The Vibrational Assignment, Rotational Isomerism and Force Constants of 1, 2-Ethanedithiol

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Many experimental data have been accumulated concerning the rotational isomerism of 1, 2-disubstituted ethanes.[1] Still, a number of molecules have not yet been studied in detail. The present work is the first of a series of papers which will deal with a group of molecules containing sulfur atoms. In this paper, we will first consider the rotational isomerism of 1, 2-ethanedithiol, and then we will determine a set of force constants in a modified Urey-Bradley force field. These force constants will then, in the subsequent paper,[2] be transferred to the other members of the series with similar structures. Finally, they will be transferred to the calculations attempted for polyethylene disulfide, which will be reported in the near future.

Experimental

The sample used for the measurements was prepared in the following way.[3]

1, 2-Dichloroethane was refluxed over thiourea in ethanol, and the product was treated by a concentrated potassium hydroxide solution and subsequently neutralized by concentrated sulfuric acid. b. p. 70°C/48 mmHg, n_D^{20} 1.5591.

A deuterated species, $DSCH_2CH_2SD$, was prepared from 1, 2-ethanedithiol by a direct exchange of hydrogen with D_2O in the presence of a small amount of potassium carbonate. However, only 30% of the hydrogen was replaced by deuterium.

The infrared spectra in the crystalline state were recorded for the sample cooled with liquid nitrogen at about -120°C. In the gaseous state the infrared spectra were recorded at ten different temperatures in the range from 60 to 220°C.

The Assignment of the Spectra

If this substance had a unique molecular form, it would show twenty-four fundamental frequencies. However, as we observed too many spectra for one molecular form and since, especially, we found that some of the spectra vanish in the crystalline state we may conclude that rotational isomers exist. Since the mass of a SH group is nearly equal to the mass of a chlorine atom, the spectra of this substance might be close to those of 1, 2-dichloroethane, which were examined in detail.[4]

Actually, this substance gives spectra very similar to those of 1, 2-dichloroethane in the region between 1000 and 1450 cm^{-1}. For 1, 2-dichloroethane we have the trans and gauche isomers, and only the trans isomer persists in the crystalline state. For 1, 2-ethanedithiol, the similarity of the spectra and the similar behavior of the spectra upon solidification suggest that the trans and gauche isomers around the C-C bond also exist.

From the well-known assignments for 1, 2-dichloroethane, the assignments of the observed frequencies are easy in this region, where we may have two CH_2 bending vibrations, two CH_2 wagging vibrations, two CH_2 twisting vibrations and one C-C stretching vibration for one molecular form. These frequencies are easily identified at nearly the same frequencies as those for 1, 2-dichloroethane. The spectra relating to the gauche isomer vanish in the crystalline state.

The spectral pattern in the region from 1000 to 650 cm^{-1} looks very different from that of 1, 2-dichloroethane. In this region, we may have two CH_2 rocking, two CSH deformation and two C-S stretching vibrations for one molecular form. A deuterated species, $DSCH_2CH_2SD$, was measured for the purpose of the use of its spectra as an aid in the assignment of the observed spectra in this region. For this deuterated species we would expect the CSH deformation vibrations alone to be shifted strongly to the lower frequency region, where no other spectra are expected. Actually, we observed that two new bands are present at 600 and 619 cm^{-1}. If the deuteration were perfect, we could expect that the frequencies of two CSH deformation vibrations would vanish or become weaker. Since, however, the deuteration was, unfortunately, not perfect, we could not identify the CSH deformation frequencies directly.

However, a simple application of the product

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[1] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York (1954).

[2] M. Hayashi, Y. Shiro and Murata, to be published.

[3] J. Spaziale, "Organic Syntheses," Vol. XXX, 35 (1950).

[4] For example, I. Nakagawa and S. Mizushima. *J. Chem. Phys.*, **21**, 2195 (1953).

rules reveals that 800 and 890 cm^{-1} should be the CSH deformation vibrations corresponding to the CSD deformation vibrations at 600 and 619 cm^{-1}; as 800 cm^{-1} disappears in the crystalline state, it is assigned to the gauche isomer.

