Microwave Spectrum, Structure and Dipole Moment of Ethanethiol. I. *Trans* Isomer

Michiro HAYASHI, Hisae IMAISHI, and Kazunori KUWADA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-sendamachi, Hiroshima 730

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The microwave spectra of *trans*-ethanethiol and its isotopic species were measured. The r_s structure of the *trans* isomer was determined from the observed moments of inertia. The *trans* isomer has a symmetrical CH_3 group, the parameters for the CH_2SH part of the molecule being approximately equal to those of methanethiol. The C-C bond length, found to be 1.529 ± 0.006 Å, is close to that of propane. The angle α(CCS), obtained as $108°34' \pm 19'$, is much smaller than that of analogous molecules. Discussion is given for this anomalously small α(CCS) angle. From the Stark shifts, the dipole moment of the *trans* isomer was determined to be $\mu_a=1.058\pm0.023$, $\mu_b=1.146\pm0.002$ and $\mu_{total}=1.560\pm0.032$ D, an angle of $28°46'$ being made with the bisector of the α(CSH) angle inclining towards the ethyl group. Since the dipole moment of methanethiol makes an angle of $18°30'$ with the bisector of the α(CSH) angle, the increase of the angle with the bisector for ethanethiol was concluded to arise from the induction moment of the ethyl group. A brief description is given for the spectra due to the *gauche* isomer.

From an interest in the internal rotation of completely asymmetric molecules, we investigated the microwave spectra of ethanethiol. The rotational spectra of ethanethiol might be influenced by two modes of internal rotation, one relating to the CH_3 group and the other to the SH group. If the barrier to the internal rotation of the SH group is sufficiently high, the rotational isomers can be observed. Actually we could observe two groups of strong spectra belonging to the ground states of the *trans* and *gauche* isomers, as well as several groups of weak spectra belonging to the vibrationally excited states.

Kadzhar, Abbasov, and Imanov[1] reported on the microwave spectra of two isotopic species of *trans*-ethanethiol. Schmidt and Quade[2] studied the normal species of *trans*-ethanethiol.

A part of our studies on the microwave spectra of ethanethiol, was reported[3] but publication of details was postponed until the spectra of a sufficient number of isotopic species necessary for determining the r_s structure of *trans*-ethanethiol were obtained.

As regards the *gauche* isomer, several strong spectra with Stark effects characteristic of the *a*-type *R* brnach transitions were observed for the normal and seven deuterated species. For the normal and CH_3CD_2SH species, the transitions of types $(J+1)_{1J+1}\leftarrow J_{1J}$ and $(J+1)_{1J}\leftarrow J_{1J-1}$ exhibited doublet structures with several MHz spacings, each component of the doublet having identical Stark shifts. The transitions of types $(J+1)_{0J+1}\leftarrow J_{0J}$, $(J+1)_{2J}\leftarrow J_{2J-1}$ and $(J+1)_{2J-1}\leftarrow J_{2J-2}$ were observed as singlets. For the CH_3CH_2SD and two of the CH_3CHDSH species, all the *a*-type transitions were observed as singlets.

For the CH_2DCH_2SH species, there are two different molecular forms expected for the *trans* isomer, (designated as *s*-CH_2DCH_2SH and *a*-CH_2DCH_2SH species, where "*s*-" and "*a*-" refer to the symmetric and asymmetric forms, respectively, with respect to the molecular plane). There are three different molecular forms expected for the *gauche* isomer, one of which corresponds to the *s*-CH_2DCH_2SH species for the *trans* isomer and the other two to the *a*-CH_2DCH_2SH species.

For these three CH_2DCH_2SH species for the *gauche* isomer, similar doublet structures were observed for the species corresponding to the *s*-CH_2DCH_2SH species of the *trans* isomer, while only singlets were observed for the other two species corresponding to the *a*-CH_2DCH_2SH species of the *trans* isomer.

The splittings of the transitions vanish for the CH_3CH_2SD species whose reduced moment of inertia around the internal rotation axis of the SH group increases, and only the singlets were observed for the species expected to have non-equivalent *gauche* minima of the internal rotation potential. Thus these spectra can be confirmed to belong to the *gauche* isomer and the doublet structures can be considered to arise from the tunnelling effect through the barrier between two *gauche* minima.

For the four species having non-equivalent *gauche* minima, the *c*-type *Q* and *R* branch transitions could also be assigned.

For the other four species, the rotational constant *A* cannot be obtained from the *a*-type transition frequencies alone since the *gauche* isomer is still a nearly symmetric top molecule. Splittings of the transitions prevent an accurate determination of the *B* and *C* rotational constants unless a theoretical analysis of the internal rotation is carried out.

