	34	0	252994.9979	0.0800
23	11	13	0	22	10	13	0	253109.0167	0.0800
23	11	12	0	22	10	13	0	253109.0167	0.0800
23	11	13	0	22	10	12	0	253109.0167	0.0800
23	11	12	0	22	10	12	0	253109.0167	0.0800
15	13	2	1	14	12	3	1	253531.0174	0.1000
15	13	3	1	14	12	2	1	253531.0174	0.1000
15	13	2	1	14	12	2	1	253531.0174	0.1000
15	13	3	1	14	12	3	1	253531.0174	0.1000
66	7	60	0	65	6	59	0	253599.3739	0.0800
78	17	61	0	78	16	62	0	253624.6051	0.1000
78	17	62	0	78	16	62	0	253624.6051	0.1000
69	4	65	0	68	5	64	0	253787.0221	0.0800
69	5	65	0	68	5	64	0	253795.5429	0.0800
69	4	65	0	68	4	64	0	253798.5299	0.0800
19	12	8	0	18	11	7	0	253800.0456	0.0800
19	12	7	0	18	11	7	0	253800.0456	0.0800
19	12	7	0	18	11	8	0	253800.0456	0.0800
19	12	8	0	18	11	8	0	253800.0456	0.0800
69	5	65	0	68	4	64	0	253807.1043	0.0800
69	4	65	1	68	5	64	1	253844.9498	0.1000
68	6	63	0	67	5	62	0	253928.8099	0.0800
70	4	67	0	69	3	66	0	253971.4993	0.0800
40	2	38	0	39	1	38	0	253985.7939	0.0800
71	3	69	0	70	3	68	0	254201.6504	0.0800
71	3	69	0	70	2	68	0	254201.6504	0.0800
71	2	69	0	70	3	68	0	254201.6504	0.0800
71	2	69	0	70	2	68	0	254201.6504	0.0800
71	3	69	1	70	2	68	1	254308.7700	0.0800
71	2	69	1	70	2	68	1	254308.7700	0.0800

71	3	69	1	70	3	68	1	254308.7700	0.0800
71	2	69	1	70	3	68	1	254308.7700	0.0800
76	17	60	0	76	16	61	0	254356.6030	0.1000
76	17	59	0	76	16	61	0	254356.6030	0.1000
76	17	60	0	76	16	60	0	254356.6030	0.1000
76	17	59	0	76	16	60	0	254356.6030	0.1000
15	13	3	0	14	12	2	0	254455.4930	0.0800
15	13	2	0	14	12	3	0	254455.4930	0.0800
15	13	2	0	14	12	2	0	254455.4930	0.0800
15	13	3	0	14	12	3	0	254455.4930	0.0800
72	1	71	0	71	2	70	0	254459.8908	0.0800
72	1	71	0	71	1	70	0	254459.8908	0.0800
72	2	71	0	71	2	70	0	254459.8908	0.0800
72	2	71	0	71	1	70	0	254459.8908	0.0800
71	2	69	2	70	3	68	2	254502.9968	0.1000
71	3	69	2	70	2	68	2	254502.9968	0.1000
71	2	69	2	70	2	68	2	254502.9968	0.1000
71	3	69	2	70	3	68	2	254502.9968	0.1000
72	1	71	1	71	1	70	1	254591.4224	0.0800
72	2	71	1	71	2	70	1	254591.4224	0.0800
72	2	71	1	71	1	70	1	254591.4224	0.0800
72	1	71	1	71	2	70	1	254591.4224	0.0800
71	3	69	3	70	3	68	3	254649.7247	0.1000
71	2	69	3	70	3	68	3	254649.7247	0.1000
71	3	69	3	70	2	68	3	254649.7247	0.1000
71	2	69	3	70	2	68	3	254649.7247	0.1000
75	17	59	0	75	16	60	0	254699.3325	0.0800
75	17	58	0	75	16	60	0	254699.3325	0.0800
75	17	58	0	75	16	59	0	254699.3325	0.0800
75	17	59	0	75	16	59	0	254699.3325	0.0800
72	2	71	4	71	2	70	4	254714.1914	0.1000
72	1	71	4	71	1	70	4	254714.1914	0.1000
72	1	71	4	71	2	70	4	254714.1914	0.1000
72	2	71	4	71	1	70	4	254714.1914	0.1000
73	0	73	0	72	0	72	0	254730.6061	0.0800
73	1	73	0	72	1	72	0	254730.6061	0.0800
73	1	73	0	72	0	72	0	254730.6061	0.0800
73	0	73	0	72	1	72	0	254730.6061	0.0800
72	1	71	2	71	1	70	2	254801.2978	0.1000
72	1	71	2	71	2	70	2	254801.2978	0.1000
72	2	71	2	71	2	70	2	254801.2978	0.1000
72	2	71	2	71	1	70	2	254801.2978	0.1000
73	0	73	1	72	1	72	1	254886.3813	0.0800
73	1	73	1	72	1	72	1	254886.3813	0.0800
73	1	73	1	72	0	72	1	254886.3813	0.0800
73	0	73	1	72	0	72	1	254886.3813	0.0800
32	9	24	0	31	8	23	0	254903.0724	0.0800
32	9	23	0	31	8	24	0	254906.2056	0.0800
73	1	73	2	72	0	72	2	255112.2647	0.1000
73	0	73	2	72	0	72	2	255112.2647	0.1000
73	0	73	2	72	1	72	2	255112.2647	0.1000
73	1	73	2	72	1	72	2	255112.2647	0.1000
73	0	73	3	72	0	72	3	255311.6361	0.1000

73	1	73	3	72	1	72	3	255311.6361	0.1000
73	1	73	3	72	0	72	3	255311.6361	0.1000
73	0	73	3	72	1	72	3	255311.6361	0.1000
73	17	57	0	73	16	58	0	255340.5080	0.0800
73	17	57	0	73	16	57	0	255340.5080	0.0800
73	17	56	0	73	16	58	0	255340.5080	0.0800
73	17	56	0	73	16	57	0	255340.5080	0.0800
72	17	56	0	72	16	56	0	255640.5383	0.0800
72	17	56	0	72	16	57	0	255640.5383	0.0800
72	17	55	0	72	16	57	0	255640.5383	0.0800
72	17	55	0	72	16	56	0	255640.5383	0.0800
28	10	18	0	27	9	18	0	256058.8655	0.0800
28	10	19	0	27	9	19	0	256058.8655	0.0800
28	10	18	0	27	9	19	0	256058.8655	0.0800
28	10	19	0	27	9	18	0	256058.8655	0.0800
37	8	30	0	36	7	29	0	256062.9253	0.0800
70	17	54	0	70	16	54	0	256200.5371	0.0800
70	17	53	0	70	16	55	0	256200.5371	0.0800
70	17	54	0	70	16	55	0	256200.5371	0.0800
70	17	53	0	70	16	54	0	256200.5371	0.0800
69	17	52	0	69	16	53	0	256461.8724	0.0800
69	17	52	0	69	16	54	0	256461.8724	0.0800
69	17	53	0	69	16	53	0	256461.8724	0.0800
69	17	53	0	69	16	54	0	256461.8724	0.0800
37	8	29	0	36	7	30	0	256531.0557	0.0800
67	13	54	0	66	13	53	0	256542.4318	0.0800
30	10	21	0	29	9	21	0	263533.0289	0.0800
30	10	21	0	29	9	20	0	263533.0289	0.0800
30	10	20	0	29	9	20	0	263533.0289	0.0800
30	10	20	0	29	9	21	0	263533.0289	0.0800
74	3	72	0	73	2	71	0	264584.8596	0.0800
74	2	72	0	73	2	71	0	264584.8596	0.0800
74	3	72	0	73	3	71	0	264584.8596	0.0800
74	2	72	0	73	3	71	0	264584.8596	0.0800
75	2	74	1	74	2	73	1	264983.0614	0.0800
75	1	74	1	74	1	73	1	264983.0614	0.0800
75	2	74	1	74	1	73	1	264983.0614	0.0800
75	1	74	1	74	2	73	1	264983.0614	0.0800
76	0	76	0	75	1	75	0	265115.7677	0.0800
76	0	76	0	75	0	75	0	265115.7677	0.0800
76	1	76	0	75	0	75	0	265115.7677	0.0800
76	1	76	0	75	1	75	0	265115.7677	0.0800
18	13	5	0	17	12	5	0	265818.9620	0.0800
18	13	6	0	17	12	5	0	265818.9620	0.0800
18	13	5	0	17	12	6	0	265818.9620	0.0800
18	13	6	0	17	12	6	0	265818.9620	0.0800
28	16	12	0	27	15	13	0	351073.5407	0.0800
28	16	13	0	27	15	12	0	351073.5407	0.0800
28	16	12	0	27	15	12	0	351073.5407	0.0800
28	16	13	0	27	15	13	0	351073.5407	0.0800
45	12	33	0	44	11	34	0	351088.4234	0.0800
45	12	34	0	44	11	34	0	351088.4234	0.0800
55	10	45	0	54	9	46	0	352620.1907	0.0800

47	23	25	0	47	22	26	0	355135.8243	0.0800
47	23	24	0	47	22	25	0	355135.8243	0.0800
47	23	25	0	47	22	25	0	355135.8243	0.0800
47	23	24	0	47	22	26	0	355135.8243	0.0800
46	23	23	0	46	22	24	0	355167.6382	0.0800
46	23	24	0	46	22	24	0	355167.6382	0.0800
46	23	24	0	46	22	25	0	355167.6382	0.0800
46	23	23	0	46	22	25	0	355167.6382	0.0800
44	23	21	0	44	22	23	0	355226.1745	0.0800
44	23	21	0	44	22	22	0	355226.1745	0.0800
44	23	22	0	44	22	22	0	355226.1745	0.0800
44	23	22	0	44	22	23	0	355226.1745	0.0800
42	23	20	0	42	22	21	0	355277.4694	0.0800
42	23	19	0	42	22	20	0	355277.4694	0.0800
42	23	20	0	42	22	20	0	355277.4694	0.0800
42	23	19	0	42	22	21	0	355277.4694	0.0800
41	23	19	0	41	22	19	0	355300.9076	0.0800
41	23	19	0	41	22	20	0	355300.9076	0.0800
41	23	18	0	41	22	19	0	355300.9076	0.0800
41	23	18	0	41	22	20	0	355300.9076	0.0800
40	23	17	0	40	22	18	0	355322.6123	0.0800
40	23	18	0	40	22	19	0	355322.6123	0.0800
40	23	18	0	40	22	18	0	355322.6123	0.0800
40	23	17	0	40	22	19	0	355322.6123	0.0800
39	23	16	0	39	22	17	0	355342.6275	0.0800
39	23	16	0	39	22	18	0	355342.6275	0.0800
39	23	17	0	39	22	18	0	355342.6275	0.0800
39	23	17	0	39	22	17	0	355342.6275	0.0800
38	23	16	0	38	22	17	0	355361.8081	0.0800
38	23	15	0	38	22	16	0	355361.8081	0.0800
38	23	16	0	38	22	16	0	355361.8081	0.0800
38	23	15	0	38	22	17	0	355361.8081	0.0800
37	23	15	0	37	22	16	0	355379.5351	0.0800
37	23	14	0	37	22	16	0	355379.5351	0.0800
37	23	15	0	37	22	15	0	355379.5351	0.0800
37	23	14	0	37	22	15	0	355379.5351	0.0800
36	23	14	0	36	22	15	0	355395.9747	0.0800
36	23	13	0	36	22	14	0	355395.9747	0.0800
36	23	13	0	36	22	15	0	355395.9747	0.0800
36	23	14	0	36	22	14	0	355395.9747	0.0800
25	17	9	0	24	16	8	0	355521.1016	0.0800
25	17	9	0	24	16	9	0	355521.1016	0.0800
25	17	8	0	24	16	8	0	355521.1016	0.0800
25	17	8	0	24	16	9	0	355521.1016	0.0800
51	11	41	0	50	10	41	0	356094.1151	0.0800
42	13	30	0	41	12	29	0	356111.2908	0.0800
42	13	29	0	41	12	29	0	356111.2908	0.0800
42	13	29	0	41	12	30	0	356111.2908	0.0800
42	13	30	0	41	12	30	0	356111.2908	0.0800
21	18	3	0	20	17	3	0	356168.9244	0.0800
21	18	4	0	20	17	4	0	356168.9244	0.0800
21	18	3	0	20	17	4	0	356168.9244	0.0800
21	18	4	0	20	17	3	0	356168.9244	0.0800

57	10	48	0	56	9	47	0	356202.9947	0.0800
38	14	24	0	37	13	24	0	357107.8550	0.0800
38	14	25	0	37	13	24	0	357107.8550	0.0800
38	14	25	0	37	13	25	0	357107.8550	0.0800
38	14	24	0	37	13	25	0	357107.8550	0.0800
98	6	93	0	97	6	92	0	357235.4764	0.0800
98	5	93	0	97	6	92	0	357235.4764	0.0800
98	5	93	0	97	5	92	0	357235.4764	0.0800
98	6	93	0	97	5	92	0	357235.4764	0.0800
99	4	95	0	98	4	94	0	357443.3774	0.0800
99	5	95	0	98	4	94	0	357443.3774	0.0800
99	4	95	0	98	5	94	0	357443.3774	0.0800
99	5	95	0	98	5	94	0	357443.3774	0.0800
22	18	5	0	21	17	5	0	359956.1063	0.0800
22	18	4	0	21	17	4	0	359956.1063	0.0800
22	18	5	0	21	17	4	0	359956.1063	0.0800
22	18	4	0	21	17	5	0	359956.1063	0.0800
40	19	21	0	39	18	21	0	443815.2812	0.0800
40	19	22	0	39	18	21	0	443815.2812	0.0800
40	19	22	0	39	18	22	0	443815.2812	0.0800
40	19	21	0	39	18	22	0	443815.2812	0.0800
36	20	17	0	35	19	17	0	444510.4313	0.0800
36	20	16	0	35	19	16	0	444510.4313	0.0800
36	20	16	0	35	19	17	0	444510.4313	0.0800
36	20	17	0	35	19	16	0	444510.4313	0.0800
33	21	12	0	32	20	13	0	448957.1252	0.0800
33	21	12	0	32	20	12	0	448957.1252	0.0800
33	21	13	0	32	20	12	0	448957.1252	0.0800
33	21	13	0	32	20	13	0	448957.1252	0.0800

Appendix F

Dimethyl Carbonate Spectral Analysis

F.1 Dimethyl Carbonate .int File

```
 dmc AA, EE, EA, AE
11 46008 1329911.     0 120   -12.9 -12.9    360  300
    2     0.1
  112     0.1
  332     0.1
  552     0.1
```

F.2 Dimethyl Carbonate .par File

```
 dmc AA, EE, EA, AE                                  Sat Thu Apr 14 11:47:48 2005
 41  278   10    0    0.0000E+000    3.0000E+010    1.0000E+000 1.0000000000
'a'  1    6    0   60    0    2    6   10        -1     99    3
     1    1    0   60    0    2    8    8        -1    199    0
     1    2    0   60    0    2    8    8        -1    299    0
     1    3    0   60    0    2    2    2        -1    199    0
     1    4    0   60    0    2    2    2        -1    299    0
     1    5    0   60    0    2    2    6         0     99    0
         910099  3.000000000001011E-001 1.00000000E-037
             99 -7.093249895311526E+001 1.16195032E+031
    -1000000000  7.109521410676506E+001 1.00000000E-037
    -1000000033 -3.554760705338249E+001 1.00000000E-037
   -11000000033  6.157026150395218E+001 1.00000000E-037
    -1000000055 -3.554760705338249E+001 1.00000000E-037
    -1000000011  1.777380352669114E+001 1.00000000E-037
   -11000000011  3.078513075197672E+001 1.00000000E-037
     2000000000 -2.558805162405164E+001 1.00000000E+037
    -2000000033  1.279402581202599E+001 1.00000000E-037
   -12000000033  2.215990273977636E+001 1.00000000E-037
    -2000000055  1.279402581202599E+001 1.00000000E-037
    -2000000011 -6.397012906013114E+000 1.00000000E-037
   -12000000011  1.107995136988829E+001 1.00000000E-037
     3000000099 -7.184739334028848E+000 1.00000000E+000
     4000000000 -2.359809593776768E-002 1.00000000E+000
    -4000000011  1.179904826039504E-002 1.00000000E-037
   -14000000011 -2.043654998849988E-002 1.00000000E-037
     1000400055 -3.095160480846307E+001 1.37411913E+010
    -1000400011  1.547580211838569E+001 1.00000000E-037
   -11000400011  2.680487590951319E+001 1.00000000E-037
     2000400055  1.108864846582044E+001 1.34572916E+010
    -2000400011 -5.548431596630979E+000 1.00000000E-037
   -12000400011  9.610165427752015E+000 1.00000000E-037
            1099  8.226300154364682E+003 1.19562662E+010
             199  2.175936215902030E+003 2.86651175E+010
     1000000100  4.095810623842150E-002 3.90830723E+004
    -1000000133 -2.047905311921122E-002 1.00000000E-037
   -11000000133  3.547076049337489E-002 1.00000000E-037
    -1000000155 -2.047905311921122E-002 1.00000000E-037
    -1000000111  1.023952655960575E-002 1.00000000E-037
   -11000000111  1.773538024668783E-002 1.00000000E-037
          40099  9.775428855827747E+001 9.24448385E+010
     1000040000  1.528206401950211E-002 1.35160053E+004
    -1000040033 -7.641032009751253E-003 1.00000000E-037
   -11000040033  1.323465566314895E-002 1.00000000E-037
    -1000040055 -7.641032009751253E-003 1.00000000E-037
    -1000040011  3.820516004875662E-003 1.00000000E-037
   -11000040011  6.617327831574674E-003 1.00000000E-037
            299 -1.225971243000191E-004 1.00000000E+037
           1199 -1.133613651949211E-002 1.00000000E+037
```

F.3 Dimethyl Carbonate .lin File

0	0	0	0					0.00	0.0001
1	1	1	3	0	0	0	4	12381.7384	0.0120
1	1	1	5	0	0	0	5	12389.9925	0.0120
1	1	1	1	0	0	0	2	12391.0100	0.0120
1	1	1	0	0	0	0	0	12396.2250	0.0120
6	1	5	4	6	0	6	4	13066.8738	0.0120
6	1	5	5	6	0	6	5	13067.2156	0.0120
6	1	5	2	6	0	6	2	13070.2968	0.0120
6	1	5	0	6	0	6	0	13073.5508	0.0120
7	1	6	4	7	0	7	4	14960.2916	0.0120
7	1	6	5	7	0	7	5	14960.5481	0.0120
7	1	6	2	7	0	7	2	14963.7606	0.0120
7	1	6	0	7	0	7	0	14967.1045	0.0120
5	0	5	0	4	1	4	0	15029.9267	0.0120
5	0	5	2	4	1	4	1	15032.1573	0.0120
5	0	5	5	4	1	4	5	15034.6068	0.0120
2	1	2	3	1	0	1	4	16347.9283	0.0120
2	1	2	5	1	0	1	5	16350.7341	0.0120
2	1	2	1	1	0	1	2	16353.1368	0.0120
2	1	2	0	1	0	1	0	16356.9482	0.0120
8	1	7	4	8	0	8	4	17251.3767	0.0120
8	1	7	5	8	0	8	5	17251.5849	0.0120
8	1	7	2	8	0	8	2	17254.9187	0.0120
8	1	7	0	8	0	8	0	17258.3580	0.0120
3	1	3	3	2	0	2	4	20120.2448	0.0120
3	1	3	5	2	0	2	5	20121.5722	0.0120
3	1	3	1	2	0	2	2	20124.2190	0.0120
3	1	3	0	2	0	2	0	20127.6808	0.0120
57	0	57	2	56	1	56	1	227481.663	0.0800
57	0	57	4	56	1	56	3	227481.663	0.0800
57	0	57	5	56	1	56	5	227481.663	0.0800
57	0	57	2	56	0	56	2	227481.663	0.0800
57	1	57	5	56	0	56	5	227481.663	0.0800
57	1	57	0	56	0	56	0	227481.663	0.0800
57	0	57	0	56	1	56	0	227481.663	0.0800
57	1	57	1	56	0	56	2	227481.663	0.0800
57	1	57	1	56	1	56	1	227481.663	0.0800
57	1	57	3	56	0	56	4	227481.663	0.0800
58	1	58	3	57	0	57	4	231437.221	0.0800
58	0	58	2	57	0	57	2	231437.221	0.0800
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58	1	58	1	57	0	57	2	231437.221	0.0800
58	1	58	1	57	1	57	1	231437.221	0.0800
58	1	58	5	57	0	57	5	231437.221	0.0800
58	0	58	5	57	1	57	5	231437.221	0.0800
58	0	58	2	57	1	57	1	231437.221	0.0800
58	1	58	0	57	0	57	0	231437.221	0.0800
58	0	58	4	57	1	57	3	231437.221	0.0800
59	0	59	2	58	1	58	1	235392.586	0.0800
59	1	59	1	58	0	58	2	235392.586	0.0800
59	0	59	2	58	0	58	2	235392.586	0.0800
59	0	59	4	58	1	58	3	235392.586	0.0800

