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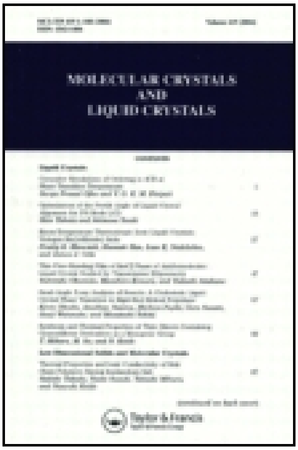

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Raman Study of Self-Trapped Phonons in Crystalline Acetanilide Under Hydrdostatic Pressure at Low Temperatures

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RAMAN STUDY OF SELF-TRAPPED PHONONS IN CRYSTALLINE ACETANILIDE UNDER HYDRDOSTATIC PRESSURE AT LOW TEMPERATURES

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Abstract We have examined pressure effect on the self-trapped states of the amide-I vibrational mode(N-C=O stretching) in crystalline acetanilide ($C_6H_5NHCOCH_3$) by means of Raman spectroscopy. The pressure dependences of the spectral position and intensity are interpreted by taking into account the changes in both inter-molecular forces and intrachain dipolar couplings. In addition, a new self-trapped state is observed upon cooling in hydrostatic pressure above ~ 2 GPa.

INTRODUCTION

The concept of the self-trapping has been applied to phonons in the polypeptide chains made of hydrogen bonded peptide groups(NHCO).[1-2]According to the theoretical investigation,[3] the self-trapping occurs if a molecular vibrational mode extending over crystal through dipole-dipole interactions is localized to deform the lattice through its interaction with longitudinal lattice modes. Acetanilide($C_6H_5NHCOCH_3$) has been recognized as a model system for a self-trapped state owing to the presence of peptide groups and quasi one-dimensional hydrogen bondings which run through the crystal parallel to the b-axis.[4-5] The amide-I mode(N-C=O stretching mode) in the peptide group is expected to be coupled strongly to the lattice modes through hydrogen bondings. The purpose of this study is to investigate spectroscopic evidences for the self-trapped state on the basis of Raman spectroscopy under hydrostatic pressure at low temperatures. The pressure dependences of both peak energy and integrated intensity of Raman band observed at 1650 cm^{-1} are interpreted well in terms of the self- trapped model by taking into account the change in intermolecular force and intrachain dipole-dipole interaction.

EXPERIMENTAL PROCEDURES AND RESULTS

Single crystals of acetanilide were grown from the saturated aqueous ethanol solution of powder sample. Raman spectrum under pressure at various temperatures was measured by using a microscope-spectrometer system combined with a continuous flowtype cryostat specially designed for high pressure cell. Figure 1 shows typical results of Raman spectra at various temperatures under high pressure for polarization of the incident laser beam $E \parallel b$. In addition to the

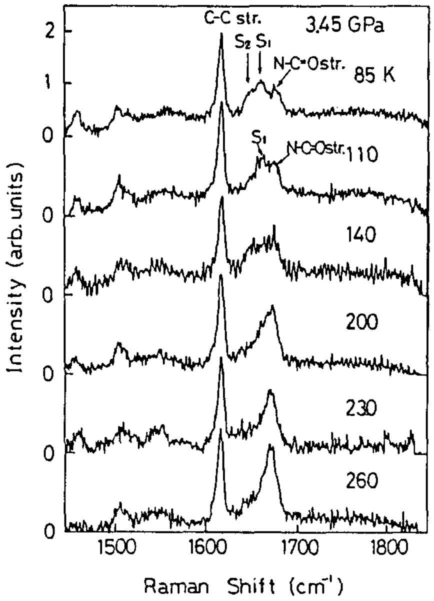

FIGURE 1 Raman spectra due to intra-molecular vibrational modes under various temperatures at 3.45 GPa.

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peak, S_1, observed at 15 cm^{-1} below that of the amide-I mode (A_g), a new band, S_2, emerges upon cooling under high pressures. Figure 2 shows the Raman spectra at various pressures. Figure 3 shows the pressure dependence of their spectral positions at 85 K. Figure 4 shows the pressure dependence of respective Raman shift of lattice modes.

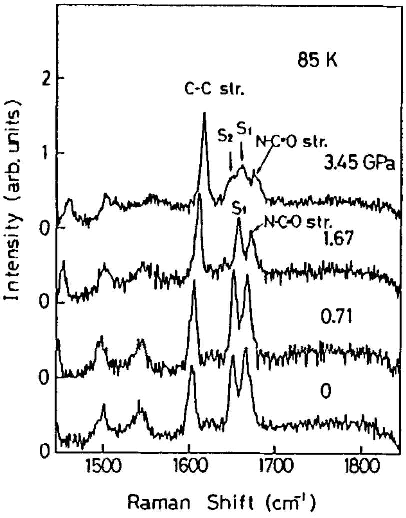

FIGURE 2 Raman spectra due to intra-molecular vibrational modes under various pressures at 85 K.

