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MOLECULAR CONFORMATIONS AND C-Cl STRETCHING VIBRATIONS OF 1-CHLORO-2-METHYLPROPANE AND C-S STRETCHING VIBRATIONS OF 2-METHYL-1-PROPANETHIOL AND L-CYSTEINE

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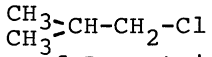
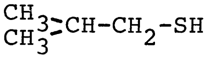
The Raman spectra of 1-chloro-2-methylpropane and 2-methyl-1-propanethiol were measured in the liquid and solid states. Conformations of these molecules were studied in relation with the characteristic CH_2-Cl and CH_2-S stretching vibrations. The molecular structure of L-cysteine was discussed on the basis of observed CH_2-S stretching frequencies.

Recently laser Raman spectra of many proteins in aqueous solution were measured, and numerous Raman lines due to vibrations of side-chain amino acid residues were observed. For detailed vibrational analyses of Raman spectra of proteins it is necessary and rewarding to establish correlations between vibrational frequencies and conformations of side-chain groups. In our previous studies, the Raman and infrared spectra of model molecules of cystine groups were studied. New correlations were found between the S-S and S-CH_2 stretching frequencies and internal rotation about the S-CH_2 and CH_2-C bonds of the $>C-CH_2-S-S-CH_2-C<$ group.[1,2] These correlations are useful for elucidating the conformations of cystine groups of proteins from the observation of the Raman lines due to S-S stretching vibrations in aqueous solution. The infrared and Raman spectra of model molecules of methionine groups were also studied. Again the CH_2-S stretching frequencies were found to depend upon the internal rotation about the C-CH_2 bond of the $>C-CH_2-S-CH_3$ group.[3]

For completing the correlation studies on the S-S and CH_2-S stretching vibrations of proteins, it is now important to study the CH_2-S stretching frequencies and internal rotation about the C-CH_2 bond of cysteine groups. In the presnet study, the molecules of 1-chloro-2-methylpropane  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH-CH_2-Cl$ and 2-methyl-1-propanethiol  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH-CH_2-SH$ were taken up as models of L-cysteine.

EXPERIMENTAL

Commercial samples of 1-chloro-2-methylpropane and 2-methyl-1-propanethiol were purified by distillation. The sample of S-deuterated 2-methyl-1-propanethiol was prepared by treating sodium 2-methyl-1-propanethiolate with deuterium oxide and sulfuric acid-d_2. The sample of L-cysteine was purified by recrystallization from hot water.

Raman spectra were measured with a JEOL (Model JRS-02AS) Raman Spectrometer with an argon-ion laser (488.0 and 514.5 nm).

1-CHLORO-2-METHYLPROPANE

The observed Raman spectra of 1-chloro-2-methylpropane are shown in Fig. 1, for the liquid and annealed solid. The Raman spectrum of the liquid is much simplified on crystallization, suggesting the coexistence of rotational isomers in the liquid state. For the molecule of 1-chloro-2-methylpropane, two isomers are possible, one belonging to the point group C_s and the other one to the point group C_1. However, these isomers may be denoted P_C and P_H, respectively. P_C and P_H indicate that the carbon and hydrogen atoms are located at the trans site with respect to the chlorine atom, respectively.$^{4)}$

The characteristic CH_2-Cl stretching vibrations of alkyl chlorides were studied by Mizushima et al.$^{4)}$ Thus, for primary alkyl chlorides, the CH_2-Cl stretching vibrations were found at 760∿700 cm^{-1} for the P_C form and at 690∿650 cm^{-1} for the P_H form. For 1-chloro-2-methylpropane in the liquid state, the two strong Raman lines at 733 and 691 cm^{-1} (Fig. 1) were assigned previously$^{4)}$ to the P_C and P_H forms, respectively.

In the present study, however, the solid sample was successfully annealed and the Raman spectrum of the crystalline sample was observed for the first time. On crystallization of the solid sample, the Raman line due to the CH_2-Cl stretching vibration of the P_H form (691 cm^{-1}) disappears whereas the Raman line due to the P_C form (733 cm^{-1}) persists with the small frequency shift of -13 cm^{-1}. The present Raman observation indicates that only the P_C form exists in the annealed solid.

