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 (~ 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.

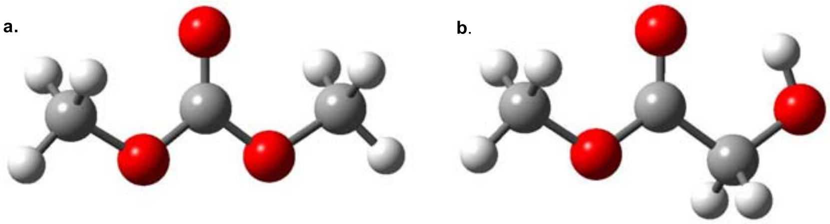

Figure 5.1: Ground state structures for a. dimethyl carbonate and b. methyl glycolate.

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 ± 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

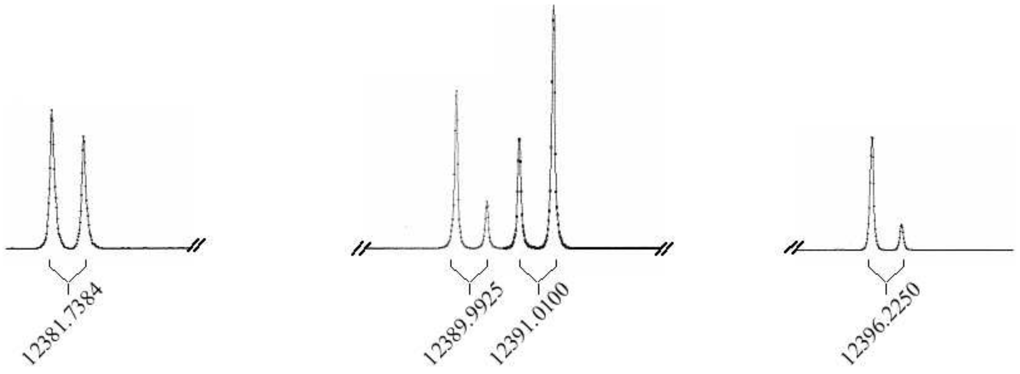

Figure 5.2: FTMW Doppler-doublet spectra of the dimethyl carbonate $1_{0,0} \rightarrow 0_{0,0}$ quartet. The frequencies are in units of MHz.

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.

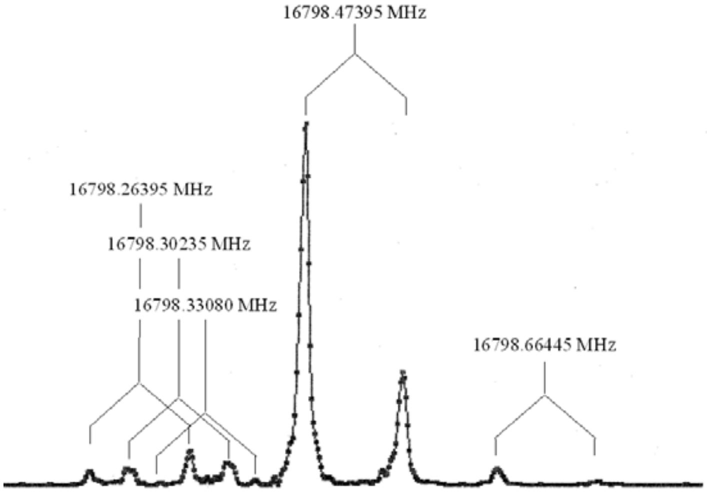

Figure 5.3: A FTMW Doppler-doublet spectrum of dimethyl carbonate for which manual de-Dopplerization was performed for line frequency determination.

