

## MILLIMETER-WAVE AND VIBRATIONAL STATE ASSIGNMENTS FOR THE ROTATIONAL SPECTRUM OF GLYCOLALDEHYDE

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### ABSTRACT

Glycolaldehyde ( $\text{CHOCH}_2\text{OH}$ ), the simplest two-carbon  $\alpha$ -hydroxy aldehyde, has become of great interest in the field of astrochemistry due to its recent detection toward the Sagittarius B2 (N-LMH) molecular cloud. The original interstellar identification was based on an extrapolation of prior microwave rotational spectroscopy of glycolaldehyde. The millimeter and submillimeter spectra of this molecule from 128 to 354 GHz were subsequently measured after the interstellar detection. We present here the millimeter spectrum of this molecule from 72 to 122.5 GHz along with a combined millimeter and submillimeter pure rotational analysis of the ground and the first three vibrationally excited states of glycolaldehyde that enables a more complete molecular partition function to be determined. These results show that excited vibrational state contributions to the partition function are an important consideration when determining the column density of a molecule with low-lying torsional states.

*Subject headings:* ISM: molecules — methods: data analysis — methods: laboratory — molecular data — radio lines: ISM

*Online material:* machine-readable table

### 1. INTRODUCTION

Glycolaldehyde, ( $\text{CHOCH}_2\text{OH}$ ), the simplest two-carbon (2C)  $\alpha$ -hydroxy aldehyde, has recently been detected toward the Galactic center Sagittarius B2(N) molecular cloud complex (Hollis et al. 2000). The glycolaldehyde emission is spatially extended by  $\geq 60''$  around the Sgr B2 (N-LMH) hot core (Hollis et al. 2001). While the more compact emission gives a rotational temperature of  $\sim 50$  K, the extended emission lines yield a rotational temperature of  $\sim 8$  K, indicating that glycolaldehyde is likely subthermally liberated from grain surfaces (Hollis et al. 2004). Polyhydroxylated aldehydes are aldoses, or sugars, and are produced biologically via glycolysis and used in the production of ATP. Thus, the presence of a species so closely related to aldoses could potentially link grain surface pathways to prebiotic interstellar chemistry.

A suite of sugars and other polyhydroxylated organic species closely related to glycolaldehyde have also been detected in the Murchison meteorite (Cooper et al. 2001). These species were detected in similar concentrations to amino acids, which have possible formation routes involving gas phase ion-molecule reactions in hot cores (Charnley 2001). This possible link between hot core gas phase reactions and the formation of  $\alpha$ -hydroxy compounds stands in stark contrast to the grain surface produc-

tion 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 these species are therefore clearly required before sugar-related chemistry in molecular clouds can be understood.

The results of the astronomical and meteoritic studies and the chemical similarity of glycolaldehyde to  $\alpha$ -hydroxy sugars has led to observational searches for more complex species. The simplest 3C polyhydroxylated ketone, or ketose, 1,3-dihydroxyacetone [ $\text{CO}(\text{CH}_2\text{OH})_2$ ] was detected in Sgr B2 (N-LMH) (Widicus Weaver & Blake 2005), but the 3C aldose glyceraldehyde ( $\text{CH}_2\text{OHCHOHCHO}$ ) was not detected in this source (Hollis et al. 2004).

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 (Widicus Weaver & Blake 2005). 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

