

Chapter 7

Aminoethanol

7.1 Introduction

Aminoalcohols are central to the gas phase formation of glycine in current hot core chemical models. The protonated forms of aminomethanol ($\text{NH}_2\text{CH}_2\text{OH}$) and aminoethanol ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$) are proposed to 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, however. The first step in the evaluation of these models is therefore the complete laboratory spectroscopic characterization of aminomethanol and aminoethanol.

Aminomethanol is not easily isolated under normal laboratory conditions. Aminoethanol, however, is commercially available, and gas phase spectra are easily obtained. Penn and Curl investigated the rotational spectrum of this molecule from 8–40 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 [65]. This data was subsequently used to determine quartic centrifugal distortion constants [66]. An internally hydrogen-bonded gauche conformer, shown in Figure 7.1, was the only conformer observed.

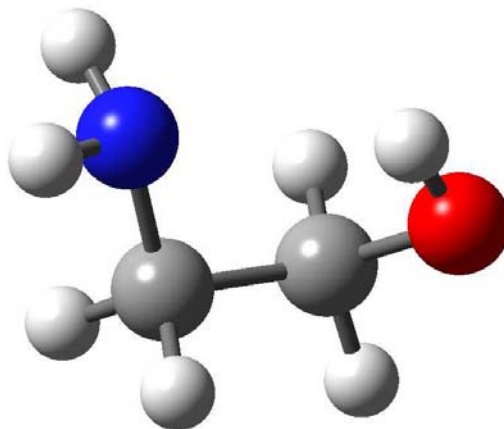


Figure 7.1: The ground state structure of 2-aminoethanol.

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.* [67], 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 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 assignments 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.

7.2 Spectroscopic Studies

7.2.1 Experimental

The experimental apparatus utilized is the JPL flow cell spectrometer. The flow cell and detection methods are outlined in reference [23], and the details of the frequency source and detectors are outlined in Chapter 6.

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. 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. A sample spectrum is shown in Figure 7.2.1. 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 because of the moderate- and high- J states accessed.

7.2.2 Data Analysis

The data were assigned using the SPFIT and SPCAT programs (see Appendix C, [30]). The lower frequency data of Penn and Curl [65] 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 2047 aminoethanol lines, approximately 85 percent of the total lines in the

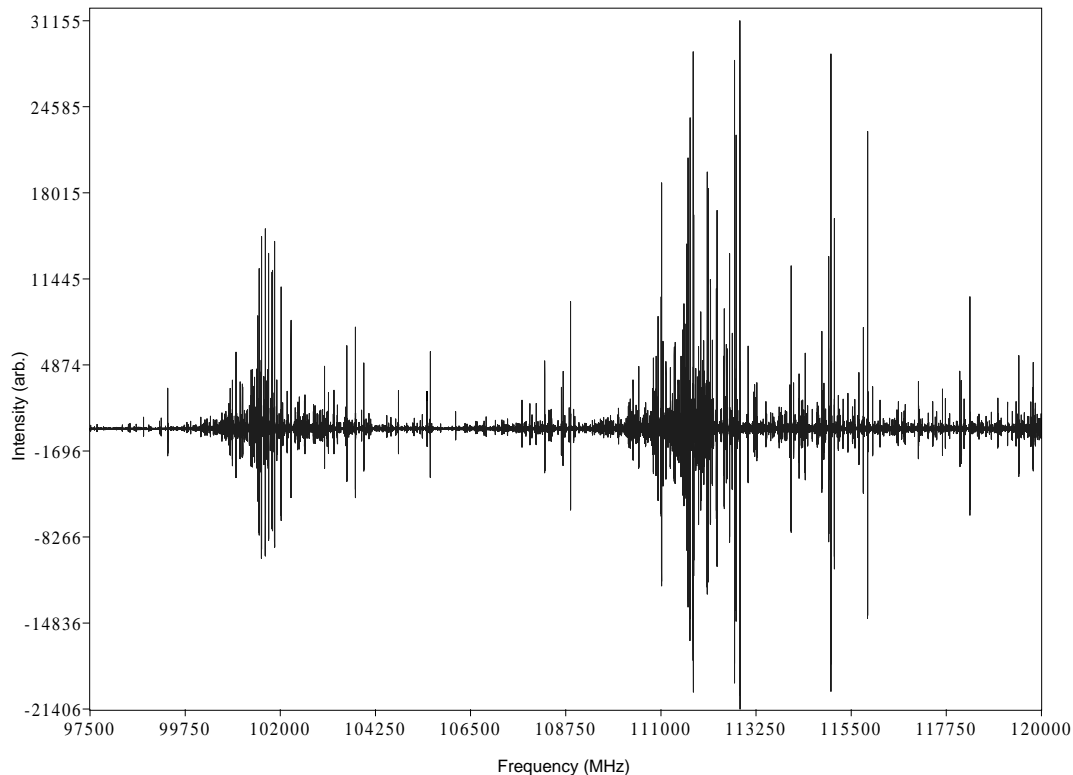


Figure 7.2: The room temperature aminoethanol spectrum from 97 to 120 GHz.

spectrum, have been assigned. The global fit microwave RMS was 113 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.

