

The millimeter and submillimeter rotational spectrum of 1,3-dihydroxyacetone[☆]

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Received 7 October 2003; in revised form 16 December 2003

Abstract

Recent detection of the 2C sugar glycolaldehyde in the Sgr B2(N-LMH) hot core source as well as the presence of several sugars and other polyhydroxylated species in the Murchison meteorite have led to interest in observational searches for higher order sugars in the interstellar medium. 1,3-Dihydroxyacetone, the simplest 3C sugar, is one of the species detected in Murchison and is of considerable importance for observational searches as the next step in complexity for interstellar sugars. However, little spectroscopic information is available for this molecule. We present here the Doppler-limited rotational spectrum of 1,3-dihydroxyacetone to 450 GHz. Assignments include the ground state up to $J = 104$ and four additional vibrational states. Standard rotational and quartic centrifugal distortion constants have been determined for each of these states.

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1. Introduction

A wide array of complex organic species have now been detected in hot protostellar cores. While astronomical models combining grain surface and gas phase reaction schemes predict the formation of even larger organics in these cores, characterization of and searches for many of even the simplest species have not been undertaken. In addition, these models do not account for the presence of many of the observed molecules. One such molecule is glycolaldehyde (CHOCH_2OH), the simplest sugar, which was detected in the hot core Sagittarius B2(N-LMH) [1]. The biological implications of interstellar sugars as well as the high level of chemical complexity of this and similar detected species have confirmed the need for further experimental and observational investigation of hot core reaction pathways.

Recent analyses of carbonaceous chondrites have led to the detection of a suite of sugars and other polyhydroxylated organic species closely related to glycolaldehyde [2]. These species were detected at concentrations similar to those of amino acids, indicating a possible link between proposed hot core gas phase reaction schemes and the formation of these compounds. 1,3-Dihydroxyacetone ($\text{CO}(\text{CH}_2\text{OH})_2$ or DHA), the second most complex sugar and the simplest 3C sugar, was one of the species detected in the Murchison meteorite. While no definitive abundance predictions can be made for dihydroxyacetone due to its absence in existing hot core models, it is reasonable to assume that its abundance may be comparable to that of glycolaldehyde or acetone, which were detected at column densities above 10^{15} cm^{-2} [1,3].

Current models for the formation of complex species involve thermal evaporation of simple organics from the grain surfaces and then subsequent gas phase reactions within the hot core to form more complicated organics [4]. However, no sugars are predicted by these hot core models, and their role in the chemistry of these cores is relatively unknown. Interstellar searches for sugars have focused on Sgr B2(N-LMH), which is found to have

[☆] Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jms.2004.01.002.

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among the highest column densities of complex molecules ever detected. To our knowledge, no other searches for more complex sugars than glycolaldehyde have been conducted. It was found that glycolaldehyde was spatially extended to $> 60''$ in this $\sim 5''$ source, unlike other related organic species which were found to be concentrated within the hot core [5]. The presence of this molecule in the colder cloud extremities rather than in the hot core suggests higher reactivity of glycolaldehyde within the warmer region. Dihydroxyacetone is expected to be a much more stable gas phase species than glycolaldehyde and it is possible that its distribution in a hot core source could be quite different from the extended nature of glycolaldehyde emission. This demonstrates the need for combined studies using both single dish observatories for spectral line searches and arrays for mapping when searching for sugars in these cores.

Lovas et al. [6] recently characterized the rotational spectrum of dihydroxyacetone to 40 GHz, fitting rotational and quartic centrifugal distortion constants to Fourier transform-microwave (FTMW) data. We simultaneously began our study of dihydroxyacetone in a similar manner, using *ab initio* studies to guide initial FTMW experiments to 18 GHz. The results of these experiments are in excellent agreement with the Lovas et al. study. We then conducted millimeter and submillimeter direct absorption experiments to provide more accurate spectral predictions for observational searches. We present here analysis of the rotational spectrum of dihydroxyacetone up to 450 GHz. Standard rotational and quartic centrifugal distortion constants have been determined for the ground state and four vibrational states of dihydroxyacetone, and ground state assignments have been extended to $J = 104$.

