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The Microwave Spectrum, Structure, and Dipole Moment of 2-Mercaptoethanol; Evidence for an Intramolecular OH···S Hydrogen Bond

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Abstract: The microwave spectrum of 2-mercaptoethanol has been observed and analyzed in the 18–40-GHz frequency region. Using data from the normal and four additional isotopic species, the structure of the observed rotamer has been shown to be all gauche (GGG). The structural results indicate the presence of an intramolecular hydrogen bond of the type OH···S, with an H···S distance of 2.565 ± 0.003 Å. Dipole moment measurements lead to the values $|\mu_a|$ = 0.619 ± 0.015, $|\mu_b|$ = 1.478 ± 0.012, and $|\mu_c|$ = 0.965 ± 0.009 D, in agreement with expectations for the observed GGG conformation. The present study appears to be the first to present concrete structural evidence for the involvement of sulfur in an intramolecular hydrogen bond in the gas phase. These results have been discussed in relation to other pertinent data.

Rotational isomerism in 1,2-disubstituted ethanes has been studied extensively.[1] The threefold C–C barrier terms lead generally to stable trans or gauche rotamers, the cis forms being sterically unfavored. In the dihaloethanes (except for the difluoro case[2a]) the trans forms are the lowest energy species,[2b] while the situation reverses for the 2-haloethanols, for which the gauche forms are lower in energy.[3-6] This latter phenomenon has been attributed to intramolecular hydrogen bonding, and was carefully investigated by Azrak and Wilson[6] by microwave spectroscopy. These workers found that the stable

Table I. Microwave Spectra of 2-Mercaptoethanol

Transition	Frequency[a]	Obsd − calcd[b]
$HSCH_2CH_2OH$		
$1_{10} \rightarrow 2_{21}$	39 423.46	−0.02
$1_{10} \rightarrow 2_{20}$	39 444.58	0.00
$1_{11} \rightarrow 2_{21}$	39 924.96	−0.04
$1_{11} \rightarrow 2_{20}$	39 946.10	0.00
$2_{12} \rightarrow 2_{21}$	27 561.16	−0.10
$2_{12} \rightarrow 2_{20}$	27 582.28	−0.09
$2_{02} \rightarrow 3_{12}$	29 746.49	0.07
$2_{02} \rightarrow 3_{13}$	26 737.97	0.14
$3_{13} \rightarrow 3_{22}$	28 326.60	0.13
$3_{13} \rightarrow 3_{21}$	28 431.75	0.04
$4_{32} \rightarrow 5_{33}$	32 229.96	−0.05
$4_{31} \rightarrow 5_{32}$	32 241.58	−0.06
$H^{34}SCH_2CH_2OH$		
$1_{10} \rightarrow 2_{21}$	39 234.82	−0.04
$1_{10} \rightarrow 2_{20}$	39 254.17	−0.01
$1_{11} \rightarrow 2_{21}$	39 715.61	0.04
$1_{11} \rightarrow 2_{20}$	39 734.94	0.06
$2_{12} \rightarrow 2_{21}$	27 637.57	−0.08
$2_{12} \rightarrow 2_{20}$	27 656.98	0.02
$4_{32} \rightarrow 5_{33}$	31 457.94	−0.02
$4_{31} \rightarrow 5_{32}$	31 468.12	0.00
$DSCH_2CH_2OD$		
$1_{10} \rightarrow 2_{21}$	36 439.18	−0.03
$1_{10} \rightarrow 2_{20}$	36 460.08	0.02
$1_{11} \rightarrow 2_{21}$	36 912.83	−0.07
$1_{11} \rightarrow 2_{20}$	36 933.82	0.07
$2_{02} \rightarrow 3_{13}$	25 369.16	0.13
$3_{03} \rightarrow 4_{14}$	30 703.24	−0.08
$4_{14} \rightarrow 5_{05}$	24 832.32	−0.01
$HSCH_2CH_2OD$		
$1_{10} \rightarrow 2_{20}$	37 841.60	−0.01
$1_{10} \rightarrow 2_{21}$	37 816.94	0.02
$1_{11} \rightarrow 2_{21}$	38 344.54	0.01
$1_{11} \rightarrow 2_{20}$	38 369.18	−0.03
$3_{03} \rightarrow 4_{14}$	31 333.64	0.06
$4_{14} \rightarrow 4_{23}$	28 031.52	0.00
$4_{04} \rightarrow 5_{15}$	37 522.72	−0.04
$DSCH_2CH_2OH$		
$1_{10} \rightarrow 2_{21}$	37 924.58	−0.01
$1_{10} \rightarrow 2_{20}$	37 942.33	0.06
$1_{11} \rightarrow 2_{21}$	38 372.52	−0.12
$1_{11} \rightarrow 2_{20}$	38 390.38	0.06
$3_{03} \rightarrow 4_{14}$	31 536.48	0.11
$4_{04} \rightarrow 5_{15}$	36 823.54	−0.09

