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C-S STRETCHING VIBRATIONS AND MOLECULAR CONFORMATIONS OF METHYL PROPYL SULFIDE AND RELATED ALKYL SULFIDES

Norimasa NOGAMI,* Hiromu SUGETA, and Tatsuo MIYAZAWA**
Institute for Protein Research, Osaka University,
Yamada-kami, Suita, Osaka 565

Raman and infrared spectra of methyl propyl sulfide, ethyl methyl sulfide, and isobutyl methyl sulfide were measured. Correlations were found between C-S stretching frequencies and internal rotation about the C-CH_2 and CH_2-S bonds of the $\geqslant$C-CH_2-S-CH_3 groups. The new correlations were applied for conformation studies of methionine groups.

Laser Raman spectroscopy has been found to be particularly useful for studying vibrational spectra and conformations of protein molecules in aqueous solutions.1) For detailed analyses of Raman scattering spectra of proteins, it is important, in advance, to establish correlations between vibrational frequencies and conformations of side chain groups as well as of polypeptide main chain. Accordingly, in our previous studies,2,3) Raman and infrared spectra of a series of dialkyl disulfides were measured and new correlations were found between the S-S and C-S stretching frequencies and internal rotation about the C-CH_2 and CH_2-S bonds of $\geqslant$C-CH_2-S-S-CH_2-C$\leqslant$ groups. The S-S stretching frequencies were in fact found to be useful for conformation studies of cystine groups of proteins in aqueous solution.4) On the other hand, C-S bonds are also found in methionine groups as well as in cystine groups of proteins. It is therefore necessary to establish correlations for the C-S stretching frequencies of methionine groups before Raman lines due to C-S stretching vibrations may be used for conformation studies of proteins having methionine and cystine groups together. In the present study, the molecules of methyl propyl sulfide and related sulfides5) were taken up as models of the methionine group and Raman and infrared spectra in the C-S stretching region were analyzed in relation to the internal rotation of the $\geqslant$C-CH_2-S-CH_3 group.

Samples of methyl propyl sulfide and isobutyl methyl sulfide were prepared from methyl iodide and sodium salts of corresponding thiols and were purified by fractional distillation. The sample of ethyl methyl sulfide was obtained from commercial sources and was purified by fractional distillation. Raman spectra were recorded with a JEOL Model JRS-02AS Raman Spectrometer with an argon-ion laser (488.0 and 514.5 nm). Infrared spectra were recorded with Hitachi EPI-G3 and EPI-L Infrared Spectrophotometers. The temperature of the sample in the low-temperature cell for Raman scattering or for infrared absorption was measured with a copper-constantan thermocouple.

METHYL PROPYL SULFIDE

The Raman and infrared spectra of methyl propyl sulfide in the region of 800-600 cm^{-1} are shown in Fig. 1. The top pair (Liquid) of spectra were observed for the liquid state at room temperature. The second pair (Solid-0) of spectra were observed after freezing the liquid sample rapidly (Raman) or after condensing the vapor sample onto a window held at 80 K (infrared). The Solid-0 samples were then annealed up to the temperature of 110 K and the second pair of spectra were drastically simplified, yielding the third pair (Solid-1) of spectra with only three bands in this region of 800-600 cm^{-1}. The Solid-1 samples were furthermore annealed up to the temperature of 170 K and all the bands were shifted, by 15-20 cm^{-1}, to higher frequency, yielding the fourth pair (Solid-2) of spectra. Annealing of the Solid-2 sample in the Raman cell did not cause any more spectral change up to the melting point. In a course of repeated sampling experiments, the Raman spectrum denoted by X was observed unexpectedly; the three bands of Solid-X were different from those of Solid-1 and Solid-2. Similarly, the infrared spectrum denoted by Y was also observed; there were observed five bands, apparently due to a mixture of Solid-X and Solid-2.