59	1	59	1	58	1	58	1	235392.586 0.0800
59	0	59	5	58	1	58	5	235392.586 0.0800
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60	1	60	1	59	0	59	2	239347.718 0.0800
60	1	60	5	59	0	59	5	239347.718 0.0800
60	0	60	2	59	1	59	1	239347.718 0.0800
60	0	60	4	59	1	59	3	239347.718 0.0800
60	1	60	3	59	0	59	4	239347.718 0.0800
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64	1	64	5	63	0	63	5	255166.699 0.0800
64	0	64	5	63	1	63	5	255166.699 0.0800
64	0	64	2	63	1	63	1	255166.699 0.0800
64	0	64	2	63	0	63	2	255166.699 0.0800
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64	0	64	4	63	1	63	3	255166.699 0.0800
65	0	65	5	64	1	64	5	259120.953 0.0800
65	0	65	0	64	1	64	0	259120.953 0.0800
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65	1	65	5	64	0	64	5	259120.953 0.0800
65	0	65	4	64	1	64	3	259120.953 0.0800
65	0	65	2	64	1	64	1	259120.953 0.0800
65	0	65	2	64	0	64	2	259120.953 0.0800
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66	0	66	0	65	1	65	0	263075.049 0.0800
66	1	66	0	65	0	65	0	263075.049 0.0800
66	1	66	3	65	0	65	4	263075.049 0.0800
66	1	66	1	65	1	65	1	263075.049 0.0800
66	1	66	5	65	0	65	5	263075.049 0.0800
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68	1	68	3	67	0	67	4	270982.525 0.0800
68	1	68	5	67	0	67	5	270982.525 0.0800
68	0	68	4	67	1	67	3	270982.525 0.0800
68	0	68	2	67	1	67	1	270982.525 0.0800

68	0	68	2	67	0	67	2	270982.525 0.0800
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68	0	68	5	67	1	67	5	270982.525 0.0800
69	0	69	5	68	1	68	5	274936.064 0.0800
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69	0	69	2	68	0	68	2	274936.064 0.0800
69	0	69	2	68	1	68	1	274936.064 0.0800
69	1	69	3	68	0	68	4	274936.064 0.0800
69	1	69	0	68	0	68	0	274936.064 0.0800
69	1	69	1	68	0	68	2	274936.064 0.0800
69	1	69	1	68	1	68	1	274936.064 0.0800
69	1	69	5	68	0	68	5	274936.064 0.0800
69	0	69	4	68	1	68	3	274936.064 0.0800
70	0	70	4	69	1	69	3	278889.280 0.0800
70	1	70	5	69	0	69	5	278889.280 0.0800
70	1	70	0	69	0	69	0	278889.280 0.0800
70	0	70	2	69	0	69	2	278889.280 0.0800
70	0	70	2	69	1	69	1	278889.280 0.0800
70	1	70	3	69	0	69	4	278889.280 0.0800
70	0	70	5	69	1	69	5	278889.280 0.0800
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71	1	71	5	70	0	70	5	282842.306 0.0800
71	0	71	4	70	1	70	3	282842.306 0.0800
71	1	71	3	70	0	70	4	282842.306 0.0800
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72	1	72	5	71	0	71	5	286794.999 0.0800
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72	1	72	1	71	0	71	2	286794.999 0.0800
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72	1	72	3	71	0	71	4	286794.999 0.0800
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72	0	72	2	71	1	71	1	286794.999 0.0800
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73	1	73	1	72	0	72	2	290747.599 0.0800
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73	1	73	0	72	0	72	0	290747.599 0.0800

74	0	74	2	73	0	73	2	294700.049 0.0800
74	0	74	2	73	1	73	1	294700.049 0.0800
74	0	74	4	73	1	73	3	294700.049 0.0800
74	0	74	0	73	1	73	0	294700.049 0.0800
74	0	74	5	73	1	73	5	294700.049 0.0800
74	1	74	0	73	0	73	0	294700.049 0.0800
74	1	74	5	73	0	73	5	294700.049 0.0800
74	1	74	1	73	0	73	2	294700.049 0.0800
74	1	74	1	73	1	73	1	294700.049 0.0800
74	1	74	3	73	0	73	4	294700.049 0.0800
75	1	75	1	74	1	74	1	298652.240 0.0800
75	0	75	0	74	1	74	0	298652.240 0.0800
75	1	75	5	74	0	74	5	298652.240 0.0800
75	0	75	5	74	1	74	5	298652.240 0.0800
75	0	75	4	74	1	74	3	298652.240 0.0800
75	0	75	2	74	1	74	1	298652.240 0.0800
75	0	75	2	74	0	74	2	298652.240 0.0800
75	1	75	1	74	0	74	2	298652.240 0.0800
75	1	75	3	74	0	74	4	298652.240 0.0800
75	1	75	0	74	0	74	0	298652.240 0.0800
76	1	76	5	75	0	75	5	302604.130 0.0800
76	0	76	2	75	1	75	1	302604.130 0.0800
76	0	76	2	75	0	75	2	302604.130 0.0800
76	0	76	0	75	1	75	0	302604.130 0.0800
76	1	76	3	75	0	75	4	302604.130 0.0800
76	0	76	4	75	1	75	3	302604.130 0.0800
76	0	76	5	75	1	75	5	302604.130 0.0800
76	1	76	0	75	0	75	0	302604.130 0.0800
76	1	76	1	75	0	75	2	302604.130 0.0800
76	1	76	1	75	1	75	1	302604.130 0.0800
77	1	77	5	76	0	76	5	306555.712 0.0800
77	1	77	1	76	0	76	2	306555.712 0.0800
77	0	77	5	76	1	76	5	306555.712 0.0800
77	1	77	1	76	1	76	1	306555.712 0.0800
77	0	77	0	76	1	76	0	306555.712 0.0800
77	0	77	2	76	1	76	1	306555.712 0.0800
77	0	77	4	76	1	76	3	306555.712 0.0800
77	1	77	0	76	0	76	0	306555.712 0.0800
77	1	77	3	76	0	76	4	306555.712 0.0800
77	0	77	2	76	0	76	2	306555.712 0.0800
78	1	78	0	77	0	77	0	310507.201 0.0800
78	1	78	1	77	1	77	1	310507.201 0.0800
78	0	78	0	77	1	77	0	310507.201 0.0800
78	1	78	1	77	0	77	2	310507.201 0.0800
78	0	78	5	77	1	77	5	310507.201 0.0800
78	0	78	2	77	0	77	2	310507.201 0.0800
78	0	78	4	77	1	77	3	310507.201 0.0800
78	0	78	2	77	1	77	1	310507.201 0.0800
78	1	78	5	77	0	77	5	310507.201 0.0800
78	1	78	3	77	0	77	4	310507.201 0.0800
79	1	79	3	78	0	78	4	314458.438 0.0800
79	1	79	1	78	0	78	2	314458.438 0.0800
79	1	79	0	78	0	78	0	314458.438 0.0800

79	1	79	1	78	1	78	1	314458.438 0.0800
79	1	79	5	78	0	78	5	314458.438 0.0800
79	0	79	0	78	1	78	0	314458.438 0.0800
79	0	79	5	78	1	78	5	314458.438 0.0800
79	0	79	4	78	1	78	3	314458.438 0.0800
79	0	79	2	78	1	78	1	314458.438 0.0800
79	0	79	2	78	0	78	2	314458.438 0.0800
82	1	82	5	81	0	81	5	326310.418 0.0800
82	1	82	3	81	0	81	4	326310.418 0.0800
82	1	82	1	81	0	81	2	326310.418 0.0800
82	0	82	2	81	0	81	2	326310.418 0.0800
82	0	82	2	81	1	81	1	326310.418 0.0800
82	0	82	0	81	1	81	0	326310.418 0.0800
82	1	82	1	81	1	81	1	326310.418 0.0800
82	0	82	5	81	1	81	5	326310.418 0.0800
82	0	82	4	81	1	81	3	326310.418 0.0800
82	1	82	0	81	0	81	0	326310.418 0.0800
83	0	83	2	82	0	82	2	330260.813 0.0800
83	0	83	0	82	1	82	0	330260.813 0.0800
83	0	83	5	82	1	82	5	330260.813 0.0800
83	1	83	0	82	0	82	0	330260.813 0.0800
83	1	83	1	82	0	82	2	330260.813 0.0800
83	1	83	3	82	0	82	4	330260.813 0.0800
83	1	83	5	82	0	82	5	330260.813 0.0800
83	0	83	4	82	1	82	3	330260.813 0.0800
83	0	83	2	82	1	82	1	330260.813 0.0800
83	1	83	1	82	1	82	1	330260.813 0.0800
84	1	84	0	83	0	83	0	334210.754 0.0800
84	1	84	3	83	0	83	4	334210.754 0.0800
84	1	84	1	83	1	83	1	334210.754 0.0800
84	1	84	1	83	0	83	2	334210.754 0.0800
84	1	84	5	83	0	83	5	334210.754 0.0800
84	0	84	5	83	1	83	5	334210.754 0.0800
84	0	84	0	83	1	83	0	334210.754 0.0800
84	0	84	2	83	1	83	1	334210.754 0.0800
84	0	84	2	83	0	83	2	334210.754 0.0800
84	0	84	4	83	1	83	3	334210.754 0.0800
85	0	85	2	84	1	84	1	338160.198 0.0800
85	1	85	3	84	0	84	4	338160.198 0.0800
85	1	85	1	84	1	84	1	338160.198 0.0800
85	1	85	1	84	0	84	2	338160.198 0.0800
85	1	85	0	84	0	84	0	338160.198 0.0800
85	0	85	5	84	1	84	5	338160.198 0.0800
85	1	85	5	84	0	84	5	338160.198 0.0800
85	0	85	2	84	0	84	2	338160.198 0.0800
85	0	85	0	84	1	84	0	338160.198 0.0800
85	0	85	4	84	1	84	3	338160.198 0.0800
87	0	87	0	86	1	86	0	346059.258 0.0800
87	0	87	5	86	1	86	5	346059.258 0.0800
87	1	87	3	86	0	86	4	346059.258 0.0800
87	1	87	1	86	0	86	2	346059.258 0.0800
87	1	87	0	86	0	86	0	346059.258 0.0800
87	0	87	2	86	0	86	2	346059.258 0.0800

87	0	87	2	86	1	86	1	346059.258 0.0800
87	1	87	5	86	0	86	5	346059.258 0.0800
87	1	87	1	86	1	86	1	346059.258 0.0800
87	0	87	4	86	1	86	3	346059.258 0.0800
88	1	88	0	87	0	87	0	350007.927 0.0800
88	1	88	3	87	0	87	4	350007.927 0.0800
88	1	88	1	87	1	87	1	350007.927 0.0800
88	1	88	1	87	0	87	2	350007.927 0.0800
88	0	88	2	87	1	87	1	350007.927 0.0800
88	1	88	5	87	0	87	5	350007.927 0.0800
88	0	88	4	87	1	87	3	350007.927 0.0800
88	0	88	5	87	1	87	5	350007.927 0.0800
88	0	88	2	87	0	87	2	350007.927 0.0800
88	0	88	0	87	1	87	0	350007.927 0.0800

Appendix G

Methyl Glycolate Spectral Analysis

G.1 Methyl Glycolate .int File

```
 mg A, E
11 46008 438220.0844     0 100   -9.9 -9.9    360  300
   1     2.68
   2     1.02
 111     2.68
 112     1.02
```

G.2 Methyl Glycolate .par File

```
mg A, E                                    20-FTue Jun 15 16:Sun Apr 10 15:35:58 2005
  85 2519   60    0    0.0000E+000    7.0000E+010    1.0000E+000 1.0000000000
'S'  1  3  0 99  0  1  2  2 -1    1  3
     1  1  0 99  0  1  1  1 -1  101  0
     1  2  0 99  0  1  1  1  1  201  0
          910099  5.119000001000022E-002 1.00000000E-030
            1099  7.974644942036493E+003 1.00000000E+037
      1000001000  2.325051263022959E-001 1.00000000E+037
     -1000001011 -1.162525631605259E-001 1.00000000E-037
    -11000001011  2.013553458992273E-001 1.00000000E-037
     -2000001000 -2.016070359736554E-004 1.00000000E-037
     -2000001011  1.008035096775923E-004 1.00000000E-037
    -12000001011  1.745968148066581E-004 1.00000000E-037
             199  2.026642269627913E+003 1.00000000E+037
      1000000100  9.131172053104843E-003 1.00000000E+037
     -1000000111 -4.565586026920719E-003 1.00000000E-037
    -11000000111  7.907826964760239E-003 1.00000000E-037
     -2000000100 -7.917711587134859E-006 1.00000000E-037
     -2000000111  3.958855467238899E-006 1.00000000E-037
    -12000000111  6.856939377116586E-006 1.00000000E-037
           40099  8.868030175854460E+001 1.00000000E+037
      1000040000  4.927630925022493E-003 1.00000000E+037
     -1000040011 -2.463815462709997E-003 1.00000000E-037
    -11000040011  4.267453561783399E-003 1.00000000E-037
     -2000040000 -4.272787791673282E-006 1.00000000E-037
     -2000040011  2.136393719733668E-006 1.00000000E-037
    -12000040011  3.700342774090576E-026 1.00000000E-037
             299 -1.897275794834111E-004 1.00000000E+037
      1000000200 -3.824016608030776E-008 1.00000000E+037
     -1000000211  1.912008304169626E-008 1.00000000E-037
    -11000000211 -3.311695527234580E-008 1.00000000E-037
     -2000000200  3.315835079080153E-011 1.00000000E-037
     -2000000211 -1.657917402877915E-011 1.00000000E-037
    -12000000211 -2.871597414423728E-011 1.00000000E-037
            1199 -1.042081898859759E-003 1.00000000E+037
      1000001100 -2.482464452802213E-006 1.00000000E+037
     -1000001111  1.241232226501234E-006 1.00000000E-037
    -11000001111 -2.149877280239513E-006 1.00000000E-037
     -2000001100  2.152564582979150E-009 1.00000000E-037
     -2000001111 -1.076282202771612E-009 1.00000000E-037
    -12000001111 -1.864175612913099E-009 1.00000000E-037
            2099 -3.255011844661971E-003 1.00000000E+037
      1000002000 -1.946775265851885E-003 1.00000000E+037
     -1000002011  9.733876330044637E-004 1.00000000E-037
    -11000002011 -1.685956835781795E-003 1.00000000E-037
     -2000002000  1.688064247430521E-006 1.00000000E-037
     -2000002011 -8.440320541416806E-007 1.00000000E-037
    -12000002011 -1.461906522096189E-006 1.00000000E-037
           40199 -2.998388885954355E-005 1.00000000E+037
           41099 -4.520438187376548E-004 1.00000000E+037
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     -1000041011  1.379557859263670E-005 1.00000000E-037
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         399  2.885640232508159E-011 1.00000000E+037
        1299  4.872203850397507E-009 1.00000000E+037
        2199 -6.347182648855119E-008 1.00000000E+037
        3099 -7.583309817208638E-006 1.00000000E+037
       41199  1.238869449022750E-009 1.00000000E+037
       42099  3.486343308658321E-008 1.00000000E+037
       40299  2.547224028627458E-011 1.00000000E+037
      990099  1.164792969543189E+007 1.00000000E+037
         -99 -1.437386200423507E+003 1.00000000E-037
 -1000000000  1.437867104550208E+003 1.00000000E-037
 -1000000011 -7.189335522751056E+002 1.00000000E-037
-11000000011  1.245229439806381E+003 1.00000000E-037
 -2000000000 -4.810042596511831E-001 1.00000000E-037
 -2000000011  2.405021299113134E-001 1.00000000E-037
-12000000011  4.165619078928177E-001 1.00000000E-037
      990099  1.683121921974000E+005 1.00000000E-037
         -99  1.748940162663000E+003 1.00000000E-037
 -1000000000 -1.749472554758000E+003 1.00000000E-037
 -1000000011  8.747362773786998E+002 1.00000000E-037
-11000000011 -1.515087675644000E+003 1.00000000E-037
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 -2000000011 -2.662571237555000E-001 1.00000000E-037
-12000000011 -4.611708661844002E-001 1.00000000E-037
 -3000000000 -8.208805783874003E-005 1.00000000E-037
 -3000000011 -8.208818198476000E-005 1.00000000E-037
 -4000000000 -6.437928615404004E-005 1.00000000E-037
 -4000000011  3.218969915170000E-005 1.00000000E-037
-14000000011 -5.575401435397000E-005 1.00000000E-037
 -5000000000  3.996546175109002E-005 1.00000000E-037
 -5000000011 -1.998274663200000E-005 1.00000000E-037
-15000000011 -3.461113883099000E-005 1.00000000E-037
 -6000000000 -2.598733962735000E-005 1.00000000E-037
 -6000000011 -2.598748458348000E-005 1.00000000E-037
 -7000000000  1.708464697003000E-005 1.00000000E-037
```