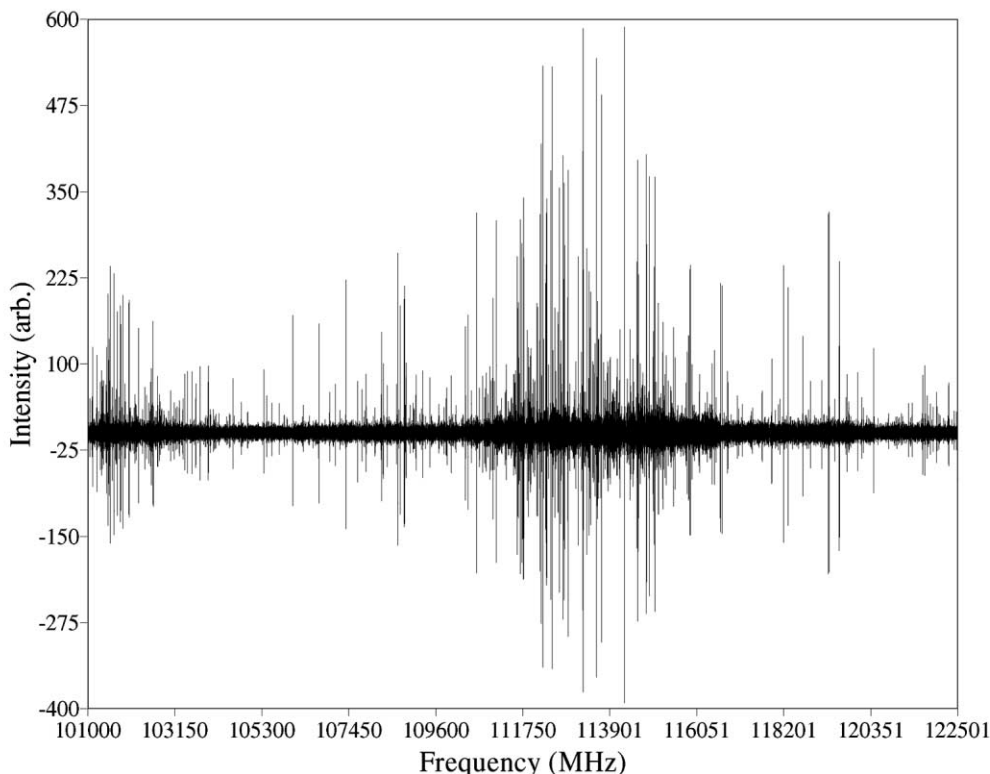


FIG. 1.—Glycolaldehyde spectrum from 101 to 122.5 GHz.

a result low-lying states can be significantly populated, often by large factors over purely collisional excitation processes (cf. Nummelin & Bergman 1999; Nummelin et al. 2000). 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 (Widicus Weaver & Blake 2005), while the glycolaldehyde column density reported by Hollis et al. (2000) was calculated using only the ground vibrational state molecular partition function. 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 (Marstokk & Møllendal 1970, 1973), with subsequent millimeter and submillimeter measurements extending the laboratory database over the 128–354 GHz interval (Butler et al. 2001). Three excited vibrational states were identified in the original microwave work and some spectral assignments were included in Marstokk & Møllendal (1970). Gas phase infrared studies of this molecule have only been completed above  $500\text{ cm}^{-1}$  (Michelsen & Klaboe 1969), and the original microwave work included energies for only two of the three vibrational states (Marstokk & Møllendal 1973). 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, spec-

tral 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, we have obtained the millimeter spectrum of glycolaldehyde from 72 to 122.5 GHz. We have also completed the combined millimeter and submillimeter pure rotational analysis of the vibrationally excited states of glycolaldehyde and used this information to determine a more complete molecular partition function.

## 2. EXPERIMENTAL

The millimeter and submillimeter spectra of glycolaldehyde from 128 to 354 GHz were obtained with the Fast Scanning Submillimeter Spectroscopic Technique (FASST) 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 Petkie et al. (1997) and Butler et al. (2001).

Additional millimeter studies from 72 to 122.5 GHz were conducted with the millimeter and submillimeter spectrometer at the Jet Propulsion Laboratory. The details of this setup are described in Friedl et al. (1995) and Widicus et al. (2003). 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  $\sim 20$  mtorr for the duration of the experiment. The line widths were less than 1 MHz, and the spectrometer resolution is better than 100 kHz. All spectra were obtained at room temperature.

The glycolaldehyde spectrum from 101 to 122.5 GHz is shown in Figure 1. The line density is quite high in this spectrum,

TABLE 1  
ASSIGNED TRANSITIONS FOR THE GROUND AND FIRST THREE VIBRATIONALLY EXCITED STATES OF GLYCOLALDEHYDE

$J'$	$K'_a$	$K'_c$	$\nu'$	$J''$	$K''_a$	$K''_c$	$\nu''$	Frequency (MHz)	$O - C$ (MHz)	Uncertainty (MHz)
8.....	3	5	0	7	4	4	0	7805.83000	0.05828	0.05000
34.....	17	17	0	35	16	20	0	8154.39000	-0.02921	0.05000
34.....	17	18	0	35	16	19	0	8154.39000	-0.02913	0.05000
19.....	8	12	0	18	9	9	0	8176.95000	0.10153	0.05000
21.....	11	10	0	22	10	13	0	8181.51000	-0.10933	0.05000
21.....	11	11	0	22	10	12	0	8181.51000	0.16133	0.05000
19.....	8	11	0	18	9	10	0	8188.74000	-0.00411	0.05000
32.....	14	19	0	31	15	16	0	8228.89000	0.01034	0.05000
8.....	5	4	0	9	4	5	0	8254.73000	0.00985	0.05000
6.....	1	6	0	5	2	3	0	8516.69000	0.00550	0.05000

NOTE.—Table 1 is available in its entirety in the electronic edition of the *Astrophysical Journal Supplement*. A portion is shown here for guidance regarding its form and content.

and strong  $bR$  branches are seen at a separation of approximately 13 GHz.