[a] All values in MHz. Measurement accuracy approximately ±0.05 MHz. [b] Computed using rotational constants of Table II.

gauche species exhibit also a gauche conformation about the C–O bond, which provides the most favorable X···HO interaction. Subsequent infrared[7] and microwave[8] studies have shown that a similar C–C gauche form is the stable conformation in 2-aminoethanol, with intramolecular hydrogen bonding once again evident (N···HO).

The ethylene glycol, 1-2-ethanedithiol, and mercaptoethanol molecules provide further interesting features relative to rotational isomerism. In particular, these species exhibit the possibility of isomerism about three bonds, and consequently there are numerous possible rotamers. Eliminating the cis forms, 1,2-ethanedithiol might exist in four C–C trans forms and six C–C gauche forms. Infrared data[9] indicate the presence of TTT and TGT forms,[10] the former being more stable. Electron diffraction studies[11] are consistent with this result, but are not definitive with regard to the C–S conformations. There seems to be no evidence that hydrogen bonding exists in the dithiol species.

For ethylene glycol, the infrared studies of Buckley and

Giguere[12] show conclusively that the molecule is C–C gauche only, with intramolecular hydrogen bonding. The most likely molecular conformation is probably either GGT or GGG, either of these permitting intramolecular hydrogen bonding. Microwave studies[13] have been unsuccessful because of tunneling complications.

Mercaptoethanol ($HSCH_2CH_2OH$) has been the least studied of this class of molecules. Rather incomplete infrared spectral data indicates the presence of both C–C trans and gauche forms in the liquid state, the former being more stable by 600 cal/mol.[14] No gas-phase data are available, and there seems to be no evidence for intramolecular hydrogen bonding. Our studies of this molecule have been undertaken in order to clarify and/or confirm the stable molecular conformation(s). Of particular interest was the question of hydrogen bonding. Viz., does it occur, and if so is it of the S···HO or the O···HS type? The latter question is particularly pertinent, and has been the subject of a recent extensive review by Zuika and Bankovskii.[15]

Experimental Section

The 2-mercaptoethanol sample used in this work was obtained from Eastman Kodak. After distillation at reduced pressure [bp 72–74 °C (~10 mTorr)] it was found to be suitable for our microwave spectral studies. Doubly deuterated ($DSCH_2CH_2OD$) samples were prepared by the liquid-phase exchange of the normal isotopic species with excess D_2O. We found that the deuterated samples underwent extremely facile exchange with glassware, and consequently all flasks and distillation apparatus were deuterated with D_2O prior to their use. After distilling the D_2O/mercaptoethanol mixture we typically obtained a sample containing about 25% of the D_2 species. Monodeuterated species ($HSCH_2CH_2OD$ and $DSCH_2CH_2OH$) were produced by gas-phase exchange with D_2O adsorbed on the walls of the microwave spectrometer sample cell. The procedure here was to simply saturate the cell for several hours with D_2O vapor, after which normal mercaptoethanol was admitted to the cell and allowed to stand a short while. This produced a mixture of deuterated species, perhaps 10% in all, containing the –OD and –SD monodeuterated species in a ratio of about –OD/–SD = 5/2, plus a very small amount of the D_2 species. The 5/2 ratio was unexpected, and seems to indicate a substantial thermodynamic preference for exchange at the hydroxyl site. Spectra of the ^{34}S molecule were obtained in its natural abundance (4%) from normal samples.