In the present paper, we deal with the r_s structure and the dipole moment of the *trans* isomer alone.

Experimental

Commercial normal species of ethanethiol was purified by gas chromatography. CH_3CH_2SD was prepared from sodium ethanethiolate and D_2O.[4] CH_2DCH_2SH, CH_3CHDSH and CH_3CD_2SH were prepared from the corresponding S-ethyl thiuronium bromides prepared from CH_2DCH_2Br, CH_3CHDBr and CH_3CD_2Br, respectively, with thiourea.[5]

The spectra of ^{34}S and ^{13}C species were measured with a sample of ethanethiol containing these species in natural isotopic abundance.

Measurements were carried out in the frequency region 8.4—34 GHz with conventional Stark modulation spectrometers with 100 kHz square- and sine-wave modulation. The $2_{12}\leftarrow 1_{01}$ transition appearing around 42500 MHz was also measured for four of the isotopic species. Measurements were usually made on an oscilloscope at dry ice temperature, a strip-chart recorder being used for the measurements for ^{34}S and ^{13}C species.

Rotational Spectra of the *Trans* Isomer

Spectra belonging to the *trans* isomer of ethanethiol were observed as singlets, indicating that the barrier to the internal rotation of the CH_3 group is relatively high. Both *a*- and *b*-type transitions could be easily assigned, for the normal and deuterated species (Table 1). For ^{34}S and two ^{13}C species, most of the *a*-type transitions were obscured under strong spectra of the normal species since the measurements were made in natural abundance. In order to ascertain the present assignments, the measurements were extended to the $2_{12}\leftarrow 1_{01}$ transitions around 42500 MHz which exhibited characteristic Stark patterns.

As the influence of the centrifugal distortion seems to be small, the rotational constants were determined by a least-squares analysis from all the observed frequencies (Table 1) so as to fit a modified rigid rotor expression which includes only the $D_J[J(J+1)]^2$ term of the centrifugal distortion formula. The rotational constants and the moments of inertia are shown in Tables 2 and 3, respectively.

The quantities ΔP_c shown in the table are quite reasonable for all the isotopic species,[6] confirming the present assignments of transitions.

Table 1. Observed frequencies in the ground state of *trans*-ethanethiol (MHz)

Transition	CH_3CH_2SH	CH_3CH_2-^{34}SH	CH_3-$^{13}CH_2SH$	$^{13}CH_3$-CH_2SH	CH_3CH_2SD	CH_3-$CHDSH$	CH_3-CD_2SH	*s*-CH_2D-CH_2SH[b)]	*a*-CH_2D-CH_2SH[c)]
$1_{10}\leftarrow 1_{01}$	23534.74	23544.86	22861.60	23466.05	22453.49	20171.84	17584.02	23816.87	21199.14
$2_{11}\leftarrow 2_{02}$	24150.41	24137.90	23496.00	24053.03	23067.61	20829.78	18253.62	24350.76	21791.18
$3_{12}\leftarrow 3_{03}$	25096.12	25047.69	24471.04	24953.56	24011.40	21845.33	19292.47	25167.95	22701.27
$4_{13}\leftarrow 4_{04}$	26397.46	26297.96	25815.45	26191.11	25312.11	23252.52	20740.42	26287.76	23955.89
$5_{14}\leftarrow 5_{05}$	28088.18	27921.00	27565.62	27796.69	27004.85	25095.70	22648.45	27735.72	25590.01
$6_{15}\leftarrow 6_{06}$	30208.45	29953.36	29766.28	29807.28	29130.76	27425.63	25074.03	29542.17	27643.49
$7_{16}\leftarrow 7_{07}$	32802.59	32437.20	32463.40	32263.60	31735.72	30296.20	28076.27	31741.71	30161.06
$1_{11}\leftarrow 0_{00}$	33298.74	33115.06	32550.94	— a)	31858.44	29728.53	26966.74	32958.10	30628.27
$2_{12}\leftarrow 1_{01}$	43062.09	42685.31	42240.57	42450.99					
$3_{03}\leftarrow 2_{12}$	8716.32	— a)	9248.88	— a)	— a)	11630.19	13728.20	— a)	9924.98
$4_{04}\leftarrow 3_{13}$	19878.92	18942.05	20371.70	18668.50	19503.83	22645.46	24566.49	16555.95	20689.26
$5_{05}\leftarrow 4_{14}$	31242.40	30060.79	— a)	29694.05	30493.81	33849.30		27114.14	31639.84
$1_{01}\leftarrow 0_{00}$	10367.48	— a)			10006.44	10198.73	10034.57	— a)	10008.63
$2_{02}\leftarrow 1_{01}$	20723.42	— a)			20001.77	20381.77	20049.57	19322.66	— a)
$2_{12}\leftarrow 1_{11}$	20131.34	19722.17			19412.65	19755.19	19416.73	18806.19	19437.49
$2_{11}\leftarrow 1_{10}$	21339.12	20885.84			20615.56	21039.41	20719.07	19856.42	20596.43
$3_{03}\leftarrow 2_{02}$	31055.56	— a)			29971.81	30028.39	30028.39	28962.11	29977.35
$3_{13}\leftarrow 2_{12}$	30189.56	— a)			29110.76	29623.06	29113.60	28204.22	29148.58
$3_{12}\leftarrow 2_{11}$	32001.21	— a)			30915.50	31549.32	31067.12	29779.28	30887.08
$3_{22}\leftarrow 2_{21}$	31102.95	— a)			30021.34	30596.20	30102.07	— a)	30025.63
$3_{21}\leftarrow 2_{20}$	31149.49	30499.87			30069.63	30658.32	30175.39	29032.42	30073.57