2. Theoretical calculations

Quantum mechanical calculations were utilized to aid in spectral predictions. These calculations used B3LYP density functional theory (DFT) [7,8] and were performed in two phases. The first phase was a coarse calculation 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 [9].

During the first phase of the calculations, the 6-31G basis set was used [10]. The four rotational degrees of freedom for dihydroxyacetone were constrained to be multiples of 60° 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 [10–12]. Separate conformers were distinguishable by unique values for the

dipole moments, and roughly 10 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 1) were then used for initial spectral predictions. The structures of these two conformers are shown in Fig. 1. The ground state conformer optimized geometry is included in the analysis of Lovas et al. [6] 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. [6] report only a *b*-type dipole moment. 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 unlikelihood of this conformer to exist under normal laboratory or interstellar conditions.

3. Experimental

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

3.1. FT-microwave studies

The FTMW experiments were conducted with the original Balle–Flygare spectrometer. The details of the setup can be found in [13]. A sample holder containing solid dihydroxyacetone was placed after the pulsed valve and heated sufficiently to obtain a dihydroxyacetone vapor pressure of ~ 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 [14] for further details on the heated nozzle). Predictions based on the theoretical calculations were used as a guide for spectral line searches. Four bR and one bQ transition were chosen for these initial searches based on their predicted linestrengths. Once the $1_{0,0} \rightarrow 0_{0,0}$ transition was observed, the single-shot signal was optimized

Table 1
Spectral parameters predicted for DHA from quantum mechanical calculations using B3LYP DFT

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

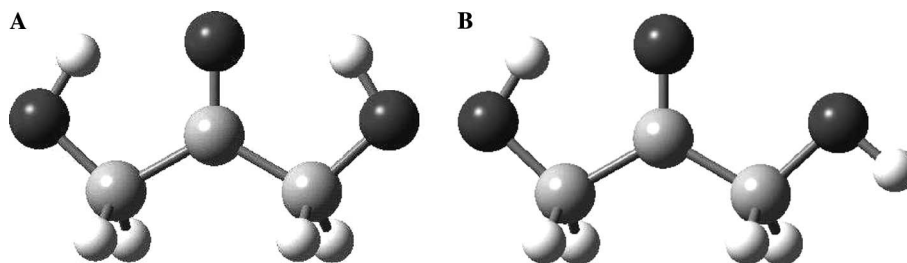


Fig. 1. Structures of the two lowest energy DHA conformers: (A) doubly hydrogen bonded conformer (ground state); and (B) singly hydrogen bonded conformer.

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 Fig. 2). Additional searches for the singly H-bonded conformer were conducted, but no lines were observed in the supersonic expansion.

3.2. Direct absorption millimeter and submillimeter studies

Studies were conducted near 100 GHz with a direct absorption flow cell spectrometer at Caltech. A Wiltron swept frequency synthesizer was used to generate microwave radiation from 10 to 20 GHz. This synthesizer was controlled by a computer and swept through a given frequency range at a frequency interval of 0.1 MHz. This radiation was then frequency modulated and multiplied to the desired frequency range by an active multiplier chain consisting of a Miteq Ka-band frequency doubler, a Miteq Ka-band power amplifier, and a Virginia diodes W-band frequency tripler. This radiation was then focused into the 2.5 m cell with a teflon lens, propagated through the cell, and detected with a room temperature Pacific Millimeter diode detector. A Stanford Research lock-in amplifier was used to narrow the detection bandwidth, amplify, and rectify the $2f$ signal. The resultant DC signal was then processed by a computer equipped with a National Instruments GPIB card and recorded as a function of frequency. 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 to 120 GHz is shown in Fig. 3. Strong bR branches are seen at a separation of approximately 4 GHz. Linewidths were on the order of 1 MHz.

