High-pressure Raman study of vibrational spectra in crystalline acetanilide

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We have studied the effect of pressure on the low-frequency lattice modes and the amide-I (N—C═O stretching) vibrational modes in crystalline acetanilide ($C_6H_5NHCOCH_3$) in the temperature range 80–300 K by means of Raman spectroscopy. The Raman intensity of the 1650-cm^{-1} band, which appears upon cooling, is enhanced by applying pressure. The energy difference between the amide-I phonon (A_g mode) and the 1650-cm^{-1} bands does not change appreciably under pressure up to at least 4 GPa. These results are analyzed in terms of the self-trapped model in which a single lattice mode couples with the amide-I excitation by taking into account the effect of pressure on the low-frequency lattice modes and on the dipole-dipole interactions associated with the amide-I vibration. A band is observed at 30 cm^{-1} below the amide-I phonon band at low temperatures with a pressure above ~ 2 GPa.

I. INTRODUCTION

Self-trapping is a concept that has been established by studying relaxation processes of an excited electronic state interacting with phonons. Recently, the concept was also applied to vibrational states in the polypeptide chains, which are made of hydrogen-bonded peptide groups (NHCO). Propagation of such a localized state of vibrational excitation is expected to be one of the mechanisms that are responsible for efficient energy storage and transfer in protein molecules consisting of polypeptides.[1]

Crystalline acetanilide can be regarded as a model system for natural proteins, since it consists of quasi-one-dimensional arrays of peptide groups linked by hydrogen bondings as indicated in Fig. 1.[2] The crystal has an ortho-
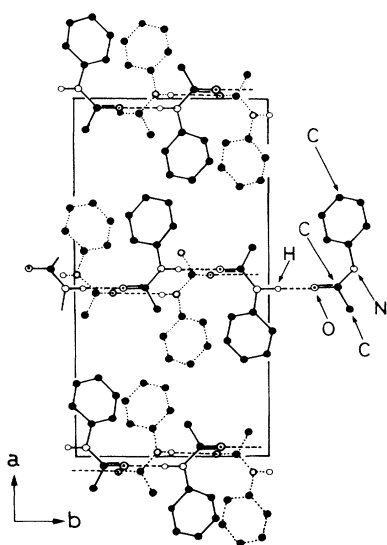

FIG. 1. Projection of the unit cell of acetanilide in the (ac) plane. Solid lines represent molecules in the plane $c/4$, dotted lines, molecules in the plane $3c/4$. Hydrogen bond chains are displayed by dashed lines.

rhombic structure.[3] Two hydrogen-bonded chains run through the crystal parallel to the b axis. The two linear chains stack parallel to the c axis and are separated from each other in the c direction by about 4 Å. In the a direction these chain pairs repeat about every 10 Å. In a linear chain, C═O bonds run parallel to the b axis, so that the direction of the dipole moment associated with N—C═O stretching vibration, which is named amide-I, is inclined by about 20° from the chain direction (b axis).[2]

The amide-I mode is extended over the crystal as phonon through the vibrational dipole-dipole interaction associated with N—C═O stretching vibration. The self-trapping takes place in the following way. The amide-I excitation deforms lattices by the interaction with lattice modes to become localized. The localization gives rise to increase in the interaction between the amide-I excitation and the lattice modes causing lattices to deform further. In this compound an amide-I mode is observed at 1666 cm^{-1}.[2] In addition, an IR and Raman-active peak is observed at 1650 cm^{-1}, which grows with decreasing temperature.[4] The first interpretation of the additional peak at 1650 cm^{-1} was given in terms of the self-trapped model in which the optical lattice mode at 130 cm^{-1} is coupled with the amide-I mode.[5] Afterwards, the model has been improved to interpret quantitatively the temperature dependence of the 1650-cm^{-1} band by taking a band of 10–20 optical phonons and/or acoustic phonons into account.[6,7] However, several other models have been proposed to explain the origin of the 1650-cm^1 band: topological defect model,[8] Fermi resonance model,[9] and coupling between hydrogen-bonded proton motion and low-frequency vibrations.[10] Recently, a transient spectroscopy has been carried out by using a pump-probe technique, indicating that the 1650-cm^{-1} band does not show a long-lived feature characterizing self-trapped states.[11] Discussions on the assignment of this band are still in progress.

