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MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF gauche-ETHANETHIOL

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Microwave spectra of gauche-ethanethiol were studied in relation to its molecular structure. The r_s structure of this molecule could be determined and was compared with that of trans isomer. Discussions were made on the angles around the carbon atom of the CH_2 group in the molecule.

In a previous paper,1) we reported the microwave spectra and molecular structure of trans-ethanethiol. Furthermore, we also added a rough description of the observed microwave spectra of gauche-ethanethiol. Recently, an independent study of the microwave spectra of gauche-ethanethiol and its four deuterated species has been published by Schmidt and Quade,3) who gave the analysis of internal rotation of the SH group based on an assumed molecular structure. We were working on the same subjects for gauche-ethanethiol as theirs. Though a part of the experimental data was already published,2) the publication of our detailed experimental results was deliberately delayed in order to determine a reliable molecular structure for the gauche isomer as well as that for the trans isomer.

Microwave spectra of a- and c-types were measured for the normal and nine isotopically substituted species of the gauche isomer which are listed in Table 1. In the table, s- and a- (e.g. s-CH_2DCH_2SH) indicate the species where the D atoms are situated in the CCS plane and out of the CCS plane, respectively, and -2 and -1 (e.g. a-CH_2DCH_2SH-2) indicate the species where the D atoms are situated at the same side and at the opposite side of the CCS plane to the H atom in the SH group, respectively.

For gauche-ethanethiol, the tunneling effect between two gauche minima in the internal rotation potential function of the SH group produces two different energy states which are hereafter referred to as the + and - states. Then, the observed spectra for some of the species exhibit doublet structure. For the normal, ^{13}C, ^{34}S and s-CH_2DCH_2SH species (hereafter referred to as Group I), the observed c-type spectra were doublets with the spacing of about 3500 MHz, the a-type spectra with $K_{-1} = 1$ were doublets with the spacing of several MHz and the a-type spectra with $K_{-1} \neq 1$ were singlets. For CH_3CH_2SD species (Group II), the c-type spectra were doublets with the spacing of about 140 MHz, while all the a-type spectra were singlets. For the species where the isotopic substitution is made for the atoms situated out of the CCS plane (Group III), all the spectra were singlets.

In order to analyze the observed spectra of the species belonging to Group I and II, we had to consider the following effective Hamiltonians which were obtained as the matrix elements of the torsional + and - states;$^{3)}$

$$<+|H|+> = A_+P_z^2 + B_+P_y^2 + C_+P_x^2, \tag{1}$$

$$<-|H|-> = A_-P_z^2 + B_-P_y^2 + C_-P_x^2 + \Delta\nu, \tag{2}$$

$$<+|H|-> = D(P_xP_y + P_yP_x) + E(P_xP_z + P_zP_x) + MP_y + QP_z, \tag{3}$$

where $\Delta\nu$ denotes pure torsional energy difference between + and - states. Since observed a-type transitions exhibited no splittings except $K_{-1} = 1$ transitions, we took account of only $D(P_xP_y + P_yP_x)$ and QP_z terms in Eq. (3). These two terms perturb mainly the $K_{-1} = 1$ levels because of the accidental degeneracies between these levels of the + and - states, whereas other terms in Eq. (3) affect the

Table 1. Observed Rotational Constants of gauche-Ethanethiol$^{a)}$ (in MHz)

Species	A	B	C	$D_J \times 10^{3\,b)}$	$\Delta\nu^{c)}$	$D^{d)}$
CH_3CH_2SH	28747.09(50)	5294.78(12)	4846.18(12)	—	1753.84(29)	12.43(37)
CH_3CH_2SD	26063.97(21)	5190.04(5)	4768.64(5)	—	70.33(14)	—
$CH_3CH_2{}^{34}SH$	28709.50(62)	5175.20(15)	4744.98(15)	—	1730.53(35)	12.07(46)
$^{13}CH_3CH_2SH$	28540.59(36)	5136.85(9)	4708.01(9)	—	1742.79(21)	11.93(28)
$CH_3{}^{13}CH_2SH$	28086.43(36)	5276.21(9)	4811.70(9)	—	1723.91(21)	13.32(24)
s-CH_2DCH_2SH	28704.62(38)	4925.35(9)	4534.49(9)	—	1789.73(23)	10.76(27)
a-CH_2DCH_2SH-1	26169.06(72)	5107.21(13)	4680.65(14)	3.7(65)	—	—
a-CH_2DCH_2SH-2	26208.79(48)	5112.49(9)	4666.76(10)	3.0(43)	—	—
CH_3CHDSH-1	25313.90(54)	5245.62(8)	4742.81(9)	3.6(60)	—	—
CH_3CHDSH-2	25243.72(60)	5229.55(9)	4749.93(10)	4.8(68)	—	—

a) Figures in parentheses indicate the uncertainty attached to the last significant figures calculated from 2.5 times the standard deviations.

b) 10^3 times the coefficient of the $[J(J+1)]^2$ term in the centrifugal distortion formula in MHz.

c) Energy difference between the + and - states.

d) Coefficient of $(P_xP_y + P_yP_x)$ term in Eq. (3).

levels which are far from degenerate. However, as the D and Q can not be determined independently, a least squares analysis was carried out using $A\pm$, $B\pm$, $C\pm$, $\Delta\nu$, and D as parameters. The centrifugal distortion effects were neglected in the calculation. It was found that the rotational constants of the + and - states were essentially equal within the experimental error limits. Since the procedure of the analysis of the internal rotation was rather complicated, the details will be published elsewhere.