Microwave spectra were obtained on a Hewlett-Packard 8460A microwave spectrometer operating in K and R bands (18–40 GHz). Radiofrequency microwave double resonance (RFMDR) spectra were obtained using the procedure described by Wodarczyk and Wilson.[16] Spectra were obtained with sample pressures of about 50 mTorr and temperatures of 20 °C or about −40 °C (using partial dry ice cooling). Sample pressures became much too low for spectral studies if the sample temperature was lowered all the way to −78 °C. Spectral frequency measurements reported in this work have an accuracy of approximately ±0.05 MHz.

Dipole moment measurements were performed by observing Stark shifts as a function of the spectrometer ground-to-base voltage. The voltage was measured with a Data Technology Model 20 digital voltmeter with a precision of about 0.1%. Calibration of the Stark cell was performed using OCS as a standard.[17]

Results

Observed Spectrum and Assignment. The observed spectrum of the normal isotopic species of mercaptoethanol was extremely dense, and initial perusals indicated that the majority of the strong lines were high-J, Q-branch lines. This was in accord with preliminary predictions, which showed strong b- and c-type Q-branch series for both C–C gauche and trans species. A careful search for several expected low-J, R-branch lines was performed and eventually these were located and assigned with the aid of their characteristic Stark effects. It was then possible to assign the various b- and c-type Q-branch series as well as several a-type R-branch lines. The spectrum was searched and assigned very carefully, since it was hoped

Table II. Rotational Constants and Moments of Inertia of 2-Mercaptoethanol

	$HSCH_2CH_2OH$	$DSCH_2CH_2OD$	$HSCH_2CH_2OD$	$DSCH_2CH_2OH$	$H^{34}SCH_2CH_2OH$
A	12152.641 ± 0.012^a	11185.594 ± 0.016	$11632.710 + 0.011$	11665.347 ± 0.037	12111.855 ± 0.09
B	3467.078 ± 0.010	3356.121 ± 0.012	3446.367 ± 0.028	3376.599 ± 0.142	3380.006 ± 0.014
C	2965.554 ± 0.009	2882.437 ± 0.009	2918.793 ± 0.008	2928.546 ± 0.032	2899.306 ± 0.014
I_a	41.5859^b	45.1812	43.4446	43.3231	41.7260
I_b	145.7651	150.5843	146.6398	149.6710	149.5201
I_c	170.4164	175.3305	173.1466	172.5699	174.3103
κ	$-0.890\ 819\ 7$	$-0.885\ 902\ 8$	$-0.878\ 905\ 4$	$-0.897\ 434\ 8$	$-0.895\ 642\ 4$

^{a} Units of rotational constants are MHz. Uncertainties are the standard deviations. ^{b} Moments of inertia are obtained using the conversion factor 505 379 amu Å^2 MHz.

to be able to locate the spectrum of a second rotameric species. A total of 100 transitions were assigned with J values up to 46. Table I lists a portion of the observed spectrum of this rotameric species, which we shall later show to be in a GGG conformation.[10]

The data for the normal isotopic form of the GGG species of Table I have been fit to the rigid rotor model, the derived rotational constants being listed in Table II. Centrifugal distortion effects became very large for the high-J transitions (not presented in Table I); consequently we also performed a centrifugal distortion analysis using a larger data set consisting of transitions with J values up to 19. In this way it was possible to fit 28 transitions with an average deviation of 0.024 MHz, and to assign transitions as high as $J = 46$. The rotational constants from the centrifugal distortion fit have the values $A = 12\ 152.79$, $B = 3467.10$, $C = 2965.57$ MHz, which do not differ substantially from the rigid rotor values of Table II. Since it was not possible to assign as many transitions for the various isotopic species (described below), we have chosen for consistency to deal only with the rigid rotor values derived from relatively low-J lines.