We assigned the bands at 718 and 699 cm^{-1} for the trans and those at 664 and 639 cm^{-1} for the gauche to the C–S stretching vibrations on the basis of the assignments given to such similar molecules as methyl mercaptan, dimethyl sulfide and ethyl methyl sulfide.[5]

There remain three unassigned observed frequencies (972, 942 and 769 cm^{-1}) in this region; all three disappear in the crystalline state, and 974 cm^{-1} is observed only in the Raman spectra. Some of these frequencies are regarded as the CH_2 rocking vibrations on the basis of the assignments given to ethyl methyl sulfide,[6] diethyl sulfide,[7] and β-chloroethyl methyl sulfide.[8]

Since the bands at 972, 942 and 796 cm^{-1} vanish in the crystalline state, they are not for the trans isomer. There are no unassigned spectra persisting in the crystalline state, and we regarded the band at 718 cm^{-1} as two overlapping frequencies, one for a C–S stretching vibration and the other for a CH_2 rocking vibration for the trans isomer. This is a reasonable choice from the selection rule of the trans isomer, as we will discuss in the following section. The other CH_2 rocking vibration is assigned to 1030 cm^{-1}. For the gauche isomer we have three possibilities: (A) 972 and 769 cm^{-1}; (B) 972 and 942 cm^{-1} and (C) 942 and 769 cm^{-1}. The band at 942 cm^{-1} is much weaker than that at 972 cm^{-1} and appears as a shoulder of 972 cm^{-1}; if we take the pair C as the CH_2 rocking vibrations, the strong band at 972 cm^{-1} remains unassigned. We compared the spectra with those of β-thiamethyl ethyl mercaptan[2]

TABLE I. INFRARED AND RAMAN SPECTRA OF 1,2-ETHANEDITHIOL (cm^{-1})

$HSCH_2CH_2SH$ Infrared			$DSCH_2CH_2SD$		Molecular[a] form	Assignment
Gas	Liquid	Solid	Raman Liquid	Infrared Liquid		
			255 w		T	C–S torsion
			267 s		G	CCS def. A
			299 w		T	CCS def. A$_g$
	400 w		403 w		G	CCS def. B
	641 m		639 m	641 m	G	C–S str. A
	662 sh		664 m	699 m	G	C–S str. B
696 s	699 s	686 vs		699 m	T	C–S str. B$_u$
710 sh	718 sh	715 s 720 s	720 s	721 s	T	CH_2 rock. A$_u$, C–S str. A$_g$
768 w	769 w		774 m	771 m	G	CH_2 rock. B
794 w	800 w		800 w	600 m	T, G	CSH def. A$_g$, A (CSD def.)
890 m	890 w	887 s	896 m	619 m	T, G	CSH def. B$_u$, B (CSD def.)
942 sh	942 sh					
970 m	972 s		974 w	965 m	G	CH_2 rock. A
1029 w	1030 m		1027 m	1008 m	T, G	CH_2 rock. B$_g$, C–C str. A
			1035 m		T	C–C str. A$_g$
1145 m	1145 s		1150 w	1143 s	G	CH_2 twist. B
	1155 sh	1155 s		1148 sh	T	CH_2 twist. A$_u$
	1203 sh		1200 w	1200 sh	G	CH_2 twist. A
1217 s	1220 vs	1221 s		1214 s	T	CH_2 wag. B$_u$
1272 s	1273 vs		1275 m	1272 s	G	CH_2 wag. A
1289 sh	1292 vs		1289 s	1293 s	T, G	CH_2 wag. A$_g$, B, twist. B$_g$
1419 s	1420 vs		1418 s	1420 s	T, G	CH_2 bend. A$_g$, B
		1423 s				
1426 s	1428 vs		1425 s	1438 s	T, G	CH_2 bend. B$_u$, A
2570 s	2570 vs	2570 s		1854 s	T, G	S–H str. (S–D str.)
	2920 vs		2920 vs		T, G	C–H str.
2950 vs		2950 vs		2950 s		
	2970 vs		2968 vs		T, G	C–H str.

a) Molecular forms around the C–C bond.