For the species belonging to Group III, the rotational constants were determined by a least squares analysis from all the observed frequencies so as to fit in with a modified rigid rotor expression which included only the $D_J[J(J+1)]^2$ term of the centrifugal distortion formula. The rotational constants are listed in Table 1. The rotational constants for the normal and s-CH_2DCH_2SH have slight discrepancies between ours and Sehmidt's, because we neglected $E(P_xP_z + P_zP_x)$ term. The parameter E can not be determined by the observed frequencies, because this term perturbs the levels in only small amounts.

Table 2. Structural Parameters[a)]

group		gauche	trans[b)]
CSH	r(SH)Å	1.336(0.010)	1.322(0.006)
	r(SC)Å	1.814(0.009)	1.820(0.005)
	α(HSC)	96° (34')	96°13'(23')
CCH₂S	r(CH)Å	1.089(0.005)	1.090(0.003)
	α(CCS)	113°37'(29')	108°34'(19')
	α(HCH)	106°35'(36')	108°54'(22')
	α(HCC)	110°42'(43')	110°14'(33')
	α(H^1CC)	111°19'(42')	
	α(H^1CS)	104°53'(57')	109°26'(30')
	α(H^2CS)	109°16'(56')	
CH₃C	r(CH_s)Å	1.091(0.007)	1.095(0.006)
	r(CH_a)Å		1.092(0.005)
	α(CCH_s)	110°30'(40')	109°40'(34')
	α(CCH_a)	110°37'(38')	110°35'(29')
	α(H_sCH_a)	109° 2'(60')	108°35'(49')
	α(H_aCH_a)	106°55'(43')	108° 7'(33')
Dihedral	τ(CCSH)	61°45'(58')	180°

$r(CH^1)=r(CH^2)$ for CH_2; $r(CH_a^1)=r(CH_a^2)=r(CH_s)$
$\alpha(CCH_a^1)=\alpha(CCH_a^2)$, $\alpha(H_sCH_a^1)=\alpha(H_sCH_a^2)$ for CH_3.

a) Figures in parentheses indicate 99 % reliability intervals.

b) Quoted from reference 1).

The atom coordinates were obtained by solving the Kraitchman equations from the moments of inertia calculated from the observed rotational constants. For the gauche isomer, as four x_c coordinates of the atoms in the CCS plane and x_b coordinate of H_s atom have small values, the solutions of the Kraitchman equations are not reliable. Then, these coordinates were obtained from the other reliable coordinates by three assumptions. (1) x_c coordinates of C atoms in the CH_2 and CH_3 groups were obtained by assuming $r(CH^1) = r(CH^2)$ and $r(CH_a^1) = r(CH_a^2)$, respectively. (2) x_b and x_c coordinates of H_s atom in the CH_3 group were obtained by assuming

$r(CH_s) = r(CH_a)$ and $r(H_sH_a^1) = r(H_sH_a^2)$. (3) x_c coordinate of S atom was obtained by the use of the first moment equation.

From the atom coordinates obtained the structural parameters were calculated and are listed in Table 2 as well as those for the trans isomer reported.

As is found from Table 2, the structural parameters of the CSH and CH_3C parts of the gauche isomer are essentially equal to those of the trans isomer.

Significant discrepancies are found in the six angles around the carbon atom in the CH_2 group. If we assume that (1) the CH_2 group is tilted by $\delta°$ towards lone pair electrons on the S atom, (2) dihedral angle $\tau(CCSH)$ is 60° ($\tau = 0°$ for the cis form) for the gauche isomer and (3) $\alpha(CCH)$ and $\alpha(HCH)$ remain unchanged between the trans and gauche isomers, the following relations can be derived;

$$\alpha(CCS)\text{trans} = \beta - \delta, \qquad \alpha(HCS)\text{trans} = \gamma + 0.6\delta$$

$$\alpha(CCS)\text{gauche} = \beta + 0.4\delta, \quad \alpha(H^1CS)\text{gauche} = \gamma - \delta, \quad \alpha(H^2CS)\text{gauche} = \gamma + 0.6\delta$$

where β and γ are the hypothetical $\alpha(CCS)$ and $\alpha(HCS)$, respectively, which are constants irrespective of the dihedral angle values and $\alpha(HCH)$ is taken as 107°45' (the average of the $\alpha(HCH)$ values obtained for the trans and gauche isomers). The observed parameters for the trans and gauche isomers can be satisfactorily explained by these relations. From the observed parameter values, β, γ and the tilt angle δ are calculated as 112°10', 107°50' and 3°36', respectively. It is interesting that the hypothetical $\alpha(CCS)$ (= β) is close to $\alpha(CCC)$ in propane (112°24')$^{4)}$ and the tilt angle (= δ) is a little larger than those of the CH_3 groups in methanethiol$^{5)}$ and dimethyl sulfide$^{6)}$; (2°30'). The tilt of the CH_2 group indicates that the internal rotation axis of the SH group is not coincided with the CS bond but a line from the C atom in the CH_2 group to the SH group making an angle of 3°36' with the CS bond.

We are working on the analysis of the SH internal rotation splittings taking the present structural results into our considerations and on the spectra in the excited CH_3 torsional states for the trans and gauche isomers.

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