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Vibrational Spectra and Molecular Structure of Ethyl Methyl Sulfide

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The Raman spectra of the liquid, unannealed solid and annealed solid, and the infrared spectra of the gas, liquid, and annealed solid of ethyl methyl sulfide were measured. Normal vibrations were treated of the *trans* and *gauche* isomers. C–S stretching, CH_2 rocking and skeletal deformation vibrations were discussed in relation with molecular structures. Only the *gauche* isomer was found to exist in the annealed solid. In the liquid state, the *gauche* isomer was found to be more stable, by 0.14 ± 0.05 kcal/mol, than the *trans* isomer. The vibrational assignment made of ethyl methyl sulfide is consistent with those of related sulfides and disulfides.

The vibrational spectra and molecular structure of ethyl methyl sulfide have been extensively studied,[2] and it has been concluded that the *trans* isomer exists in the crystalline state. In our previous studies, however, the molecules of dialkyl sulfides[3,4] and dialkyl disulfides[5,6] were taken up as models of methionine and cystine groups of protein side-chains. The Raman spectra of ethyl methyl sulfide, methyl propyl sulfide, and isobutyl methyl sulfide were analyzed in the region 800—600 cm^{-1}. A systematic assignment was made of the normal vibrations of these three molecules, and the Raman lines of the annealed solid of ethyl methyl sulfide were assigned to the *gauche* isomer rather than the *trans* isomer.[3]

In the present study, a normal coordinate treatment was made of the *trans* and *gauche* isomers of ethyl methyl sulfide and the vibrational spectra (C–S stretching, CH_2 rocking, and skeletal deformation vibrations) were analyzed for establishing the molecular conformation of ethyl methyl sulfide in the crystalline state.

Experimental

The sample of ethyl methyl sulfide was obtained from commercial sources and was purified by fractional distillation. Raman spectra were recorded with a JEOL Raman Spectrometer (Model JRS-02AS) with an argon-ion laser. Infrared spectra were recorded with a Hitachi EPI-G3 Infrared Spectrophotometer.

Normal Coordinate Treatment

As an aid for analyzing the vibrational spectra in the low frequency region, normal vibrations were treated for the *trans* (C_s) and *gauche* (C_1) isomers of ethyl methyl sulfide. The structural parameters used in the calculations were the bond lengths of $r(\text{C–S}) = 1.81$ Å, $r(\text{C–C}) = 1.54$ Å, and $r(\text{C–H}) = 1.09$ Å, bond angles of $\phi(\text{C–S–C}) = 98.67°$ and the tetrahedral angles for carbon atoms. The internal-rotation angles were taken as 180° and 60° for the *trans* and *gauche* forms, respectively. The force constants of the Urey-Bradley type were mostly transferred from dialkyl disulfides,[7] except that the bending constant H(C–S–C) [$=0.244$ mdyn/Å·rad²] and repulsion constant F(C–S–C) [$=0.210$ mdyn/Å] were transferred from dimethyl sulfide.[8]

C–S Stretching Vibrations

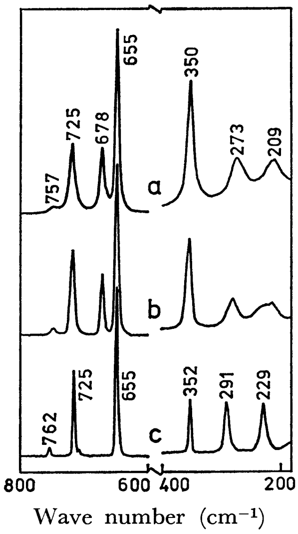

Fig. 1. The Raman spectra of ethyl methyl sulfide; (a) liquid at 300 K, (b) unannealed solid at 150 K, and (c) annealed solid at 130 K.

The Raman spectra of ethyl methyl sulfide in the 800∼200 cm^{-1} region are shown in Fig. 1. The top spectrum (a) was observed for the liquid at room temperature. The second spectrum (b) was observed after freezing the sample rapidly. Then the frozen solid sample was readily annealed and the third spectrum (c) was observed. The infrared spectra of the liquid and annealed solid of ethyl methyl sulfide are shown in Figs. 2(b) and (c).

For each of the *trans* and *gauche* isomers of ethyl methyl sulfide, three fundamental vibrations are expected to lie in the 800—600 cm^{-1} region, including two C–S stretching and one CH_2 rocking vibrations. In fact, the Raman [Fig. 1(c)] and infrared [Fig. 2(c)] spectra of the annealed solid exhibit only three bands, indicating the presence of only one isomer. The band observed at 762 cm^{-1} (weak in Raman scattering but strong in infrared absorption) is assigned to the CH_2 rocking vibration while the bands at 725 and 655 cm^{-1} are assigned to the CH_3–S and CH_2–S stretching vibrations, respectively. For the liquid or unannealed solid, an additional band is observed at 678 cm^{-1} and is assigned to the CH_2–S stretching vibration of the other isomer. From the comparison of these C–S stretching frequencies with those of methyl propyl sulfide and isobutyl methyl sulfide,[3,4] the Raman lines of ethyl methyl sulfide at 725 and 655 cm^{-1} are assigned to the *gauche* isomer and the Raman line at 678 cm^{-1} is assigned to the *trans* isomer.