Spectra of the two monodeuterated species, the dideuterio species, and the ^{34}S species could not be assigned by using ordinary Stark spectroscopy because of the very high background spectrum of the normal species. Instead, we used the RFMDR technique[16] to great advantage for this task. The key energy levels are the $2_{20}/2_{21}$ pair, which are separated by about 20 MHz for the various species. Consequently, it was possible to locate the four b- and c-type $1 \rightarrow 2$ transitions using this particular double resonance. In some cases the $2 \rightarrow 2$ transitions were also located by this method, as well as $4 \rightarrow 5$ and $5 \rightarrow 6$ transitions using a double resonance involving the $5_{33}/5_{32}$ pair of levels (approximately 15-MHz separation). Our initial effort at locating these transitions was aided by isotope shift predictions based on the normal isotopic species, which was clearly of the C–C gauche form. (Dipole moment measurements and approximate structural calculations based on the normal isotopic species had already been performed, and these results ruled out species having cis or trans conformations about the C–C bond.)

Table I lists the observed transitions used in the rigid rotor analysis for the various isotopic species, and Table II summarizes the rotational constants. Additional high-J, Q-branch lines were assigned and measured also to confirm the fit. The assignment of the spectral data to the correct monodeuterated species (–SD or –OD) is not intuitively obvious from the rotational constants alone, but is confirmed to be the correct one by the structural results described below.

No rotamer other than the GGG form could be discovered. Several sets of vibrational satellites were observed, and will be described later.

Dipole Moment Measurements. Second-order Stark effect measurements have been performed on five components of the normal isotopic species. Table III presents the experimental values of the Stark shift coefficients, $\Delta\nu/E^2$, and the derived values of the dipole moment components obtained by a

Table III. Stark Coefficients and Dipole Moment of 2-Mercaptoethanol

		$\Delta\nu/E^2$	
Transition	M	Obsd^a	Calcd
$1_{11} \rightarrow 2_{20}$	0	$0.4908\ (0.0009)$	0.4851
$2_{02} \rightarrow 3_{13}$	2	$3.2040\ (0.0043)$	3.2158
	1	$-0.0759\ (0.0006)$	-0.0752
	0	$-1.1653\ (0.0033)$	-1.1723
$4_{14} \rightarrow 4_{23}$	4	$-5.5764\ (0.0447)$	-5.8539
	$|\mu_a|$	$= 0.619 \pm 0.015^b$	
	$|\mu_b|$	$= 1.478 \pm 0.012$	
	$|\mu_c|$	$= 0.965 \pm 0.009$	
	$|\mu_T|$	$= 1.871 \pm 0.019$	

^{a} Units are 10^{-5} MHz/(V/cm)^2. Values in parentheses are the standard deviations. ^{b} Units are debye and uncertainties are 3σ.

weighted least-squares fit. The theory of Golden and Wilson[18] was used for this analysis.

For comparison purposes we have computed the dipole moment components for the GGG conformation by expressing μ as a vector sum of the moments of methanol and methanethiol.[19,20] The orientation of these moments in mercaptoethanol was taken to be the same as in the component molecules (relative to the COH and CSH fragments). Our computed values are: $|\mu_a| = 0.58$, $|\mu_b| = 1.37$, $|\mu_c| = 1.06$, and $|\mu_T| = 1.82$ D.

Structure. While it is not possible to derive a complete structure of high accuracy from the available data (normal plus four isotopic species), it is possible to specify the conformation unambiguously, and also to specify the various structural parameters within a reasonably small range. The data for the mondeuterated and normal isotopic species can be used immediately to derive the r_s coordinates[21] of the appropriate atoms by means of Kraitchman's equations.[22] These results are presented in column 1 of Table IV. It can be seen that each of the coordinate sets contains one very small coordinate whose uncertainty is consequently rather large due to zero-point vibration effects. This presents no difficulty in the ensuing conformational analysis, but degrades somewhat the accuracy of the few Kraitchman structural parameters which we shall quote later.