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[5] M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 627 (1957).

[6] M. Hayashi, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957).

[7] M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1804 (1956).

[8] M. Hayashi, ibid., **80**, 1084 (1959).

and found that a band corresponding to 940 cm^{-1} does not exist, while bands corresponding to 972 and 769 cm^{-1} are found at 959 and 776 cm^{-1}. Therefore, we took the pair A as the CH_2 rocking vibrations.

For 1, 2-dichloroethane and also for many molecules with a $-CH_2CH_2-$ structure, it is well-known that the frequency difference of two CH_2 rocking vibrations strongly depends on the azimuthal angle around the C–C bond.

For 1, 2-dichloroethane the frequency differences are 221 cm^{-1} for the trans and 62 cm^{-1} for the gauche; their ratio is 0.28. For 1, 2-ethanedithiol, according to the above assignments, the frequency differences are 312 cm^{-1} for the trans and 203 cm^{-1} for the gauche, while their ratio is 0.65. This ratio seems too large compared with that for 1, 2-dichloroethane. However, 0.64 is also obtained for both β-thiamethyl ethyl mercaptan and β-chloroethyl mercaptan.

Furthermore, a refined calculation of nomal vibrations, which will be described afterwards, gave a reasonable set of force costants from this assignment, while the solved force constants obtained from the other possibilities are not acceptable.

From the observed frequencies we have:

$$\begin{aligned} \sum \nu_i^2(\mathrm{T}) &= 6.334\times 10^7 \\ \sum \nu_i^2(\mathrm{G}) &= 6.321\times 10^7 \end{aligned} \qquad (0.21\%\ \text{difference})$$

Therefore, the assignments of the observed frequencies are quite satisfactory. Recently, Fujiyama et al.[9] published a discussion of the vibrational spectra of succinonitrile. According to their assignment, the CH_2 rocking frequencies of this substance also have a large ratio of frequency differences (0.62). For the CH_2 rocking vibrations, then, the difference of the ratio from that of 1, 2-dichloroethane might arise from the influence of some special character of sulfur atoms attached to the $-CH_2CH_2-$ group. The assignments are given in Table I.

The Molecular Form of Isomers

In the preceding section, we have assumed that the isomers are the trans and gauche forms around the C–C bond.

The assignment of the spectra discussed above leads to the conclusion that the spectra in the crystalline state show the mutual exclusion rule between the infrared and the Raman spectra. Therefore, the isomer in this state should have the center of symmetry. This requires that the isomer have the trans form around the C–C bond.

We made the calculation of normal vibrations for skeletal frequencies in order to find the molecular form of the isomer disappearing in the crystalline state.

In this treatment, SH and CH_2 group were regarded as dynamic units, and, accordingly, only the internal rotation around the C–C bond was taken into consideration. About the force constants used in the Urey-Bradley potential function adopted for this treatment, one of the present authors reported that reasonable values were obtained from the observed vibrational frequencies of molecules with similar structures, such as dimethyl sulfide, methyl mercaptan and ethyl mercaptan.[5] These are $K(CH_2\text{-}SH)=2.60$, $K(CH_2\text{-}CH_2)=3.7$, $H(CH_2\text{-}CH_2\text{-}SH)=0.15$ and $F(CH_2\cdots SH)=0.50$ md./Å. The calculation was carried out for seven different molecular forms around the C–C bond. Skeletal deformation frequencies produce large frequency changes, as Fig. 1 shows, where arrows indicate the observed Raman lines below 450 cm^{-1}. The Raman line observed at 299 cm^{-1} is understood to be one of the skeletal deformation vibrations for the trans form, and the other frequency is considered to be Raman-inactive from the symmetry of the trans isomer, while the lines at 267 and 407 cm^{-1} are regarded as the frequencies for the gauche form around the C–C bond. Therefore, we concluded that the isomer disappearing in the crystalline state is the gauche form around the C–C bond.