a) Overlapped with another transition. b) "*s*-" refers to the symmetric form with respect to the molecular plane. c) "*a*-" refers to the asymmetric form with respect to the molecular plane.

Table 2. Observed rotational constants (MHz) of *trans*-ethanethiol[a)]

Species	*A*	*B*	*C*	$D_J\times 10^3$ (MHz)[b)]	R. M. S.[c)] (MHz)
CH_3CH_2SH	28416.89 (0.74)	5485.77 (0.09)	4881.92 (0.10)	−4.68 (4.09)	0.22
$CH_3CH_2{}^{34}SH$	28330.19 (0.58)	5367.00 (0.07)	4785.13 (0.07)	−5.06 (3.33)	0.21
$CH_3{}^{13}CH_2SH$	27706.34 (0.49)	5466.02 (0.06)	4844.68 (0.06)	0.29 (5.69)[d)]	0.19
$^{13}CH_3CH_2SH$	28212.58 (0.56)	5322.41 (0.05)	4746.32 (0.05)	−10.05 (3.25)[d)]	0.22
CH_3CH_2SD	27156.24 (0.90)	5304.38 (0.10)	4702.68 (0.11)	−3.52 (4.58)	0.26
CH_3CHDSH	24950.46 (0.65)	5420.40 (0.08)	4778.38 (0.08)	−4.26 (3.40)	0.19
CH_3CD_2SH	22275.58 (0.81)	5342.61 (0.09)	4691.45 (0.09)	−2.56 (6.73)	0.23
s-CH_2DCH_2SH	28387.68 (0.78)	5095.38 (0.09)	4570.42 (0.10)	−3.13 (4.05)	0.24
a-CH_2DCH_2SH	25914.08 (0.88)	5294.10 (0.10)	4714.56 (0.10)	−5.52 (4.60)	0.26

a) Figures in parentheses indicate the uncertainty calculated from 2.5 times the standard deviations. b) Coefficient of the $[J(J+1)]^2$ term of centrifugal distortion contributions. c) Indicates root mean square deviation between the calculated and observed transition frequencies by use of solved rotational constants. d) The D_J value could not be determined satisfactorily for lack of a sufficient number of observed frequencies.

TABLE 3. OBSERVED MOMENTS OF INERTIA (amu·Å^2) OF *trans*-ETHANETHIOL[a)]

Species	I_a	$\delta^{b)}$	I_b	$\delta^{b)}$	I_c	$\delta^{b)}$	$P_c^{c)}$	ΔP_c
CH_3CH_2SH	17.78435(46)	0.07726	92.12490(156)	0.44172	103.52003(201)	0.45573	3.19461(129)	——
$CH_3CH_2{}^{34}SH$	17.83878(36)	0.07732	94.16352(128)	0.44531	105.61381(163)	0.46011	3.19425(105)	−0.00036(167)
$CH_3{}^{13}CH_2SH$	18.24045(31)	0.07503	92.45775(108)	0.43743	104.31558(133)	0.45581	3.19131 (87)	−0.00330(156)
$^{13}CH_3CH_2SH$	17.91315(35)	0.07626	94.95247 (94)	0.43834	106.47744(116)	0.45239	3.19409 (77)	−0.00052(150)
CH_3CH_2SD	18.60994(61)	0.09200	95.27519(185)	0.46272	107.46555(239)	0.46112	3.20979(154)	0.01518(201)
CH_3CHDSH	20.25518(52)	0.07804	93.23585(129)	0.43843	105.76313(170)	0.45337	3.86395(110)	0.66934(170)
CH_3CD_2SH	22.68745(82)	0.07988	94.59347(162)	0.43883	107.72277(204)	0.45457	4.77907(137)	1.58446(188)
s-CH_2DCH_2SH	17.80266(48)	0.08151	99.18314(179)	0.44655	110.57552(229)	0.44375	3.20514(147)	0.01053(196)
a-CH_2DCH_2SH	19.50199(65)	0.07595	95.46016(187)	0.43988	107.19473(243)	0.45205	3.88370(157)	0.68910(203)