The conformation of the molecule about the C–C bond can be stated immediately to be gauche by a study of the sulfur atom principal axis coordinates given in Table IV. No cis or trans conformation employing reasonable heavy-atom structural parameters can yield the sulfur coordinates of Table IV, a conclusion independent of the SH and OH conformations. For example, for a TTT molecular conformation having normal structural parameters, $a = -1.65$, $b = 0.14$, and $c = 0$, while a typical cis conformation, TCT, yields $a = 1.30$, $b = -0.31$, and $c = 0$. Although the cis values are rather close to the experimental ones, it turns out that unreasonable heavy-atom deformations are required to bring the a coordinate into agreement. An additional difficulty with attempting to fit a

Table IV. Atomic Coordinates in Angstroms

Atom	Coordinate	$|r_s|$ [a]	r_s [b]	Effective [c]
S	a	1.388 ± 0.001	-1.388 ± 0.002	-1.390
	b	0.272 ± 0.001	0.272 ± 0.006	0.268
	c	0.017 ± 0.019	0.017 ± 0.02	0.016
H (hydroxy)	a	0.929 ± 0.001	0.929 ± 0.002	0.929
	b	1.373 ± 0.001	1.373 ± 0.002	1.367
	c	0.042 ± 0.018	0.042 ± 0.040	0.008
H (thiol)	a	1.465 ± 0.002	-1.465 ± 0.003	-1.466
	b	$0.0 \quad \pm 0.08$ [d]	0.05 ± 0.05	0.068
	c	1.336 ± 0.002	1.336 ± 0.003	1.338

[a] Coordinates (unsigned) obtained by using normal and monodeuterated isotopic species. Uncertainties are those produced by one standard deviation of the rotational constants. [b] r_s coordinates with signs selected according to discussion in text. Uncertainties here include estimate of vibration–rotation effects. [c] Effective coordinates computed using geometrical parameters of Table V. [d] This coordinate was imaginary and was set equal to zero. The uncertainty represents the square root of the value needed to make b^2 positive.
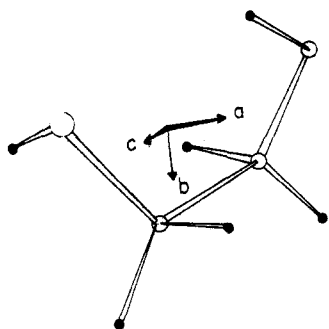

Figure 1. Perspective drawing of 2-mercaptoethanol. Thiol group is at left, hydroxyl group at right.

cis structure is that the S···O nonbonding distance is appreciably shorter than the sum of the sulfur and oxygen van der Waals radii. Of course, even without the ^{34}S data the cis and trans species can be ruled out, since the observed rotational constants of the normal species are quite distinctive of the correct conformation. A trans heavy-atom structure, being elongated along the a axis, yields a typical A rotational constant of 25 000 MHz, far too large to be confused with the observed results. Expected rotational constants for a cis structure are much closer to those observed, but the A constant is typically 10% smaller and the B constant about 20% larger. Finally, the quantity $I_a + I_b - I_c$ ($= 16.93$ amu Å^2) argues against any conformation having planar heavy atoms, since out-of-plane hydrogen atoms could contribute no more than 12–13 amu Å^2 to this quantity.

The heavy-atom structure can be approximately specified by fitting the heavy-atom framework (S–C(1)–C(2)–O) to the moments of inertia of the normal and ^{34}S isotopic species. By considering all possible orientations of the OH and SH groups, and using reasonable CH$_2$ parameters, the heavy-atom coordinates are found to be constrained to the following approximate range of values.

S: $a = -1.39 \pm 0.03$; $b = 0.28 \pm 0.04$; $c = 0.04 \pm 0.04$
C(1): $a = -0.09 \pm 0.03$; $b = -0.91 \pm 0.02$; $c = -0.28 \pm 0.04$
C(2): $a = 1.26 \pm 0.03$; $b = -0.53 \pm 0.02$; $c = 0.32 \pm 0.03$
O: $a = 1.72 \pm 0.03$; $b = 0.74 \pm 0.02$; $c = -0.13 \pm 0.07$ (1)

This preliminary determination of the heavy-atom coordinates is possible because the hydroxyl and thiol protons make very little contribution to the principal moments of inertia. Note that the sulfur values of eq 1 agree with the r_s results of Table IV and provide the proper signs.

