

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.

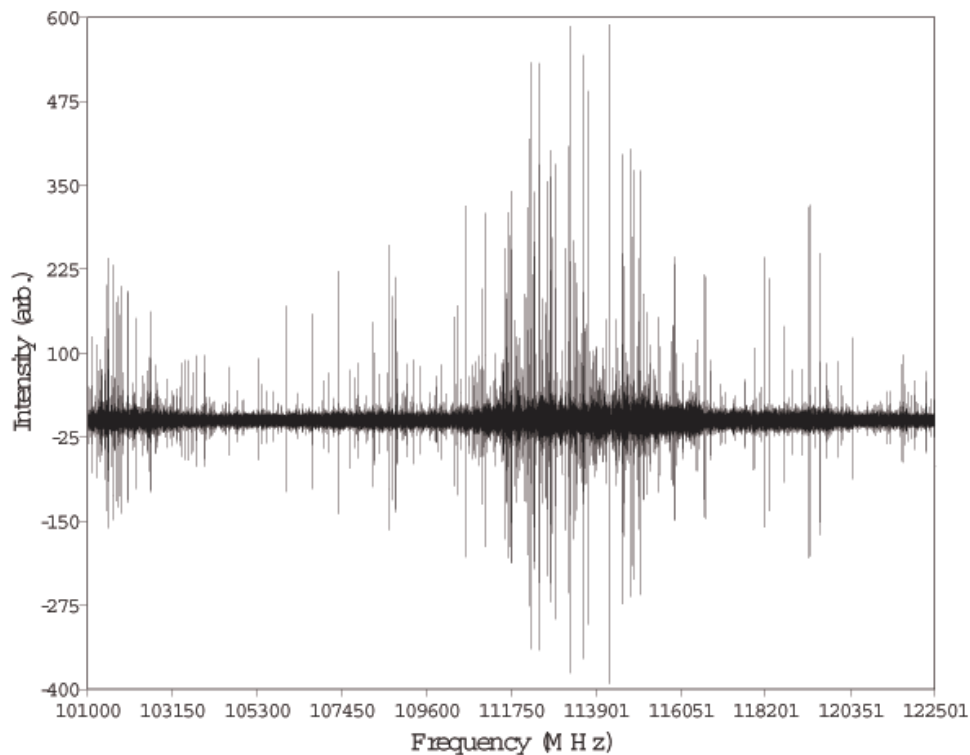


Figure 6.1: The room temperature glycolaldehyde spectrum from 101 to 122.5 GHz.

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' -

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, ~ 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 ± 30 cm^{-1} and 260 ± 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	Units
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.

^aThe 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:

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

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 (≤ 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 $\sim 2.26 \times 10^{15} \text{ cm}^{-2}$ at 200 K, rather than the reported value of $\sim 1.5 \times 10^{15} \text{ cm}^{-2}$ [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 $\sim 10\text{-}20''$ [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.