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

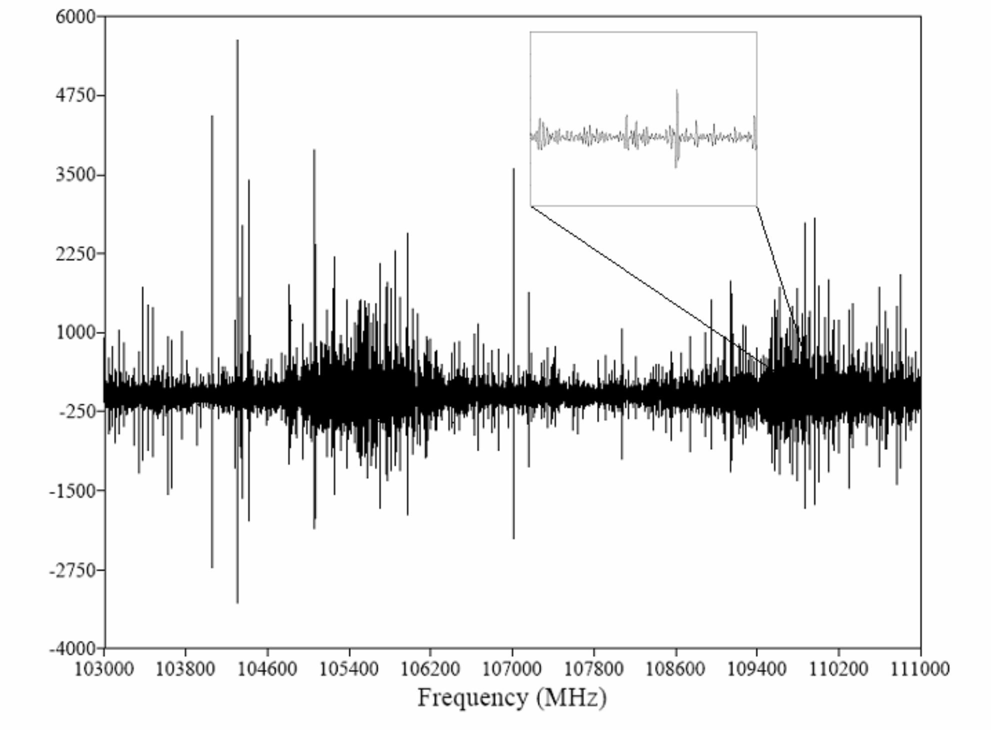

Figure 5.4: The room temperature methyl glycolate spectrum from 103 to 111 GHz.

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 $\sim$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 ∼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.