Having the heavy-atom conformation in hand, we turn now to the OH and SH groups. First, we need to consider how the monodeuterated data of Tables I and II were assigned to the correct functional group (OH and SH). This assignment can

be verified by computing the S–H distance using all possible sign combinations for each of the two sets of $|r_s|$ hydrogen atom coordinates. In this calculation, the sulfur atom signs are now known to be those appropriate for a gauche heavy-atom molecule. These signs can be found in eq 1. The key point is that a correct assignment must lead to a typical S–H distance, about 1.32 Å.[23] Using the r_s data labeled "hydroxyl", the best obtainable S–H distance is 1.19 Å, which is far too short. Even if the poor c coordinates are arbitrarily assigned values of 0.1, which is surely an upper limit, the best S–H value is still only 1.21 Å. On the other hand, the r_s data labeled "thiol" leads to a sensible S–H distance for two possible a and c sign choices: $a < 0, c < 0$, or $a < 0, c > 0$. The small hydrogen b coordinate and the small sulfur c coordinate again do not affect the argument. Thus the isotope assignment is verified, and the choice between the two remaining possibilities for the thiol hydrogen can be made by investigating the two possible locations relative to the heavy-atom framework (see eq 1). Using the former sign choice ($a < 0, c < 0$), we find that $\angle$HSC(1) $< 80°$, which is clearly impossible. Consequently the correct thiol hydrogen sign choice is $a < 0, c > 0$, which leads to an entirely reasonable value for $\angle$HSC(1).

Finally, we can now make the proper sign choice for the hydroxyl hydrogen r_s coordinates, since this atom must be situated in a normal bonding configuration relative to the oxygen atom. Investigation of the heavy-atom parameters in eq 1 leads to the choice $a > 0$ and $b > 0$. The net result of all these sign choices is that the molecule exists in the GGG conformation as shown in Figure 1. Also, column 2 of Table IV summarizes the sign choices made for the various coordinates (including the small ones, which are discussed below).

Although the molecular conformation has been determined unambiguously, a complete structure of high quality cannot be obtained, since only three atoms have been located by isotopic substitution. An additional difficulty is caused by the small r_s coordinate appearing for each of the three isotopically substituted atoms. This produces both a sign uncertainty and a relatively large uncertainty in magnitude due to zero-point vibration effects. A partial resolution of this problem can be obtained by utilizing the second-difference method of Pierce,[24] since the SH and OH hydrogens can be located in both the normal and the D_2 molecular principal axis systems. While the transformation between these two axis systems cannot be specified with sufficient accuracy to provide precise numerical values of the small hydrogen coordinates, it is possible to provide information about the correct signs. Using the moments of inertia of the normal and three deuterated species, and using a transformation developed from the proposed molecular geometry, the thiol hydrogen c coordinate and the hydroxyl hydrogen b coordinate are each predicted to be positive. These results now permit the hydrogen coordinates to be specified with some degree of confidence. For the hydroxyl hydrogen,

Table V. Structural Parameters of 2-Mercaptoethanol

r_s Parameters[a]

S–H = 1.340 ± 0.022
S⋯H = 2.565 ± 0.003
H⋯H = 3.026 ± 0.028

Effective Structural Parameters[a]

Assumed:

C–H = 1.094	∠HCH = 108.9[b]
∠OCH = 109.8	∠CCH = 110.7[c]
∠SCH = 109.4	∠HCH = 109.8[c]
∠CCH = 110.2[b]	

Adjusted:

C–S = 1.806 ± 0.010	∠CCS = 113.5 ± 1.0
C–C = 1.538 ± 0.010	∠CCO = 111.4 ± 1.0
C–O = 1.423 ± 0.010	∠COH = 104.4 ± 1.5
O–H = 1.015 ± 0.015	∠CSH = 96.5 ± 2.0
S–H = 1.340 ± 0.015	∠(SCC)–(CCO) = 58.3 ± 1.0[d]
	∠(CCO)–(COH) = 307.3 ± 2.0[d]
	∠(CCS)–(CSH) = 67.1 ± 2.0[d]

[a] Distances in Å, angles in degrees. [b] Hydroxyl end of molecule. [c] Thiol end of molecule. [d] For these dihedral angles, 0° corresponds to the cis conformations. For the OH and SH angles, a positive angle represents a CCW rotation when viewed from oxygen or sulfur toward carbon.

we choose c = 0.042 ± 0.040 Å, where the coordinate is the r_s value and the uncertainty includes largely that due to vibration rotation effects (estimated as 0.0015/0.042). For the thiol hydrogen, we choose b = 0.05 ± 0.05 Å, where the value and uncertainty are chosen with the assumption that the coordinate must be between 0 and 0.10 Å. Using these coordinate values and the remaining r_s values in column 2 of Table IV, we have computed the S–H, H⋯H, and S⋯H r_s distances as presented in Table V. (For the small c coordinate of S we choose the value 0.017 ± 0.02. The sign and uncertainty have been chosen here to conform to the maximum allowable range which satisfies the experimental moments of inertia for reasonable heavy-atom structural parameters.)