a) Conversion factor is 505376 MHz·amu·Å^2. Figures in parentheses indicate the uncertainty attached to the last significant figures estimated from 2.5 times the standard deviations. Only the effect of uncertainty in measured frequencies is taken into account. b) $\delta = I_{obsd} - I_{calcd}$. I_{calcd} is calculated on the basis of the structure shown in Table 4. c) $P_c = (I_a + I_b - I_c)/2$. d) $\Delta P_c = (P_c)_{isotopic} - (P_c)_{parent}$.

The r_s Structure of the *Trans* Isomer

Our data are sufficient to determine the r_s coordinates of all the atoms in the *trans* isomer by the substitution method. The *trans* isomer possesses a plane of symmetry perpendicular to the *c*-axis, so that the isotopic substitution of an atom in this plane would leave $P_c (= (I_a + I_b - I_c)/2)$ unaltered if the molecule is rigid. If such were the case, one of the three moments of inertia of the isotopic species would be calculated from the other two. Any two of the three moments of inertia would be sufficient for calculation of the x_a and x_b coordinates of the atom by the following specialized Kraitchman equation for the in-plane atom.

$$\left.\begin{aligned} |x_a| &= [(\Delta I_b/\mu)(1+\Delta I_a/(I_a^0 - I_b^0))]^{1/2} \\ |x_b| &= [(\Delta I_a/\mu)(1+\Delta I_b/(I_b^0 - I_a^0))]^{1/2} \\ |x_c| &= 0 \\ \Delta I_g &= I_g - I_g^0,\ \mu = \Delta m M/(M+\Delta m) \end{aligned}\right\} \quad (1)$$

where M is the molecular weight of the parent species, Δm is the mass increment of the substituted atom in the isotopic species and I_g^0 and I_g indicate the g-th moment of inertia for the parent and isotopic species, respectively.

However, since isotopic substitution of such an atom usually alters P_c slightly, the computed coordinates will depend on which pair of moments is used, or whether all three moments are used in the Kraitchman equation.

In order to check the dependence of the computed coordinates on the choice of the moments, the following five different cases were compared. a) All the three moments were used equally in the following general Kraitchman equation.

$$\left.\begin{aligned} |x_a| &= [(\Delta P_a/\mu)(1+\Delta P_b/(I_a^0 - I_b^0))(1+\Delta P_c/(I_a^0 - I_c^0))]^{1/2} \\ |x_b| &= [(\Delta P_b/\mu)(1+\Delta P_c/(I_b^0 - I_c^0))(1+\Delta P_a/(I_b^0 - I_a^0))]^{1/2} \\ |x_c| &= [(\Delta P_c/\mu)(1+\Delta P_a/(I_c^0 - I_a^0))(1+\Delta P_b/(I_c^0 - I_b^0))]^{1/2} \\ P_a &= (-I_a + I_b + I_c)/2,\ P_b = (I_a - I_b + I_c)/2 \\ P_c &= (I_a + I_b - I_c)/2,\ \Delta P_g = P_g - P_g^0,\ g = \text{a, b and c} \end{aligned}\right\} \quad (2)$$

where P_g^0 and P_g indicate the quantities P_g for the parent and isotopic species, respectively. In this case the x_c coordinate, which should be zero from the symmetry, can also be calculated if $\Delta P_c > 0$, but will be disregarded. b) All the three moments were used but ΔP_c was set to zero. c) ΔI_a and ΔI_b were used in the specialized Kraitchman equation (1). d) ΔI_c and ΔI_b were used assuming $\Delta P_c = 0$. e) ΔI_a and ΔI_c were used assuming $\Delta P_c = 0$.

The coordinates calculated in the five cases were in good agreement with each other for the two C atoms and the S atom within estimated uncertainty of the observed moments of inertia. Therefore, the averages of the five values were used for the r_s coordinates of these atoms.

However, the difference in the coordinate values for the five cases was found to exceed the estimated experimental uncertainty for the hydrogen atom in the SH group and for the in-plane hydrogen atom (H_s) in the CH_3 group. Since $\Delta P_c > 0$, the apparent x_c coordinates in case a) can be calculated for these atoms. They are 0.130 and 0.107 Å, respectively, and indicate the serious influence of the zero point energy contribution to the coordinates of these atoms.