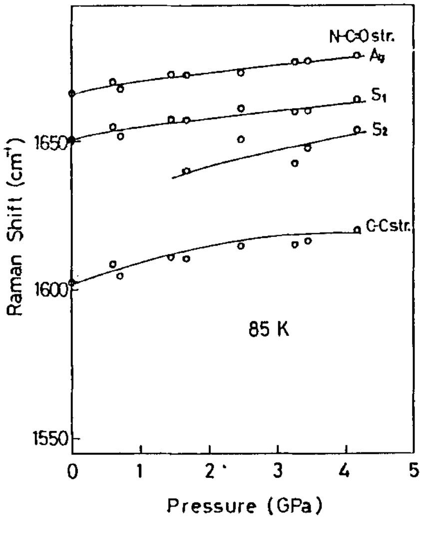

FIGURE 3 Pressure dependence of Raman frequencies of intra-molecular vibrational modes at 85 K.

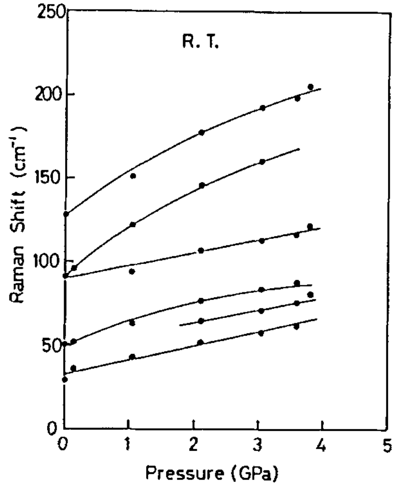

FIGURE 4 Pressure dependence of frequencies of lattice modes.

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DISCUSSION

Neglecting the energy dispersion of the self trapped state, the optical excitation energy of the self-trapped state is given by [3]

$$\omega_s = \omega_0 - (\Delta_1 - 2J), \tag{1}$$

where ω_0 is the optical excitation energy of the amide-I phonon (A_g mode), Δ_1 the energy gain due to self-trapping of the phonon, J the dipole-dipole interaction between adjacent vibrational dipoles owing to N-C=O stretching modes. The higher energy peak (B_{1g} mode) for the Davydov splitting of the amide-I phonon is observed for E⊥b and not observed for E∥b as shown in Fig.1 . These spectral results give J = 3.5 cm^{-1} under ambient condition. Assigning the peak, S_1, at 1650 cm^{-1} to the self-trapped state, Δ_1 is estimated to be 23 cm^{-1} by using eq.(1). The expression of Δ_1 is give by [4]

$$\Delta_1 = \chi^2/2M\omega_1^2 , \tag{2}$$

where χ is the coupling constant between the amide-I and lattice modes, ω_1 is the frequency of lattice mode coupling with the amide-I phonon, M the reduced mass associated with the lattice mode. The Raman frequencies of the lattice modes increase with increasing pressure, indicating that the inter-molecular forces stiffen under pressure. Thus Δ_1 decreases as pressure increases. The energy separation, however, of the self-trapped state from the amide-I phonon remains nearly unchanged under pressure up to 4 GPa as indi-

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cated in Fig.3, implying that J also decreases to leave $\Delta_1 - 2J$ nearly constant. The increase in the intermolecular forces also causes an increase in the Franck-Condon factor of optical excitation to the self-trapped state through the reduction of lattice deformation. This feature is consistent with the result that the integrated Raman intensity increases with increasing pressure. If the pressure exceeds about 2 GPa, a new band, S_2, appears at about 30 cm^{-1} below the amide-I phonon line (A_g mode). The energy separation from the amide-I phonon remains nearly unchanged under pressure. In addition, the integrated intensity of the new band increases upon cooling as well as that of the peak, S_1, for the self-trapped state. These results suggest that the new band is also due to a self-trapped state of the amide-I phonon. Extraporating data in Fig.3 to lower pressures, we obtain $\omega_s = 1633 \pm 5$ cm^{-1} under atmospheric pressure. The Δ_2 for the new self-trapped state is estimated to be 39 ± 5 cm^{-1} under atmospheric pressure by using eq.(1), indicating that the new self-trapped state is caused by its coupling with another lattice mode rather than the same mode as for Δ_1. Provided the coupling strength for the new self-trapped state, S_2, is same as that for the self-trapped state, S_1, we obtain $\omega_2 \sim 0.77\omega_1$. This ratio is interpreted by assigning ω_1 and ω_2 to lattice modes observed at 130 and 94 cm^{-1}, respectively.

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