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Millimeter wavelength measurements of the rotational spectrum of 2-aminoethanol

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Abstract

Aminoethanol is a predicted precursor to the amino acid alanine in the interstellar medium and is therefore of great interest for observational studies. However, previous work involving the rotational spectrum of this molecule is limited to centimeter wavelengths and additional laboratory work is necessary to support astronomical heterodyne spectroscopy. This work presents the Doppler-limited rotational spectrum of aminoethanol measured in selected regions between 72 and 305 GHz. Measurements of ground state and v_{27} transitions have been extended up to $J = 51$ and $J = 43$, respectively. Additional rotational transitions were assigned for the v_{25} , v_{26} , $v_{25} + v_{27}$, $2v_{27}$ and $v_{26} + v_{27}$ hot bands, resulting in improved rotational and centrifugal distortion constants for these states.

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1. Introduction

Presently there are over one hundred known interstellar molecules, the great majority of which are organic [1]. Theoretical models of grain surface chemistry predict precursors to the more complex compounds, such as simple alcohols and aminoalcohols, to be abundant under certain conditions [2–4]. 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 themselves. 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. In these models, the temperature of the so-called hot cores (~ 300 K) near young stars leads to thermal evaporation of simple molecules such as alcohols and aminoalcohols from the grain surface. These molecules can then undergo gas phase reactions to form more complex species such as amino

acids, sugars, and other biologically important molecules.

The recent detection of glycolaldehyde (CHOCH_2OH), the simplest sugar, in the hot core Sagittarius B2(N-LMH) [5] has confirmed the need for further experimental and observational investigation of these models. One proposed pathway involves both grain surface and hot core gas phase chemistry for the formation of amino acids. In this pathway, the protonated forms of aminomethanol ($\text{NH}_2\text{CH}_2\text{OH}$) and aminoethanol ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$) 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. The first step in the evaluation of this model is therefore the complete laboratory spectroscopic characterization of aminomethanol and aminoethanol.

Prebiotic monomers such as aminoalcohols are expected to have strong torsional transitions in the terahertz (THz) frequency range. Terahertz observational searches for such modes are potentially much more sensitive than pure rotational spectroscopy, and the CASIMIR (Caltech Airborne Submillimeter Interstellar Medium Investigations Receiver) instrument on the

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Stratospheric Observatory for Infrared Astronomy (SOFIA) and the HIFI package on the Herschel Observatory will carry out the first high sensitivity THz astronomical surveys. Laboratory THz data for prebiotic molecules is vital to these observational programs. Due to experimental limitations in this range, however, the spectral search is more straightforward at microwave and millimeter wavelengths, resulting in this window being the most natural starting point when available spectra are limited. This data can then be extrapolated to higher frequencies and used as a guide for further laboratory THz studies.

Aminomethanol is not easily isolated under normal laboratory conditions. However, aminoethanol is commercially available and the gas phase spectra are easily obtained. Penn and Curl investigated the rotational spectrum of this molecule from 8 to 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 [6]. This data was subsequently used to determine quartic centrifugal distortion constants [7]. An internally hydrogen-bonded gauche conformer, shown in Fig. 1, was the only conformer observed in this work.

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. [8], 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 previous 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 assign-

ments of Penn and Curl can be attributed to the ν_{27} and $2\nu_{27}$ states. These torsionally excited states have vibrational energies below $\sim 350\text{cm}^{-1}$ 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. Improved rotational, quartic and sextic inertial constants have been determined for these states.

2. Experimental

The experimental apparatus utilized is the millimeter and submillimeter spectrometer at the Jet Propulsion Laboratory. The flow cell and detection methods are outlined in reference [9]. The source frequencies were obtained using a directly synthesized beam projected from the output of a multiplier chain [10].

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 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. 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 Fig. 2). Second and third harmonics of this multiplier were produced on a whisker-contacted Shottky diode allowing scans of up to

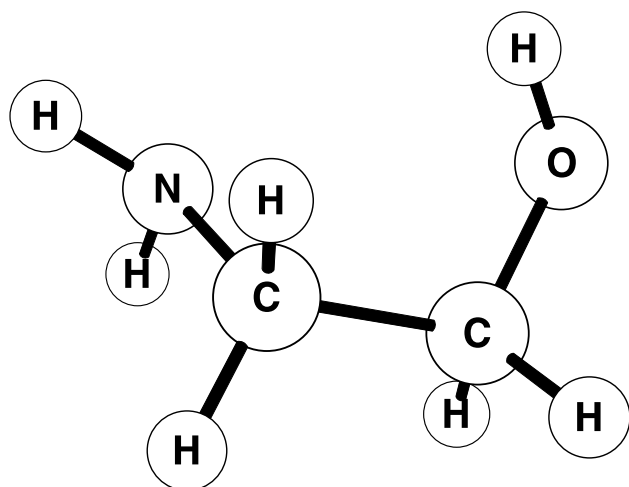


Fig. 1. The ground state structure of 2-aminoethanol from [6].