CH_2 rocking frequencies were also found to be sensitive to molecular conformations. For the molecule of 1-chloro-2-methylpropane, the two Raman lines at 819 and 805 cm^{-1} are assigned to the P_C and P_H forms, respectively. Similarly in the low-frequency region, the Raman lines at 430, 408, and 338 cm^{-1} are assigned to the P_C form while those at 523 and 376 cm^{-1} are assigned to the P_H form.

The energy difference between the P_H and P_C forms [$\Delta E=E(P_H)-E(P_C)$] was studied by the measurement of the temperature dependence of the Raman spectra in the liquid state. Thus the relative intensity of the Raman lines at 733 cm^{-1}(P_C) and 691 cm^{-1}(P_H) over the temperature range 292∿167 K, and ΔE was found to be 0.03±0.05 kcal/mol.

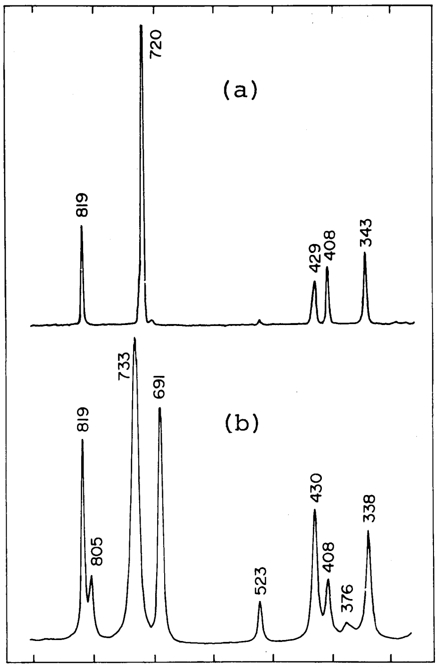


Fig. 1. The Raman spectra of 1-chloro-2-methylpropane, (a) annealed solid (80 K); (b) liquid (293 K).

2-METHYL-1-PROPANETHIOL

The observed Raman spectra of 2-methyl-1-propanethiol are shown in Fig. 2. Cooled solid samples never crystallized even after repeated sampling and annealing experiments. However, the Raman spectra of 2-methyl-1-propanethiol are very much similar to those of 1-chloro-2-methylpropane, as shown in Figs. 1 and 2.

In previous studies of the vibrational spectra of dialkyl disulfides, characteristic CH_2-S stretching frequencies were found to be similar to CH_2-Cl stretching frequencies of corresponding alkyl chlorides.1) The Raman lines of 2-methyl-1-propanethiol at 709 and 668 cm^{-1} are now assigned to the CH_2-S stretching vibrations of the P_C and P_H forms, respectively, indicating that these two isomers coexist in the liquid state. The two Raman lines were observed for cooled solid samples, again indicating the coexistence of two rotational isomers.

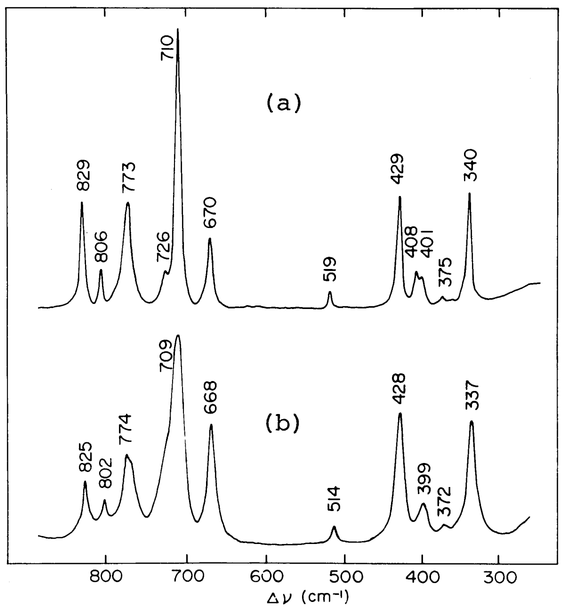


Fig. 2. The Raman spectra of 2-methyl-1-propanethiol; (a) solid (80 K); (b) liquid (293 K).