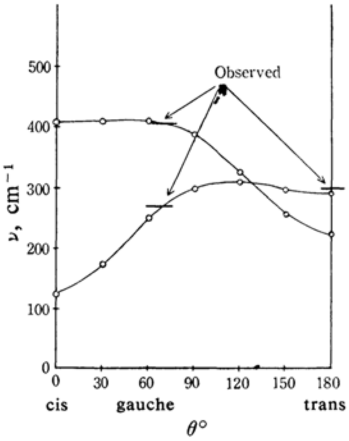

Fig. 1. Observed and calculated frequencies of skeletal deformation modes.

When we take the rotational isomerism around two C–S bonds into consideration, we would have ten different isomers altogether. Four of them have the trans form, and six have the gauche form, around the C–C bond. The form with the center of symmetry arises twice among the four trans isomers.

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[9] T. Fujiyama, K. Tokumaru and T. Shimanouchi, *Spectrochim. Acta*, **20**, 415 (1964).

We will use symbols T, G and G′ for each rotational axis to designate their molecular forms. For example, GTG′ means an isomer with the gauche, the trans and the gauche form for the first C–S, C–C and the second C–S bond respectively, where the gauche form for the second C–S bond is obtained by a 120° rotation of the hydrogen in the second SH group from its trans position to the opposite direction against the hydrogen in the first SH group. In these notations, two trans forms with a center of symmetry can be expressed as TTT and GTG′ respectively.

Since a Raman line at 255 cm^{-1} is found from the refined normal vibration calculation described in the following section, as a C–S torsion, we have no unassigned spectra persisting in the crystalline state.

Since it is hard to consider that two sets of the spectra arising from TTT and GTG′ would overlap perfectly, and since the results of the normal vibration treatment also indicate that perfect overlapping never happens between two sets of the spectra of TTT and GTG′, we have concluded that only one molecular form exists in the crystalline state. About the molecular form disappearing in the crystalline state, we have not enough information to determine how many molecular forms there are and what the molecular forms are. We have only an unassigned band at 942 cm^{-1} which disappears in the crystalline state; this fact suggests that two or more molecular forms probably exist. From the above discussion about skeletal deformation vibrations, it may be said that the main molecular form is the gauche form around the C–C bond. However, the complete determination of the molecular forms around the C–S bonds is a difficult problem on the basis only of the experimental data available at present.

However, it is worthwhile to note that, as we will discuss in detail, the force constants as determined by the least-squares treatment on the assumption of such molecular forms as TTT and TGT, are considered to be reasonable and can be successfully transferred to other substances with similar structures, while the force constats obtained on the assumption of such molecular forms as GTG′ and GGG are not only unreasonable but also less transferable. We believe that this is a good reason to conclude that the isomer in the crystalline state is TTT with C_{2h} symmetry and that the main isomer vanishing in the crystalline state is TGT with C_2 symmetry.

Energy Difference between Isomers

In the gaseous state at ten different temperatures, we made measurements of the relative absorption intensity of the bands at 1289 and 1272 cm^{-1}, which were assigned to the CH_2 wagging frequencies for the trans and gauche isomers respectively.

From the observed optical densities, we found that the energy difference of the isomer is 0.6_3 kcal./mol. where the trans is more stable than the gauche. In order to check the accuracy of this, the measurement was made for 1, 2-dichloroethane, which was reported to have an energy difference of 1.1_4 kcal./mol.,[1] we obtained a very satisfactory agreement.

An attempt was made to measure the intensities in the liquid state at room temperature, at the temperature of ice water, and at the temperature of an ice-alcohol mixture. However, no change could be seen in the absorption intensities. This shows that the isomer have almost the same energy in the liquid state.

