C-S Stretching Vibrations and Molecular Conformations of Isobutyl Methyl Sulfide and Related Alkyl Sulfides

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The Raman and infrared spectra of isobutyl methyl sulfide and related alkyl sulfides were measured. The Raman spectra of the liquid, unannealed solid, and annealed solid of isobutyl methyl sulfide were compared and skeletal normal vibrations of possible rotational isomers were treated. Three rotational isomers were found to coexist in the liquid state whereas only one isomer was observed in the annealed solid. The energy differences among the three rotational isomers were measured. The correlations between the CH_2–S stretching frequencies and molecular conformations were established, in common, for the molecules of isobutyl methyl sulfide, methyl propyl sulfide and ethyl methyl sulfide.

In our previous studies,[2,3] Raman and infrared spectra of a series of dialkyl disulfides were analysed. The S–S and C–S stretching frequencies of the $\rangle C\text{–}CH_2\text{–}S\text{–}S\text{–}CH_2\text{–}C\langle$ group were found to depend upon the internal rotation about the CH_2–S and C–CH_2 bonds, respectively. The correlation for S–S stretching vibrations is useful for studying conformations of cystine groups of proteins in aqueous solution. On the other hand, C–S bonds are involved in methionine groups as well as in cystine groups of proteins. Accordingly, the molecule of methyl propyl sulfide was taken up as a model of the methionine group.[4] New correlations were found between C–S stretching frequencies and the internal rotation about the C–CH_2 and CH_2–S bonds of the $\rangle C\text{–}CH_2\text{–}S\text{–}CH_3$ group. The Raman lines due to C–S stretching vibrations are now useful for studying conformations of methionine groups of proteins in aqueous solution.

In the present study, the Raman and infrared spectra of isobutyl methyl sulfide $CH_3\text{–}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}\text{–}CH_2\text{–}S\text{–}CH_3$ were analysed. This molecule possibly serves as a model of *S*-methylcystein,

$$NH_3^+\text{–}\underset{\displaystyle COO^-}{\overset{\displaystyle |}{CH}}\text{–}CH_2\text{–}S\text{–}CH_3$$

The correlations for the C–S stretching frequencies of isobutyl methyl sulfide were compared with those of ethyl methyl sulfide, methyl propyl sulfide and isopropyl methyl sulfide.

Experimental

Isobutyl methyl sulfide, methyl propyl sulfide, and isopropyl methyl sulfide were prepared from methyl iodide and sodium salts of corresponding thiols. Ethyl methyl sulfide was obtained from commercial sources. All these samples were purified by distillation.

Raman spectra were recorded with a JEOL Raman Spectrometer (Model JRS-02AS) with an argon-ion laser (514.5 and 488.0 nm). Infrared spectra were recorded with a Hitachi EPI-G3 Infrared Spectrophotometer. The temperature of the sample in the low temperature cell for Raman scattering was measured with a copper-constantan thermocouple.

Normal Coordinate Treatment

As an aid for analysing the vibrational spectra in the low frequency region, normal vibrations were treated for the possible rotational isomers of isobutyl methyl sulfide. Methyl, methylene and methine groups were treated as single dynamic units. The structural parameters used in the calculation were the bond lengths of r(C–S)=1.81 Å and r(C–C)=1.54 Å, bond angles of ϕ(C–S–C)=98.67° and the tetrahedral angles for carbon atoms. The dihedral angles were 180° and ±60° for the *trans* (T) and *gauche* (G, G′) forms, respectively. The force constants of the Urey-Bradley type were transferred from related molecules (Table 1).

Table 1. Force constants[a]

K(CH_3–S)	2.8	H(C–S–C)	0.16[b]
K(CH_2–S)	2.3	H(C–C–S)	0.15
K(C–C)	3.6	H(C–C–C)	0.25
F(C–S–C)	0.21[b]	Y(C–S)	0.05
F(C–C–S)	0.47	Y(C–C)	0.07
F(C–C–C)	0.33		

a) K(stretching) and F(repulsion), in unit of mdyn/Å; H(bending) in unit of mdyn/Å·rad^2; and Y(internal-rotation) in unit of mdyn·Å/rad^2. This set was used previously.[4] b) These were transferred from dimethyl sulfide.[7] Others were from dialkyl disulfide (Sugeta, Go, and Miyazawa).