### 3. DATA ANALYSIS

The data were assigned using the SPFIT and SPCAT program suite (Pickett et al. 1998). The rotational constants, centrifugal distortion constants, and dipole moments determined in previous spectral studies (Marstokk & Møllendal 1970; Butler et al. 2001) and a standard asymmetric-top Hamiltonian in the  $J'$ -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, and these assignments are listed in Table 1. 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 fits 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 (Marstokk & Møllendal 1970). 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 2.

The rotational quantum numbers, the observed frequencies, and the residuals (observed—calculated frequencies) included in the combined fit are listed in Table 1. The spectral assignments

TABLE 2  
SPECTRAL PARAMETERS DETERMINED FOR THE GROUND AND FIRST THREE EXCITED VIBRATIONAL STATES OF GLYCOLALDEHYDE

Parameter	Ground Vibrational State	First Excited Vibrational State	Second Excited Vibrational State	Third Excited Vibrational State	Units
$E$ .....	0	~195	~260	~313	cm <sup>-1</sup>
$A$ .....	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
$\Delta_J$ .....	6.222339 (55)	6.280203 (216)	6.196436 (251)	6.35860 (131)	kHz
$\Delta_{JK}$ .....	-20.397978 (222)	-19.94946 (55)	-21.59964 (89)	-23.25808 (149)	kHz
$\Delta_K$ .....	47.72338 (47)	48.27689 (292)	51.9581 (45)	53.2488 (60)	kHz
$\delta_J$ .....	1.8337838 (135)	1.8342152 (305)	1.849366 (67)	1.859377 (139)	kHz
$\delta_K$ .....	8.87889 (41)	7.61421 (102)	10.89546 (160)	8.9558 (41)	kHz
$\Phi_J$ .....	-6.465 (42)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	mHz
$\Phi_{JK}$ .....	0.15657 (108)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	Hz
$\Phi_{KJ}$ .....	-0.7721 (34)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	Hz
$\Phi_K$ .....	1.05703 (292)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	Hz
$\phi_J$ .....	2.5042 (167)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	mHz
$\phi_{JK}$ .....	12.98 (82)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	mHz
$\phi_K$ .....	0.1909 (107)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	Hz
$J_{\max}$ .....	66	61	48	39	
$K_{\max}$ .....	29	14	15	15	
Number of lines.....	1657	672	491	340	
Fit rms.....	0.110	0.130	0.129	0.120	MHz

NOTE.—Errors (1  $\sigma$ ) are listed in parentheses in units of last significant figure.

<sup>a</sup> The sextic distortion constants were fitted as global constants across all states.

and other predicted rotational frequencies are available through the submillimeter and microwave spectral line catalog (Pickett et al. 1998).<sup>1</sup> The rotational and centrifugal distortion constants determined for each state are listed in Table 2.

#### 4. 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 fit,  $\sim 0.1$  MHz, agrees with the resolution of both spectrometers used in this study. While the rotational constants determined from this fit 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 the fits (see Table 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  $J \lesssim 80$ .

Neglecting centrifugal distortion, the partition function for an asymmetric rotor such as glycolaldehyde is given by

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

where  $\prod [e^{-E_i/2kT}/(1 - e^{-E_i/kT})]$  is the total vibrational state partition function, the  $E_i$ -values are the energies of the normal modes of vibration,  $[(\pi/ABC)(kT/h)^3]^{1/2}$  is the rotational partition function, and  $A$ ,  $B$ , and  $C$  are the rotational constants. The rotational constants determined for each vibrational state are used such that the molecular partition function is approximated as

$$Q(T) \approx \sum_{i=0}^3 e^{-E_i/kT} \sqrt{\frac{\pi}{A_i B_i C_i}} \left( \frac{kT}{h} \right)^3. \quad (2)$$

The original microwave study derived energies of  $195 \pm 30$  and  $260 \pm 40$   $\text{cm}^{-1}$  for the first two excited vibrational states, which agree with those values obtained in this study (Marstokk & Møllendal 1973). 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  $\text{cm}^{-1}$  (Senent 2004), 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.

The tabulated values for the glycolaldehyde partition function at a range of temperatures are given in Table 3 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 combina-

TABLE 3  
GLYCOLALDEHYDE MOLECULAR PARTITION FUNCTION  
VALUES AT VARIOUS TEMPERATURES

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

tion 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.

The partition function values in Table 3 were calculated assuming that the vibrational and rotational excitation temperatures are the same, which is often the case in hot cores (Nummelin & Bergman 1999; Olmi et al. 2003). 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 (cf. Nummelin & Bergman 1999; Nummelin et al. 2000). 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 (Hollis et al. 2000). 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  $\sim 1.5 \times 10^{15} \text{ cm}^{-2}$  (Hollis et al. 2000). However, recent Green Bank Telescope 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  $\geq 10''$ – $20''$  (Hollis et al. 2004). 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.

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<sup>1</sup> See <http://spec.jpl.nasa.gov>.

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