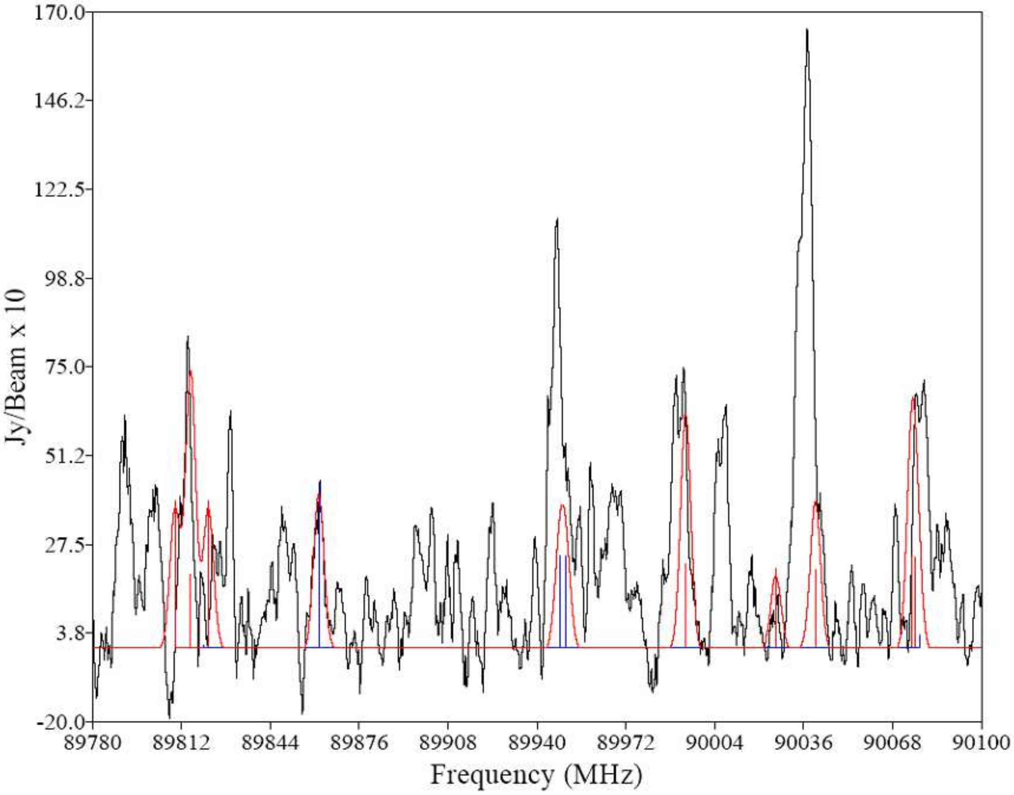

Figure 5.5: The simulated spectrum of methyl glycolate at 200 K (red) compared to a Sgr B2(N-LMH) 3 mm survey spectrum. The vertical lines correspond to line center positions, with red representing methyl glycolate lines and blue representing formic acid lines. Formic acid is the only identified species 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)	$Ag_u \times 10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit ^{b} ($\times 10^{-16}$ 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-

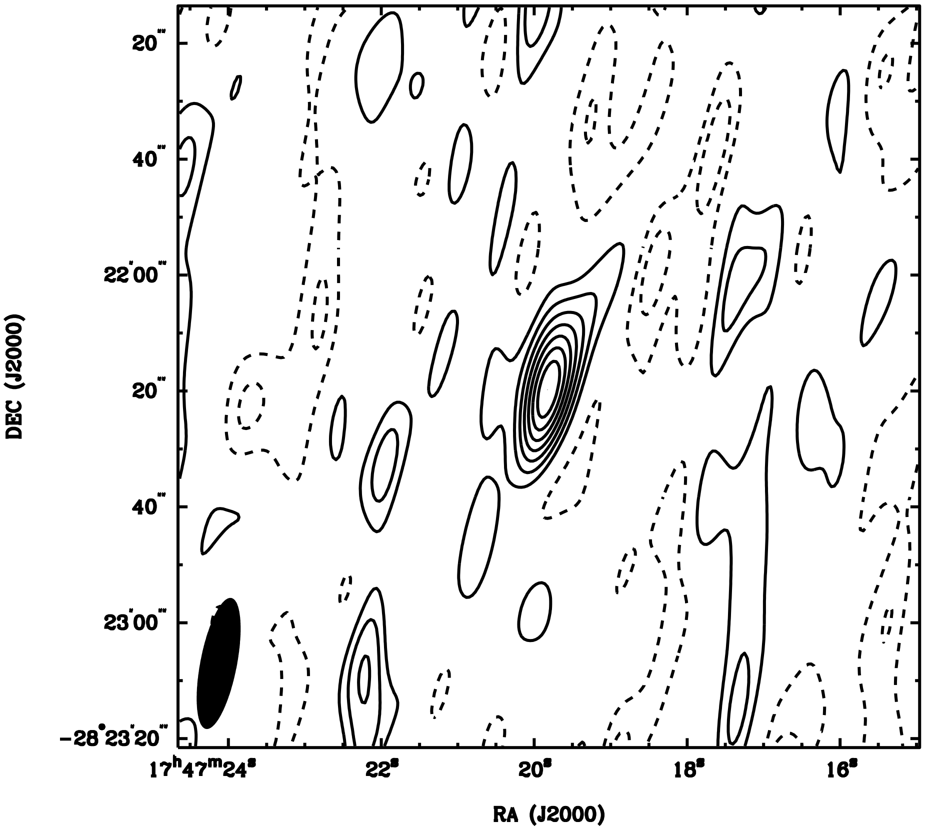

Figure 5.6: A map of the possible methyl glycolate emission feature at 89815 MHz in Sgr B2(N-LMH).

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.