G.3 Methyl Glycolate .lin File

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 0  0  0  0                                    0.00      0.0001 1.00
 2  0  2  0  1  0  1  0                     8095.0       1.00   1.00
 2  1  1  0  1  1  0  0                     8461.0       1.00   1.00
 5  1  4  0  5  0  5  0                    10959.6       0.15   1.00
 3  1  3  0  2  1  2  0                    11620.2       0.15   1.00
 3  0  3  0  2  0  2  0                    12113.3       1.00   1.00
17  3 15  0 16  4 12  0                    12432.51      0.1000 1.00
 3  1  2  0  2  1  1  0                    12684.29      0.1000 1.00
20  2 19  0 19  3 16  0                    13315.15      0.1000 1.00
19  2 18  0 18  3 15  0                    14324.03      0.1000 1.00
17  2 16  0 16  3 13  0                    14504.49      0.1000 1.00
18  2 17  0 17  3 14  0                    14719.92      0.1000 1.00
 4  1  4  0  3  1  3  0                    15480.83      0.1000 1.00
18  3 16  0 17  4 13  0                    15791.13      0.1000 1.00
 4  0  4  0  3  0  3  0                    16095.80      0.1000 1.00
 4  3  2  0  3  3  1  0                    16236.7       0.15   1.00
 4  3  1  0  3  3  0  0                    16236.7       0.15   1.00
 4  2  2  0  3  2  1  0                    16321.3       0.15   1.00
 4  1  3  0  3  1  2  0                    16898.1       0.15   1.00
 5  1  5  0  4  1  4  0                    19330.1       0.15   1.00
 5  0  5  0  4  0  4  0                    20033.7       0.15   1.00
 5  2  4  0  4  2  3  0                    20240.0       0.15   1.00
 5  4  1  0  4  4  0  0                    20292.8       0.15   1.00
 5  4  2  0  4  4  1  0                    20292.8       0.15   1.00
 5  2  3  0  4  2  2  0                    20472.4       0.15   1.00
 7  2  5  0  7  1  6  0                    20573.77      0.1000 1.00
 5  1  4  0  4  1  3  0                    21098.9       0.15   1.00
 6  2  4  0  6  1  5  0                    21113.45      0.1000 1.00
 6  1  6  0  5  1  5  0                    23167.2       0.15   1.00
 6  0  6  0  5  0  5  0                    23919.3       0.15   1.00
 6  2  5  0  5  2  4  0                    24266.7       0.15   1.00
 6  5  1  0  5  5  0  0                    24348.9       0.15   1.00
 6  5  2  0  5  5  1  0                    24348.9       0.15   1.00
 6  4  2  0  5  4  1  0                    24359.5       0.15   1.00
 6  4  3  0  5  4  2  0                    24359.5       0.15   1.00
 6  2  4  0  5  2  3  0                    24666.1       0.1500 1.00
 6  1  5  0  5  1  4  0                    25282.06      0.1000 1.00
41 13 29  0 42 12 30  0                    26448.29      0.1000 1.00
24  4 21  0 23  5 18  0                    26581.30      0.1000 1.00
37 12 26  0 38 11 27  0                    27065.87      0.1000 1.00
14  2 12  0 13  3 11  0                    27378.81      0.1000 1.00
33 11 23  0 34 10 24  0                    27676.20      0.1000 1.00
25  9 17  0 26  8 18  0                    28863.23      0.1000 1.00
 7  2  5  2  6  2  4  2                    28901.81      0.1000 0.612
 7  2  6  2  6  2  5  2                    28901.81      0.1000 0.612
 7  2  5  0  6  2  4  0                    28903.78      0.1000 0.613
28  5 24  0 27  6 21  0                    29463.97      0.1000 1.00
48 15 34  0 49 14 35  0                    29481.00      0.1000 1.00
25  4 22  0 24  5 19  0                    30026.98      0.1000 1.00
18  3 16  2 18  2 17  2                    30381.06      0.1000 0.100
18  3 15  2 18  2 16  2                    30381.06      0.1000 0.100
18  3 15  0 18  2 16  0                    30391.19      0.1000 0.200
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17	3	14	0	17	2	15	0	30406.75	0.1000	0.094
40	13	28	0	41	12	29	0	30719.68	0.1000	1.00
19	3	17	2	19	2	18	2	30774.18	0.1000	0.108
19	3	16	2	19	2	17	2	30774.18	0.1000	0.108
19	3	16	0	19	2	17	0	30783.32	0.1000	0.108
8	1	7	1	7	1	6	1	30800.03	0.1000	0.851
8	1	8	1	7	1	7	1	30800.03	0.1000	0.851
8	1	8	0	7	1	7	0	30800.03	0.1000	0.852
17	2	15	2	17	1	16	2	30977.62	0.1000	0.080
17	2	16	2	17	1	17	2	30977.62	0.1000	0.080
17	2	15	0	17	1	16	0	30981.72	0.1000	0.080
32	6	27	0	31	7	24	0	31118.38	0.1000	1.00
36	12	25	0	37	11	26	0	31327.88	0.1000	1.00
13	1	13	2	13	0	14	2	31416.52	0.1000	0.039
13	1	12	2	13	0	13	2	31416.52	0.1000	0.039
13	1	12	0	13	0	13	0	31421.57	0.1000	0.079
8	0	8	0	7	0	7	0	31526.60	0.1000	1.805
8	0	9	2	7	0	8	2	31526.60	0.1000	0.902
8	0	8	2	7	0	7	2	31526.60	0.1000	0.902
20	3	18	2	20	2	19	2	31615.03	0.1000	0.117
20	3	17	2	20	2	18	2	31615.03	0.1000	0.117
20	3	17	0	20	2	18	0	31623.17	0.1000	0.234
9	0	9	0	8	1	8	0	31849.91	0.1000	0.100
9	0	10	2	8	1	7	1	31851.77	0.1000	0.050
9	0	9	2	8	1	8	1	31851.77	0.1000	0.050
32	11	22	0	33	10	23	0	31926.73	0.1000	1.00
8	2	6	1	7	2	5	1	32282.30	0.1000	0.887
8	2	7	0	7	2	6	0	32282.30	0.1000	0.887
8	2	7	1	7	2	6	1	32282.30	0.1000	0.887
14	3	11	0	14	2	12	0	32347.59	0.1000	1.00
8	7	2	2	7	7	1	2	32462.08	0.1000	0.212
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8	7	2	1	7	7	1	1	32462.08	0.1000	0.212
8	7	1	2	7	7	0	2	32462.08	0.1000	0.212
8	7	1	1	7	7	0	1	32462.08	0.1000	0.212
8	7	1	0	7	7	0	0	32462.08	0.1000	0.212
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8	6	3	0	7	6	2	0	32470.17	0.1000	0.805
8	5	3	1	7	5	2	1	32483.47	0.1000	0.569
8	5	4	1	7	5	3	1	32483.47	0.1000	0.569
8	5	4	0	7	5	3	0	32483.47	0.1000	0.569
8	5	4	2	7	5	3	2	32483.47	0.1000	0.569
8	5	3	2	7	5	2	2	32483.47	0.1000	0.569
8	5	3	0	7	5	2	0	32483.47	0.1000	0.569
8	4	4	2	7	4	3	2	32508.14	0.1000	0.709
8	4	4	1	7	4	3	1	32508.14	0.1000	0.709
8	4	5	1	7	4	4	1	32508.14	0.1000	0.709
8	4	5	2	7	4	4	2	32508.14	0.1000	0.709
8	4	5	0	7	4	4	0	32508.14	0.1000	0.709
8	4	4	0	7	4	3	0	32509.14	0.1000	0.709
8	3	6	0	7	3	5	0	32538.30	0.1000	1.642
8	3	6	1	7	3	5	1	32555.60	0.1000	0.804
8	3	5	1	7	3	4	1	32555.60	0.1000	0.804

8	3	6	2	7	3	5	2	32581.76	0.1000	0.805
8	3	5	2	7	3	4	2	32581.76	0.1000	0.805
8	3	5	0	7	3	4	0	32599.47	0.1000	1.649
21	3	18	2	21	2	19	2	32932.61	0.1000	0.129
21	3	19	2	21	2	20	2	32932.61	0.1000	0.129
21	3	18	0	21	2	19	0	32939.72	0.1000	0.129
24	9	16	0	25	8	17	0	33085.80	0.1000	1.00
8	2	6	2	7	2	5	2	33179.07	0.1000	0.937
8	2	7	2	7	2	6	2	33179.07	0.1000	0.937
8	2	6	0	7	2	5	0	33179.79	0.1000	0.937
32	6	26	0	31	7	25	0	33298.20	0.1000	1.00
13	3	10	0	13	2	11	0	33393.51	0.1000	1.00
15	2	13	0	14	3	12	0	33533.92	0.1000	1.00
29	5	25	0	28	6	22	0	33573.31	0.1000	1.00
8	1	7	0	7	1	6	0	33576.57	0.1000	1.009
8	1	8	2	7	1	7	2	33576.57	0.1000	1.009
8	1	7	2	7	1	6	2	33576.57	0.1000	1.009
47	15	33	0	48	13	34	0	33755.16	0.1000	1.00
18	2	16	2	18	1	17	2	34188.92	0.1000	0.094
18	2	17	2	18	1	18	2	34188.92	0.1000	0.094
18	2	16	0	18	1	17	0	34192.84	0.1000	0.094
43	14	30	0	44	13	31	0	34369.56	0.1000	1.00
28	5	23	0	27	6	22	0	34395.67	0.1000	1.00
12	3	9	0	12	2	10	0	34508.83	0.1000	1.00
9	1	8	1	8	1	7	1	34594.45	0.1000	1.206
9	1	9	1	8	1	8	1	34594.45	0.1000	1.206
9	1	9	0	8	1	8	0	34594.45	0.1000	1.206
22	3	20	2	22	2	21	2	34744.85	0.1000	0.143
22	3	19	2	22	2	20	2	34744.85	0.1000	0.143
22	3	19	0	22	2	20	0	34750.96	0.1000	0.287
39	13	27	0	40	12	28	0	34976.46	0.1000	1.00
14	1	14	2	14	0	15	2	35227.66	0.1000	0.048
14	1	13	2	14	0	14	2	35227.66	0.1000	0.048
14	1	13	0	14	0	14	0	35233.10	0.1000	0.048
9	0	10	2	8	0	9	2	35258.20	0.1000	1.262
9	0	9	0	8	0	8	0	35258.20	0.1000	2.525
9	0	9	2	8	0	8	2	35258.20	0.1000	1.262
33	6	28	0	32	7	25	0	35568.97	0.1000	1.00
35	12	24	0	36	11	25	0	35574.48	0.1000	1.00
27	4	24	0	26	5	21	0	35990.73	0.1000	1.00
10	0	10	0	9	1	9	0	36211.06	0.1000	1.00
9	2	8	1	8	2	7	1	36267.67	0.1000	1.270
9	2	7	1	8	2	6	1	36267.67	0.1000	1.270
9	2	8	0	8	2	7	0	36267.67	0.1000	1.270
9	8	2	2	8	8	1	2	36518.40	0.1000	0.264
9	8	1	2	8	8	0	2	36518.40	0.1000	0.264
9	8	1	1	8	8	0	1	36518.40	0.1000	0.264
9	8	2	0	8	8	1	0	36518.40	0.1000	0.264
9	8	1	0	8	8	0	0	36518.40	0.1000	0.264
9	8	2	1	8	8	1	1	36518.40	0.1000	0.264
9	7	3	1	8	7	2	1	36525.70	0.1000	0.506
9	7	2	0	8	7	1	0	36525.70	0.1000	0.506
9	7	3	0	8	7	2	0	36525.70	0.1000	0.506

9	7	2	1	8	7	1	1	36525.70	0.1000	0.506
9	7	2	2	8	7	1	2	36525.70	0.1000	0.506
9	7	3	2	8	7	2	2	36525.70	0.1000	0.506
9	6	3	0	8	6	2	0	36537.21	0.1000	1.447
9	6	4	1	8	6	3	1	36537.21	0.1000	0.724
9	6	3	2	8	6	2	2	36537.21	0.1000	0.724
9	6	4	2	8	6	3	2	36537.21	0.1000	0.724
9	6	3	1	8	6	2	1	36537.21	0.1000	0.724
9	6	4	0	8	6	3	0	36537.21	0.1000	1.447
9	5	5	1	8	5	4	1	36556.31	0.1000	0.914
9	5	4	2	8	5	3	2	36556.31	0.1000	0.914
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9	5	4	0	8	5	3	0	36556.31	0.1000	0.914
9	4	6	0	8	4	5	0	36591.13	0.1000	1.075
9	4	6	2	8	4	5	2	36592.33	0.1000	1.075
9	4	5	1	8	4	4	1	36592.33	0.1000	1.075
9	4	6	1	8	4	5	1	36592.33	0.1000	1.075
9	4	5	2	8	4	4	2	36592.33	0.1000	1.075
9	4	5	0	8	4	4	0	36594.40	0.1000	1.076
9	3	7	0	8	3	6	0	36623.21	0.1000	2.408
9	3	7	2	8	3	6	2	36717.62	0.1000	1.176
9	3	6	2	8	3	5	2	36717.62	0.1000	1.176
9	3	6	0	8	3	5	0	36734.07	0.1000	2.423
23	3	20	0	23	2	21	0	37061.18	0.1000	1.00
23	9	15	0	24	8	16	0	37290.92	0.1000	1.00
9	2	8	2	8	2	7	2	37484.53	0.1000	1.357
9	2	7	2	8	2	6	2	37484.53	0.1000	1.357
9	2	7	0	8	2	6	0	37485.17	0.1000	1.357
30	5	26	0	29	6	23	0	37541.12	0.1000	1.00
9	1	8	0	8	1	7	0	37675.77	0.1000	1.426
9	1	9	2	8	1	8	2	37675.77	0.1000	1.426
9	1	8	2	8	1	7	2	37675.77	0.1000	1.426
19	2	17	0	19	1	18	0	37751.76	0.1000	1.00
46	15	32	0	47	14	33	0	38017.00	0.1000	1.00
10	1	10	0	9	1	9	0	38374.63	0.1000	1.643
10	1	10	1	9	1	9	1	38374.63	0.1000	1.642
10	1	9	1	9	1	8	1	38374.63	0.1000	1.642
28	4	25	0	27	5	22	0	38379.74	0.1000	1.00
33	6	27	0	32	7	26	0	38619.67	0.1000	1.00
42	14	29	0	43	13	30	0	38623.04	0.1000	1.00
10	0	10	0	9	0	9	0	38955.48	0.1000	1.00
38	13	26	0	39	12	27	0	39220.22	0.1000	1.00
16	2	14	0	15	3	13	0	39795.00	0.1000	1.00
34	12	23	0	35	11	24	0	39807.18	0.1000	1.00
24	3	21	0	24	2	22	0	39858.54	0.1000	1.00
3	3	1	0	3	2	2	0	39890.02	0.1000	1.00
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22	1	21	1	21	1	20	1	83059.7079	0.1000	
22	1	22	1	21	1	21	1	83059.7079	0.1000	
22	0	22	0	21	0	21	0	83080.6619	0.1000	
22	0	23	2	21	0	22	2	83080.6619	0.1000	

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20	2	18	2	19	2	17	2	83358.4022	0.1000
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20	2	18	0	19	2	17	0	83359.9490	0.1000
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21	3	19	0	20	3	18	0	84975.7870	0.1000
21	17	5	0	20	17	4	0	85203.6717	0.1000
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21	16	5	0	20	16	4	0	85213.3887	0.1000
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21	15	6	0	20	15	5	0	85224.7171	0.1000
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21	14	8	0	20	14	7	0	85238.2522	0.1000
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21	13	9	2	20	13	8	2	85254.5417	0.1000
21	13	8	2	20	13	7	2	85254.5417	0.1000
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21	12	9	1	20	12	8	1	85274.7407	0.1000
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21	11	11	0	20	11	10	0	85300.3624	0.1000
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21	10	12	2	20	10	11	2	85333.4748	0.1000
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23	1	23	0	22	1	22	0	86759.6506	0.1000
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21	4	17	2	20	4	16	2	87010.8423	0.1000
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21	4	17	0	20	4	16	0	87012.2089	0.1000
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22	3	19	1	21	3	18	1	88881.8018	0.1000
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22	20	2	2	21	20	1	2	89240.9532	0.1000
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59	18	42	2	58	18	41	2	240325.7766	0.1000
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59	17	42	0	58	17	41	0	240486.9458	0.1000
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65	15	51	0	64	15	50	0	265831.5826	0.1000
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65	14	52	1	64	14	51	1	266233.8415	0.1000
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65	8	58	0	64	8	57	0	266266.6712	0.1000
63	8	56	2	62	8	55	2	266420.9942	0.1000
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64	10	55	2	63	10	54	2	266560.9729	0.1000
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67	6	62	1	66	6	61	1	266650.3658	0.1000
67	6	61	1	66	6	60	1	266650.3658	0.1000
67	6	62	0	66	6	61	0	266653.7420	0.1000
67	5	62	2	66	5	61	2	266677.7136	0.1000
67	5	63	2	66	5	62	2	266677.7136	0.1000
69	3	67	2	68	4	64	1	266965.2877	0.1000
69	4	65	1	68	4	64	1	266965.2877	0.1000
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69	3	66	0	68	4	65	0	266967.5121	0.1000
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70	2	69	2	69	2	68	2	267221.1109	0.1000
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66	22	44	0	65	22	43	0	268539.0486 0.1000
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66	21	45	2	65	21	44	2	268661.6776 0.1000
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66	21	46	2	65	21	45	2	268661.6776 0.1000
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65	11	54	0	64	11	53	0	268663.9310 0.1000
66	20	47	2	65	20	46	2	268802.6294 0.1000
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66	17	49	2	65	17	48	2	269385.7548 0.1000
66	17	50	2	65	17	49	2	269385.7548 0.1000
66	16	50	2	65	16	49	2	269660.1606 0.1000
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66	16	51	1	65	16	50	1	269662.5159 0.1000
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66	15	52	0	65	15	51	0	269997.4332 0.1000

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67	7	61	1	66	7	60	1	270308.5060	0.1000
67	7	60	1	66	7	59	1	270308.5060	0.1000
67	7	61	0	66	7	60	0	270312.4990	0.1000
68	6	62	1	67	6	61	1	270327.517	0.1500
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68	5	63	0	67	5	62	0	270350.8238	0.1000
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67	6	61	2	66	6	60	2	270571.8763	0.1000
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67	6	61	0	66	6	60	0	270576.3300	0.1000
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66	13	53	2	65	13	52	2	270962.8549	0.1000
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66	12	54	0	65	12	53	0	271740.1567	0.1000
66	9	58	1	65	9	57	1	272383.6555	0.1000
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66	9	58	0	65	9	57	0	272386.0048	0.1000
67	22	46	0	66	22	45	0	272637.8688	0.1000
67	22	45	2	66	22	44	2	272637.8688	0.1000
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67	22	46	2	66	22	45	2	272637.8688	0.1000
67	21	47	0	66	21	46	0	272765.9836	0.1000
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67	21	47	1	66	21	46	1	272768.3413	0.1000
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66	10	56	1	65	10	55	1	273035.7324	0.1000
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67	18	49	2	66	18	48	2	273285.7393	0.1000
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67	18	50	1	66	18	49	1	273288.1166	0.1000
67	18	49	1	66	18	48	1	273288.1166	0.1000
67	17	51	2	66	17	50	2	273524.7108	0.1000
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67	17	50	1	66	17	49	1	273526.8425	0.1000
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69	6	63	1	68	6	62	1	274004.3493	0.1000
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67	15	53	0	66	15	52	0	274167.2957	0.1000