Since the x_b coordinate of H_s is small, the serious influence of the zero point energy is not surprising and makes it impossible to calculate from the expreimental data for this coordinate. Then, this coordinate is considered to be better determined from other coordinates by the use of some special assumptions such as the first moment equation and so on.

However, even for the x_a coordinate of H_s and the x_a and x_b coordinates of the hydrogen atom in the SH group which are not so small and for which the solutions of the Kraitchman equation can be regarded to be reliable, the half differences between the largest and smallest values of the coordinates for the five cases $(|x_{max}| - |x_{min}|)/2$ are calculated to be 0.00219, 0.00447 and 0.00565 Å, respectively, while the uncertainties are 0.00114, 0.00174 and 0.00324 Å, respectively. The structural parameters such as r(SH), α(CSH), $r(CH_s)$, $\alpha(CCH_s)$ and $\alpha(H_aCH_s)$, which are related to these coordinates will then strongly depend on the choice of the moments of inertia.

The same situation was reported for ethyl choride[7)] by Schwendeman and Jacobs, and for propane[8)] by Lide. Taking the above into account, case a) was used for the r_s coordinate of the hydrogen atom in

Table 4. Atom coordinates (Å)[a)] and the structural parameters of *trans*-ethanethiol

Atom	x_a	x_b	x_c
H (SH)	1.76920 (142)	0.92278 (287)	0.0
S	1.02635 (128)	−0.17049 (715)	0.0
C (CH_2)	−0.58101 (412)	0.68306 (319)	0.0
C (CH_3)	−1.69064 (137)	−0.36850 (593)	0.0
H (CH_2)	−0.65758 (274)	1.31230 (285)	±0.88703 (219)
H_s (CH_3)	−2.66712 (93)	0.12609 (1155)	0.0
H_a (CH_3)	−1.61659 (155)	−1.00514 (250)	±0.88425 (326)

Skeleton		CH_2 group		CH_3 group	
r(SH)	1.322 Å (0.006)	r(CH)	1.090 Å (0.003)	$r(CH_s)$	1.095 Å (0.006)
r(SC)	1.820 Å (0.005)	α(SCH)	109°26′ (30′)	$r(CH_a)$	1.092 Å (0.005)
r(CC)	1.529 Å (0.006)	α(HCC)	110°14′ (33′)	$\alpha(CCH_s)$	109°40′ (34′)
α(CSH)	96°13′ (23′)	α(HCH)	108°54′ (22′)	$\alpha(CCH_a)$	110°35′ (29′)
α(CCS)	108°34′ (19′)			$\alpha(H_sCH_a)$	108°53′ (49′)
				$\alpha(H_aCH_a)$	108° 7′ (33′)

a) Figures in parentheses are 99% reliability intervals attached to the last significant figures.

the SH group and the x_a coordinate of the H_s atom. The x_b coordinate of the H_s atom was then determined from the first moment equation.

As for the hydrogen in the CH_2 group, two independent sets of r_s coordinates are available from the observed moments of inertia for CH_3CHDSH and CH_3-CD_2SH species.

For the substituted atom in CH_3CD_2SH species whose coordinates satisfy relations $(x_a)_1=(x_a)_2$, $(x_b)_1=(x_b)_2$ and $(x_c)_1=-(x_c)_2$, where 1 and 2 designate the substituted atom number, the Kraitchman equation can be written as

$$\left.\begin{aligned} |x_a| &= [(\Delta P_a/\mu)(1+\Delta P_b/(I_a^0-I_b^0))]^{1/2} \\ |x_b| &= [(\Delta P_b/\mu)(1+\Delta P_a/(I_b^0-I_a^0))]^{1/2} \\ |x_c| &= [\Delta P_c/2\Delta m]^{1/2},\ \mu=2\Delta mM/(M+2\Delta m) \end{aligned}\right\} \quad (3)$$

Actually, the two sets of computed coordinates were found to be in good agreement within experimental uncertainty in spite of the expected large difference of the zero point energy contributions between the two species. The averages of the two sets of the coordinate values were then used for the r_s coordinates of this atom.

Since no other isotopic species useful for determining the coordinates of the H_a atom in the CH_3 group is available at present, the influence of the zero point energy to these coordinates cannot be evaluated from a unique solution of the general Kraitchman equation (2) alone.

Coordinates of the atoms and structural parameters are given in Table 4.

It is seen that a slightly asymmetric CH_3 structure was obtained from the above procedures though it is within the range of uncertainties for the structural parameters.

Completion of the determination of the structure of *trans*-ethanethiol is of interest since it is desirable to know to what extent the structure correlations found in the analogous molecules are applicable.