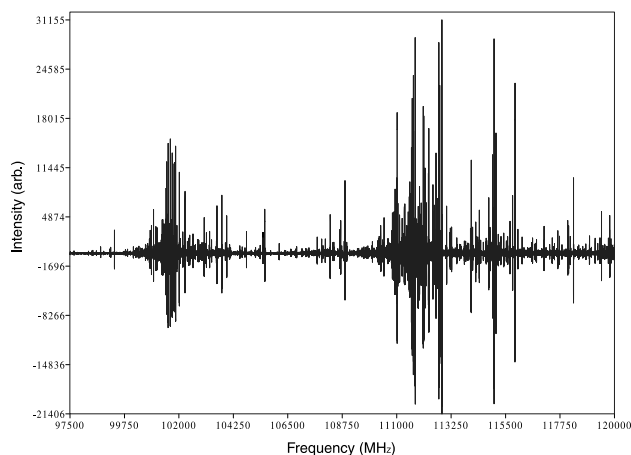


Fig. 2. A single scan covering 23 GHz from 97 to 120 GHz.

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. Linewidths were on the order of 1 MHz. Strong aR branches are seen at a separation of approximately 11 GHz. No nitrogen hyperfine splitting patterns were observed.

3. Data analysis

The data were assigned using the SPFIT and SPCAT programs [11]. The lower frequency data of Penn and Curl [6] 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 2030 lines, approximately 85 percent of the total lines in the spectrum, have been assigned for aminoethanol. The global fit microwave rms was 111 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. These assignments and other predicted rotational frequencies are available through the submillimeter and microwave spectral line catalog [11] available at <http://spec.jpl.nasa.gov>. An electronic file containing the fitting parameters, transitions frequencies, and residuals has been deposited with the journal.

Initial assignments of excited vibrational levels for the fundamental vibrational 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 1 and 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.

4. Discussion

The rotational spectrum of aminoethanol has been characterized up to 305 GHz. We have extended measurements of ground state transitions and assigned

Table 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 |
| $-\Delta_J$ | -6.18488(67) | -6.10549(63) | -6.29271(66) | -6.29079 (66) | kHz |
| $-\Delta_{JK}$ | 0.02319299(213) | 0.02413757(235) | 0.02399144 (268) | 0.02386650(231) | MHz |
| $-\Delta_K$ | -0.0532367(101) | -0.0596786(112) | -0.056270(42) | -0.0541637(111) | MHz |
| $-\delta_J$ | -1.809587(130) | -1.784947(137) | -1.857728(194) | -1.845020(147) | kHz |
| $-\delta_K$ | -0.0106488(40) | -0.0111940(43) | -0.0108574 (60) | -0.0104006(46) | MHz |
| Φ_J | -0.01392(34) | | | | Hz |
| Φ_{JK} | 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 | 556 | 431 | 254 | 362 | |
| Fit rms | 0.084 | 0.143 | 0.135 | 0.132 | |

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 2
Spectral parameters determined for overtone and combination vibrational states of aminoethanol

| State | $2\nu_{27}$ | $\nu_{26} + \nu_{27}$ | $\nu_{25} + \nu_{27}$ | |
|----------------|------------------|-----------------------|-----------------------|------------------|
| <i>E</i> | 208 | 268 | 409 | cm ⁻¹ |
| <i>A</i> | 14697.53155(166) | 14572.0760(128) | 14631.2449(263) | MHz |
| <i>B</i> | 5464.38187(50) | 5503.29600(91) | 5458.88835(144) | MHz |
| <i>C</i> | 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) | -0.013363(39) | -0.012183(47) | MHz |
| # Lines | 238 | 101 | 88 | |
| Fit rms | 0.120 | 0.127 | 0.150 | MHz |

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.

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 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 between 300 and 400 cm⁻¹ are perturbed from regular asymmetric top energy levels. Analysis of these states is beyond the scope of the present work.

The assignment of the rotational spectrum of aminoethanol at millimeter frequencies has led to observational searches for aminoethanol. Initial work with the Owen's Valley Radio Observatory Millimeter Array focused on strong aR transitions near 112.7 GHz. No aminoethanol lines were detected in the hot core sources of Orion KL or W51. However, observational searches for strong aminoethanol lines predicted near 250 GHz should be substantially more sensitive and are planned with the Caltech Submillimeter Observatory for the fall of 2002.

In addition, this data has been extrapolated to sub-millimeter and terahertz frequencies and laboratory characterization of aminoethanol in these frequency ranges is planned. This work will provide the basis for future observational searches with SOFIA and the Herschel Observatory.

Finally laboratory characterization of aminomethanol is underway with the original Balle-Flygare Fourier-Transform microwave spectrometer, now relocated to Pasadena. Millimeter spectroscopic studies and observational searches similar to those for aminoethanol are planned for this molecule.

Acknowledgments

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