Normal Vibration Calculation

We have attempted to make the normal vibration calculation, including all the vibrational freedoms, in order to get a reliable set of force constants which can then be transferred to molecules with similar structures.

For 1, 2-dichloroethane we have established that the usual simple Urey-Bradley force field is not enough to reproduce the observed frequencies. Modifications of the force field have, therefore, been proposed:[10]

1) Torsional freedom is added, with the torsional force constant Y.

2) C–H bond interaction constants, p, are introduced.

3) Angle-interaction constants, l, are considered.

4) Trans and gauche interaction constants, t and g, are added between the angles of different CH_2 groups.

For 1, 2-ethanedithiol we did not know to what extent the force field should be modified. Therefore, we made a trial calculation in a simple Urey-Bradley force field with torsional freedoms for TTT and TGT isomers.

Since we have no observed C–C torsional bands and since the 255 cm^{-1} Raman line is still uncertain as a C–S torsional vibration at this stage, the torsional force constant Y(C–S) for the C–S torsional frequencies was computed from the barrier height reported for methyl mercaptan,[11] while the Y(C–C) for the C–C torsional frequencies was assumed to be the same value as that for 1, 2-dichloroethane.

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[10] T. Shimanouchi, "Proc. Intern. Sym. Mol. Str. and Spectroscopy," Tokyo, C 216 (1962).

[11] T. Kojima and T. Nishikawa, *J. Phys. Soc. Japan*, **12**, 680 (1957).

Since the results have indicated that the 255 cm^{-1} Raman line can be regarded as one of the C–S tortional bands for TTT isomers (species B_g), we made a slight change in Y(C–S) in order to predict the frequency better. 0.05 md. Å was obtained as a Y(C–S) force constant, which made the barrier height 1.7 kcal./mol. This is a little higher than that for methyl mercaptan (1.27 kcal./mol.). The assumed Y(C–C) is 0.15 md. Å, which corresponds to the barrier height of 4.8 kcal./mol. We have fixed these two values throughout the following treatments. The first column of Table II presents the set of force constants which best predicts the observed frequencies in the simple Urey-Bradley force field. This set has been obtained by adjusting the force constants little by little in order best to predict the observed frequencies for TTT and TGT isomers. From a comparison of the observed and the calculated frequencies for 1, 2-ethanedithiol, it has been found that the force field should also be modified. Especially, as is shown in the second column of Table III, the CH_2 wagging, twisting and rocking frequencies strongly suggest the necessity of some modifications of the force field. For example, the observed frequency differences of two CH_2 wagging, two CH_2 twisting and two rocking vibrations are 68, 140, and 317 cm^{-1} for TTT, and 19, 58, and 203 cm^{-1} for TGT, respectively. The calculated values, 12, 9, and 106 cm^{-1} for TTT and 69, 20, and 160 cm^{-1} for TGT, are much smaller than the observed.

TABLE II. FORCE CONSTANTS

$F' = -(1/10)F$

Force const.		No. 1	No. 2	No. 3	No. 4
K(S–H)	(md./Å)	3.65	3.49	3.46	3.41
K(C–S)	(md./Å)	1.80	1.96	1.92	1.90
K(C–C)	(md./Å)	2.36	2.25	2.20	2.20
K(C–H)	(md./Å)	4.35	4.32	4.33	4.31
H(HSC)	(md./Å)	0.18	0.13	0.09	0.06
H(SCC)	(md./Å)	0.11	0.09	0.05	0.05
H(HCC)	(md./Å)	0.16	0.14	0.16	0.15
H(HCS)	(md./Å)	0.14	0.30	0.29	0.28
H(HCH)	(md./Å)	0.46	0.34	0.33	0.33
F(H·S·C)	(md./Å)	0.35	0.36	0.62	0.70
F(S·C·C)	(md./Å)	0.61	0.53	0.56	0.56
F(H·C·C)	(md./Å)	0.43	0.47	0.46	0.47
F(H·C·S)	(md./Å)	0.43	0.21	0.19	0.23
F(H·C·H)	(md./Å)	0.01	0.20[b]	0.20[b]	0.20[b]
κ	(md.·Å)	−0.01	0.07	0.06	0.06
Y(C–S)	(md.·Å)	0.05	0.05	0.05	0.05
Y(C–C)	(md.·Å)	0.15[b]	0.15[b]	0.15[b]	0.15[b]
p[c]	(md./Å)		−0.11	−0.11	−0.11
l[c]	(md.·Å)		0.05	0.06	0.06
t[c]	(md.·Å)			0.14	0.14
g[c]	(md.·Å)			−0.05	−0.05
t'[c]	(md.·Å)				−0.04
g'[c]	(md.·Å)				−0.04
Averaged error in %		2.3	1.7	0.4	0.4