The higher frequency (sub)millimeter studies were conducted with a similar millimeter and submillimeter spectrometer at the Jet Propulsion Laboratory. The basic flow cell design and detection methods for the JPL spectrometer are outlined in [15]. The source frequencies were obtained using a directly synthesized beam projected from the output of a multiplier chain [16]. Second and third harmonics of this multiplier were produced on a whisker-contacted Shottky diode, and the detector used was 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 on the order of 1 MHz. No sample heating was required for these experiments due to the strength of the submillimeter lines. A pressure of approximately 10 mTorr was maintained for the duration of the experiment.

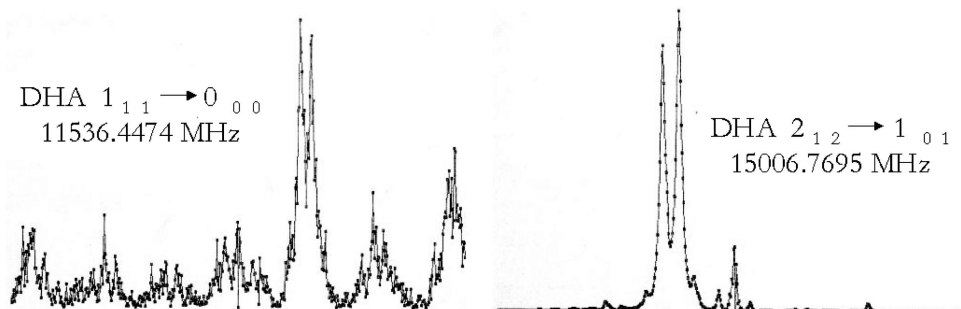


Fig. 2. Single-shot dihydroxyacetone spectra from the FT-microwave experiments.

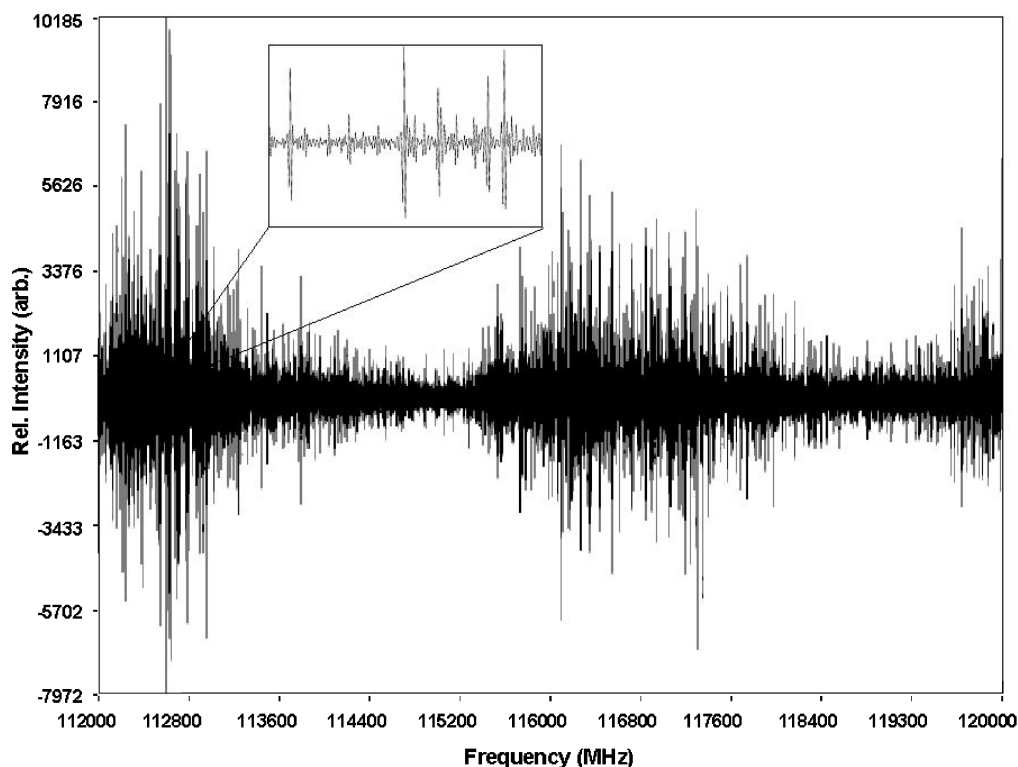


Fig. 3. A 3 mm scan covering 8 GHz from 112 to 120 GHz.