The Raman lines due to the C-S-H bending vibrations of propanethiol were observed at about 800 cm^{-1}.6) However, for studying the assignment of the C-S-H bending vibration of 2-methyl-1-propanethiol, the Raman spectrum of the S-deuterated species in the liquid state was also observed. The Raman line of the normal species at 774 cm^{-1} (Fig. 2) was found to shift, on S-deuteration, to 614 cm^{-1}. Accordingly, this Raman line is now assigned to the C-S-H bending vibration. In fact, the corresponding line is not observed in the Raman spectrum of 1-chloro-2-methylpropane (Fig. 1).

From the comparison with the Raman spectrum of 1-chloro-2-methylpropane, the Raman lines of 2-methyl-1-propanethiol at 825 and 802 cm^{-1} may be assigned to the CH_2 rocking vibrations of the P_C and P_H forms, respectively.

The relative intensity of the Raman lines of 2-methyl-1-propanethiol at 709 cm^{-1}(P_C) and 668 cm^{-1}(P_H) was measured over the temperature range $294\sim214$ K. The P_C form was found to be more stable in the liquid state, with the energy difference of 0.21 ± 0.10 kcal/mol.

L-CYSTEINE

For the molecule of L-cysteine, there are three rotational isomers, P_H, P_C, and P_N. In the monoclinic crystal the P_H and P_N forms coexist with the abundance ratio of 1:1,7) while in the orthorhombic crystal only the P_H form exists.8)

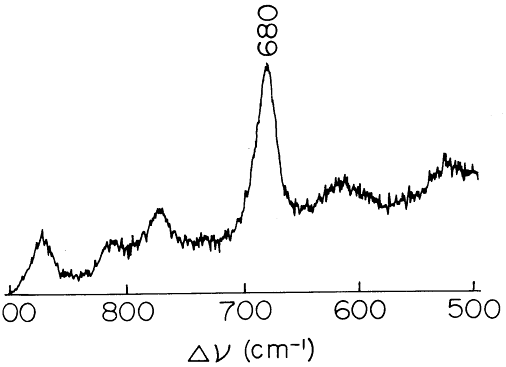


Fig. 3. The Raman spectrum of L-cysteine in aqueous solution (pH 5).

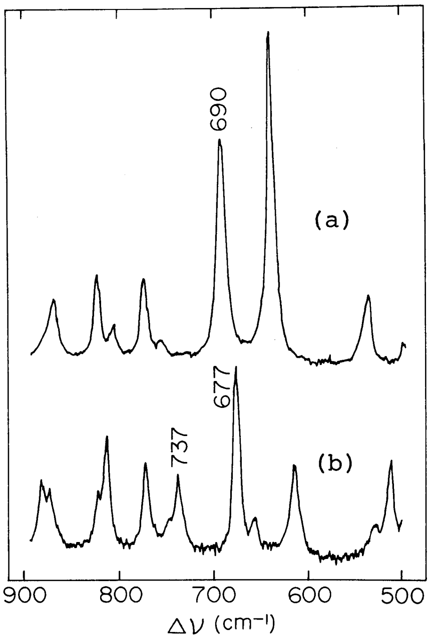
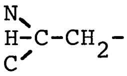


Fig. 4. The Raman spectrum of L-cysteine crystals; (a) orthorhombic, (b) monoclinic.

The  $\overset{N\diagdown}{\underset{C\diagup}{H-C}}-CH_2-SH$ group of the cysteine molecule is closely related with the molecule of 2-methyl-1-propanethiol and accordingly the conformation of the cysteine molecule may also be studied on the basis of the Raman lines due to C-S stretching vibrations.

The Raman spectrum of L-cysteine in aqueous solution is shown in Fig. 3. The strong Raman line at 680 cm^{-1} may be assigned to the CH_2-S stretching vibration of the P_H form. On the other hand, well-defined Raman lines were not observed in the region 750∿710 cm^{-1} where the CH_2-S stretching vibrations of the P_C and P_N forms should appear. Accordingly, from the observation of the Raman scattering, the P_H form appears to exist primarily in aqueous solution.

The Raman spectra of two crystalline samples of L-cysteine are shown in Fig. 4. The strong Raman line observed at about 680 cm^{-1} in either spectrum may be assigned to the P_H form. The spectrum (b) exhibits the additional line at 737 cm^{-1}, which is due to the P_N (or P_C) form. Accordingly, the spectrum (a) corresponds to the orthorhombic crystal and (b) to the monoclinic crystal.

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