Initial assignments of excited vibrational levels for the fundamental torsional 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 7.1 and 7.2. 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.

The files associated with the analysis, including the parameters and rest frequencies, can be found in Appendix I. 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].

7.2.3 Discussion

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

Table 7.1: Spectral parameters determined for the ground and fundamental vibrational states of aminoethanol.

state	gs	ν_{27}	ν_{26}	ν_{25}	cm^{-1}
E	0	104	164	305	
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	573	431	254	362	
Fit RMS	0.084	0.143	0.135	0.132	

Note: 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 7.2: Spectral parameters determined for overtone and combination vibrational states of aminoethanol.

state	$2\nu_{27}$	$\nu_{26} + \nu_{27}$	$\nu_{25} + \nu_{27}$	
E	208	268	409	cm^{-1}
A	14697.53155(166)	14572.0760(128)	14631.2449(263)	MHz
B	5464.38187(50)	5503.29600(91)	5458.88835(144)	MHz
C	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)	-0.013395(39)	-0.012183(47)	MHz
# Lines	238	101	88	
Fit RMS	0.120	0.127	0.150	MHz

Note: 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.

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, which lie between 300 and 400 cm^{-1} , are perturbed from the regular asymmetric top energy levels. Analysis of these states is beyond the scope of the present work.

7.3 Observational Studies

The laboratory studies of aminoethanol provided the necessary information to guide observational searches for this species. These searches were conducted with the CSO and OVRO observatories. No lines were detected for this molecule with either observatory, but upper limits for the column density have been calculated from the astronomical data. The observations and results are outlined below.

7.3.1 CSO Observations

7.3.1.1 Observations

Searches for aminoethanol in the Sgr B2(N-LMH), Orion Compact Ridge, and W51e2 sources were conducted with the CSO using the 230 GHz DSB heterodyne receiver on the nights of 2002 October 11–14 and 2004 July 3–5. Spectral windows corresponding to the frequencies of two aminoethanol lines were observed in each source, and 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 in Table 7.3. All observed lines are asymmetry doublets whose transitions occur within the ground vibrational state. Typical system temperatures ranged from 200-600 K, and the source positions and velocities selected were $\alpha(1950)=17^h 44^m 10^s.1$, $\delta(1950)= -28^\circ 21' 17''$ and 64 km/s for the Sgr B2(N-LMH) hot core, $\alpha(2000)=05^h 35^m 14^s.5$, $\delta(2000)= -05^\circ 22' 30''.4$ and 9 km/s for the Orion Compact Ridge, and $\alpha(1950)=19^h 23^m 43^s.5$, $\delta(1950)= 14^\circ 30' 34''$ and 55 km/s for the W51e2 hot core. The chopping secondary with a 70'' throw was used along with chopper-wheel calibration and the facility 1.5 GHz, 500 MHz, and 50 MHz AOS back ends to minimize the spectral baseline fluctuations. The FWHM of the CSO at these frequencies is $\sim 30''$, and all data are placed on the T_{MB} temperature scale using a main beam efficiency of 70%.

7.3.1.2 Results

No transitions were detected in any of the sources observed, and so the column density upper limit was calculated from the observed spectral intensity at the expected line position, which was placed on the T_{MB} temperature scale using a main beam efficiency of 70%. These limits are presented in Table 7.3. A linewidth of 5 km/s and a rotational temperature of 150

Table 7.3: Aminoethanol column density upper limits in Orion, W51, and Sgr B2 from CSO observations.

$J'_{K'_a, K'_c} - J''_{K''_a, K''_c}$	ν_0^a (MHz)	$Ag_u \times 10^2$ (s ⁻¹)	E_u (K)	T_{MB}^b (K)	N_T upper limit ^c ($\times 10^{-13}$ cm ⁻²)
Orion					
26 _{1,25} → 25 _{1,24}	246825.322	3.1364	165.04	0.05(2)	3.03(42)
26 _{2,25} → 25 _{2,24}		3.1364	165.04		
27 _{0,27} → 26 _{0,26}	249709.769	7.5484	169.66	0.20(2)	5.15(71)
27 _{1,27} → 26 _{1,26}		7.5484	169.66		
W51e2					
27 _{0,27} → 26 _{0,26}	249709.769	7.5484	169.66	0.03(2)	1.33(31)
27 _{1,27} → 26 _{1,26}		7.5484	169.66		
28 _{0,28} → 27 _{0,27}	258826.376	8.7195	182.08	0.08(2)	7.34(74)
28 _{1,28} → 27 _{1,27}		8.7195	182.08		
Sgr B2(N-LMH)					
27 _{0,27} → 26 _{0,26}	249709.769	7.5484	169.66	0.063(5)	2.96(30)
27 _{1,27} → 26 _{1,26}		7.5484	169.66		
28 _{0,28} → 27 _{0,27}	258826.376	8.7195	182.08	0.030(5)	5.90(14)
28 _{1,28} → 27 _{1,27}		8.7195	182.08		

^a One σ uncertainties are 0.1 MHz.