Isobutyl Methyl Sulfide

The Raman spectra of isobutyl methyl sulfide in the 850—150 cm^{-1} region are shown in Fig. 1. The top spectrum (Liquid) was observed for the liquid state. The second spectrum (Solid-1) was observed after freezing the sample rapidly. This solid sample was then annealed and the third spectrum (Solid-2) was observed.

Possible rotational isomers of isobutyl methyl sulfide are shown in Fig. 2. The conformations of the X$\rangle$C–CH_2–S– group are denoted with the atom located at the *trans* site (X) with respect to the sulfur atom. Thus, P_C and P_H refer to the conformations with carbon and hydrogen atoms, respectively, at the site X. The internal rotation about the CH_2–S bond is denoted by

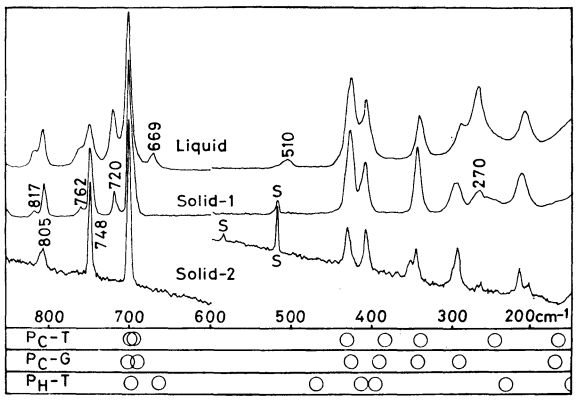

Fig. 1. The Raman spectra of the liquid (Liquid, at 300 K), unannealed solid (Solid-1, at 120 K), and annealed solid (Solid-2, at 120 K) samples of isobutyl methyl sulfide. Calculated frequencies are given with open circles. Spontaneous emission lines of the laser plasma are indicated as S.

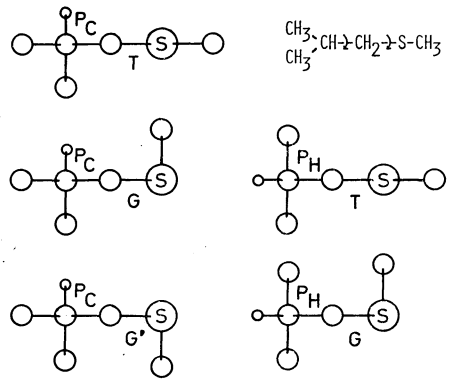

Fig. 2. Possible conformations of isobutyl methyl sulfide. Arrangements of sulfur and carbon atoms and methine hydrogen atom are given.

T (*trans*), G (right-handed *gauche*) and G′ (left handed *gauche*).

For each rotational isomer of isobutyl methyl sulfide, two C–S stretching vibrations are expected to appear in the region of 800—600 cm^{-1}. In fact, two strong Raman lines were observed at 748 and 701 cm^{-1} for Solid-2, indicating the presence of only one rotational isomer (to be called A hereafter). All the Raman lines of the isomer A were also observed in the spectrum of Solid-1, together with two additional lines at 762 and 720 cm^{-1}. These Raman lines are assigned to the C–S stretching vibrations of the second isomer (B), providing the evidence for the coexistence of two rotational isomers in the unannealed solid sample. All the Raman lines of the isomers A and B were also observed in the spectrum of the liquid state. The additional Raman line of the liquid at 669 cm^{-1} is assigned to the C–S stretching vibration of the third isomer (C).

The three rotational isomers (A, B, and C) are possibly the more stable ones among the five isomers shown in Fig. 2. The two isomers, P_C-G′ and P_H-G, are considered to be less stable because of strong steric repulsion between the terminal methyl groups. Accordingly the other isomers, P_C-T, P_C-G, and P_H-T, are expected to correspond to the three isomers experimentally observed in the Raman scattering.