Comparison of the structural parameters of the CH_2SH part of *trans*-ethanethiol with those of methanethiol[9)] reveals that r(SC) remains unchanged between them, while those of both ethane- and methanethiol are definitely greater than that of dimethyl sulfide (1.802±0.002 Å).[10)]

r(SH) and α(CSH) of ethanethiol are essentially equal to those of methanethiol within experimental error.

A comparison of the structural parameters of the CH_2 part of the molecule with those of ethyl halides,[7,11)] propane[8)] and ethylsilane[12)] is given in Table 5.

r(CC) of ethanethiol has a value between that of ethylsilane and those of ethyl chloride and bromide, being roughly equal to that of propane.

The value 108°34′ obtained for α(SCC) of ethanethiol is abnormally small compared with the value for α(XCC) (X=Cl, Br, Si and C) of analogous molecules, for which they are always larger than tetrahedral. On the other hand, the value 108°54′ obtained for α(HCH) is smaller than tetrahedral.

The following angular constraint can be imposed on sp^3 hybrids for the present case if each hybrid is orthonormal or localized.[13)] That is, the α(HCH) angle should be larger than tetrahedral if the α(XCC) angle is smaller than tetrahedral.

This is approximately valid for CH_3CH_2X molecules except *trans*-ethanethiol (Table 5). On the other hand, though this rule is valid for the α(HCC) and α(HCX) angles of all the molecules listed, the α(HCX) angle of *trans*-ethanethiol is the largest, except that of propane for which these two angles should be equal for the sake of symmetry.

This anomalous feature found in *trans*-ethanethiol can be easily explained if the ethyl group is tilted in the molecular plane towards the lone pair electrons of the S atom.

When the tilt angle is assumed to be equal to that of methanethiol and of dimethyl sulfide (2°30′), the α(CCS) and α(HCS) angles of ethanethiol are considered to contain contributions in amounts of −2°30′ and +1°15′ respectively. In order to compare these angles with those of other molecules having the non-tilted ethyl group, the corrected angle values should be used.

TABLE 5. COMPARISON OF THE STRUCTURAL PARAMETERS OF *trans*-ETHANETHIOL WITH THOSE OF SIMILAR MOLECULES[a)]

	CH_3CH_2SH	CH_3SH	CH_3CH_2Cl	CH_3CH_2Br	$CH_3CH_2CH_3$	$CH_3CH_2SiH_3$
CSH						
r(SH) (Å)	1.322(0.006)	1.332(0.010)				
r(SC) (Å)	1.820(0.005)	1.819(0.005)				
α(HSC)	96°13′ (23′)	96°30′ (30′)				
CCH_2X						
r(CH) (Å)	1.090(0.003)	1.092(0.010)[b)]	1.089(0.010)	1.087(0.010)	1.096(0.002)	1.097(0.002)
r(CC) (Å)	1.529(0.006)		1.520(0.003)	1.518(0.004)	1.526(0.002)	1.540(0.002)
α(CCX)	108°34′ (19′)	109°11′ [b)]	111° 2′ (8′)	111° 2′ (15′)	112°24′ (12′)	113°11′ (12′)
α(HCH)	108°54′ (22′)	109°45′ (30′)[b)]	109°12′ (30′)	109°54′ (30′)	106° 6′ (12′)	105°46′ (24′)
α(HCC)	110°14′ (33′)		111°36′ (30′)	112°15′ (30′)	109°34′[c)]	110°10′[c)]
α(HCX)	109°26′ (30′)		106°41′[c)]	105°25′ (30′)	109°34′[c)]	108°45′[c)]
CH_3C						
$r(CH_s)$ (Å)	1.095(0.006)		1.091(0.010)[d)]	1.093(0.010)[d)]	1.089(0.009)	1.093(assumed)[f)]
$r(CH_a)$ (Å)	1.092(0.005)				1.094[e)]	1.093(0.002)
$\alpha(CCH_s)$	109°40′ (34′)		110°26′[e)]	110° 4′[e)]	111°48′ (1°)	111°57′ (1°)
$\alpha(CCH_a)$	110°35′ (29′)				110°36′[e)]	111° 2′ (30′)
$\alpha(H_sCH_a)$	108°35′ (49′)		108°30′ (30′)[d)]	108°52′ (30′)[d)]	108° 6′[e)]	107°15′ (1°)
$\alpha(H_aCH_a)$	108° 7′ (33′)				107°18′[e)]	106°59′ (30′)

a) Figures in parentheses indicate 99% reliability intervals. b) Parameters for the CH_3 group, that is, $r(CH)_{ave}$, $\alpha(H_sCS)$, and $\alpha(H_aCS)$, respectively, where $\alpha(H_sCS)$ was calculated from $\alpha(H_aCS)$. c) Calculated by the present authors from the reported coordinates. d) Averaged values given by the original authors. e) The uncertainty is not described by the original authors. f) Assumed to be equal to $r(CH_a)$ by the original authors.