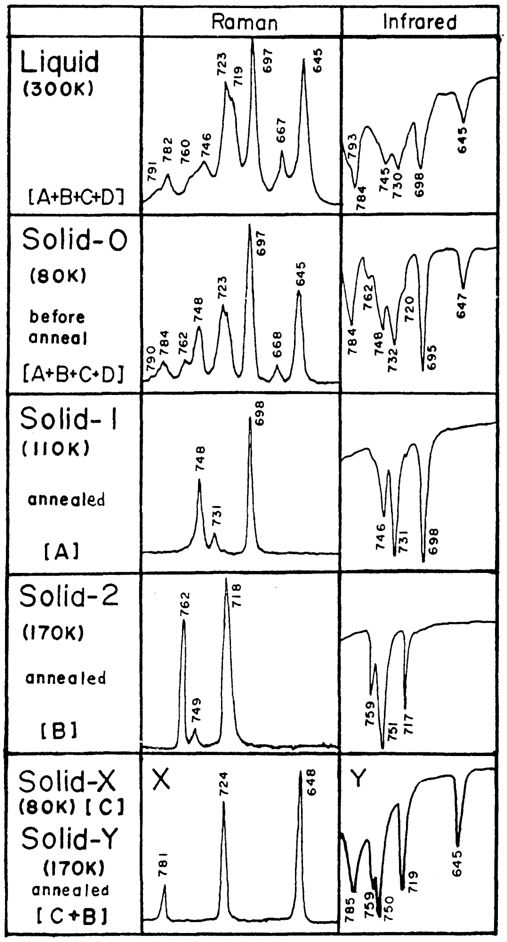

Fig. 1. The Raman and infrared spectra of methyl propyl sulfide.

For each rotational isomer of methyl propyl sulfide, three vibrations are expected to appear in the region 800-600 cm^{-1}, including two C-S stretching vibrations and one CH_2 rocking vibration. In fact, only three distinct bands were observed in the spectra of Solid-1, Solid-2, and Solid-X, indicating the presence of only one isomer in each solid. These isomers will be called as A (in Solid-1), B (in Solid-2), and C (in Solid-X). The Raman and infrared bands of the liquid state (and Solid-0) are now assigned to the A, B, and C isomers, except those at 791 and 667 cm^{-1}, which are due to the fourth isomer (D).

The observed bands of isomer-A at 731 cm^{-1} and of isomer-B at 749 cm^{-1} (weak in Raman scattering but strong in infrared absorption) are assigned to CH_2 rocking vibrations. Similarly, the weak Raman lines of isomer-C at 781 cm^{-1} and of isomer-D at 791 cm^{-1} are also assigned to CH_2 rocking vibrations. As in the case of propyl chloride,[6] these Raman lines of isomer-A and B correspond to the trans form while those of isomer-C and D correspond to the gauche form of the $-CH_2-CH_2-$ group.

As an aid for studying the internal rotation of methyl propyl sulfide, skeletal normal vibrations were treated.[7] The force constants of the Urey-Bradley type were transferred from

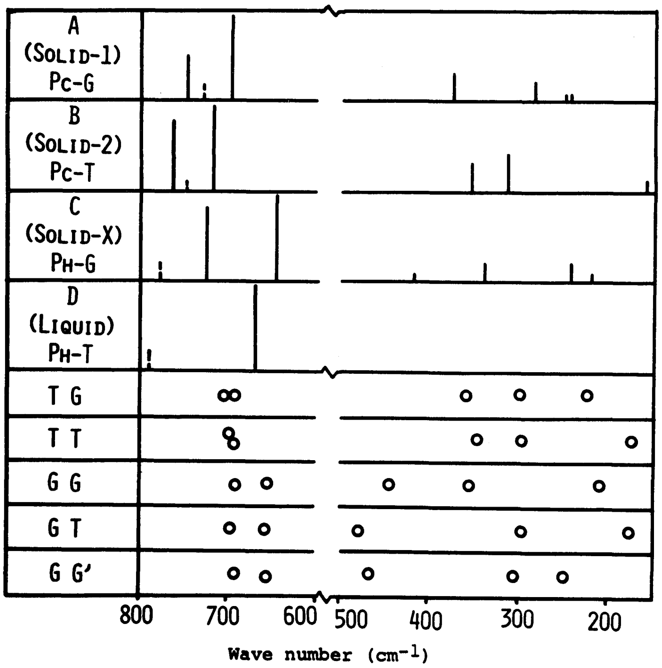

Fig. 2. The observed Raman frequencies (bars) and calculated frequencies (open circles) of methyl propyl sulfide. Observed CH_2 rocking frequencies are shown with broken bars.

related molecules. Fig. 2 shows observed Raman frequencies, together with the frequencies calculated for possible isomers, where the first symbol (T, trans; G, gauche) refers to the internal rotation about the CH_2-CH_2 bond and the second symbol about the CH_2-S bond. From the comparison of the observed and calculated frequencies in the region of 500-150 cm^{-1}, the isomer-A, B, and C are identified as TG (or in other notation, P_C-G), TT (P_C-T), and GG (P_H-G) forms, respectively. Here in parentheses, P_C and P_H refer to the conformations of the $>$C-CH_2-S- group which have carbon and hydrogen atoms, respectively, at the trans site with respect to the sulfur atom.8)

The C-S stretching frequencies in the region of 800-600 cm^{-1} may now be discussed in relation to the P_C and P_H forms. Similar to the case of dialkyl disulfides,2,3) the C-S stretching frequencies of the P_C forms of methyl propyl sulfide (TG and TT) are observed higher than those of the P_H form (GG). The C-S stretching frequency (667 cm^{-1}) of isomer-D corresponds to the P_H form. The isomer-D is probably GT (P_H-T) rather than GG', since the latter is considered to be much less stable because of strong steric repulsion between the terminal methyl groups. These assignments for methyl propyl sulfide are confirmed by spectral comparison with those of ethyl methyl sulfide and isobutyl methyl sulfide.