4. Data analysis

The data were assigned using the SPFIT and SPCAT programs [17]. The rotational constants obtained with the *ab initio* studies, the dipole moments from [6], 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 fit was 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. These assignments and other predicted rotational frequencies are accessible through the submillimeter and microwave spectral line catalog [17] available at <http://spec.jpl.nasa.gov>. An electronic file containing the parameters, rest frequencies, and residuals has been deposited with the journal. The rotational and centrifugal distortion constants determined for each state are listed in Table 2.

As no vibrational spectral studies have been conducted for dihydroxyacetone, assignments of the vibrational state energies were based on the relative intensities of the observed lines to the ground state lines. Approximate relative energies were determined for each vibrational state and are included in Table 2. The rotational and quartic centrifugal distortion constants were determined independently for three vibrational states. Only a partial fit has been completed for the highest energy vibrational state due to its relatively weak

Table 2
Spectral parameters determined for dihydroxyacetone

State	ν_0	ν_1	ν_2	ν_3	ν_4
E (cm ⁻¹)	0	~93	~147	~150	~183
A (MHz)	9801.294341(269)	9764.48006(113)	9701.67778(178)	9662.11092(271)	10329.1(106)
B (MHz)	2051.525611(76)	2049.846696(274)	2051.55037(42)	2050.02151(45)	2065.17(41)
C (MHz)	1735.164871(77)	1736.322262(248)	1737.92899(33)	1739.41934(37)	1735.12347(60)
Δ_J (kHz)	0.1823699(94)	0.183278(33)	0.185158(62)	0.187123(60)	
Δ_{JK} (kHz)	0.657039(88)	0.84847(40)	0.50245(102)	0.60623(79)	
Δ_K (kHz)	5.36670(50)	5.4775(57)	3.4799(110)	7.1160(185)	
δ_J (kHz)	0.02767300(181)	0.0274086(134)	0.0276239(291)	0.0265674(279)	
δ_K (kHz)	0.569401(157)	0.64161(96)	0.35886(184)	0.31951(205)	
# Lines	1284	490	312	241	34
Fit RMS (MHz)	0.098	0.099	0.142	0.178	0.268

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.

linestrengths. In this case, the quartic distortion constants were held to the values fit to the ground state. The microwave RMS determined for this state is therefore considerably higher than those determined for the others.

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 spectral prediction.

It was found 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, predicted frequencies for the strongest transitions differ by 10–15 MHz from the experimentally measured line positions. This corresponds to a velocity shift of >15 km/s from the source velocity. Interstellar detection of this molecule would be quite difficult based on these parameters. Due to the relative rigidity of this molecule 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.

Observational searches for dihydroxyacetone have begun. Preliminary results from observations with the Caltech submillimeter observatory (CSO) indicate a strong possibility for the presence of this species in Sagittarius B2(N-LMH). Additional observational work to confirm this potential detection is scheduled with the CSO, the Green Bank Telescope, and the Owens Valley Millimeter Array.

Acknowledgments

The experimental work was funded in part by the NASA Exobiology and SARA programs, Grant Nos. NAG5-11423 and NAG5-13457. D.R.K. is grateful for a graduate fellowship from the Fannie and John Hertz Foundation. We thank the JPL Microwave, Millimeter, and Submillimeter Spectroscopy Group, particularly Dr. Brian Drouin, for use of the millimeter/submillimeter apparatus and assistance during data collection. We would like to thank Dr. Tryggvi Emilsson for his guidance and advice with the FTMW experiments. We would also like to acknowledge the diligence of Ms. Kathryn Dyl and Ms. Maryam Ali during the initial FTMW experiments. The computational resources were provided by the Materials and Process Simulation Center at Caltech. We also gratefully acknowledge the support and services rendered by the CIT and JPL staff.

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