According to the self-trapped model, dipole-dipole interactions and intermolecular forces play important roles in the process of the localization and in the spectroscopic property. These quantities can be controlled by applying

hydrostatic pressure on a crystalline sample. In this study we have investigated the consistency of the self-trapped model for the 1650-cm^{-1} band under various conditions generated by hydrostatic pressure. We have measured Raman scattering by the amide-I and the low-frequency lattice modes under hydrostatic pressure up to 4 GPa at temperature in the range 80–300 K. The mode assignment of amide-I phonons is carried out by taking into account the dipole-dipole interactions associated with the N—C=O stretching vibration. The behavior of both the frequency and the intensity of the 1650-cm^{-1} band under pressure is analyzed semiquantitatively by assuming the self-trapped model in which a single lattice mode interacts with the amide-I mode.

II. EXPERIMENTAL PROCEDURES

Single crystals of acetanilide were grown from a saturated aqueous ethanol solution of powder sample. Typical dimensions of the samples were about $10 \times 4 \times 0.2$ mm.[3] The 4765 Å or 4880 Å line of an Ar ion laser was employed as the light source and the light beam was focused on an area of $\phi = 12 \times 10^{-4}$ mm.[2] The scattered light was observed in the nearly back-scattering configuration. The Raman spectrum under pressure at various temperatures was measured by using a microscope-spectrometer system combined with a continuous flow cryostat specially designed for a high-pressure cell. The sample temperature was controlled with an Oxford Model ITC4 temperature controller to an accuracy of $\pm 1°$. The hydrostatic pressure was generated by using the clamp-type diamond-anvil cell. Sumitomo 3M Flourinert FC77 was used for hydrostatic environment inside the pressure cell. The spectrum under atmospheric pressure was obtained by using a conventional photon counting system with a Nalumi 1000D-WN double monochromator and a Hamamatsu R464 photomultiplier. The spectrum under high pressure was obtained by using a Spex Model 1877A triple stage spectrometer with a PAR Model 1254 SIT multichannel detector.

III. EXPERIMENTAL RESULTS

Figure 2(a) shows Raman spectra at various temperatures under atmospheric pressure in the region of the amide-I modes. These spectra are taken for the depolarized laser beam in order to investigate temperature dependence of B_{1g} mode of amide-I phonon as well as A_g mode. The two peaks are observed at 1679 and 1665 cm^{-1}, respectively, at room temperature under atmospheric pressure. The assignment of the symmetry is carried out by referring to the literature.[5,9] The peak energy for the B_{1g} mode decreases upon cooling, while that for the A_g mode remains nearly unchanged. In addition to these peaks, there is a peak S_1 at 1650 cm^{-1} whose intensity grows with decreasing temperature in contrast to A_g and B_{1g} peaks whose intensities decrease upon cooling. These features are in good agreement with results in the literature.[5,9] Figure 2(b) indicates the temperature dependence of the observed Raman shifts. Spectral splitting between the A_g and B_{1g} decreases if temperature de-

creases. Figure 3 shows Raman spectra observed for the depolarized laser beam under various pressures at room temperature. The peak energy for the B_{1g} mode of the amide-I phonon decreases with increasing pressure, while that for the A_g mode remains nearly unchanged. In consequence, the peak for the B_{1g} mode merges into the A_g mode above 0.5 GPa.

Figures 4(a) and 5(a) indicate Raman spectra of lattice modes observed at various temperatures and under various pressures, respectively. Figures 4(b) and 5(b) show
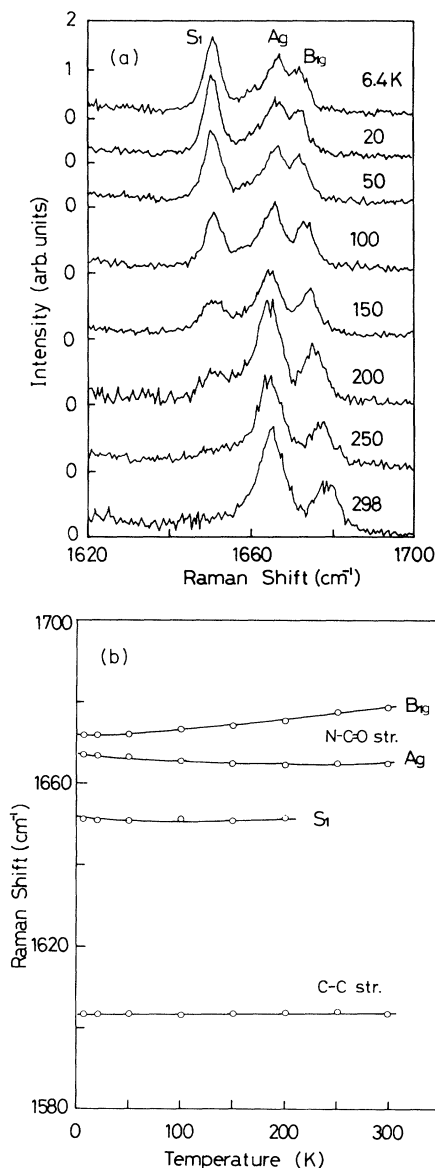