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67	15	52	1	66	15	51	1	274169.3963	0.1000
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74	1	74	1	73	0	73	2	275178.7643	0.1000
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67	13	55	0	66	13	54	0	275182.6020	0.1000
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67	9	59	1	66	9	58	1	276341.9966	0.1000
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68	23	46	0	67	23	45	0	276620.4808	0.1000
68	23	45	0	67	23	44	0	276620.4808	0.1000
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68	22	47	2	67	22	46	2	276737.9794	0.1000
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68	20	49	2	67	20	48	2	277026.4421	0.1000
68	19	50	2	67	19	49	2	277205.4247	0.1000
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68	18	51	2	67	18	50	2	277415.9605	0.1000
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67	11	56	0	66	11	55	0	277510.0830	0.1000
68	8	61	1	67	8	60	1	277541.2619	0.1000
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69	7	63	1	68	7	62	1	277662.0443	0.1000
69	7	62	1	68	7	61	1	277662.0443	0.1000
68	17	51	2	67	17	50	2	277666.2043	0.1000
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71	5	66	1	70	5	65	1	277814.1494	0.1000
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66	8	58	0	65	8	57	0	277834.9732	0.1000
68	16	53	2	67	16	52	2	277968.5666	0.1000
68	16	52	2	67	16	51	2	277968.5666	0.1000
68	16	53	1	67	16	52	1	277970.9198	0.1000
68	16	52	1	67	16	51	1	277970.9198	0.1000
72	4	68	1	71	3	69	2	278028.5043	0.1000
72	4	68	1	71	4	67	1	278028.5043	0.1000
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72	4	69	0	71	4	68	0	278030.5460	0.1000
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73	3	71	1	72	3	70	1	278288.8070	0.1000
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66	9	57	0	65	9	56	0	279280.2183	0.1000
68	12	57	0	67	12	56	0	280183.7901	0.1000
66	8	59	1	65	7	58	2	280327.1530	0.1000
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69	21	49	2	68	21	48	2	280980.0896	0.1000
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69	20	49	2	68	20	48	2	281140.9108	0.1000
69	20	50	2	68	20	49	2	281140.9108	0.1000
69	18	51	2	68	18	50	2	281548.6085	0.1000
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69	12	58	0	68	12	57	0	284452.3679 0.1000
69	12	57	1	68	12	56	1	284471.1733 0.1000
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70	24	47	0	69	24	46	0	284700.8129 0.1000
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70	23	48	2	69	23	47	2	284814.9104 0.1000
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70	23	48	1	69	23	47	1	284817.1769 0.1000
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68	8	61	2	67	8	60	2	284942.2042 0.1000
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70	8	62	1	69	8	61	1	284978.2471 0.1000
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70	21	50	2	69	21	49	2	285089.3030 0.1000
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71	6	66	2	70	6	65	2	285099.0529 0.1000
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73	5	69	1	72	5	68	1	285182.0003 0.1000
73	5	68	1	72	5	67	1	285182.0003 0.1000
73	4	69	0	72	4	68	0	285184.8023 0.1000
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70	20	50	2	69	20	49	2	285257.6859 0.1000
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70	20	50	1	69	20	49	1	285260.1305 0.1000
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69	11	59	0	68	11	58	0	285285.3116 0.1000
69	11	59	1	68	11	58	1	285287.2687 0.1000
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74	4	71	1	73	3	70	2	285403.3840 0.1000
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70	19	51	0	69	19	50	0	285453.6691 0.1000
70	19	52	0	69	19	51	0	285453.6691 0.1000
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70	19	52	1	69	19	51	1	285456.1141 0.1000
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69	10	59	1	68	10	58	1	285491.1396 0.1000
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70	18	53	2	69	18	52	2	285683.8400 0.1000
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70	18	53	1	69	18	52	1	285686.4600 0.1000
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70	7	63	0	69	7	62	0	285877.8051 0.1000
76	2	75	1	75	1	74	2	285952.2014 0.1000
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70	17	53	2	69	17	52	2	285958.4362 0.1000
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70	17	53	1	69	17	52	1	285961.0677 0.1000
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70	16	54	1	69	16	53	1	286293.5000	0.1000
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69	11	58	0	68	11	57	0	286514.7351	0.1000
70	15	55	0	69	15	54	0	286701.8001	0.1000
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70	14	57	0	69	14	56	0	287219.3382	0.1000
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70	14	56	1	69	14	55	1	287222.7980	0.1000
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70	13	58	0	69	13	57	0	287887.7943	0.1000
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68	9	60	2	67	9	59	2	287996.9765	0.1000
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68	9	59	0	67	9	58	0	287999.1488	0.1000
70	9	62	0	69	9	61	0	288033.8731	0.1000
69	8	61	0	68	8	60	0	288396.8737	0.1000
72	7	66	0	71	7	65	0	288681.1364	0.1000
71	8	64	0	70	8	63	0	288683.2114	0.1000
73	6	68	1	72	6	67	1	288714.4657	0.1000
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70	12	59	0	69	12	58	0	288725.7554	0.1000
70	12	58	1	69	12	57	1	288741.0620	0.1000
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76	2	74	0	75	3	73	0	289356.7773	0.1000
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71	19	53	2	70	19	52	2	289580.6575	0.1000
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70	10	61	1	69	10	60	1	289591.5305	0.1000
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71	15	56	0	70	15	55	0	290888.8176	0.1000
71	15	57	1	70	15	56	1	290890.6707	0.1000
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87	7	80	0	86	8	79	0	347349.3815	0.1000
87	8	80	1	86	8	79	1	347376.2404	0.1000
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87	8	80	1	86	7	79	2	347417.2814	0.1000
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88	6	83	2	87	7	80	1	347426.8502	0.1000
88	6	82	2	87	7	81	1	347426.8502	0.1000
88	7	82	1	87	7	81	1	347428.9737	0.1000
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88	6	83	2	87	6	82	2	347428.9737	0.1000
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86	9	78	1	85	9	77	1	347469.1620	0.1000
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89	5	85	2	88	5	84	2	347584.3843	0.1000
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90	5	85	1	89	5	84	1	347802.7889 0.1000
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90	5	86	1	89	5	85	1	347802.7889 0.1000
93	1	92	2	92	1	91	2	348628.3023 0.1000
93	2	91	1	92	2	90	1	348628.3023 0.1000
93	1	92	2	92	2	91	1	348628.3023 0.1000
93	1	93	2	92	2	90	1	348628.3023 0.1000
93	1	93	2	92	1	92	2	348628.3023 0.1000
93	2	91	1	92	1	92	2	348628.3023 0.1000
93	2	92	1	92	2	91	1	348628.3023 0.1000
93	2	92	1	92	1	91	2	348628.3023 0.1000
94	0	95	2	93	0	94	2	348925.4715 0.1000
94	0	95	2	93	1	92	1	348925.4715 0.1000
94	1	93	1	93	0	94	2	348925.4715 0.1000
94	0	94	2	93	1	93	1	348925.4715 0.1000
94	1	94	1	93	1	93	1	348925.4715 0.1000
94	1	94	1	93	0	93	2	348925.4715 0.1000
94	1	93	1	93	1	92	1	348925.4715 0.1000
94	1	94	0	93	1	93	0	348925.4715 0.1000
94	0	94	0	93	1	93	0	348925.4715 0.1000
94	0	94	0	93	0	93	0	348925.4715 0.1000
94	1	94	0	93	0	93	0	348925.4715 0.1000
94	0	94	2	93	0	93	2	348925.4715 0.1000

Appendix H

Glycolaldehyde Spectral Analysis

H.1 Glycolaldehyde .int File

```
glycolaldehyde !!
 0001 710xx  62921.0030,  0, 80, -9.9,-9.9, 360.
 001  0.12
 002  2.73
 003  0.00
 111  0.12
 112  2.73
 113  0.00
 221  0.12
 222  2.73
 223  0.00
 331  0.12
 332  2.73
 333  0.00
```

H.2 Glycolaldehyde .par File

```
   glycolaldehyde                                  20-FEB-Tue Mar 08 16:53:30 2005
  43 3160   20    0    0.0000E+000    8.0000E+000    1.0000E+000 1.0000000000
a   1    4   0   90
              0  1.055623781112654E-052 1.00000000E-030
             11  5.850000000000000E+006 1.00000000E-020
             22  7.800000000000000E+006 1.00000000E-020
             33  9.410000000000000E+006 1.00000000E-020
          10000  1.844626074448348E+004 8.10000000E+020
          20000  6.525996379120887E+003 3.16000000E+020
          30000  4.969235800589177E+003 2.97000000E+020
           1100  2.039797750931777E-002 1.22000000E+020
           2000 -4.772337539696791E-002 1.87000000E+020
            200 -6.222339192607588E-003 2.52000000E+020
          40100 -1.833783791154165E-003 9.80000000E+020
          41000 -8.878891564129571E-003 2.66000000E+020
            399 -6.465478187768077E-009 1.00764150E+020
           1299  1.565742184756087E-007 2.50287500E+020
           2199 -7.720841178790587E-007 7.15017900E+020
           3099  1.057027541563161E-006 5.55354000E+020
          40299 -2.504187458139837E-009 5.23012700E+020
          41199 -1.297885693365799E-008 2.29641120E+020
          42099  1.908733515453502E-007 2.18783450E+020
          10011  1.846355355190025E+004 8.10000000E+020
          20011  6.482544600805613E+003 3.16000000E+020
          30011  4.965052865673245E+003 2.97000000E+020
           1111  1.994945899240820E-002 1.22000000E+020
           2011 -4.827689303628609E-002 1.87000000E+020
            211 -6.280202567628707E-003 2.52000000E+020
          40111 -1.834215249663875E-003 9.80000000E+020
          41011 -7.614211111745850E-003 2.66000000E+020
          10022  1.857657913024933E+004 8.10000000E+020
          20022  6.477994714671660E+003 3.16000000E+020
          30022  4.938517530230890E+003 2.97000000E+020
           1122  2.159963648307887E-002 1.22000000E+020
           2022 -5.195805934463164E-002 1.87000000E+020
            222 -6.196435813429423E-003 2.52000000E+020
          40122 -1.849365592830345E-003 9.80000000E+020
          41022 -1.089545573548198E-002 2.66000000E+020
          10033  1.852485586468521E+004 8.10000000E+020
          20033  6.445623992696672E+003 3.16000000E+020
          30033  4.933536970451043E+003 2.97000000E+020
           1133  2.325807581751820E-002 1.22000000E+020
           2033 -5.324883990577034E-002 1.87000000E+020
            233 -6.358601292949328E-003 2.52000000E+020
          40133 -1.859377387402884E-003 9.80000000E+020
          41033 -8.955798475850508E-003 2.66000000E+020
```

H.3 Glycolaldehyde .lin File

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34 17 17  0 35 16 20  0     8154.390     0.0500
34 17 18  0 35 16 19  0     8154.390     0.0500
19  8 12  0 18  9  9  0     8176.950     0.0500
21 11 10  0 22 10 13  0     8181.510     0.0500
21 11 11  0 22 10 12  0     8181.510     0.0500
19  8 11  0 18  9 10  0     8188.740     0.0500
32 14 19  0 31 15 16  0     8228.890     0.0500
 8  5  4  0  9  4  5  0     8254.730     0.0500
 6  1  6  0  5  2  3  0     8516.690     0.0500
 8  5  3  0  9  4  6  0     8738.800     0.0500
 7  1  7  0  6  2  4  0     9742.620     0.0500
43 19 24  0 42 20 23  0     9876.970     0.0500
43 19 25  0 42 20 22  0     9876.970     0.0500
23 12 11  0 24 11 14  0    10184.780     0.0500
23 12 12  0 24 11 13  0    10184.780     0.0500
17  7 11  0 16  8  8  0    10204.580     0.0500
36 18 18  0 37 17 21  0    10230.210     0.0500
36 18 19  0 37 17 20  0    10230.210     0.0500
17  7 10  0 16  8  9  0    10252.520     0.0500
30 13 18  0 29 14 15  0    10305.860     0.0500
30 13 17  0 29 14 16  0    10305.880     0.0500
10  6  5  0 11  5  6  0    10431.280     0.0500
10  6  4  0 11  5  7  0    10561.110     0.0500
 2  0  2  0  1  1  1  0    10927.300     0.0500
 1  1  0  0  1  0  1  0    13477.170     0.0500
13  5  9  0 12  6  6  0    14078.250     0.0500
27 14 13  0 28 13 16  0    14209.210     0.0500
27 14 14  0 28 13 15  0    14209.210     0.0500
14  8  6  0 15  7  9  0    14459.930     0.0500
13  5  8  0 12  6  7  0    14759.520     0.0500
 2  1  1  0  2  0  2  0    15176.620     0.0500
 4  1  3  0  3  2  2  0    15261.660     0.0500
11  4  8  0 10  5  5  0    15495.140     0.0500
 9  3  7  0  8  4  4  0    15614.970     0.0500
29 15 14  0 30 14 17  0    16232.810     0.0500
29 15 15  0 30 14 16  0    16232.810     0.0500
16  9  7  0 17  8 10  0    16432.220     0.0500
24 10 14  0 23 11 13  0    16518.370     0.0500
 3  1  2  0  3  0  3  0    17980.930     0.0500
31 16 15  0 32 15 18  0    18265.330     0.0500
31 16 16  0 32 15 17  0    18265.330     0.0500
 5  4  2  0  6  3  3  0    18344.220     0.0500
35 15 20  0 34 16 19  0    18441.090     0.0500
35 15 21  0 34 16 18  0    18441.090     0.0500
22  9 14  0 21 10 11  0    18590.690     0.0500
22  9 13  0 21 10 12  0    18597.470     0.0500
44 22 22  0 45 21 25  0    18658.070     0.0500
44 22 23  0 45 21 24  0    18658.070     0.0500
 5  4  1  0  6  3  4  0    19016.710     0.0500
46 20 26  0 45 21 25  0    19886.260     0.0500
46 20 27  0 45 21 24  0    19886.260     0.0500
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33	17	16	0	34	16	19	0	20307.800	0.0500
33	17	17	0	34	16	18	0	20307.800	0.0500
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20	11	10	0	21	10	11	0	20389.010	0.0500
33	14	19	0	32	15	18	0	20560.230	0.0500
33	14	20	0	32	15	17	0	20560.230	0.0500
7	5	3	0	8	4	4	0	20584.980	0.0500
20	8	13	0	19	9	10	0	20671.400	0.0500
20	8	12	0	19	9	11	0	20698.690	0.0500
7	5	2	0	8	4	5	0	20774.120	0.0500
46	23	23	0	47	22	26	0	20800.100	0.0500
46	23	24	0	47	22	25	0	20800.100	0.0500
8	2	7	0	7	3	4	0	20907.720	0.0500
44	19	25	0	43	20	24	0	22090.920	0.0500
44	19	26	0	43	20	23	0	22090.920	0.0500
4	1	3	0	4	0	4	0	22142.600	0.0500
9	3	6	0	8	4	5	0	22252.790	0.0500
35	18	17	0	36	17	20	0	22361.010	0.0500
35	18	18	0	36	17	19	0	22361.010	0.0500
9	6	4	0	10	5	5	0	22636.270	0.0500
31	13	18	0	30	14	17	0	22674.840	0.0500
31	13	19	0	30	14	16	0	22674.840	0.0500
9	6	3	0	10	5	6	0	22685.650	0.0500
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18	7	11	0	17	8	10	0	22857.160	0.0500
48	24	24	0	49	23	27	0	22957.690	0.0500
55	24	31	0	54	25	30	0	22995.920	0.0500
55	24	32	0	54	25	29	0	22995.920	0.0500
1	1	1	0	0	0	0	0	23415.570	0.0500
3	0	3	0	2	1	2	0	23415.570	0.0500
42	18	24	0	41	19	23	0	24283.240	0.0500
42	18	25	0	41	19	22	0	24283.240	0.0500
37	19	18	0	38	18	21	0	24425.600	0.0500
37	19	19	0	38	18	20	0	24425.600	0.0500
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16	6	11	0	15	7	8	0	24776.430	0.0500
50	25	25	0	51	24	28	0	25131.410	0.0500
50	25	26	0	51	24	27	0	25131.410	0.0500
16	6	10	0	15	7	9	0	25175.350	0.0500
53	23	30	0	52	24	29	0	25298.080	0.0500
53	23	31	0	52	24	28	0	25298.080	0.0500
26	14	12	0	27	13	15	0	26364.970	0.0500
26	14	13	0	27	13	14	0	26364.970	0.0500
10	3	8	0	9	4	5	0	26383.710	0.0500
40	17	23	0	39	18	22	0	26464.850	0.0500
40	17	24	0	39	18	21	0	26464.850	0.0500
5	1	4	0	5	0	5	0	27871.110	0.0500
5	2	3	0	5	1	4	0	31727.070	0.0500
6	2	4	0	6	1	5	0	31833.030	0.0500
47	20	27	0	46	21	26	0	32109.270	0.0500
47	20	28	0	46	21	25	0	32109.270	0.0500
32	17	15	0	33	16	18	0	32411.070	0.0500
32	17	16	0	33	16	17	0	32411.070	0.0500

19	11	8	0	20	10	11	0	32513.170	0.0500
19	11	9	0	20	10	10	0	32513.170	0.0500
4	2	2	0	4	1	3	0	32672.520	0.0500
45	23	22	0	46	22	25	0	32813.060	0.0500
45	23	23	0	46	22	24	0	32813.060	0.0500
34	14	20	0	33	15	19	0	32964.770	0.0500
34	14	21	0	33	15	18	0	32964.770	0.0500
11	2	10	0	10	3	7	0	33188.680	0.0500
21	8	14	0	20	9	11	0	33309.350	0.0500
7	2	5	0	7	1	6	0	33345.230	0.0500
2	1	2	0	1	0	1	0	33354.010	0.0500
21	8	13	0	20	9	12	0	33368.940	0.0500
3	2	1	0	3	1	2	0	34225.470	0.0500
45	19	26	0	44	20	25	0	34352.290	0.0500
45	19	27	0	44	20	24	0	34352.290	0.0500
34	18	16	0	35	17	19	0	34445.940	0.0500
34	18	17	0	35	17	18	0	34445.940	0.0500
21	12	9	0	22	11	12	0	34489.830	0.0500
21	12	10	0	22	11	11	0	34489.830	0.0500
8	6	3	0	9	5	4	0	34666.740	0.0500
8	6	2	0	9	5	5	0	34683.360	0.0500
47	24	23	0	48	23	26	0	34945.410	0.0500
47	24	24	0	48	23	25	0	34945.410	0.0500
56	24	32	0	55	25	31	0	35103.660	0.0500
56	24	33	0	55	25	30	0	35103.660	0.0500
32	13	19	0	31	14	18	0	35125.700	0.0500
32	13	20	0	31	14	17	0	35125.700	0.0500
6	1	5	0	6	0	6	0	35214.810	0.0500
19	7	13	0	18	8	10	0	35452.060	0.0500
19	7	12	0	18	8	11	0	35677.560	0.0500
2	2	0	0	2	1	1	0	35903.320	0.0500
4	0	4	0	3	1	3	0	35970.050	0.0500
11	3	9	0	10	4	6	0	36307.710	0.0500
23	13	10	0	24	12	13	0	36471.610	0.0500
23	13	11	0	24	12	12	0	36471.610	0.0500
36	19	17	0	37	18	20	0	36491.380	0.0500
36	19	18	0	37	18	19	0	36491.380	0.0500
8	2	6	0	8	1	7	0	36532.280	0.0500
43	18	25	0	42	19	24	0	36584.220	0.0500
43	18	26	0	42	19	23	0	36584.220	0.0500
10	7	4	0	11	6	5	0	36659.740	0.0500
10	7	3	0	11	6	6	0	36663.850	0.0500
49	25	24	0	50	24	27	0	37093.400	0.0500
49	25	25	0	50	24	26	0	37093.400	0.0500
17	6	12	0	16	7	9	0	37486.350	0.0500
10	3	7	0	9	4	6	0	37877.790	0.0500
17	6	11	0	16	7	10	0	38295.950	0.0500
25	14	11	0	26	13	14	0	38459.400	0.0500
25	14	12	0	26	13	13	0	38459.400	0.0500
38	20	18	0	39	19	21	0	38548.470	0.0500
38	20	19	0	39	19	20	0	38548.470	0.0500
41	17	24	0	40	18	23	0	38807.070	0.0500
41	17	25	0	40	18	22	0	38807.070	0.0500

15	5	11	0	14	6	8	0	39067.810	0.0500
51	26	26	0	52	25	27	0	39257.470	0.0500
13	4	10	0	12	5	7	0	39291.210	0.0500
28	11	18	0	27	12	15	0	39463.760	0.0500
28	11	17	0	27	12	16	0	39465.720	0.0500
52	22	30	0	51	23	29	0	39770.110	0.0500
52	22	31	0	51	23	28	0	39770.110	0.0500
2	2	1	0	2	1	2	0	40430.540	0.0500
27	15	12	0	28	14	15	0	40454.080	0.0500
27	15	13	0	28	14	14	0	40454.080	0.0500
39	16	23	0	38	17	22	0	41023.260	0.0500
39	16	24	0	38	17	21	0	41023.260	0.0500
53	27	26	0	54	26	29	0	41438.530	0.0500
53	27	27	0	54	26	28	0	41438.530	0.0500
9	2	7	0	9	1	8	0	41576.880	0.0500
26	10	17	0	25	11	14	0	41654.060	0.0500
26	10	16	0	25	11	15	0	41662.080	0.0500
15	5	10	0	14	6	9	0	41749.640	0.0500
50	21	29	0	49	22	28	0	42080.630	0.0500
50	21	30	0	49	22	27	0	42080.630	0.0500
29	16	13	0	30	15	16	0	42456.500	0.0500
29	16	14	0	30	15	15	0	42456.500	0.0500
3	1	3	0	2	0	2	0	42571.150	0.0500
16	10	6	0	17	9	9	0	42587.970	0.0500
16	10	7	0	17	9	8	0	42587.970	0.0500
42	22	20	0	43	21	23	0	42699.830	0.0500
42	22	21	0	43	21	22	0	42699.830	0.0500
3	2	2	0	3	1	3	0	42851.190	0.0500
37	15	22	0	36	16	21	0	43235.510	0.0500
37	15	23	0	36	16	20	0	43235.510	0.0500
24	9	16	0	23	10	13	0	43867.490	0.0500
7	1	6	0	7	0	7	0	43997.950	0.0500
8	2	6	0	7	3	5	0	44159.510	0.0500
48	20	28	0	47	21	27	0	44377.690	0.0500
48	20	29	0	47	21	26	0	44377.690	0.0500
31	17	14	0	32	16	17	0	44467.390	0.0500
31	17	15	0	32	16	16	0	44467.390	0.0500
18	11	7	0	19	10	10	0	44561.410	0.0500
18	11	8	0	19	10	9	0	44561.410	0.0500
44	23	21	0	45	22	24	0	44795.390	0.0500
44	23	22	0	45	22	23	0	44795.390	0.0500
12	3	10	0	11	4	7	0	44999.740	0.0500
6	1	5	0	5	2	4	0	45145.320	0.0500
35	14	21	0	34	15	20	0	45447.730	0.0500
35	14	22	0	34	15	19	0	45447.730	0.0500
57	29	28	0	58	28	31	0	45853.190	0.0500
57	29	29	0	58	28	30	0	45853.190	0.0500
22	8	15	0	21	9	12	0	46102.180	0.0500
4	2	3	0	4	1	4	0	46115.780	0.0500
20	12	8	0	21	11	11	0	46536.240	0.0500
20	12	9	0	21	11	10	0	46536.250	0.0500
7	6	2	0	8	5	3	0	46562.760	0.0500
46	24	22	0	47	23	25	0	46905.090	0.0500