It has been established that the C–Cl[6] and C–S[2] stretching frequencies of the P_H form are lower than those of the P_C form. The Raman line of the isomer C at 669 cm^{-1} is clearly due to the P_H-form. Furthermore, the Raman line of the isomer C at 510 cm^{-1} closely corresponds to the frequency (~470 cm^{-1}) calculated for the P_H-T isomer (Fig. 1). The vibrational frequencies calculated for the P_C-T and P_C-G forms in the 300 cm^{-1} region correspond to the Raman lines at 270 cm^{-1} (the isomer B) and at 299 cm^{-1} (the isomer A), respectively (Fig. 1). Thus, the isomers A, B, and C are now identified as the P_C-G, P_C-T, and P_H-T forms, respectively.

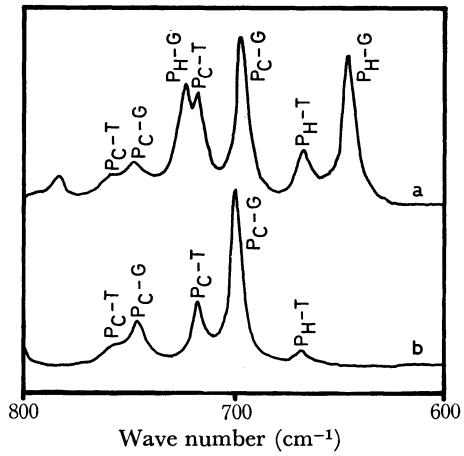

Fig. 3. Assignments of the Raman lines of methyl propyl sulfide (a) and isobutyl methyl sulfide (b) in the liquid state.

TABLE 2. OBSERVED FREQUENCIES (cm^{-1}), RELATIVE INTENSITIES,[a] AND VIBRATIONAL ASSIGNMENTS OF ISOBUTYL METHYL SULFIDE

Liquid		Solid-1	Solid-2	Assignments
Infrared	Raman	Raman	Raman	
	212m	215w	205vw 218w	skel. def.
	269 s	270w	—	skel. def. (P_C-T)
	292m	299w	297m	skel. def. (P_C-G)
	345m	347 s	349m 357w	skel. def.
408w	412 s	413 s	412m	skel. def.
427vw	431 s	431 s	434m	skel. def.
—	510vw	—	—	skel. def. (P_H-T)
670w	669m	—	—	CH_2–S str. (P_H-T)
700 s	701vs	700vs	701vs	C–S sym. str. (P_C-G)
718m	720 s	720m	—	CH_3–S str. (P_C-T)
748 s	745 s	748vs	748vs	C–S asym. str. (P_C-G)
758w	757m	762w	—	CH_2–S str. (P_C-T)
803 s	805 s	805m	805m	CH_2 rock. (P_C-G)
813w	815m	817w	—	CH_2 rock. (P_C-T)
849 s	851w	850w	851w	
862w	—	—	—	

a) vs: very strong, s: strong, m: medium, w: weak, vw: very weak.

The vibrational assignments of the infrared and Raman frequencies of isobutyl methyl sulfide are listed in Table 2. The Raman lines due to the C–S stretching vibrations of isobutyl methyl sulfide and methyl propyl sulfide[4] are compared in Fig. 3. The assignments to molecular conformations of these two sulfides correspond to each other case surprisingly well. It may be noted that, for the molecule of methyl propyl sulfide, the rotational isomers P_H-G and P_H-G′ are possible. However, the isomer P_H-G′ is considered to be much less stable because of strong steric repulsion between the terminal methyl groups. On the other hand, the isomer P_H-G is expected to be more stable and, in fact, the Raman lines due to this isomer were observed as shown in Fig. 3.

Energy Difference. The relative intensities of the Raman lines at 669 cm^{-1} (P_H-T), 720 cm^{-1} (P_C-T), and 701 cm^{-1} (P_C-G) were measured over the temperature range from 180 to 290 K. The P_C-G isomer was found to be most stable. The energy difference between the P_C-T and P_C-G isomers is 0.2 ± 0.1 kcal/mol and the energy difference between the P_H-T and P_C-G isomers is 0.8 ± 0.1 kcal/mol, in the liquid state.

C–S Stretching Frequencies of Alkyl Sulfides

For each of the P_C-G, P_C-T, and P_H-G forms of isobutyl methyl sulfide and methyl propyl sulfide, two Raman lines due to C–S stretching vibrations were observed as shown in Fig. 3. For the P_H-T form, however, only one Raman line due to the C–S stretching vibration was observed and the other Raman line was missing.