a) Averaged error between the observed and the calculated frequencies.

b) Assumed.

c) p; C–H bands interaction.
l; angles interaction in a CH_2 group.
t, g; trans and gauche interaction between different CH_2 group.
t', g'; trans and gauche interaction between a CH_2 group and a CSH group.

As the first trial of the modification, we have added p and l, that is, the C–H bond interaction and the angle interaction terms. The set of force constants obtained is listed in the second column of Table II. As the third column of Table III shows, the above-mentioned frequency differences are improved very much. However, a large difference still remains in the CH_2 twisting frequencies for TTT.

As the second trial of the modification, we have added the trans and gauche interaction

TABLE III. OBSERVED AND CALCULATED FREQUENCIES OF CH_2 HYDROGEN DEFORMATION VIBRATIONS (cm^{-1})

Molecular form			Obs.		Calcd. No. 1		No. 2		No. 3		No. 4	
TTT	CH_2 wag.	A_g	1292	(68)	1202	(12)	1289	(88)	1305	(90)	1305	(88)
		B_u	1220		1214		1201		1215		1217	
	CH_2 twist.	A_u	1153	(140)	1152	(9)	1154	(19)	1161	(130)	1160	(131)
		B_g	1292		1143		1173		1291		1291	
	CH_2 rock.	A_u	718	(312)	701	(106)	730	(235)	714	(308)	715	(308)
		B_g	1030		807		965		1022		1023	
TGT	CH_2 wag.	A	1273	(19)	1182	(69)	1281	(13)	1257	(42)	1257	(42)
		B	1292		1251		1294		1299		1299	
	CH_2 twist.	A	1203	(58)	1147	(29)	1164	(18)	1195	(45)	1197	(47)
		B	1145		1137		1146		1150		1150	
	CH_2 rock.	A	972	(203)	829	(160)	923	(158)	974	(198)	974	(199)
		B	769		769		765		776		775	

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES OF 1,2-ETHANEDITHIOL (cm^{-1})

	Trans (TTT)				Gauche (TGT)			
	Obs.	Calcd.			Obs.	Calcd.		Assignment
		No. 1[a]	No. 3[b]			No. 1[a]	No. 3[b]	
A_g	2920	2910	2908	A	2920	2913	2901	C–H str.
	2570	2583	2570		2570	2583	2570	S–H str.
	1420	1411	1426		1428	1429	1426	CH_2 bend.
	1292	1202	1305		1273	1182	1257	CH_2 wag.
	1035	1027	1037		1030	1023	1020	C–C str.
	800	815	806		800	815	802	CSH def.
	718	723	721		639	615	642	C–S str.
	299	297	301		267	284	267	CCS def.
A_u	2968	2975	2972		2968	2965	2963	C–H str.
	1155	1152	1161		1203	1147	1195	CH_2 twist.
	718	701	714		972	829	974	CH_2 rock.
	—	232	236		—	209	210	C–S torsion
	—	115	118		—	102	100	C–C torsion
B_g	2968	2963	2961	B	2968	2972	2969	C–H str.
	1292	1143	1291		1145	1137	1150	CH_2 twist.
	1030	807	1022		769	769	776	CH_2 rock.
	255	249	255		—	229	236	C–S torsion
B_u	2920	2934	2929		2920	2930	2925	C–H str.
	2570	2583	2570		2570	2583	2570	S–H str.
	1428	1429	1420		1420	1424	1422	CH_2 bend.
	1220	1214	1215		1292	1251	1299	CH_2 wag.
	890	878	889		890	883	886	CSH def.
	699	695	690		664	641	665	C–S str.
	—	227	173		403	408	401	CCS def.