46	24	23	0	47	23	24	0	46905.090	0.0500
13	4	9	0	12	5	8	0	47087.860	0.0500
20	13	7	0	21	12	10	0	72431.5097	0.1000
20	13	8	0	21	12	9	0	72431.5097	0.1000
33	19	14	0	34	18	17	0	72457.0934	0.1000
33	19	15	0	34	18	16	0	72457.0934	0.1000
35	6	30	0	34	7	27	0	72635.3909	0.1000
24	8	16	0	23	9	15	0	72660.4126	0.1000
12	3	9	0	11	4	8	0	72673.0690	0.1000
35	13	22	0	34	14	21	0	73032.3974	0.1000
9	3	7	0	9	2	8	0	73611.6767	0.1000
29	5	25	0	28	6	22	0	73868.5555	0.1000
22	14	8	0	23	13	11	0	74416.2998	0.1000
22	14	9	0	23	13	10	0	74416.2998	0.1000
22	7	16	0	21	8	13	0	74455.8948	0.1000
35	20	15	0	36	19	18	0	74472.3433	0.1000
35	20	16	0	36	19	17	0	74472.3433	0.1000
9	2	8	0	9	1	9	0	74676.4956	0.1000
10	1	9	0	10	0	10	0	74953.1331	0.1000
8	1	7	0	7	2	6	0	75347.4860	0.1000
33	12	22	0	32	13	19	0	75425.2733	0.1000
18	5	14	0	17	6	11	0	75515.3079	0.1000
11	4	7	0	11	3	8	0	75836.4677	0.1000
20	6	15	0	19	7	12	0	76017.2575	0.1000
22	7	15	0	21	8	14	0	76084.3824	0.1000
44	17	27	0	43	18	26	0	76210.6936	0.1000
44	17	28	0	43	18	25	0	76210.6936	0.1000
11	9	2	0	12	8	5	0	76279.5778	0.1000
11	9	3	0	12	8	4	0	76279.5778	0.1000
24	15	9	0	25	14	12	0	76401.8767	0.1000
24	15	10	0	25	14	11	0	76401.8767	0.1000
7	1	7	0	6	0	6	0	76790.5979	0.1000
22	4	19	0	21	5	16	0	77467.7821	0.1000
10	3	8	0	10	2	9	0	77799.2258	0.1000
31	11	21	0	30	12	18	0	77865.8983	0.1000
31	11	20	0	30	12	19	0	77884.5792	0.1000
17	4	14	0	16	5	11	0	78065.7308	0.1000
20	5	15	0	20	4	16	0	78184.0268	0.1000
13	10	3	0	14	9	6	0	78304.9511	0.1000
13	10	4	0	14	9	5	0	78304.9511	0.1000
26	16	10	0	27	15	13	0	78389.3398	0.1000
26	16	11	0	27	15	12	0	78389.3398	0.1000
13	2	11	0	13	1	12	0	78402.0038	0.1000
39	22	17	0	40	21	20	0	78529.7801	0.1000
39	22	18	0	40	21	19	0	78529.7801	0.1000
10	2	8	0	9	3	7	0	78585.3729	0.1000
42	16	26	0	41	17	25	0	78598.9591	0.1000
42	16	27	0	41	17	24	0	78598.9591	0.1000
16	3	13	0	16	2	14	0	79098.8099	0.1000
19	5	14	0	19	4	15	0	79209.7824	0.1000
4	2	3	0	3	1	2	0	79388.4359	0.1000
21	5	16	0	21	4	17	0	79544.8437	0.1000
10	4	6	0	10	3	7	0	79717.0570	0.1000

19	4	15	0	19	3	16	0	79800.4243	0.1000
15	11	4	0	16	10	7	0	80316.7671	0.1000
15	11	5	0	16	10	6	0	80316.7671	0.1000
29	10	20	0	28	11	17	0	80366.7040	0.1000
28	17	11	0	29	16	14	0	80379.9922	0.1000
28	17	12	0	29	16	13	0	80379.9922	0.1000
29	10	19	0	28	11	18	0	80437.3729	0.1000
20	6	14	0	19	7	13	0	81058.8919	0.1000
15	4	11	0	14	5	10	0	81383.0612	0.1000
51	20	31	0	50	21	30	0	81478.1003	0.1000
51	20	32	0	50	21	29	0	81478.1003	0.1000
18	5	13	0	18	4	14	0	82207.0188	0.1000
17	12	5	0	18	11	8	0	82319.1197	0.1000
17	12	6	0	18	11	7	0	82319.1197	0.1000
30	18	12	0	31	17	15	0	82374.8901	0.1000
30	18	13	0	31	17	14	0	82374.8901	0.1000
10	2	9	0	10	1	10	0	82411.6831	0.1000
8	0	8	0	7	1	7	0	82470.6118	0.1000
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9	4	5	0	9	3	6	0	82922.0573	0.1000
27	9	19	0	26	10	16	0	82923.5975	0.1000
27	9	18	0	26	10	17	0	83182.5469	0.1000
22	5	17	0	22	4	18	0	83529.9788	0.1000
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8	4	4	0	8	3	5	0	85288.3543	0.1000
25	8	18	0	24	9	15	0	85458.8964	0.1000
11	1	10	0	11	0	11	0	85476.6282	0.1000
8	1	8	0	7	0	7	0	85782.2074	0.1000
36	13	24	0	35	14	21	0	85874.1443	0.1000
36	13	23	0	35	14	22	0	85876.4382	0.1000
21	14	7	0	22	13	10	0	86306.1685	0.1000
21	14	8	0	22	13	9	0	86306.1685	0.1000
25	8	17	0	24	9	16	0	86357.2456	0.1000
47	18	29	0	46	19	28	0	86366.3404	0.1000
47	18	30	0	46	19	27	0	86366.3404	0.1000
19	5	15	0	18	6	12	0	86567.7827	0.1000
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7	4	3	0	7	3	4	0	86862.3880	0.1000
23	7	17	0	22	8	14	0	87663.2812	0.1000
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6	4	2	0	6	3	3	0	87812.1534	0.1000
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34	12	23	0	33	13	20	0	88374.8468	0.1000
34	12	22	0	33	13	21	0	88384.3681	0.1000
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36	21	16	0	37	20	17	0	88395.1476	0.1000
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6	4	3	0	6	3	4	0	88463.7004	0.1000
8	4	5	0	8	3	6	0	88530.4087	0.1000
5	4	2	0	5	3	3	0	88556.5854	0.1000
4	4	0	0	4	3	1	0	88591.5911	0.1000

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21	6	16	0	20	7	13	0	88668.8941	0.1000
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25	16	9	0	26	15	12	0	90284.0665	0.1000
25	16	10	0	26	15	11	0	90284.0665	0.1000
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11	4	8	0	11	3	9	0	90922.1788	0.1000
32	11	22	0	31	12	19	0	90940.1694	0.1000
32	11	21	0	31	12	20	0	90977.1204	0.1000
13	3	10	0	12	4	9	0	91485.5015	0.1000
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24	6	18	0	24	5	19	0	93048.4534	0.1000
9	0	9	0	8	1	8	0	93052.6650	0.1000
30	10	21	0	29	11	18	0	93582.7186	0.1000
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41	15	26	0	40	16	25	0	93760.0946	0.1000
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16	12	4	0	17	11	7	0	94144.9024	0.1000
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29	18	11	0	30	17	14	0	94265.6564	0.1000
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31	19	12	0	32	18	15	0	96261.0732	0.1000
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39	14	26	0	38	15	23	0	96273.6602	0.1000
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21	4	17	0	21	3	18	0	101116.3718	0.1000
15	2	13	0	15	1	14	0	101232.1850	0.1000
57	22	35	0	56	23	34	0	101331.0489	0.1000
57	22	36	0	56	23	33	0	101331.0489	0.1000
35	12	24	0	34	13	21	0	101459.0124	0.1000
35	12	23	0	34	13	22	0	101478.0886	0.1000
46	17	29	0	45	18	28	0	101497.1613	0.1000
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37	22	15	0	38	21	18	0	102277.8171	0.1000
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26	17	9	0	27	16	12	0	104133.2784	0.1000
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31	10	22	0	30	11	19	0	106969.7887	0.1000
31	10	21	0	30	11	20	0	107226.8239	0.1000
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30	19	11	0	31	18	14	0	108116.8450	0.1000
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36	22	14	0	37	21	17	0	114114.3946	0.1000
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38	23	15	0	39	22	18	0	116123.4735	0.1000
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26	7	19	0	26	6	20	0	119302.6257	0.1000
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29	19	10	0	30	18	13	0	119944.0175	0.1000
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25	7	18	0	25	6	19	0	126236.3906	0.1000
26	7	20	0	25	8	17	0	126638.6079	0.1000
23	4	19	0	23	3	20	0	126725.3994	0.1000
20	3	17	0	20	2	18	0	126916.903	0.1000
17	3	15	0	17	2	16	0	127293.928	0.1000
36	8	28	0	36	7	29	0	127418.244	0.1000
33	7	26	0	33	6	27	0	127599.366	0.1000
17	6	11	0	17	5	12	0	127708.047	0.1000
20	5	16	0	20	4	17	0	128021.497	0.1000
12	1	11	0	11	2	10	0	128797.144	0.1000
19	4	16	0	19	3	17	0	129120.218	0.1000
6	3	4	0	5	2	3	0	129608.915	0.1000
11	2	10	0	10	1	9	0	129902.763	0.1000
13	2	11	0	12	3	10	0	129990.984	0.1000
15	3	12	0	14	4	11	0	130394.653	0.1000
16	6	10	0	16	5	11	0	131008.309	0.1000
31	8	23	0	31	7	24	0	131746.089	0.1000
30	6	24	0	30	5	25	0	131963.337	0.1000
24	7	17	0	24	6	18	0	133281.928	0.1000
18	2	16	0	18	1	17	0	133410.634	0.1000
15	6	9	0	15	5	10	0	133453.705	0.1000
21	5	17	0	21	4	18	0	133572.230	0.1000
13	0	13	0	12	1	12	0	133662.112	0.1000
13	1	13	0	12	0	12	0	133886.093	0.1000
39	9	30	0	39	8	31	0	134339.726	0.1000
16	1	15	0	16	0	16	0	134489.420	0.1000
38	9	29	0	38	8	30	0	134549.194	0.1000
18	6	13	0	18	5	14	0	134743.293	0.1000
17	6	12	0	17	5	13	0	134883.5702	0.1000
6	3	3	0	5	2	4	0	134891.243	0.1000
4	4	0	0	3	3	1	0	134892.022	0.1000
19	6	14	0	19	5	15	0	135013.789	0.1000
33	10	23	0	32	11	22	0	135104.8770	0.1000
14	6	8	0	14	5	9	0	135222.100	0.1000
16	6	11	0	16	5	12	0	135299.790	0.1000
37	8	29	0	37	7	30	0	135767.363	0.1000
20	6	15	0	20	5	16	0	135833.2720	0.1000
15	6	10	0	15	5	11	0	135872.3960	0.1000
18	3	16	0	18	2	17	0	136156.730	0.1000
13	6	7	0	13	5	8	0	136487.178	0.1000
14	6	9	0	14	5	10	0	136504.366	0.1000
27	5	22	0	27	4	23	0	136989.690	0.1000
13	6	8	0	13	5	9	0	137123.476	0.1000
20	4	17	0	20	3	18	0	137148.831	0.1000
21	6	16	0	21	5	17	0	137332.9125	0.1000
12	6	6	0	12	5	7	0	137390.638	0.1000

40	9	31	0	40	8	32	0	137527.609	0.1000
12	2	11	0	11	1	10	0	137677.039	0.1000
12	6	7	0	12	5	8	0	137684.121	0.1000
37	9	28	0	37	8	29	0	137842.9001	0.1000
11	6	5	0	11	5	6	0	138037.210	0.1000
11	6	6	0	11	5	7	0	138161.724	0.1000
7	3	5	0	6	2	4	0	138436.807	0.1000
40	13	28	0	39	14	25	0	138504.055	0.1000
21	3	18	0	21	2	19	0	138511.940	0.1000
40	13	27	0	39	14	26	0	138539.487	0.1000
9	6	3	0	9	5	4	0	138830.8409	0.1000
9	6	4	0	9	5	5	0	138847.1524	0.1000
8	6	2	0	8	5	3	0	139063.260	0.1000
8	6	3	0	8	5	4	0	139068.020	0.1000
12	7	5	0	11	7	4	0	139069.892	0.1000
12	7	6	0	11	7	5	0	139069.892	0.1000
30	8	22	0	30	7	23	0	139158.1141	0.1000
7	6	1	0	7	5	2	0	139222.843	0.1000
7	6	2	0	7	5	3	0	139223.910	0.1000
6	6	0	0	6	5	1	0	139327.749	0.1000
6	6	1	0	6	5	2	0	139327.749	0.1000
29	8	22	0	28	9	19	0	139332.455	0.1000
23	17	6	0	24	16	9	0	139526.070	0.1000
23	17	7	0	24	16	8	0	139526.070	0.1000
26	6	21	0	25	7	18	0	139594.617	0.1000
22	6	17	0	22	5	18	0	139623.1219	0.1000
24	4	20	0	24	3	21	0	139684.5802	0.1000
36	23	13	0	37	22	16	0	139712.113	0.1000
36	23	14	0	37	22	15	0	139712.113	0.1000
23	7	16	0	23	6	17	0	139818.0198	0.1000
26	7	19	0	25	8	18	0	139841.390	0.1000
31	9	22	0	30	10	21	0	139924.953	0.1000
22	5	18	0	22	4	19	0	139945.999	0.1000
30	6	25	0	29	7	22	0	140041.520	0.1000
13	1	12	0	12	2	11	0	140280.293	0.1000
18	4	14	0	17	5	13	0	141807.9683	0.1000
23	6	18	0	23	5	19	0	142784.691	0.1000
19	2	17	0	19	1	18	0	143447.497	0.1000
14	0	14	0	13	1	13	0	143640.936	0.1000
36	9	27	0	36	8	28	0	143672.293	0.1000
14	1	14	0	13	0	13	0	143765.650	0.1000
17	1	16	0	17	0	17	0	143846.112	0.1000
17	2	16	0	17	1	17	0	144131.721	0.1000
41	9	32	0	41	8	33	0	144173.634	0.1000
19	3	17	0	19	2	18	0	145189.816	0.1000
22	7	15	0	22	6	16	0	145451.200	0.1000
21	4	18	0	21	3	19	0	145608.187	0.1000
14	2	12	0	13	3	11	0	145774.840	0.1000
31	6	25	0	31	5	26	0	145884.435	0.1000
13	2	12	0	12	1	11	0	146019.311	0.1000
8	3	6	0	7	2	5	0	146201.513	0.1000
5	4	2	0	4	3	1	0	146384.136	0.1000
5	4	1	0	4	3	2	0	146445.050	0.1000

24	6	19	0	24	5	20	0	146861.261	0.1000
38	8	30	0	38	7	31	0	146985.738	0.1000
23	5	19	0	23	4	20	0	147058.898	0.1000
29	8	21	0	29	7	22	0	147081.254	0.1000
29	8	21	0	28	9	20	0	147183.452	0.1000
43	10	33	0	43	9	34	0	147559.286	0.1000
34	10	25	0	33	11	22	0	148156.857	0.1000
44	10	34	0	44	9	35	0	148555.387	0.1000
7	3	4	0	6	2	5	0	148713.203	0.1000
21	5	16	0	20	6	15	0	149067.851	0.1000
20	16	4	0	21	15	7	0	149254.892	0.1000
20	16	5	0	21	15	6	0	149254.892	0.1000
33	22	11	0	34	21	14	0	149487.309	0.1000
33	22	12	0	34	21	13	0	149487.309	0.1000
22	3	19	0	22	2	20	0	149616.394	0.1000
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42	10	32	0	42	9	33	0	149966.847	0.1000
28	7	22	0	27	8	19	0	150032.447	0.1000
21	7	14	0	21	6	15	0	150034.498	0.1000
52	18	34	0	51	19	33	0	150147.805	0.1000
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13	8	5	0	12	8	4	0	150558.596	0.1000
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14	1	13	0	13	2	12	0	151243.012	0.1000
35	9	26	0	35	8	27	0	151294.199	0.1000
25	6	20	0	25	5	21	0	151856.880	0.1000
41	13	28	0	40	14	27	0	152088.7748	0.1000
25	4	21	0	25	3	22	0	152230.981	0.1000
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9	3	7	0	8	2	6	0	152975.220	0.1000
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45	10	35	0	45	9	36	0	153169.544	0.1000
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18	2	17	0	18	1	18	0	153311.222	0.1000
15	0	15	0	14	1	14	0	153597.9863	0.1000
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35	7	28	0	35	6	29	0	153633.4177	0.1000
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22	4	19	0	22	3	20	0	154393.287	0.1000
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24	5	20	0	24	4	21	0	154806.249	0.1000
14	2	13	0	13	1	12	0	154847.6520	0.1000
41	10	31	0	41	9	32	0	155308.460	0.1000
32	9	23	0	31	10	22	0	155546.193	0.1000
19	7	12	0	19	6	13	0	156342.0320	0.1000
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22	7	16	0	22	6	17	0	156664.068	0.1000
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15	14	1	0	16	13	4	0	156875.049	0.1000

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28	20	8	0	29	19	11	0	157262.979	0.1000
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26	6	21	0	26	5	22	0	157736.748	0.1000
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37	11	27	0	36	12	24	0	158792.794	0.1000
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29	7	23	0	28	8	20	0	159973.507	0.1000
23	3	20	0	23	2	21	0	160274.772	0.1000
32	6	26	0	32	5	27	0	160368.701	0.1000
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17	7	11	0	17	6	12	0	160694.022	0.1000
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16	7	9	0	16	6	10	0	161131.157	0.1000
32	22	10	0	33	21	13	0	161237.000	0.1000
32	22	11	0	33	21	12	0	161237.000	0.1000
46	10	36	0	46	9	37	0	161347.289	0.1000
16	7	10	0	16	6	11	0	161501.910	0.1000
27	8	19	0	27	7	20	0	161708.1143	0.1000
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27	7	21	0	27	6	22	0	161951.7515	0.1000
15	7	8	0	15	6	9	0	162035.7798	0.1000
35	10	26	0	34	11	23	0	162173.194	0.1000
47	11	36	0	47	10	37	0	162179.914	0.1000
15	7	9	0	15	6	10	0	162210.5616	0.1000
44	14	31	0	43	15	28	0	162342.311	0.1000
44	14	30	0	43	15	29	0	162375.127	0.1000
19	1	18	0	19	0	19	0	162405.193	0.1000
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40	10	30	0	40	9	31	0	162889.707	0.1000
25	5	21	0	25	4	22	0	163074.671	0.1000
49	11	38	0	49	10	39	0	163110.151	0.1000
53	18	35	0	52	19	34	0	163150.859	0.1000
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23	4	20	0	23	3	21	0	163412.088	0.1000

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11	7	4	0	11	6	5	0	164020.164	0.1000
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26	4	22	0	26	3	23	0	164215.046	0.1000
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29	5	24	0	29	4	25	0	164306.6540	0.1000
27	6	22	0	27	5	23	0	164432.500	0.1000
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7	7	0	0	7	6	1	0	164667.414	0.1000
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33	9	25	0	32	10	22	0	164829.681	0.1000
31	8	24	0	30	9	21	0	165150.121	0.1000
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43	9	34	0	43	8	35	0	166753.670	0.1000
46	11	35	0	46	10	36	0	166838.963	0.1000
26	8	18	0	26	7	19	0	167587.185	0.1000
17	3	14	0	16	4	13	0	168524.1167	0.1000
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50	11	39	0	50	10	40	0	169190.713	0.1000
7	4	3	0	6	3	4	0	169682.471	0.1000
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22	5	17	0	21	6	16	0	171459.814	0.1000
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26	5	22	0	26	4	23	0	171751.2676	0.1000
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39	10	29	0	39	9	30	0	171862.410	0.1000
33	9	24	0	32	10	23	0	172112.100	0.1000
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47	10	37	0	47	9	38	0	172756.558	0.1000
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15	13	2	0	14	13	1	0	173279.0769	0.1000
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17	0	17	0	16	1	16	0	173479.0003	0.1000