^b Assumed uncertainties are listed in parentheses in units of last significant figure.

^c One σ uncertainties are listed in parentheses in units of last significant figure.

K, typical values observed for species in the Compact Ridge, were assumed for the Orion calculations [25]. A line width of 10 km/s and a rotational temperature of 100 K, the values found for methyl cyanide in the W51e2 source, were assumed for the W51e2 calculations [42]. A line width of 10 km/s, the approximate linewidth observed for dihydroxyacetone in the Sgr B2(N-LMH) source (see Section 4.4), and a rotational temperature of 200 K, the most

commonly quoted temperature for this source [28], were assumed for the Sgr calculations. The vibrational state contributions to the partition function were included in this analysis.

7.3.2 OVRO Observations

7.3.2.1 Observations

Searches for aminoethanol in the Orion and W51e2 sources were conducted with the OVRO Millimeter Array between 2001 October 1–November 4. The source positions used were $\alpha(2000)=05^h 35^m 14^s .5$, $\delta(2000)= -05^\circ 22' 30'' .4$ for Orion, which is coincident with the Orion Compact Ridge source, and $\alpha(2000)=19^h 23^m 43^s .9$, $\delta(2000)= 14^\circ 30' 34'' .0$ for W51e2. The source velocities used were 9 and 55 km/s, respectively. These observations were conducted in the L and C configurations. Each source was observed for approximately 8 hours in each full track, and one track in each configuration was completed for Orion, while two half tracks in each configuration were completed for W51e2. Two aminoethanol lines were observed simultaneously, and the parameters for these lines, specifically the vibrational ground state transition quantum numbers, rest frequencies, Einstein A-coefficients times the upper state degeneracy, and upper state energies, are listed in Table 7.4. The beam sizes for these observations were $6''.8 \times 4''.8$ and $5''.6 \times 4''.5$ for Orion and W51e2, respectively. The quasars 3C84, 3C345, and 3C454.3 were observed for flux and bandpass calibration, and observations of Uranus were conducted for bootstrapping the quasar fluxes. Observations of phase and amplitude calibrators were conducted in approximately half hour intervals throughout the tracks.

Table 7.4: Aminoethanol column density upper limits in Orion and W51 from OVRO observations.

$J'_{K'_a, K'_c} - J''_{K''_a, K''_c}$	ν_0^a (MHz)	$Ag_u \times 10^2$ (s^{-1})	E_u (K)	T_{MB}^b (K)	N_T upper limit ^c ($\times 10^{-13} \text{ cm}^{-2}$)
Orion					
$12_{1,12} \rightarrow 11_{1,11}$	112742.2238	0.1386	35.94	0.27(9)	5.05(68)
$11_{4,7} \rightarrow 10_{4,6}$	112779.8117	0.1118	39.52	0.45(9)	10.4(14)
W51e2					
$12_{1,12} \rightarrow 11_{1,11}$	112742.2238	0.1386	35.94	0.59(13)	89.5(185)
$11_{4,7} \rightarrow 10_{4,6}$	112779.8117	0.1118	39.52	0.52(13)	99.8(206)

^a One σ uncertainties are 0.1 MHz.

^b Uncertainties are listed in parentheses in units of last significant figure and are based on an assumed flux uncertainty of ± 0.02 Jy/Beam.

^c One σ uncertainties are listed in parentheses in units of last significant figure.

7.3.2.2 Results

Boxcar fits to an internal noise source modified by second order polynomial fits to observations of the quasars were used for bandpass calibration. The quasars were also used to establish the flux density scale, with fluxes bootstrapped from observations of Uranus. Bandpass, phase, and flux calibrations were applied to the data with the MMA software package [43]. The MIRIAD data reduction software package [44] was used for subsequent spectral analysis. Neither transition was observed in either source, and so the column density upper limits were calculated as described for the CSO observations. The calculated aminoethanol column density upper limits are presented in Table 7.4.

7.3.3 Discussion

The upper limit for the aminoethanol column density in the Orion Compact Ridge, W51e2, and Sgr B2(N-LMH) hot core sources is on the order of $\sim 3 \times 10^{13} \text{ cm}^{-2}$ for an extended source and $\sim 9 \times 10^{14} \text{ cm}^{-2}$ for a compact source. Aminoethanol is expected to be present in amounts similar to those observed for ethanol if it is formed by the simple grain surface mechanisms proposed in reference [3]. Ethanol column densities in these sources are on the order of $\sim 10^{15} \text{ cm}^{-2}$ [24, 68]. Emission from ethanol is extended in the Orion and Sgr clouds, and similar behavior would be expected for aminoethanol if it was formed by a similar process [18, 68]. Grain surface formation pathways should therefore be reinvestigated, as the aminoethanol upper limits found here are two orders of magnitude below the expected levels. The only mechanism that has been proposed for the interstellar formation of amino acids involves gas phase ion-molecule reactions of aminoalcohols [3], and so these results call into question the viability of amino acid formation in hot cores.