Energy Difference between Rotational Isomers. Relative intensities of the Raman lines at 678 cm^{-1} (*trans*) and 655 cm^{-1} (*gauche*) were measured over the temperature range from 290 K to 180 K. Thus, the *gauche* isomer was found to be slightly more stable than the *trans* isomer, with the energy difference of 0.14±0.05 kcal/mol.

The temperature dependence of the relative intensities of the Raman lines at 725 and 655 cm^{-1} was also measured. The apparent energy difference of 0.05±0.05 kcal/mol is consistent with the assignment of the liquid Raman line at 725 cm^{-1} to the overlap of the CH_3–S stretching vibrations of the *trans* and *gauche* isomers.[4]

Skeletal Deformation Vibrations

For each isomer of ethyl methyl sulfide, two skeletal deformation vibrations and one CH_3–CH_2 torsional vibration are expected to lie in the 400—200 cm^{-1} region. Generally in the Raman scattering, skeletal vibrations are strongly observed but CH_3–CH_2 torsional vibrations are hardly observed. However, if the CH_3–CH_2 torsional mode is extensively hybridized with skeletal deformation modes, "CH_3–CH_2 torsional" vibration may well be observed in Raman spectra. Such hybridization was found to be the case for the *gauche* isomer of ethyl methyl sulfide. The potential energy distribution calculated for the *gauche* isomer indicates that the skeletal deformation modes and CH_3–CH_2 torsional mode are appreciably hybridized to yield the normal vibrations at 291 and 229 cm^{-1}. Indeed, three well-defined Raman lines were observed for the annealed solid [Fig. 1(c)]. This observation is consistent with the presence of the *gauche* isomer in the annealed solid, since such hybridization is not expected to occur for the *trans* isomer belonging to the point group C_s.

CH_2 Rocking Vibrations

In our previous studies on dialkyl disulfides, the correlations were found between the CH_2 rocking frequencies and internal rotation about the CH_2–S bond of CH_3–CH_2–S–S group.[6] For the case of ethyl methyl disulfide [Fig. 2(d)], the infrared bands of the liquid at 781 and 761 cm^{-1} were assigned to the *trans* and *gauche* forms, respectively, of the CH_3–CH_2–S–S group. Similarly for diethyl disulfide, the infrared bands at 781 and 762 cm^{-1} were found to be due to the *trans* and *gauche* forms, respectively. Thus, the CH_2 rocking frequency of the *trans* form is higher, by about 20 cm^{-1}, than that of the *gauche* form. This correlation may now be applied to the case of ethyl methyl sulfide. The infrared bands of the liquid at 785 and 760 cm^{-1} are assigned to the *trans* and *gauche* isomers respectively. The observation of the infrared band at 764 cm^{-1} indicates that the *gauche* isomer exists in the annealed solid.

CH_2 rocking frequencies were also observed for the rotational isomers of isobutyl methyl sulfide, $(CH_3)_2$-CH–CH_2–S–CH_3. The infrared bands of the liquid at 813 and 803 cm^{-1} are due to the P_C-T and P_C-G forms, where the second symbol (T or G) refers to the internal rotation about the CH_2–S bond.[4] In the case of methyl propyl sulfide CH_3CH_2–CH_2–S–CH_3, there are two CH_2 rocking vibrations for each isomer and the lower frequency vibration lies in the 800—700 cm^{-1} region. The infrared bands (see Fig. 1 of Ref. 3) observed at 751 and 731 cm^{-1} are assigned to the P_C-T and P_C-G forms and those at 793 and 785 cm^{-1} to the P_H-T and P_H-G forms, respectively.[3] In all these cases, the CH_2 rocking frequency of the *trans* form (P_C-T or P_H-T) is higher, by 8∼25 cm^{-1}, than that of the *gauche* form (P_C-G or P_H-G).

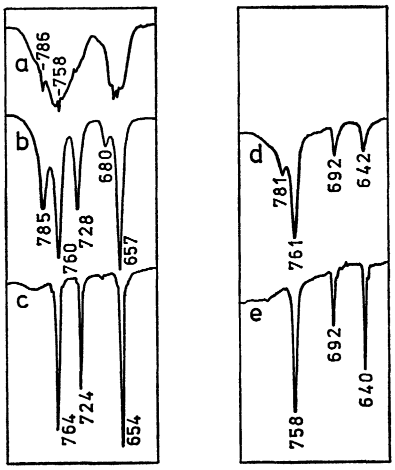

Fig. 2. Left: the infrared spectra of ethyl methyl sulfide; (a) vapor at 130 Torr and 300 K, (b) liquid at 300 K, and (c) annealed solid at 80 K. Right: the infrared spectra of ethyl methyl disulfide; (d) liquid at 300 K and (e) annealed solid at 80 K.[6]

Gas Phase. The electron diffraction of ethyl methyl sulfide was studied by Oyanagi *et al.*,[9] and the *gauche* isomer was found to be more abundant than the *trans* isomer in the gas phase. In our present study, the infrared spectrum of the gas phase was measured at the gas pressure of 130 Torr and room temperature [Fig. 2(a)]. The infrared bands due to CH_2 rocking vibrations were observed at 786 cm^{-1} (*trans*) and 758 cm^{-1} (*gauche*). The absorption band of the *gauche* isomer is stronger than that of the *trans* isomer. This observation is consistent with the result of the electron diffraction study.

To summarize, the present analyses of the Raman and infrared spectra (C–S stretching, CH_2 rocking and skeletal deformation vibrations) indicate that the *gauche* isomer of ethyl methyl sulfide exists in the annealed solid.

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