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13	8	5	0	13	7	6	0	189198.622	0.1000
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39	11	28	0	38	12	27	0	189349.8538	0.1000
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30	9	21	0	30	8	22	0	189826.663	0.1000
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22	2	21	0	22	1	22	0	190073.264	0.1000
56	13	43	0	56	12	44	0	190103.755	0.1000
37	10	28	0	36	11	25	0	190326.2389	0.1000
26	3	23	0	26	2	24	0	190405.786	0.1000
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26	4	23	0	26	3	24	0	191202.313	0.1000
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35	9	27	0	34	10	24	0	191525.1591	0.1000
52	11	41	0	52	10	42	0	191721.145	0.1000
34	8	27	0	34	7	28	0	192393.240	0.1000
18	1	17	0	17	2	16	0	192424.708	0.1000
18	2	17	0	17	1	16	0	192887.326	0.1000
59	13	46	0	59	12	47	0	193169.3285	0.1000
19	0	19	0	18	1	18	0	193340.112	0.1000
19	1	19	0	18	0	18	0	193345.989	0.1000
43	11	32	0	43	10	33	0	193384.770	0.1000
9	4	5	0	8	3	6	0	193705.169	0.1000

49	12	37	0	49	11	38	0	194401.921	0.1000
23	5	18	0	22	6	17	0	194460.620	0.1000
29	9	20	0	29	8	21	0	194698.589	0.1000
7	5	3	0	6	4	2	0	194816.890	0.1000
7	5	2	0	6	4	3	0	194835.498	0.1000
33	7	27	0	33	6	28	0	196158.042	0.1000
55	13	42	0	55	12	43	0	196379.532	0.1000
56	12	44	0	56	11	45	0	196674.097	0.1000
34	8	27	0	33	9	24	0	196771.795	0.1000
37	10	27	0	36	11	26	0	196953.1574	0.1000
29	4	25	0	29	3	26	0	197068.808	0.1000
31	6	26	0	31	5	27	0	197302.471	0.1000
45	9	36	0	45	8	37	0	197559.145	0.1000
42	12	31	0	41	13	28	0	197579.5991	0.1000
17	3	15	0	16	2	14	0	198094.221	0.1000
35	8	28	0	35	7	29	0	198098.741	0.1000
33	9	25	0	33	8	26	0	198133.440	0.1000
32	9	24	0	32	8	25	0	198261.283	0.1000
18	2	16	0	17	3	15	0	198541.218	0.1000
28	9	19	0	28	8	20	0	198587.759	0.1000
34	9	26	0	34	8	27	0	198666.675	0.1000
38	7	31	0	38	6	32	0	198701.970	0.1000
42	12	30	0	41	13	29	0	198781.051	0.1000
31	9	23	0	31	8	24	0	198912.138	0.1000
36	10	26	0	36	9	27	0	198915.532	0.1000
9	2	7	0	8	1	8	0	198941.386	0.1000
10	4	7	0	9	3	6	0	198949.934	0.1000
17	6	12	0	16	6	11	0	199008.3060	0.1000
23	1	22	0	23	0	23	0	199247.780	0.1000
23	2	22	0	23	0	23	0	199257.4302	0.1000
23	2	22	0	23	1	23	0	199257.447	0.1000
29	5	25	0	29	4	26	0	199266.903	0.1000
26	6	20	0	25	7	19	0	199839.796	0.1000
30	9	22	0	30	8	23	0	199946.967	0.1000
35	9	27	0	35	8	28	0	199985.150	0.1000
27	3	24	0	27	2	25	0	200074.537	0.1000
62	14	48	0	62	13	49	0	200082.794	0.1000
10	3	7	0	9	2	8	0	200381.915	0.1000
25	2	23	0	25	1	24	0	200505.833	0.1000
27	4	24	0	27	3	25	0	200565.235	0.1000
25	3	23	0	25	2	24	0	200589.167	0.1000
32	5	27	0	32	4	28	0	201213.215	0.1000
29	9	21	0	29	8	22	0	201234.381	0.1000
40	11	30	0	39	12	27	0	201423.012	0.1000
27	9	18	0	27	8	19	0	201677.521	0.1000
35	6	29	0	35	5	30	0	202012.624	0.1000
60	13	47	0	60	12	48	0	202117.087	0.1000
36	9	28	0	36	8	29	0	202190.849	0.1000
63	14	49	0	63	13	50	0	202232.881	0.1000
19	1	18	0	18	2	17	0	202433.999	0.1000
28	9	20	0	28	8	21	0	202659.416	0.1000
19	2	18	0	18	1	17	0	202702.032	0.1000
49	10	39	0	49	9	40	0	202704.311	0.1000

29	7	22	0	28	8	21	0	202761.401	0.1000
19	3	16	0	18	4	15	0	202971.961	0.1000
20	0	20	0	19	1	19	0	203266.824	0.1000
20	1	20	0	19	0	19	0	203270.058	0.1000
42	11	31	0	42	10	32	0	203513.717	0.1000
35	8	28	0	34	9	25	0	203693.726	0.1000
47	14	33	0	46	15	32	0	203936.2596	0.1000
36	9	28	0	35	10	25	0	203978.184	0.1000
27	9	19	0	27	8	20	0	204127.703	0.1000
26	9	17	0	26	8	18	0	204143.394	0.1000
38	10	29	0	37	11	26	0	204242.780	0.1000
34	7	28	0	34	6	29	0	204468.176	0.1000
36	8	29	0	36	7	30	0	204677.848	0.1000
48	12	36	0	48	11	37	0	204873.199	0.1000
40	11	29	0	39	12	28	0	205112.563	0.1000
54	13	41	0	54	12	42	0	205310.632	0.1000
37	9	29	0	37	8	30	0	205352.895	0.1000
21	4	17	0	20	5	16	0	205356.320	0.1000
32	8	24	0	31	9	23	0	205375.975	0.1000
26	9	18	0	26	8	19	0	205568.532	0.1000
18	3	16	0	17	2	15	0	205980.745	0.1000
25	9	16	0	25	8	17	0	206131.426	0.1000
35	10	25	0	35	9	26	0	206139.223	0.1000
8	5	4	0	7	4	3	0	206272.009	0.1000
8	5	3	0	7	4	4	0	206340.313	0.1000
38	8	31	0	37	9	28	0	206396.8954	0.1000
32	6	27	0	32	5	28	0	206486.536	0.1000
10	4	6	0	9	3	7	0	206487.258	0.1000
25	9	17	0	25	8	18	0	206932.580	0.1000
11	4	8	0	10	3	7	0	206947.034	0.1000
53	11	42	0	53	10	43	0	207016.941	0.1000
42	8	34	0	42	7	35	0	207121.417	0.1000
30	4	26	0	30	3	27	0	207283.584	0.1000
24	9	15	0	24	8	16	0	207754.439	0.1000
36	8	29	0	35	9	26	0	207926.434	0.1000
24	9	16	0	24	8	17	0	208189.448	0.1000
24	1	23	0	24	0	24	0	208431.027	0.1000
24	2	23	0	24	1	24	0	208436.452	0.1000
6	6	0	0	5	5	1	0	208657.878	0.1000
6	6	1	0	5	5	0	0	208657.878	0.1000
30	5	26	0	30	4	27	0	208691.332	0.1000
37	8	30	0	36	9	27	0	208958.2059	0.1000
23	9	14	0	23	8	15	0	209095.415	0.1000
35	9	26	0	34	10	25	0	209178.806	0.1000
23	9	15	0	23	8	16	0	209323.191	0.1000
38	9	30	0	38	8	31	0	209502.938	0.1000
28	3	25	0	28	2	26	0	209637.575	0.1000
19	2	17	0	18	3	16	0	209724.930	0.1000
26	2	24	0	26	1	25	0	209798.376	0.1000
26	3	24	0	26	2	25	0	209846.824	0.1000
22	9	13	0	22	8	14	0	210214.827	0.1000
22	9	14	0	22	8	15	0	210329.420	0.1000
57	12	45	0	57	11	46	0	210844.042	0.1000

18	6	13	0	17	6	12	0	211048.1887	0.1000
21	9	12	0	21	8	13	0	211155.302	0.1000
21	9	13	0	21	8	14	0	211210.671	0.1000
20	9	11	0	20	8	12	0	211948.652	0.1000
20	9	12	0	20	8	13	0	211974.443	0.1000
43	12	32	0	42	13	29	0	211985.4277	0.1000
37	8	30	0	37	7	31	0	212038.919	0.1000
34	10	24	0	34	9	25	0	212153.853	0.1000
33	5	28	0	33	4	29	0	212348.031	0.1000
20	1	19	0	19	2	18	0	212404.760	0.1000
20	2	19	0	19	1	18	0	212558.295	0.1000
19	9	10	0	19	8	11	0	212618.053	0.1000
19	9	11	0	19	8	12	0	212629.3045	0.1000
39	7	32	0	39	6	33	0	212992.263	0.1000
41	11	30	0	41	10	31	0	213006.249	0.1000
18	9	9	0	18	8	10	0	213181.782	0.1000
18	9	10	0	18	8	11	0	213186.359	0.1000
21	0	21	0	20	1	20	0	213191.872	0.1000
21	1	21	0	20	0	20	0	213193.594	0.1000
35	7	29	0	35	6	30	0	213243.147	0.1000
17	9	8	0	17	8	9	0	213653.979	0.1000
17	9	9	0	17	8	10	0	213655.907	0.1000
12	4	9	0	11	3	8	0	213689.912	0.1000
43	12	31	0	42	13	30	0	213986.091	0.1000
16	9	7	0	16	8	8	0	214047.188	0.1000
16	9	8	0	16	8	9	0	214047.188	0.1000
46	9	37	0	46	8	38	0	214053.513	0.1000
66	15	51	0	66	14	52	0	214105.5618	0.1000
15	9	6	0	15	8	7	0	214371.634	0.1000
15	9	7	0	15	8	8	0	214371.634	0.1000
19	3	17	0	18	2	16	0	214480.949	0.1000
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61	13	48	0	61	12	49	0	214611.815	0.1000
39	9	31	0	39	8	32	0	214634.061	0.1000
14	9	5	0	14	8	6	0	214636.294	0.1000
14	9	6	0	14	8	7	0	214636.294	0.1000
38	10	28	0	37	11	27	0	214680.468	0.1000
11	9	2	0	11	8	3	0	215150.428	0.1000
11	9	3	0	11	8	4	0	215150.428	0.1000
10	9	1	0	10	8	2	0	215250.378	0.1000
10	9	2	0	10	8	3	0	215250.378	0.1000
9	9	0	0	9	8	1	0	215324.366	0.1000
9	9	1	0	9	8	2	0	215324.366	0.1000
47	12	35	0	47	11	36	0	215759.743	0.1000
53	13	40	0	53	12	41	0	215995.553	0.1000
59	14	45	0	59	13	46	0	216180.179	0.1000
33	10	23	0	33	9	24	0	217053.668	0.1000
31	4	27	0	31	3	28	0	217271.523	0.1000
24	5	19	0	23	6	18	0	217603.637	0.1000
25	1	24	0	25	0	25	0	217607.886	0.1000
25	1	24	0	25	1	25	0	217607.886	0.1000
25	2	24	0	25	0	25	0	217610.928	0.1000
25	2	24	0	25	1	25	0	217610.928	0.1000

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39	10	30	0	38	11	27	0	217826.100	0.1000
32	10	22	0	32	9	23	0	221009.903	0.1000
40	11	29	0	40	10	30	0	221427.108	0.1000
34	10	25	0	34	9	26	0	221467.277	0.1000
11	3	8	0	10	2	9	0	222166.871	0.1000
21	1	20	0	20	2	19	0	222352.345	0.1000
36	7	30	0	36	6	31	0	222372.067	0.1000
21	2	20	0	20	1	19	0	222439.736	0.1000
43	8	35	0	43	7	36	0	222443.752	0.1000
33	10	24	0	33	9	25	0	223080.406	0.1000
41	10	32	0	41	9	33	0	223104.460	0.1000
20	3	18	0	19	2	17	0	223444.033	0.1000
14	4	11	0	13	3	10	0	223738.630	0.1000
32	10	23	0	32	9	24	0	224788.393	0.1000
22	4	18	0	21	5	17	0	225262.566	0.1000
38	9	30	0	37	10	27	0	225350.639	0.1000
34	6	29	0	34	5	30	0	225366.268	0.1000
46	12	34	0	46	11	35	0	226264.765	0.1000
37	6	31	0	37	5	32	0	226414.055	0.1000
40	7	33	0	40	6	34	0	226495.087	0.1000
31	10	22	0	31	9	23	0	226506.916	0.1000
42	10	33	0	42	9	34	0	226602.289	0.1000
26	1	25	0	26	0	26	0	226779.119	0.1000
26	1	25	0	26	1	26	0	226779.119	0.1000
26	2	25	0	26	0	26	0	226780.643	0.1000
26	2	25	0	26	1	26	0	226780.643	0.1000
30	10	20	0	30	9	21	0	226816.342	0.1000
58	14	44	0	58	13	45	0	226921.127	0.1000
30	7	23	0	29	8	22	0	227023.183	0.1000
32	4	28	0	32	3	29	0	227092.274	0.1000
58	12	46	0	58	11	47	0	227257.581	0.1000
15	4	12	0	14	3	11	0	227463.645	0.1000
52	13	39	0	52	12	40	0	227472.309	0.1000
41	9	33	0	41	8	34	0	227627.191	0.1000
32	5	28	0	32	4	29	0	227648.137	0.1000
51	15	36	0	50	16	35	0	228020.2349	0.1000
30	10	21	0	30	9	22	0	228173.931	0.1000
28	2	26	0	28	1	27	0	228316.696	0.1000
28	3	26	0	28	2	27	0	228332.744	0.1000
33	8	25	0	32	9	24	0	228355.668	0.1000
30	3	27	0	30	2	28	0	228550.837	0.1000
39	11	28	0	39	10	29	0	228601.266	0.1000
39	8	32	0	39	7	33	0	228656.864	0.1000
30	4	27	0	30	3	28	0	228658.615	0.1000
10	5	6	0	9	4	5	0	228801.186	0.1000
29	10	19	0	29	9	20	0	228968.327	0.1000
10	5	5	0	9	4	6	0	229329.610	0.1000
29	10	20	0	29	9	21	0	229746.703	0.1000
44	12	32	0	43	13	31	0	229771.787	0.1000
62	13	49	0	62	12	50	0	229987.6336	0.1000
42	11	32	0	41	12	29	0	230000.070	0.1000
36	9	27	0	35	10	26	0	230242.966	0.1000

47	9	38	0	47	8	39	0	230337.910	0.1000
16	4	13	0	15	3	12	0	230703.694	0.1000
28	10	18	0	28	9	19	0	230766.991	0.1000
40	10	31	0	39	11	28	0	230829.621	0.1000
21	2	19	0	20	3	18	0	230898.473	0.1000
43	10	34	0	43	9	35	0	231109.198	0.1000
28	10	19	0	28	9	20	0	231200.378	0.1000
8	6	3	0	7	5	2	0	231723.266	0.1000
8	6	2	0	7	5	3	0	231724.332	0.1000
37	7	31	0	37	6	32	0	231756.098	0.1000
21	3	18	0	20	4	17	0	232261.725	0.1000
22	1	21	0	21	2	20	0	232286.032	0.1000
27	10	17	0	27	9	18	0	232288.413	0.1000
22	2	21	0	21	1	20	0	232335.448	0.1000
27	10	18	0	27	9	19	0	232522.255	0.1000
21	3	19	0	20	2	18	0	232734.994	0.1000
23	1	23	0	22	1	22	0	233037.2824	0.1000
23	0	23	0	22	1	22	0	233037.357	0.1000
23	1	23	0	22	0	22	0	233037.730	0.1000
23	0	23	0	22	0	22	0	233037.8032	0.1000
39	9	31	0	38	10	28	0	233345.103	0.1000
35	5	30	0	35	4	31	0	233447.816	0.1000
26	10	16	0	26	9	17	0	233587.371	0.1000
26	10	17	0	26	9	18	0	233709.718	0.1000
17	4	14	0	16	3	13	0	233797.250	0.1000
39	10	29	0	38	11	28	0	233837.734	0.1000
38	11	27	0	38	10	28	0	234554.579	0.1000
25	10	15	0	25	9	16	0	234703.932	0.1000
25	10	16	0	25	9	17	0	234765.736	0.1000
38	9	30	0	38	7	31	0	234861.2710	0.1000
35	6	30	0	35	5	31	0	234939.582	0.1000
43	9	35	0	42	10	32	0	235203.895	0.1000
12	4	8	0	11	3	9	0	235272.809	0.1000
42	9	34	0	42	8	35	0	235311.366	0.1000
24	10	14	0	24	9	15	0	235667.765	0.1000
24	10	15	0	24	9	16	0	235697.889	0.1000
45	12	33	0	45	11	34	0	235825.953	0.1000
27	1	26	0	27	0	27	0	235945.215	0.1000
27	1	26	0	27	1	27	0	235945.215	0.1000
27	2	26	0	27	0	27	0	235946.128	0.1000
27	2	26	0	27	1	27	0	235946.128	0.1000
23	10	13	0	23	9	14	0	236500.632	0.1000
23	10	14	0	23	9	15	0	236515.024	0.1000
44	10	35	0	44	9	36	0	236602.398	0.1000
51	10	41	0	51	9	42	0	236677.974	0.1000
33	4	29	0	33	3	30	0	236789.630	0.1000
44	8	36	0	44	7	37	0	236993.599	0.1000
18	4	15	0	17	3	14	0	237108.132	0.1000
33	5	29	0	33	4	30	0	237133.525	0.1000
22	10	12	0	22	9	13	0	237220.486	0.1000
22	10	13	0	22	9	14	0	237226.808	0.1000
29	2	27	0	29	1	28	0	237551.380	0.1000
29	3	27	0	29	2	28	0	237560.473	0.1000

40	8	33	0	40	7	34	0	237677.299	0.1000
38	6	32	0	38	5	33	0	237729.673	0.1000
21	10	11	0	21	9	12	0	237840.832	0.1000
21	10	12	0	21	9	13	0	237843.626	0.1000
31	3	28	0	31	2	29	0	237935.145	0.1000
31	4	28	0	31	3	29	0	237999.195	0.1000
42	11	32	0	42	10	33	0	238080.773	0.1000
43	11	33	0	43	10	34	0	238202.621	0.1000
20	10	10	0	20	9	11	0	238373.542	0.1000
20	10	11	0	20	9	12	0	238374.740	0.1000
41	11	31	0	41	10	32	0	238635.678	0.1000
19	10	9	0	19	9	10	0	238828.548	0.1000
19	10	10	0	19	9	11	0	238828.548	0.1000
57	14	43	0	57	13	44	0	238829.880	0.1000
40	9	32	0	39	10	29	0	238830.616	0.1000
51	13	38	0	51	12	39	0	238860.120	0.1000
44	11	34	0	44	10	35	0	239127.807	0.1000
18	10	8	0	18	9	9	0	239214.752	0.1000
18	10	9	0	18	9	10	0	239214.752	0.1000
41	7	34	0	41	6	35	0	239218.228	0.1000
42	11	31	0	41	12	30	0	239315.497	0.1000
37	11	26	0	37	10	27	0	239429.800	0.1000
17	10	7	0	17	9	8	0	239540.197	0.1000
17	10	8	0	17	9	9	0	239540.197	0.1000
11	5	7	0	10	4	6	0	239674.131	0.1000
40	11	30	0	40	10	31	0	239728.721	0.1000
16	10	6	0	16	9	7	0	239811.872	0.1000
16	10	7	0	16	9	8	0	239811.872	0.1000
15	10	5	0	15	9	6	0	240036.289	0.1000
15	10	6	0	15	9	7	0	240036.289	0.1000
42	9	34	0	41	10	31	0	240153.5838	0.1000
14	10	4	0	14	9	5	0	240219.171	0.1000
14	10	5	0	14	9	6	0	240219.171	0.1000
13	10	3	0	13	9	4	0	240366.513	0.1000
13	10	4	0	13	9	5	0	240366.513	0.1000
25	5	20	0	24	6	19	0	240402.1624	0.1000
12	10	2	0	12	9	3	0	240482.834	0.1000
12	10	3	0	12	9	4	0	240482.834	0.1000
11	10	1	0	11	9	2	0	240572.910	0.1000
11	10	2	0	11	9	3	0	240572.910	0.1000
10	10	0	0	10	9	1	0	240641.381	0.1000
10	10	1	0	10	9	2	0	240641.381	0.1000
11	5	6	0	10	4	7	0	240890.626	0.1000
45	11	35	0	45	10	36	0	240961.350	0.1000
19	4	16	0	18	3	15	0	240986.942	0.1000
22	3	19	0	21	4	18	0	245139.9353	0.1000
7	7	0	0	6	6	1	0	245536.2033	0.1000
7	7	1	0	6	6	0	0	245536.2033	0.1000
21	5	17	0	20	5	16	0	245604.521	0.1000
20	4	17	0	19	3	16	0	245711.1634	0.1000
48	9	39	0	48	8	40	0	245964.1087	0.1000
45	12	33	0	44	13	32	0	246302.6578	0.1000
34	4	30	0	34	3	31	0	246394.7753	0.1000