TABLE 6. STARK COEFFICENTS AND DIPOLE MOMENT OF *trans*-ETHANETHIOL[a)]

Transition	M	$\Delta\nu/E^2\times 10^4$ MHz/(V/cm)^2 Obsd	Calcd	Range of E (V/cm)
$1_{10}\leftarrow 1_{01}$	1	4.757(0.06)	4.873	20→ 200
$2_{11}\leftarrow 2_{01}$	1	0.578(0.01)	0.568	200→ 450
	2	1.042(0.02)	1.041	100→ 450
$1_{11}\leftarrow 0_{00}$	0	0.954(0.02)	0.894	100→ 450
$2_{12}\leftarrow 1_{01}$	0	−0.225(0.001)	−0.223	200→ 600
	1	0.041(0.001)	0.032	200→1000
$1_{01}\leftarrow 0_{00}$	0	0.645(0.007)	0.646	200→ 300
$2_{02}\leftarrow 1_{01}$	1	−0.894(0.002)	−0.073	300→ 700
$2_{12}\leftarrow 1_{11}$	0	−0.488(0.02)	−0.471	100→ 300
	1	4.044(0.05)	4.040	50→ 120
$2_{11}\leftarrow 1_{10}$	0	0.142(0.001)	0.140	400→ 700
	1	−4.420(0.5)	−4.342	50→ 120

$\mu_{total}=1.560$ D (0.032), $\mu_a=1.058$ D (0.023), $\mu_b=1.146$ D (0.022)

a) Figures in parentheses indicate the uncertainty calculated from 2.5 times the standard deviations.

They are 108°34′+2°30′=111°4′ and 109°26′−1°15′=108°11′ for α(CCS) and α(HCS), respectively, which are plausible as values expected from angles of similar molecules.

Dipole Moment

The electric dipole moment and its components for the parent species were quantitatively determined by Stark-effect measurements of eight *a*- and *b*-type rotational transitions. Two Stark components of different M values could be resolved for some of the transitions. Before and after the measurements, the electric field was calibrated using the OCS molecule as a standard.[14)] The results are given in Table 6.

Since the molecule is a slightly asymmetric top having a relatively large μ_a dipole component, some transitions used for the Stark-effect measurements exhibit fast Stark shifts due to the first-order effect. On the other hand, in the relatively higher range of applied field strength, the frequency shift $\Delta\nu$ changes linearly against the squares of the field strength E^2 within experimental error for all the transitions used, so that the fourth-order effect[15)] might not be noticeable. Analysis of the present Stark-effect measurements is possible by the usual second-order perturbation treatment with the appropriate first-order corrections,[16)] but the method by direct diagonalization of the energy matrices[17)] was used in order to make calculation with an electronic computer easier. As the J quantum number for the transitions used is at most 2, the energy matrices were truncated at J=4 after confirming that the truncation error was negligible.

The theoretical Stark coefficients are shown in Table 6 where $\Delta\nu/E^2$ is the value at the field strength 200 V/cm. Agreement is very good for both *a*- and *b*-type transitions.

The obtained dipole moments are $\mu_a=1.058\pm0.023$, $\mu_b=1.146\pm0.022$ and $\mu_{total}=1.560\pm0.032$ D.

The dipole moment of *trans*-ethanethiol determined by microwave spectroscopy can be compared with the value 1.33 D obtained by dielectric constant measurement[18)] in the gaseous state. The reported values for methanethiol by microwave spectroscopy and dielectric constant measurement are 1.532 D[9)] and 1.26 D,[19)] respectively. The values obtained by the former measurement are larger for both molecules.