Finally, we have determined a complete, effective molecular structure by finding the set of structural parameters which best reproduce the experimental moments of inertia. In this procedure the methylene parameters have been fixed at the values found for ethanol[25] and ethanethiol.[23] With these choices made, there remain 12 structural parameters to determine. These have been obtained by an iterative solution of the moment of inertia equations. Since there are 15 experimental moments, this fitting procedure has been performed in several independent ways. The best set of effective structural parameters listed in Table V represents the average values from the various independent fitting schemes. This set of parameters satisfies the complete set of experimental moments with an average deviation of 0.009% and a maximum deviation of 0.042%. The listed parameter uncertainties have been chosen to be somewhat larger than the maximum range of values found from the various fits. Some measure of the validity of the effective structure can be found by comparing the effective structure coordinates with the previously determined r_s coordinates. This comparison can be made in Table IV, where column 3 contains the effective coordinates. Clearly, the agreement is quite satisfactory in all cases.

Excited Vibrational States. The observed spectrum shows only one other set of relatively intense transitions. Assignment of a total of 26 of these lines leads to the following rotational constants for the normal isotopic species: A = 12 249.98 ± 0.012, B = 3441.74 ± 0.01, C = 2949.85 ± 0.01 MHz. Relative intensity measurements show this species to lie 180 ± 20 cm^{-1} above the ground state. The latter result suggests this is the v = 1 state of the C–C torsion, which occurs at 210 cm^{-1}

in ethylene glycol,[12] ca. 140 cm^{-1} in aminoethanol,[8] and is predicted to be at about 100 cm^{-1} in ethanedithiol.[9]

Evidence that this spectrum does not arise from a second distinct rotational isomer comes from our assignment of the -OD isotopic species, whose rotational constants are: A = 11714.38, B = 3420.44, and C = 2902.72 MHz. With these data, the hydrogen r_s coordinates are computed to be $|a|$ = 0.946, $|b|$ = 1.380, and $|c|$ = 0.101 Å, which differ little from those of the hydroxyl in Table IV, and are indeed qualitatively reasonable for the v = 1 state of the C–C torsion. We have also predicted the v = 1 rotational constants of the normal species by assuming that this state is represented by the v = 0 structure except for the C–C torsional angle, which is increased by 2°. These predictions yield A = 12 248.83, B = 3432.83, and C = 2952.00 MHz, in reasonable agreement with the observed values. The entire collection of data provides strong evidence that the assigned satellites arise from the v = 1 state of the C–C torsion.

In addition we have observed, but not assigned, several weaker satellites having intensities 5–10 times less than the ground state. These satellites lie very near to the v = 0 lines, and consequently they cannot be produced by other rotameric species. They most likely arise from the other torsional and heavy-atom angle deformation modes.

Discussion

The experimental data show unambiguously that the observed molecular conformation of mercaptoethanol is the GGG form shown in Figure 1. Note that the dihedral angles of Table V place each of the torsional minima near the expected staggered positions appropriate for the dominant threefold potential function of tetrahedral carbon. For the heavy-atom dihedral angle, ∠(SCC)–(CCO), the present result can be compared to that for aminoethanol,[8] 55.4 ± 2°, and chloroethanol,[6] 63.2 ± 0.6°. The remaining heavy-atom bond distances and angles require no special consideration, other than to note that they are very similar to the corresponding values in ethanol[25] and ethanethiol.[23]