12	3	9	0	11	2	10	0	246431.1615	0.1000
34	5	30	0	34	4	31	0	246605.3780	0.1000
35	11	24	0	35	10	25	0	246687.0380	0.1000
21	7	14	0	20	7	13	0	246734.168	0.1000
30	2	28	0	30	1	29	0	246772.8984	0.1000
30	2	28	0	30	2	29	0	246772.8984	0.1000
30	3	28	0	30	2	29	0	246778.0844	0.1000
36	11	26	0	36	10	27	0	246852.4810	0.1000
41	8	34	0	41	7	35	0	247022.7955	0.1000
32	3	29	0	32	2	30	0	247285.0571	0.1000
32	4	29	0	32	3	30	0	247322.7509	0.1000
47	11	37	0	47	10	38	0	247616.9231	0.1000
39	6	33	0	39	5	34	0	248606.8697	0.1000
35	11	25	0	35	10	26	0	248796.6747	0.1000
28	6	22	0	27	7	21	0	248963.7804	0.1000
34	11	23	0	34	10	24	0	249406.5519	0.1000
50	13	37	0	50	12	38	0	249480.8133	0.1000
12	5	8	0	11	4	7	0	250063.9720	0.1000
46	10	37	0	46	9	38	0	250283.5561	0.1000
34	11	24	0	34	10	25	0	250667.5467	0.1000
45	8	37	0	45	7	38	0	250683.6260	0.1000
56	14	42	0	56	13	43	0	250963.6262	0.1000
39	7	33	0	39	6	34	0	250973.7824	0.1000
43	12	31	0	43	11	32	0	251182.1933	0.1000
23	2	21	0	22	2	20	0	251655.228	0.1000
55	16	39	0	54	17	38	0	251992.037	0.1000
24	2	23	0	23	2	22	0	252137.210	0.1000
24	1	23	0	23	1	22	0	252141.647	0.1000
22	3	19	0	21	3	18	0	252932.246	0.1000
34	8	26	0	33	9	25	0	253111.668	0.1000
37	9	28	0	36	10	27	0	253256.656	0.1000
48	13	35	0	47	14	34	0	254312.093	0.1000
40	10	30	0	39	11	29	0	254722.259	0.1000
22	13	9	0	21	13	8	0	254807.211	0.1000
22	13	10	0	21	13	9	0	254807.211	0.1000
46	12	35	0	45	13	32	0	255603.307	0.1000
22	10	12	0	21	10	11	0	255817.786	0.1000
22	10	13	0	21	10	12	0	255817.786	0.1000
11	2	9	0	10	1	10	0	256289.269	0.1000
22	9	14	0	21	9	13	0	256434.546	0.1000
22	9	13	0	21	9	12	0	256438.289	0.1000
21	5	16	0	20	5	15	0	256494.761	0.1000
53	15	39	0	52	16	36	0	256520.309	0.1000
22	5	18	0	21	5	17	0	256710.296	0.1000
18	5	13	0	18	2	16	0	256952.516	0.1000
53	15	38	0	52	16	37	0	256997.551	0.1000
22	8	15	0	21	8	14	0	257315.734	0.1000
22	8	14	0	21	8	13	0	257378.805	0.1000
44	11	34	0	43	12	31	0	257494.480	0.1000
44	12	33	0	44	11	34	0	260582.8666	0.1000
40	7	34	0	40	6	35	0	260691.1928	0.1000
49	9	40	0	49	8	41	0	260713.885	0.1000
26	11	15	0	26	10	16	0	261033.2766	0.1000

26	11	16	0	26	10	17	0	261040.8568	0.1000
24	4	20	0	23	5	19	0	261042.1365	0.1000
50	12	39	0	50	11	40	0	261111.4101	0.1000
24	2	22	0	23	3	21	0	261258.0725	0.1000
24	3	22	0	23	2	21	0	261655.7083	0.1000
45	9	37	0	45	8	38	0	261738.7242	0.1000
25	11	14	0	25	10	15	0	261795.5789	0.1000
25	11	15	0	25	10	16	0	261799.0606	0.1000
41	12	29	0	41	11	30	0	261830.5454	0.1000
25	1	24	0	24	2	23	0	262048.2953	0.1000
25	2	24	0	24	1	23	0	262056.8431	0.1000
26	5	21	0	25	6	20	0	262376.4743	0.1000
43	12	32	0	43	11	33	0	262446.8227	0.1000
24	11	13	0	24	10	14	0	262464.2849	0.1000
24	11	14	0	24	10	15	0	262465.8663	0.1000
55	14	41	0	55	13	42	0	262545.3171	0.1000
43	7	36	0	43	6	37	0	262721.2702	0.1000
61	15	46	0	61	14	47	0	262745.269	0.1000
26	0	26	0	25	0	25	0	262794.4634	0.1000
26	0	26	0	25	1	25	0	262794.4634	0.1000
26	1	26	0	25	0	25	0	262794.4634	0.1000
26	1	26	0	25	1	25	0	262794.4634	0.1000
23	11	12	0	23	10	13	0	263048.8580	0.1000
23	11	13	0	23	10	14	0	263049.5726	0.1000
60	12	48	0	60	11	49	0	263231.132	0.1000
38	5	33	0	38	4	34	0	263378.6997	0.1000
30	1	29	0	30	0	30	0	263416.823	0.1000
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22	11	11	0	22	10	12	0	263558.2106	0.1000
22	11	12	0	22	10	13	0	263558.2106	0.1000
38	6	33	0	38	5	34	0	263755.7453	0.1000
46	12	34	0	45	13	33	0	263793.8930	0.1000
21	11	10	0	21	10	11	0	263999.2974	0.1000
21	11	11	0	21	10	12	0	263999.2974	0.1000
51	12	40	0	51	11	41	0	264244.9318	0.1000
20	11	9	0	20	10	10	0	264379.4408	0.1000
20	11	10	0	20	10	11	0	264379.4408	0.1000
42	12	31	0	42	11	32	0	264520.3478	0.1000
13	5	8	0	12	4	9	0	264653.9105	0.1000
19	11	8	0	19	10	9	0	264704.8131	0.1000
19	11	9	0	19	10	10	0	264704.8131	0.1000
18	11	7	0	18	10	8	0	264981.3779	0.1000
18	11	8	0	18	10	9	0	264981.3779	0.1000
50	11	40	0	50	10	41	0	265083.3740	0.1000
32	2	30	0	32	1	31	0	265184.8144	0.1000
32	2	30	0	32	2	31	0	265184.8144	0.1000
32	3	30	0	32	1	31	0	265186.4792	0.1000
32	3	30	0	32	2	31	0	265186.4792	0.1000
17	11	6	0	17	10	7	0	265214.6435	0.1000
17	11	7	0	17	10	8	0	265214.6435	0.1000
16	11	5	0	16	10	6	0	265408.7955	0.1000

16	11	6	0	16	10	7	0	265408.7955 0.1000
36	4	32	0	36	3	33	0	265410.3504 0.1000
36	5	32	0	36	4	33	0	265487.4332 0.1000
15	11	4	0	15	10	5	0	265569.1217 0.1000
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14	11	3	0	14	10	4	0	265699.4278 0.1000
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23	4	20	0	22	3	19	0	265700.8217 0.1000
13	11	2	0	13	10	3	0	265803.9567 0.1000
13	11	3	0	13	10	4	0	265803.9567 0.1000
40	12	28	0	40	11	29	0	265812.2739 0.1000
64	13	51	0	64	12	52	0	265880.402 0.1000
12	11	1	0	12	10	2	0	265886.074 0.1000
12	11	2	0	12	10	3	0	265886.074 0.1000
34	3	31	0	34	2	32	0	265907.257 0.1000
34	4	31	0	34	3	32	0	265920.151 0.1000
11	11	0	0	11	10	1	0	265949.3352 0.1000
11	11	1	0	11	10	2	0	265949.3352 0.1000
11	6	6	0	10	5	5	0	266101.0261 0.1000
11	6	5	0	10	5	6	0	266154.1635 0.1000
43	8	36	0	43	7	37	0	266324.3929 0.1000
41	12	30	0	41	11	31	0	266696.8351 0.1000
14	5	10	0	13	4	9	0	268398.660 0.1000
24	3	21	0	23	4	20	0	268416.336 0.1000
9	7	2	0	8	6	3	0	268609.979 0.1000
9	7	3	0	8	6	2	0	268609.979 0.1000
39	12	27	0	39	11	28	0	269135.286 0.1000
41	6	35	0	41	5	36	0	269432.542 0.1000
41	7	35	0	41	6	36	0	270427.996 0.1000
25	2	23	0	24	3	22	0	271230.142 0.1000
14	4	10	0	13	3	11	0	271268.989 0.1000
46	9	38	0	46	8	39	0	271288.631 0.1000
25	3	23	0	24	2	22	0	271463.843 0.1000
38	12	26	0	38	11	27	0	271941.928 0.1000
26	1	25	0	25	2	24	0	271962.324 0.1000
26	2	25	0	25	1	24	0	271967.004 0.1000
51	11	41	0	51	10	42	0	272660.785 0.1000
27	0	27	0	26	0	26	0	272710.107 0.1000
27	0	27	0	26	1	26	0	272710.107 0.1000
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54	14	40	0	54	13	41	0	273050.507 0.1000
38	12	27	0	38	11	28	0	273089.274 0.1000
39	5	34	0	39	4	35	0	273099.187 0.1000
44	7	37	0	44	6	38	0	273742.349 0.1000
47	13	34	0	47	12	35	0	273856.386 0.1000
37	4	33	0	37	3	34	0	274846.940 0.1000
37	5	33	0	37	4	34	0	274893.356 0.1000
15	5	11	0	14	4	10	0	275818.070 0.1000
25	4	21	0	24	5	20	0	276655.160 0.1000
36	12	25	0	36	11	26	0	276811.490 0.1000
51	13	39	0	51	12	40	0	277102.845 0.1000
25	3	22	0	24	4	21	0	279230.190 0.1000

34	12	22	0	34	11	23	0	279841.994	0.1000
34	12	23	0	34	11	24	0	279962.141	0.1000
10	7	3	0	9	6	4	0	280128.651	0.1000
10	7	4	0	9	6	3	0	280128.651	0.1000
42	7	36	0	42	6	37	0	280159.811	0.1000
52	11	42	0	52	10	43	0	280941.324	0.1000
47	9	39	0	47	8	40	0	281044.450	0.1000
26	2	24	0	25	3	23	0	281171.542	0.1000
33	12	21	0	33	11	22	0	281261.911	0.1000
26	3	24	0	25	2	23	0	281307.699	0.1000
33	12	22	0	33	11	23	0	281326.447	0.1000
16	5	12	0	15	4	11	0	281836.749	0.1000
27	1	26	0	26	2	25	0	281874.605	0.1000
27	2	26	0	26	1	25	0	281877.197	0.1000
8	8	0	0	7	7	1	0	282409.318	0.1000
8	8	1	0	7	7	0	0	282409.318	0.1000
32	12	20	0	32	11	21	0	282525.698	0.1000
32	12	21	0	32	11	22	0	282559.358	0.1000
28	0	28	0	27	0	27	0	282624.338	0.1000
28	0	28	0	27	1	27	0	282624.338	0.1000
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40	5	35	0	40	4	36	0	282739.067	0.1000
25	4	22	0	24	3	21	0	282760.626	0.1000
27	5	22	0	26	6	21	0	283099.091	0.1000
34	3	32	0	34	1	33	0	283561.355	0.1000
34	3	32	0	34	2	33	0	283561.355	0.1000
47	13	35	0	47	12	36	0	283766.288	0.1000
36	3	33	0	36	2	34	0	284450.676	0.1000
36	4	33	0	36	3	34	0	284454.987	0.1000
56	13	44	0	56	12	45	0	284520.772	0.1000
30	12	19	0	30	11	20	0	284666.074	0.1000
29	12	17	0	29	11	18	0	285554.234	0.1000
29	12	18	0	29	11	19	0	285558.325	0.1000
45	8	38	0	45	7	39	0	285992.950	0.1000
28	12	16	0	28	11	17	0	286352.688	0.1000
28	12	17	0	28	11	18	0	286354.641	0.1000
17	5	13	0	16	4	12	0	286455.360	0.1000
27	12	15	0	27	11	16	0	287062.478	0.1000
27	12	16	0	27	11	17	0	287063.374	0.1000
48	8	40	0	48	7	41	0	287331.284	0.1000
23	5	19	0	22	4	18	0	299065.0102	0.1000
54	11	44	0	54	10	45	0	299125.687	0.1000
40	13	27	0	40	12	28	0	299130.280	0.1000
44	6	38	0	44	5	39	0	299297.386	0.1000
40	13	28	0	40	12	29	0	299485.9888	0.1000
14	6	9	0	13	5	8	0	299546.9147	0.1000
44	7	38	0	44	6	39	0	299549.5955	0.1000
52	9	43	0	52	8	44	0	299842.1413	0.1000
27	3	24	0	26	4	23	0	299966.7260	0.1000
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14	6	8	0	13	5	9	0	300296.262	0.1000
53	14	40	0	53	13	41	0	300400.211	0.1000
49	9	41	0	49	8	42	0	300886.0302	0.1000
28	2	26	0	27	3	25	0	301006.819	0.1000
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39	13	26	0	39	12	27	0	301069.075	0.1000
39	13	27	0	39	12	28	0	301272.234	0.1000
27	4	24	0	26	3	23	0	301333.3359	0.1000
29	1	28	0	28	2	27	0	301693.376	0.1000
29	2	28	0	28	1	27	0	301694.185	0.1000
42	5	37	0	42	4	38	0	301837.275	0.1000
42	6	37	0	42	5	38	0	301890.940	0.1000
36	2	34	0	36	1	35	0	301907.588	0.1000
36	2	34	0	36	2	35	0	301907.588	0.1000
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24	5	20	0	23	4	19	0	302051.1189	0.1000
28	5	23	0	27	6	22	0	302255.244	0.1000
30	0	30	0	29	0	29	0	302447.485	0.1000
30	0	30	0	29	1	29	0	302447.485	0.1000
30	1	30	0	29	0	29	0	302447.485	0.1000
30	1	30	0	29	1	29	0	302447.485	0.1000
52	14	39	0	52	13	40	0	302698.695	0.1000
38	13	25	0	38	12	26	0	302797.693	0.1000
38	13	26	0	38	12	27	0	302911.4377	0.1000
38	3	35	0	38	2	36	0	302933.4864	0.1000
56	15	41	0	55	16	40	0	302934.6746	0.1000
40	4	36	0	40	3	37	0	302962.191	0.1000
40	5	36	0	40	3	37	0	302971.9203	0.1000
27	4	23	0	26	5	22	0	303846.6360	0.1000
37	13	24	0	37	12	25	0	304347.051	0.1000
37	13	25	0	37	12	26	0	304409.0241	0.1000
47	8	40	0	47	7	41	0	305700.7973	0.1000
36	13	23	0	36	12	24	0	305740.6185	0.1000
36	13	24	0	36	12	25	0	305773.7531	0.1000
25	5	21	0	24	4	20	0	306150.484	0.1000
36	8	28	0	35	9	27	0	306625.964	0.1000
49	14	35	0	49	13	36	0	306724.707	0.1000
35	13	22	0	35	12	23	0	306995.971	0.1000
35	13	23	0	35	12	24	0	307013.045	0.1000
59	11	48	0	59	10	49	0	307135.039	0.1000
34	13	21	0	34	12	22	0	308128.178	0.1000
34	13	22	0	34	12	23	0	308137.026	0.1000
45	6	39	0	45	5	40	0	309036.685	0.1000
32	13	19	0	32	12	20	0	310070.388	0.1000
32	13	20	0	32	12	21	0	310072.403	0.1000
28	3	25	0	27	4	24	0	310078.941	0.1000
15	6	10	0	14	5	9	0	310162.493	0.1000
49	14	36	0	49	13	37	0	310431.127	0.1000
48	14	34	0	48	13	35	0	310646.724	0.1000
31	13	18	0	31	12	19	0	310898.836	0.1000
31	13	19	0	31	12	20	0	310899.848	0.1000

29	2	27	0	28	3	26	0	310911.580	0.1000
28	4	25	0	27	3	24	0	310913.543	0.1000
29	3	27	0	28	2	26	0	310937.593	0.1000
37	2	35	0	37	1	36	0	311070.396	0.1000
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37	3	35	0	37	1	36	0	311070.396	0.1000
37	3	35	0	37	2	36	0	311070.396	0.1000
56	10	46	0	56	9	47	0	311173.1575	0.1000
43	5	38	0	43	4	39	0	311316.256	0.1000
43	6	38	0	43	5	39	0	311348.625	0.1000
26	5	22	0	25	4	21	0	311440.737	0.1000
53	9	44	0	53	8	45	0	311557.135	0.1000
30	1	29	0	29	1	28	0	311600.323	0.1000
30	1	29	0	29	2	28	0	311600.323	0.1000
30	2	29	0	29	1	28	0	311600.323	0.1000
30	2	29	0	29	2	28	0	311600.323	0.1000
30	13	17	0	30	12	18	0	311643.777	0.1000
30	13	18	0	30	12	19	0	311643.777	0.1000
15	6	9	0	14	5	10	0	311707.382	0.1000
39	3	36	0	39	2	37	0	312155.092	0.1000
39	4	36	0	39	3	37	0	312156.108	0.1000
29	13	16	0	29	12	17	0	312311.140	0.1000
29	13	17	0	29	12	18	0	312311.140	0.1000
31	0	31	0	30	0	30	0	312355.871	0.1000
31	0	31	0	30	1	30	0	312355.871	0.1000
31	1	31	0	30	0	30	0	312355.871	0.1000
31	1	31	0	30	1	30	0	312355.871	0.1000
28	13	15	0	28	12	16	0	312908.326	0.1000
28	13	16	0	28	12	17	0	312908.326	0.1000
48	14	35	0	48	13	36	0	313006.1085	0.1000
56	15	41	0	56	14	42	0	313130.215	0.1000
27	13	14	0	27	12	15	0	313440.618	0.1000
27	13	15	0	27	12	16	0	313440.618	0.1000
26	13	13	0	26	12	14	0	313913.806	0.1000
26	13	14	0	26	12	15	0	313913.806	0.1000
47	14	33	0	47	13	34	0	314013.886	0.1000
25	13	12	0	25	12	13	0	314332.069	0.1000
13	7	7	0	12	6	6	0	314510.710	0.1000
13	7	6	0	12	6	7	0	314523.880	0.1000
24	13	11	0	24	12	12	0	314701.204	0.1000
23	13	10	0	23	12	11	0	315024.554	0.1000
48	7	41	0	48	6	42	0	315094.774	0.1000
53	10	44	0	53	9	45	0	315140.284	0.1000
22	13	9	0	22	12	10	0	315306.771	0.1000
22	13	10	0	22	12	11	0	315306.771	0.1000
47	14	34	0	47	13	35	0	315485.838	0.1000
48	8	41	0	48	7	42	0	315516.039	0.1000
63	15	49	0	63	14	50	0	315650.196	0.1000
20	13	7	0	20	12	8	0	315761.586	0.1000
20	13	8	0	20	12	9	0	315761.586	0.1000
28	4	24	0	27	5	23	0	315895.541	0.1000
19	13	6	0	19	12	7	0	315941.377	0.1000
19	13	7	0	19	12	8	0	315941.377	0.1000