FIG. 2. Temperature dependence of amide-I modes: (a) Raman spectra of amide-I modes (N—C=O stretching) in acetanilide at various temperatures under atmospheric pressure. Incident laser beam is depolarized. (b) Temperature dependence of Raman shifts of amide-I (N—C=O stretching) and C—C stretching modes in acetanilide under atmospheric pressure.
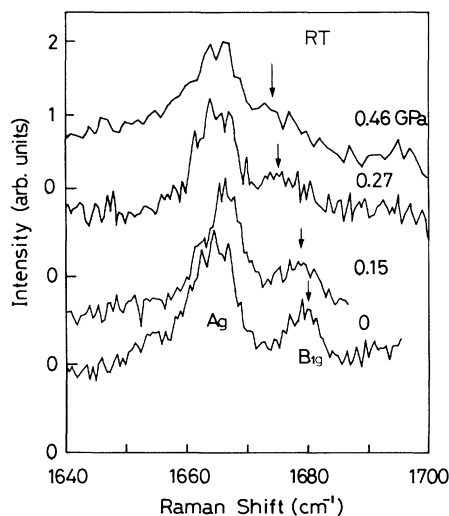
FIG. 3. Raman spectra of amide-I modes (N—C=O stretching) in acetanilide under various pressures at room temperature. Incident laser beam is depolarized. The arrow shows the shift of B_{1g} mode.

temperature and pressure dependences of the Raman shifts of lattice modes, respectively. The Raman shifts of all the lattice modes increase continuously with decreasing temperature or with increasing pressure. No structural phase transformation takes place under hydrostatic pressure up to 4 GPa at least.

Figure 6 shows typical results of Raman spectra of the amide-I vibrational region observed at various temperatures under high pressures for polarization of the incident laser beam $E \| b$. If pressure exceeds about 2 GPa, a Raman band, S_2, appears at a frequency about 30 cm^{-1} below the peak for the amide-I phonon. The intensity of this band increases upon cooling. Figure 7 shows the Raman spectra under various pressures at 85 K. The Raman shifts and intensity of the amide-I mode, S_1 and S_2 are determined by deconvolution analysis of the observed spectra in which we assume Lorentzian line shape. A typical example of the deconvolved spectrum is indicated in Fig. 8. The results for the Raman shifts of S_1 and S_2 are plotted in Fig. 9(a) along with that of the amide-I mode (A_g). The energy difference between the amide-I phonon and the S_1 band does not change appreciably under pressure up to 4 GPa at 85 K. Extrapolating the data points of the band, S_2, in Fig. 9(a) toward lower pressures, we obtain $\omega_s = 1663 \pm 5$ cm^{-1} under atmospheric pressure at 85 K. This band is never observed at atmospheric pressure even if temperature decreases. Figure 9(b) indicates the temperature dependence of the integrated Raman intensity of the S_1 band under various pressures. The intensity is given relative to that for the C—C stretching mode. The respective curves in Fig. 9(b) are obtained by least-squares fits, taking power series up to order 2 into account. The relative intensity increases with increasing pressure at any temperature observed. Figure 9(c) shows pressure dependence of the line width associated with C—C stretching, amide-I and S_1 band at

about 90 K. The respective lines are obtained by least-squares fits.

IV. DISCUSSION

A. Mode assignment of amide-I phonons

Structural features of crystalline acetanilide mentioned in the Introduction allow us to take four molecules into account for mode assignment of the amide-I phonons. It has been determined that the amide-I modes essentially consist of four modes, which are designated M_1, M_2, M_3,
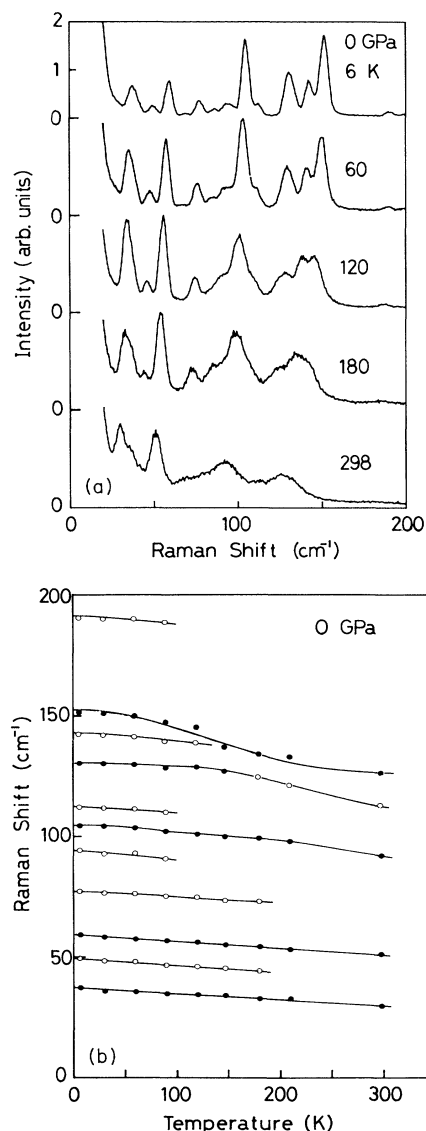