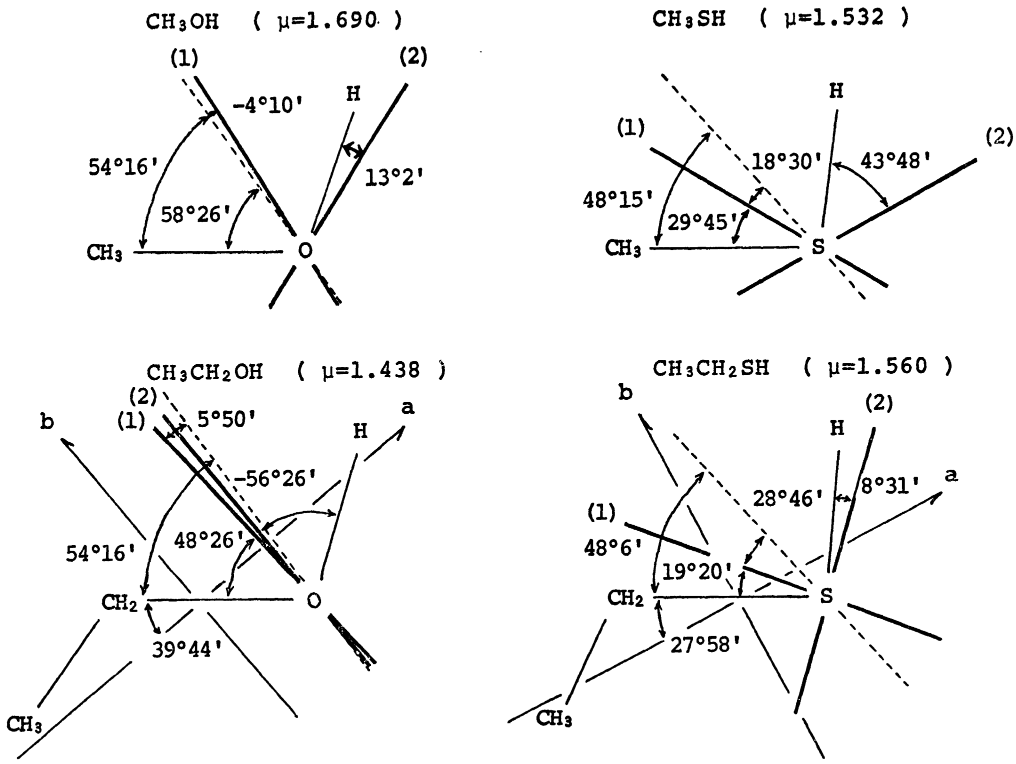

Fig. 1. Directions of the dipole moments for CH_3SH, CH_3CH_2SH, CH_3OH, and CH_3CH_2OH.
—— Direction of the dipole moment.
---- Bisector of the angle CXH, X=O, S.
←— The principal inertial axis.

From the dipole components obtained, the dipole moment of *trans*-ethanethiol is inclined by either 47°18′ or 132°42′ against the *a*-principal inertial axis (Fig. 1). Usually the direction of the dipole moment can be determined uniquely if a comparison is made between the isotopic species. However, for *trans*-ethanethiol, the rotation of the principal axes due to the isotopic substitution is estimated to be too small when compared with the experimental error limit for the available isotopic species.

In order to find the correct direction of the dipole moment, a comparison was made between methanethiol, ethanethiol, methanol[20] and ethanol.[21] The reported values of the CXH angles of these molecules are 96°30′ 96°13′, 108°32′ and 108°32′, respectively. The possible directions of the dipole moment in the molecule are designated as (1) and (2) in Fig. 1, the dotted line indicating the bisector of the CXH angle.

The CS and CO bonds are found to make angles of 27°58′ and 39°44′, respectively, with the *a*-axis for *trans*-ethanethiol and ethanol from the structure analysis. Direction (1) then makes angles of 29°45′, 19°20′, 58°26′ and 48°26′ with the CX bonds of methanethiol, ethanethiol, methanol and ethanol, respectively, which correspond to the angles 17°30′, 28°46′, −4°10′ and 5°50′ against the bisectors, respectively.

Direction (2) makes angles of 43°48′, 8°31′, 13°2′ and −56°26′ with the XH bonds, respectively. A regularity can be found for direction (1) in the angles with the CX bonds and with the bisectors of the CXH angles. No such regularity can be found for direction (2). Since both of the two possible directions for ethanol are almost parallel to the bisector of the COH angle, this strongly suggests that the correct direction of the dipole moments for this series of molecules can be regarded as (1) which is more parallel to the bisector of the CXH angle than (2).

The angle between the dipole moment and the bisector of the CXH angle increases by about 10° when the methyl group is replaced by the ethyl group for both mercaptan and alcohol. The dipole moments of the present series are considered to consist of the C–X and X–H bond moments and the moment along the bisector of the CXH angle which is produced by the long pair electrons on the atom X. The directions of these moments are considered to be from H to X for the X–H bond moment, from C to X for the C–X bond moment and from X to the outside of the CXH angle for the lone pair moment. Thus, if the lone pair moment and the X–H bond moment remain unchanged on replacement of the alkyl group, the above change in direction of the dipole moment indicates that the apparent C–X bond moment increases as the methyl group is replaced by the ethyl group. This is similar to the so-called inductive effect for the case of alkyl halides.[22]

If the X–H and lone pair moments between methane- and ethanethiol and between methanol and ethanol are assumed to be equal, the C–X bond moments of the ethyl group are calculated to be larger than those of the methyl group by about 0.36 and 0.33 D, respectively.

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