18	13	5	0	18	12	6	0	316093.614	0.1000
18	13	6	0	18	12	7	0	316093.614	0.1000
17	13	4	0	17	12	5	0	316221.174	0.1000
17	13	5	0	17	12	6	0	316221.174	0.1000
16	13	3	0	16	12	4	0	316326.874	0.1000
16	13	4	0	16	12	5	0	316326.874	0.1000
15	13	2	0	15	12	3	0	316413.132	0.1000
15	13	3	0	15	12	4	0	316413.132	0.1000
14	13	1	0	14	12	2	0	316482.3864	0.1000
14	13	2	0	14	12	3	0	316482.3864	0.1000
46	14	32	0	46	13	33	0	316939.473	0.1000
11	8	3	0	10	7	4	0	317013.950	0.1000
11	8	4	0	10	7	3	0	317013.950	0.1000
46	14	33	0	46	13	34	0	317840.641	0.1000
27	5	23	0	26	4	22	0	317850.313	0.1000
55	15	40	0	55	14	41	0	319416.7089	0.1000
45	14	31	0	45	13	32	0	319511.358	0.1000
29	5	24	0	28	6	23	0	319696.105	0.1000
51	8	43	0	51	7	44	0	319804.655	0.1000
45	14	32	0	45	13	33	0	320052.754	0.1000
29	3	26	0	28	4	25	0	320098.586	0.1000
38	2	36	0	38	1	37	0	320227.8970	0.1000
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38	3	36	0	38	1	37	0	320227.8970	0.1000
38	3	36	0	38	2	37	0	320227.8970	0.1000
16	6	11	0	15	5	10	0	320265.794	0.1000
31	6	25	0	30	7	24	0	320425.533	0.1000
29	4	26	0	28	3	25	0	320603.586	0.1000
30	2	28	0	29	3	27	0	320812.762	0.1000
30	3	28	0	29	2	27	0	320827.525	0.1000
40	3	37	0	40	2	38	0	321366.095	0.1000
40	4	37	0	40	3	38	0	321366.095	0.1000
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32	0	32	0	31	0	31	0	322262.880	0.1000
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47	6	41	0	47	5	42	0	328309.8159	0.1000
47	7	41	0	47	6	42	0	328369.9037	0.1000

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31	3	28	0	30	4	27	0	339987.124	0.1000
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53	9	45	0	53	8	46	0	340715.5942	0.1000
22	14	8	0	22	13	9	0	340926.4916	0.1000
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21	14	7	0	21	13	8	0	341113.326	0.1000
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42	15	27	0	42	14	28	0	354727.102	0.1000
42	15	28	0	42	14	29	0	354735.725	0.1000
41	15	26	0	41	14	27	0	355969.8659	0.1000
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21	1	21	1	20	0	20	1	212960.7591	0.1000
31	4	27	1	31	3	28	1	213455.9257	0.1000
19	9	10	1	19	8	11	1	213491.2636	0.1000
19	9	11	1	19	8	12	1	213500.3044	0.1000
18	9	9	1	18	8	10	1	214022.5154	0.1000
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12	4	9	1	11	3	8	1	214177.0183	0.1000
17	9	8	1	17	8	9	1	214468.2120	0.1000
17	9	9	1	17	8	10	1	214469.5323	0.1000
31	5	27	1	31	4	28	1	214555.0433	0.1000
30	3	27	1	30	2	28	1	225094.9817	0.1000
42	10	33	1	42	9	34	1	225152.2902	0.1000
28	2	26	1	28	1	27	1	225159.6786	0.1000
28	3	26	1	28	2	27	1	225179.9800	0.1000
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30	10	21	1	30	9	22	1	229639.7697	0.1000
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29	10	19	1	29	9	20	1	230528.9634	0.1000
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22	7	15	3	22	6	16	3	149220.6188	0.1000
14	1	13	3	13	2	12	3	149837.3448	0.1000
22	4	19	3	22	3	20	3	152078.1943	0.1000
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25	5	21	3	25	4	22	3	160596.7725	0.1000
21	3	19	3	21	2	20	3	161289.9911	0.1000
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6	6	1	3	5	5	0	3	209461.1318	0.1000
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25	10	16	3	25	9	17	3	237834.7097	0.1000
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7	7	0	3	6	6	1	3	246495.5451	0.1000

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27	13	14	3	27	12	15	3	317141.9268	0.1000
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35	0	35	3	34	0	34	3	349411.0380	0.1000
35	0	35	3	34	1	34	3	349411.0380	0.1000
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Appendix I

Aminoethanol Spectral Analysis

I.1 Aminoethanol .int File

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 003  0.42
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 112  0.89
 113  0.42
 221  2.65
 222  0.89
 223  0.42
 331  2.65
 332  0.89
 333  0.42
 441  2.65
 442  0.89
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 551  2.65
 552  0.89
 553  0.42
 661  2.65
 662  0.89
 663  0.42
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I.2 Aminoethanol .par File

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             22  6.235683126400000E+006 1.00000000E-020
             33  9.143669969000001E+006 1.00000000E-020
             44  4.916596311200000E+006 1.00000000E-020
             55  8.034437874400000E+006 1.00000000E-020
             66  1.226151153220000E+007 1.00000000E-020
          10000  1.450872691481113E+004 8.97093826E+030
          10011  1.461109477646003E+004 1.08813523E+030
          10022  1.469753099708661E+004 1.52920352E+030
          10033  1.452458317956908E+004 2.13980318E+030
          10044  1.449242303649748E+004 1.25299518E+030
          10055  1.457207599536213E+004 5.89953695E+030
          10066  1.463125165988415E+004 8.87990268E+030
          20000  5.546493840167291E+003 3.82909887E+030
          20011  5.502573626317491E+003 3.87692710E+030
          20022  5.464381924917447E+003 5.06044801E+030
          20033  5.537514504514986E+003 4.91840065E+030
          20044  5.545552371740057E+003 4.25296345E+030
          20055  5.503295885610964E+003 3.00083969E+030
          20066  5.458887750081936E+003 4.82265058E+030
          30000  4.570487013274089E+003 3.90031159E+030
          30011  4.547558969631417E+003 3.90020773E+030
          30022  4.527520009816749E+003 4.75506001E+030
          30033  4.559957663792010E+003 4.70269864E+030
          30044  4.559708841734267E+003 4.19408056E+030
          30055  4.534741537277679E+003 3.57265868E+030
          30066  4.530877561043026E+003 3.90407808E+030
            200 -6.184938070916333E-003 1.08951313E+030
            211 -6.105444681623311E-003 1.04032629E+030
            222 -5.832532506427557E-003 1.20979184E+030
            233 -6.292826498617173E-003 1.09123758E+030
            244 -6.290943192254260E-003 1.01293238E+030
            255 -6.298678115934773E-003 6.02017545E+030
            266 -6.318982889840100E-003 1.32151568E+030
           1100  2.319334580939019E-002 2.49398414E+030
           1111  2.413843793349043E-002 2.97134864E+030
           1122  2.356738717641051E-002 3.56527917E+030
           1133  2.399237171450826E-002 3.21031801E+030
           1144  2.386679028278053E-002 2.76895838E+030
           1155  2.503137620436886E-002 3.90429489E+030
           1166  2.504923407304352E-002 5.85840992E+030
           2000 -5.323135154076776E-002 1.37291796E+030
           2011 -5.969222258447504E-002 1.71616575E+030
           2022 -6.091216384407538E-002 1.79458577E+030
           2033 -5.626961339638703E-002 3.60404779E+030
           2044 -5.416104779615454E-002 1.88552782E+030
           2055 -1.009067062636328E-001 8.67219251E+030
           2066 -6.854943841976517E-002 1.87132404E+030
          40100 -1.809584282706530E-003 1.33869374E+030
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40155 -1.877143962863214E-003 5.50866504E+030
40166 -1.858137106279261E-003 8.69816476E+030
41000 -1.064828968540390E-002 4.53852332E+030
41011 -1.119240772001303E-002 4.67808485E+030
41022 -1.187406203850443E-002 7.12894758E+030
41033 -1.085783812955233E-002 6.29868944E+030
41044 -1.040010100952899E-002 5.19853690E+030
41055 -1.339215560007355E-002 3.84692763E+030
41066 -1.218654275664320E-002 7.34571070E+030
  399 -1.373956550037875E-008 1.01331730E+030
 1299  2.104542989423229E-007 1.46708010E+030
 2199 -1.180318212665764E-006 4.28757562E+030
 3099  1.826226300619005E-006 6.58693204E+030
40299 -5.976511788142836E-009 1.00000000E+037
41199 -9.917494427459096E-008 1.00000000E+037
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I.3 Aminoethanol .lin File

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2	1	2	0	1	1	1	0	19257.73	0.10
1	1	0	0	0	0	0	0	20054.70	0.10
2	0	2	0	1	0	1	0	20158.29	0.10
2	1	1	0	1	1	0	0	21209.72	0.10
2	1	2	0	1	0	1	0	28220.00	0.10
2	2	0	0	2	1	1	0	26962.24	0.10
3	1	3	0	2	1	2	0	28841.55	0.10
3	0	3	0	2	0	2	0	30051.58	0.10
3	1	2	0	2	1	1	0	31765.35	0.10
3	1	3	0	2	0	2	0	36903.35	0.10
3	2	1	0	2	2	0	0	30649.48	0.10
3	2	2	0	2	2	1	0	30351.24	0.10
3	2	2	0	3	1	3	0	31323.69	0.10
3	3	0	0	2	2	0	0	77573.6478	0.070
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8	6	2	0	8	5	4	0	103617.5559	0.070
8	6	2	0	8	5	3	0	103616.1212	0.070
8	6	3	0	8	5	4	0	103617.5559	0.070
8	6	3	0	8	5	3	0	103616.1212	0.070
9	2	8	0	8	1	7	0	102932.4481	0.070
9	6	3	0	9	5	4	0	103497.4425	0.070
9	6	3	0	9	5	5	0	103502.5892	0.070
9	6	4	0	9	5	4	0	103497.4420	0.070
9	6	4	0	9	5	5	0	103502.5889	0.070
10	1	9	0	9	1	8	0	101863.9901	0.070
10	2	8	0	9	2	7	0	105548.1523	0.070
10	2	9	0	9	1	8	0	109774.7972	0.070
10	3	7	0	9	3	6	0	103975.9166	0.070
10	3	8	0	9	3	7	0	101722.9298	0.070
10	4	6	0	9	4	5	0	102252.8632	0.070
10	4	7	0	9	4	6	0	102018.3898	0.070
10	5	5	0	9	5	4	0	101814.9066	0.070
10	5	6	0	9	5	5	0	101804.5864	0.070
10	6	4	0	9	6	3	0	101647.4318	0.070
10	6	4	0	10	5	5	0	103329.9926	0.070
10	6	5	0	9	6	4	0	101647.4318	0.070
10	7	3	0	9	7	2	0	101555.3036	0.070
10	7	4	0	9	7	3	0	101555.3036	0.070
10	8	2	0	9	8	1	0	101499.3270	0.070

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10	9	1	0	9	9	0	0	101464.2868	0.070
10	9	2	0	9	9	1	0	101464.2868	0.070
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11	0	11	0	10	1	10	0	103251.3035	0.070
11	1	11	0	10	0	10	0	104096.8534	0.070
11	1	11	0	10	1	10	0	103571.8907	0.070
11	2	10	0	10	2	9	0	108864.2389	0.070
11	6	5	0	11	5	6	0	103098.7733	0.070
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12	6	6	0	12	5	7	0	102782.6432	0.070
12	6	6	0	12	5	8	0	102880.7907	0.070
12	6	7	0	12	5	7	0	102779.3498	0.070
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13	6	7	0	13	5	9	0	102568.8622	0.070
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14	6	9	0	14	5	9	0	101744.8782	0.070
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17	6	11	0	17	5	13	0	101170.6202	0.070
17	6	12	0	17	5	13	0	100952.6196	0.070
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18	2	17	0	18	1	18	0	103400.5349	0.070
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18	6	13	0	18	5	14	0	100618.8196	0.070
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19	1	18	0	19	1	19	0	109451.4688	0.070
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19	2	18	0	19	1	19	0	109629.1261	0.070
19	5	15	0	19	3	16	0	107055.2133	0.070
19	6	13	0	19	5	15	0	101204.0503	0.070
19	6	14	0	19	5	15	0	100418.2903	0.070
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20	5	16	0	20	3	17	0	104787.3764	0.070
20	6	14	0	20	5	16	0	101821.6412	0.070
20	6	15	0	20	5	16	0	100423.3522	0.070
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21	2	19	0	21	2	20	0	108197.1208	0.070

21	3	19	0	21	1	20	0	109497.2904	0.070
21	3	19	0	21	2	20	0	109432.3037	0.070
21	5	16	0	21	4	18	0	108732.6670	0.070
21	5	17	0	21	3	18	0	103747.3645	0.070
21	6	16	0	21	5	17	0	100712.2337	0.070
22	4	19	0	22	2	20	0	103754.0200	0.070
22	4	19	0	22	3	20	0	102958.2954	0.070
22	5	18	0	22	3	19	0	103988.0888	0.070
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23	6	18	0	23	5	19	0	102447.7613	0.070
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24	7	17	0	24	6	18	0	108406.1818	0.070
25	5	21	0	25	4	22	0	108937.7309	0.070
25	6	20	0	25	5	21	0	106146.4712	0.070
25	7	18	0	25	6	19	0	104617.5650	0.070
26	4	22	0	26	3	23	0	102186.3051	0.070
26	6	21	0	26	5	22	0	108830.6131	0.070
26	7	19	0	26	6	20	0	100252.9396	0.070
27	4	23	0	27	4	24	0	109621.2807	0.070
27	9	18	0	26	10	17	0	100610.3128	0.070
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31	11	20	0	30	12	19	0	102987.6456	0.070
32	8	24	0	32	7	25	0	107900.3380	0.070
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37	14	23	0	36	15	22	0	106804.2738	0.070
39	9	30	0	39	8	31	0	108966.6017	0.070
39	15	24	0	38	16	23	0	108093.0216	0.070
40	9	31	0	40	8	32	0	104519.0452	0.070
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42	9	33	0	42	8	34	0	100119.7604	0.070
43	9	34	0	43	8	35	0	100771.7593	0.070
44	9	35	0	44	8	36	0	103528.8518	0.070
45	9	36	0	45	8	37	0	108384.0963	0.070
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11	8	3	0	10	8	2	0	111689.7293	0.070
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11	10	1	0	10	10	0	0	111610.2517	0.070
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12	0	12	0	11	1	11	0	112549.2444	0.070
12	1	11	0	11	2	10	0	114267.6514	0.070
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12	2	11	0	11	2	10	0	118307.0103	0.070
13	2	11	0	12	3	10	0	112680.7453	0.070
15	2	13	0	14	3	11	0	114781.4822	0.070
15	3	12	0	14	4	11	0	112659.1220	0.070
16	5	12	0	16	3	13	0	119346.8636	0.070
17	5	13	0	17	3	14	0	114585.8710	0.070
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21	3	19	0	20	4	17	0	115129.2600	0.070
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21	7	14	0	21	6	16	0	118399.4565	0.070
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22	3	20	0	22	1	21	0	115690.4136	0.070
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22	5	17	0	22	4	19	0	118331.8426	0.070

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23	7	16	0	23	6	17	0	111542.0698	0.070
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23	7	17	0	23	6	18	0	117106.7085	0.070
23	7	17	0	23	6	17	0	110865.9917	0.070
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24	6	18	0	24	5	20	0	113550.1443	0.070
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24	7	18	0	24	6	19	0	116749.9906	0.070
25	3	22	0	25	2	23	0	118355.9749	0.070
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25	5	21	0	25	3	22	0	111591.0073	0.070
25	7	18	0	25	6	20	0	118604.6991	0.070
25	7	19	0	25	6	20	0	116614.6632	0.070
26	5	22	0	26	3	23	0	115908.1033	0.070
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26	7	20	0	26	6	21	0	116779.2199	0.070
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27	5	22	0	26	7	19	0	115162.7814	0.070
27	5	23	0	27	4	24	0	119674.7502	0.070
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37	9	29	0	37	8	29	0	112657.5846	0.070
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47	10	37	0	47	9	38	0	110283.2893	0.070
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49	10	39	0	49	9	40	0	113234.0042	0.070
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29	5	25	0	28	4	24	0	299985.9245	0.070
29	5	24	0	28	5	23	0	304017.5097	0.070
29	7	22	0	28	7	21	0	302449.3420	0.070
30	4	26	0	29	4	25	0	303630.3554	0.070
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32	1	31	0	31	2	30	0	301482.4917	0.070
33	0	33	0	32	0	32	0	304381.7906	0.070
33	0	33	0	32	1	32	0	304381.7906	0.070
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14	2	13	1	14	0	14	1	78444.8982	0.070
14	2	13	1	14	1	14	1	78366.0186	0.070
14	4	10	1	14	3	12	1	75841.7938	0.070
15	3	13	1	15	1	14	1	75817.0919	0.070
15	3	13	1	15	2	14	1	74469.0635	0.070
15	4	11	1	14	5	10	1	74891.3846	0.070
15	4	12	1	15	3	13	1	73404.9274	0.070
15	5	10	1	15	4	11	1	78265.2782	0.070
15	5	11	1	15	4	11	1	77527.2992	0.070
16	3	14	1	16	2	15	1	79561.6696	0.070
16	4	13	1	16	3	14	1	76049.8271	0.070
16	5	11	1	16	4	12	1	75405.9247	0.070
17	2	15	1	17	1	16	1	78694.5453	0.070
17	2	15	1	17	2	16	1	78143.3432	0.070
17	4	14	1	17	3	15	1	79225.1390	0.070
17	5	12	1	17	4	13	1	72100.7721	0.070
20	3	17	1	20	2	18	1	77326.8426	0.070
20	3	17	1	20	3	18	1	75095.1801	0.070
23	4	19	1	23	3	20	1	73591.7352	0.070
23	6	18	1	23	5	18	1	76378.9297	0.070
24	4	20	1	24	4	21	1	77212.0344	0.070
24	6	18	1	24	5	19	1	77590.5311	0.070
25	6	19	1	25	5	20	1	74076.1658	0.070
27	5	22	1	27	4	23	1	77405.0558	0.070
28	5	23	1	28	5	24	1	76624.7069	0.070
29	6	23	1	29	5	24	1	72297.3529	0.070
30	6	24	1	30	5	25	1	75961.3484	0.070
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6	5	1	1	6	4	2	1	86046.6564	0.070
6	5	2	1	6	4	3	1	86052.4443	0.070
7	2	6	1	6	1	5	1	89211.2514	0.070
7	5	2	1	7	4	3	1	85939.2093	0.070
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24	8	16	1	23	9	15	1	84167.6153	0.070
25	4	21	1	25	4	22	1	87401.5296	0.070
28	5	23	1	28	4	24	1	85301.5328	0.070
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29	7	22	1	29	6	23	1	89867.0197	0.070
30	7	23	1	30	6	24	1	85802.7929	0.070
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35	8	28	1	35	7	28	1	81483.1566	0.070
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25	4	21	1	25	3	22	1	90622.6995	0.070

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25	5	21	1	25	4	22	1	108249.4884	0.070
25	6	20	1	25	5	21	1	106652.3621	0.070
25	7	18	1	25	6	19	1	107955.0395	0.070
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26	7	19	1	26	6	20	1	103856.9573	0.070
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11	8	3	1	10	8	2	1	110933.4365	0.070
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11	9	2	1	10	9	1	1	110888.6128	0.070
11	9	3	1	10	9	2	1	110888.6128	0.070
11	10	1	1	10	10	0	1	110860.2162	0.070
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30	18	12	3	29	18	11	3	304106.6651	0.070
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