With regard to the light atoms, i.e., the hydroxyl and thiol hydrogens, it is clear that the geometrical features have some particularly interesting characteristics. The first of these is the fact that the molecule does not adopt a TGT conformation, which might be expected to be the most stable one from the point of view of steric interactions. In particular, the hydroxyl hydrogen finds itself in a gauche position lying 2.565 Å away from the sulfur atom, a value considerably shorter than the sum of the van der Waals radii, 3.05 Å.[26] In addition, the O–H bond length is appreciably longer than the value in methanol (0.945 Å)[27] or ethanol (0.971 Å).[25] Providing further evidence of an unusual hydroxyl group is the bond angle, ∠COH (104.4°), which is significantly smaller than the value in methanol (108.5°).[27] On the other hand, the thiol parameters are essentially normal, e.g., the S–H distances in methanethiol[20] and ethanethiol[23] are 1.335 and 1.322 Å, respectively.

All of these structural facts point toward an intramolecular OH⋯S hydrogen bond as the stabilizing influence favoring the experimental conformation. This nonlinear hydrogen bond is, in fact, very similar geometrically to those observed in aminoethanol[8] and chloroethanol.[6] For example, the O–H bond lengths in these molecules are 1.14 and 1.008 Å, respectively, the former value showing an especially strong hydrogen bond interaction. In addition, for these same two molecules, the OH⋯X distance is appreciably less than the van der Waals distance, the shortening being nearly 0.6 Å for aminoethanol[8] and 0.4 Å for chloroethanol.[6]

Evidence for the involvement of sulfur in hydrogen bonding has been available for some years,[15,28,29] although quantitative evidence for OH⋯S or SH⋯O bonding is relatively slim. Sri-

nivasan and Chacko[28] reviewed meager crystallographic evidence and found several likely cases of OH···S bonding, although the hydrogens were not located. In these intermolecular cases, the O···S distances were in the range 3.2–3.4 Å, similar to the intramolecular value obtained in the present study (3.148 Å). Typical of infrared studies has been that of David and Hallam,[29] who suggested that both OH···S and SH···O bonded species existed in solutions of o-hydroxythiophenol, indicating that the SH group may act as either a donor or acceptor. Gas-phase evidence for intramolecular hydrogen bonding involving sulfur seems to be nonexistent. In particular, a structural study of ethanedithiol in the gas phase[11] provided no evidence for SH···S hydrogen bonding in this analogue of mercaptoethanol. As mentioned previously, the liquid-phase infrared studies of mercaptoethanol[14] provided very little detailed evidence concerning geometry (except for the heavy atoms), and no evidence for hydrogen bonding was presented by the authors of this work.

Our study provides no evidence for a conformation of mercaptoethanol involving an SH···O hydrogen bond, which would be obtained by rotating each functional group by about 180°. Such a species would have a microwave spectrum similar to, but easily distinguishable from, the observed spectrum. We estimate that such a rotamer is less stable by at least 800 cal/mol, since otherwise we should have detected its microwave spectrum.

Snyder et al.[30] have recently assessed the strengths of OH···O, OH···S, SH···O, and SH···S intramolecular hydrogen bonds using an empirical potential function. Their results indicate that the bond strengths are in the approximate order OH···O ∼ OH···S > SH···O ∼ SH···S. Our failure to observe an SH···O species, the nonexistence of an observable SH···S interaction in ethanedithiol,[9] and the observed OH···O interaction[12] in ethylene glycol are thus consistent with the work of Snyder.[30] More recently Dietrich[31] et al. have performed ab initio studies of such hydrogen bond systems, but the results were not definitive.

As previously mentioned, published infrared data[14] suggest that a trans conformation should be 600 cal/mol more stable than the gauche form observed in this study. Our failure to observe such a species might be caused by its low dipole moment. For a TTT conformation (as found for ethanedithiol[11]), we have predicted the dipole moment components using the model described in a previous section. This calculation yields $|\mu_a| = 0.43$, $|\mu_b| = 0.38$, and $|\mu_c| = 0$. On this basis, the dominant a-type spectrum of the trans species should be ca. 1.3 times more intense than the a-type lines of the gauche species. These latter lines were observed, although they were often difficult to find among the intense Q-branch spectrum.

Nevertheless, it seems that the trans species would have been observed if it were as stable as indicated by the infrared work. This suggests a possible misidentification of the infrared bands used in the relative energy determination.[14]

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