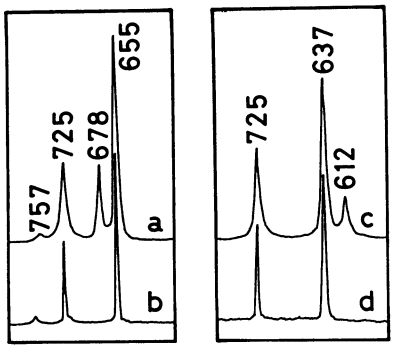

Fig. 4. The Raman spectra of the liquid (a) and annealed solid (b) of ethyl methyl sulfide and of the liquid (c) and annealed solid (d) of isopropyl methyl sulfide.

For studying the C–S stretching vibrations of the P_H-T form, Raman spectra were also measured of the liquid and annealed solid of ethyl methyl sulfide (Fig. 4).[7] The assignments of observed Raman lines to molecular conformations may be done with reference to the correlations found for the molecule of isobutyl methyl sulfide and methyl propyl sulfide. Thus the Raman lines of the annealed solid of ethyl methyl sulfide at 725 and 655 cm^{-1} may be assigned to the C–S stretching vibrations of the P_H-G form while the Raman line of the liquid at 678 cm^{-1} may be assigned to the P_H-T form.[8] The temperature dependence of the intensities of these three Raman lines suggests that the missing Raman line of the P_H-T form is overlapped by the Raman line of the P_H-G form at 725 cm^{-1}. This frequency is nearly equal to the average value (716 cm^{-1}) of the two CH_3–S stretching frequencies of dimethyl sulfide (antisymmetric: 741 cm^{-1}, symmetric: 691 cm^{-1}).[5] Accordingly the Raman line of ethyl methyl sulfide at 725 cm^{-1} is assigned to the CH_3–S stretching vibration. Similarly, the Raman line of methyl *tert*-butyl sulfide at 722 cm^{-1} is assigned to the CH_3–S stretching vibration.[12]

The CH_3–S stretching vibration was also studied for the molecule of isopropyl methyl sulfide. The Raman spectra of the liquid and annealed solid were observed, as shown in Fig. 4.[10] The Raman lines at 725 and 637 cm^{-1} have been assigned to the C_1 isomer and the line at 612 cm^{-1} to the C_S isomer.[11–13] The missing Raman line of the C_S isomer is now considered to be overlapped by the Raman line (at 725 cm^{-1}) due to the CH_3–S stretching vibration of the C_1 isomer.

Table 3. Characteristic C–S stretching frequencies (cm^{-1}) of alkyl sulfides

Molecule	Conformation				
	P_C-T	P_C-G	P_H-T	P_H-G	Mode
H, H, H–C–CH_2–S–CH_3	—	—	~725	725	S–CH_3
	—	—	678	655	CH_2–S
H, H, CH_3–C–CH_2–S–CH_3	719	(697)	~720	724	S–CH_3
	760	(746)	667	645	CH_2–S
H, CH_3, CH_3–C–CH_2–S–CH_3	720	(699)	~720	—	S–CH_3
	755	(743)	669	—	CH_2–S

The present analyses of the Raman spectra of isobutyl methyl sulfide and related alkyl sulfide lead to the conclusion that the CH_3–S stretching vibration is observed around 725 cm^{-1}, fairly independent of the changes in molecular conformations (except for the P_C-G form, see Table 3). On the other hand, the CH_2–S stretching frequencies are sensitive to the changes in molecular conformations. For the molecule of methyl propyl sulfide, the CH_2–S stretching frequencies are 645 (P_H-G), 667 (P_H-T), and 760 cm^{-1} (P_C-T). For the exceptional case of the P_C-G isomer, CH_3–S and S–CH_2 stretching modes are hybridized to yield normal vibrations at 746 cm^{-1} (pseudo-asymmetric) and 697 cm^{-1} (pseudo-symmetric). The average value (722 cm^{-1}) of these frequencies is, in fact, nearly equal to the 'intrinsic' frequency (725 cm^{-1}) of the CH_3–S stretching vibration.

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