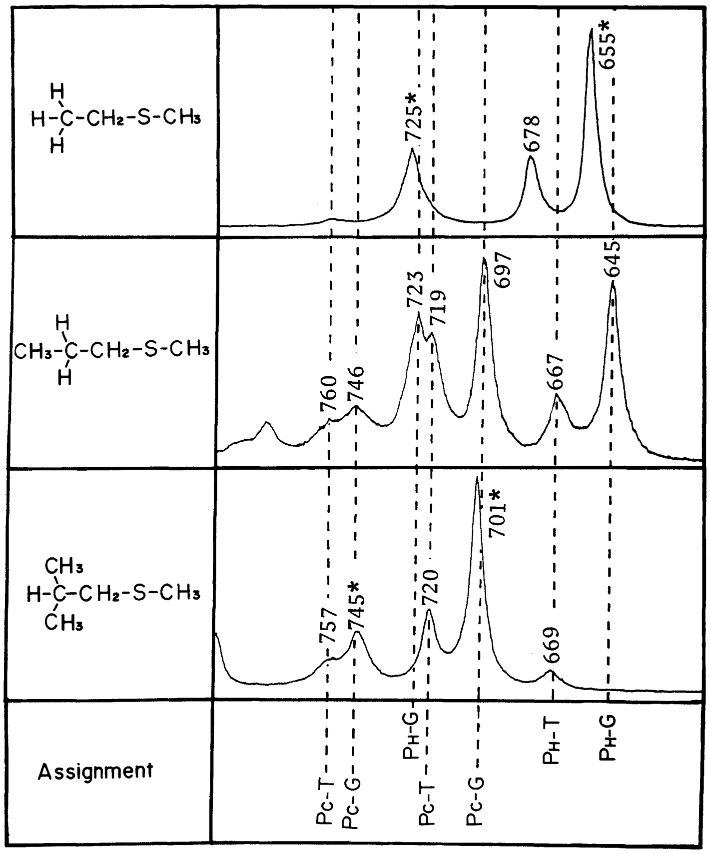

Fig. 3. The Raman spectra of ethyl methyl sulfide, methyl propyl sulfide, and isobutyl methyl sulfide.

ETHYL METHYL SULFIDE AND ISOBUTYL METHYL SULFIDE

The Raman spectra of ethyl methyl sulfide (top), methyl propyl sulfide (middle), and isobutyl methyl sulfide (bottom) in the liquid state at room temperature are shown in Fig. 3, for the region of 800-600 cm^{-1}. The superscript * in the spectra of ethyl methyl sulfide and isobutyl methyl sulfide indicates the Raman lines which are also observed in the crystalline state.

In the molecule of ethyl methyl sulfide, a hydrogen atom always occupies the trans site with respect to the sulfur atom and there is no possibility of P_C-G or P_C-T forms. Indeed, the Raman lines due to the P_C-G and P_C-T forms of methyl propyl sulfide are not observed for ethyl methyl sulfide. The Raman lines of ethyl methyl sulfide at 725 and 655 cm^{-1} are now assigned to the P_H-G form, while the Raman line at 678 cm^{-1} is assigned to the P_H-T form.

For isobutyl methyl sulfide, on the other hand, Raman lines of the P_H-G form are not expected to appear, because of strong steric repulsion between terminal methyl groups of the P_H-G form. In fact, the Raman lines of methyl propyl sulfide at 723 and 645 cm^{-1} are not observed for isobutyl methyl sulfide. All the other Raman lines of propyl methyl sulfide in the region of 800-600 cm^{-1} are also observed for isobutyl methyl sulfide as shown in Fig. 3. Thus the Raman lines of ethyl methyl sulfide, methyl propyl sulfide, and isobutyl methyl sulfide are systematically interpreted, providing supports to the correlations between C-S stretching frequencies and conformations of methyl propyl sulfide. These correlations may now be used for conformation studies of methionine derivatives.

ACETYLMETHIONINE METHYLAMIDE

For acetylmethionine methylamide (L and DL), a very strong Raman line at ∿700 cm^{-1} and a strong line at ∿755 cm^{-1} were observed in the solid state, indicating the predominance of the P_C-G form (TG) of the methionine side chain. These samples were generously given by Dr. Y. Koyama of Kwansei Gakuin University.

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* Present address: Department of Chemistry, Faculty of Science, The University of of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

** To whom correspondences may be addressed; present address: Department of Biophysics and Biochemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

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