a) Using a simple Urey-Bradley force field corresponding to a set of force constants No. 1 in Table II.

b) Using a modified Urey-Bradley force field corresponding to a set of force constants No. 3 in Table II.

terms between the angles of different CH_2 groups. As the fourth column of Table III shows, a very satisfactory agreement has thus been obtained. The set of force constants in this modified Urey-Bradley force field was obtained by the application of the least-squares method. We have twenty-two force constants, of which two for torsinal freedoms are fixed at the values mentioned before.

Forty-two observed frequencies could be predicted with an average error of 0.4%; the maximum error was 1.5%.

By the use of the set of force constants so obtained, the frequencies for $DSCH_2CH_2SD$ species were calculated; the observed frequencies have been reproduced with an average error of 0.8%. The calculated and the observed frequencies are tabulated in Table IV.

As we mentioned before, we tried to check the molecular forms. At first, as may be seen in Table V, we calculated the frequencies for GTG′ and GGG isomers as well as for TTT and TGT isomers. We concluded that the C–C stretching, CH_2 rocking, CSH deformation and C–S stretching frequencies for GTG′ and GGG isomers can be observed separately from those for TTT and TGT isomers if they exist. As we have no unassigned spectra in the expected region, however, GTG′ and GGG isomer may not exist.

Secondly, we tried, by the least-squares method, to get a set of force constants on the assumption that the molecular forms were GTG′ and GGG isomers. In this attempt, we found that the force constants did not converge well in a reasonable range of values. Therefore, we might say that GTG′ and GGG isomers are not actual molecular forms. We have concluded that TTT and TGT are the actual molecular forms, as we mentioned in the preceding section.

Another modification of the force field has also been attempted. As the last modification, we introduced the trans and gauche interaction terms between the angles of different CH_2 groups. Similar interaction terms, t' and g',

TABLE V. OBSERVED AND CALCULATED FREQUENCIES IN DIFFERENT MOLECULAR FORMS OF 1, 2-ETHANEDITHIOL[a)] (cm^{-1})

	Obs.	Calcd.		Obs.	Calcd.	
		TTT	GTG′		TGT	GGG
CC str.	1035	1037	1016	1030	1020	992
CS str.	718	720	691	664	665	650
	699	696	694	639	642	630
CH_2 rock.	1030	1022	1011	972	974	970
	718	719	718	769	776	779
CSH def.	890	892	898	890	886	896
	800	804	877	800	802	845

a) Frequencies unaffected by the molecular forms are omitted from the table.

are possible between the angles of a CH_2 group and a CSH angle. The last column of Table V shows a set of force constants adjusted in this modified force field by the least-squares method. However, as we see in the last column of Table III, this modification has no appreciable influence on the CH_2 wagging, twisting and rocking vibrations or on the CSH deformation vibrations, and no appreciable improvement of the average errors could be obtained. Therefore, we have concluded at present that this kind of modification is not necessary for 1, 2-ethanedithiol.

The transferability of the force constants has been checked by the use of the set of the force constants of the second modification of the Urey-Bradley force field. For *n*-propyl mercaptan, β-thiamethyl ethyl mercaptan, β-halogenoethyl mercaptan and 1, 2-dithiamethyl ethane, the set can predict the observed frequencies with a very satisfactory agreement,[2)] as will be reported on in the subsequent papers of this series.

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