FIG. 4. Temperature dependence of lattice modes in acetanilide: (a) Raman spectra of lattice modes observed at various temperatures under atmospheric pressure. (b) Temperature dependence of Raman shifts of lattice modes under atmospheric pressure. Solid and open circles denote intense and weak-shoulder bands, respectively.

and M_4, as indicated schematically in Fig. 10. In fact, at room temperature two Raman peaks with symmetry A_g and B_{1g} are observed at 1665 and 1679 cm^{-1}, respectively, and an IR peak with symmetry B_{2u} at 1666 cm^{-1}. Taking the nearest-neighbor and the next-nearest-neighbor dipole-dipole couplings into account, we find that the difference of frequency between M_1 and M_3 modes is given by $4J_{1a} + 2J_{2c}$, and the difference between M_1 and M_2 modes by $2J_{2a} + 2J_{2c}$, where J_{1a} is the intrachain dipole-dipole interaction, J_{2a} and J_{2c} the interchain dipole-dipole interactions defined in Fig. 10. Since J_{2a} is nearly equal to J_{2c}, we obtain the difference between M_1 and M_2 modes to be $\sim 4J_{2c}$.

Assuming that the intrachain dipole-dipole coupling is

larger than the interchain dipole-dipole coupling, we obtain the assignment of the IR and Raman features as indicated in Table I. No detectable amount of spectral splitting is observed between A_g and B_{2u} modes, while the difference between A_g and B_{1g} modes amounts to about 14 cm^{-1} at room temperature. From this assignment we obtain $J_{2c} \ll 1$ cm^{-1} and $J_{1a} = 3.5$ cm^{-1} at room temperature and atmospheric pressure. The value of J_{1a} thus obtained agrees well with that estimated theoretically.[12] The spectral splitting between A_g and B_{1g} decreases with decreasing temperature and with increasing pressure as indicated in Figs. 2 and 3, respectively. This result suggests that the magnitude of J_{1a} reduces monotonically with decreasing temperature and with increasing pressure. The pressure coefficient of J_{1a} is obtained to be -3.5 ± 0.8 cm^{-1}/GPa at pressure below 1 GPa.

The dipole-dipole interaction is also affected by the intermolecular distance and by the direction of the dipole moments. According to results of x-ray diffraction, intermolecular distances associated with b axis are reduced by about 0.7% upon cooling to about 90 K without significant change in the orientation of the molecules.[5,13] This decrease in the intermolecular distance causes the dipole-dipole interaction to increase by about 2%. According to our interpretation for the assignment of amide-I modes, the dipole-dipole interactions decrease by about 50% as temperature decreases to about 90 K. This feature indicates that the change in the dipole-dipole interaction is caused almost entirely by the change in the magnitude of the dipole moment, which decreases by about 25% upon cooling to about 90 K.

In a fully deuterated sample, the A_g and B_{1g} modes of the amide-I phonon are observed at 1635 and 1664 cm^{-1}, respectively, at room temperature.[14] On the basis of our assignment, the magnitude of J_{1a} for deuterated sample is estimated to be about 7 cm^{-1}, being twice as large as that of the hydrogenated sample. In contrast to the hydrogenated sample, the spectral interval between these modes is not changed as temperature decreases, so that J_{1a} turns out to be insensitive to temperature.

These results suggest that the dipole-dipole interaction associated with amide-I modes is affected strongly by the hydrogen bond in a linear chain consisting of peptide groups, and is reduced as the hydrogen bond stiffens under low temperature and/or hydrostatic pressure.

B. Analysis of the 1650-cm^{-1} band under high pressure on the basis of the self-trapped model

The energy gain due to self-trapping is given by the equilibrium condition between the increase in elastic en-
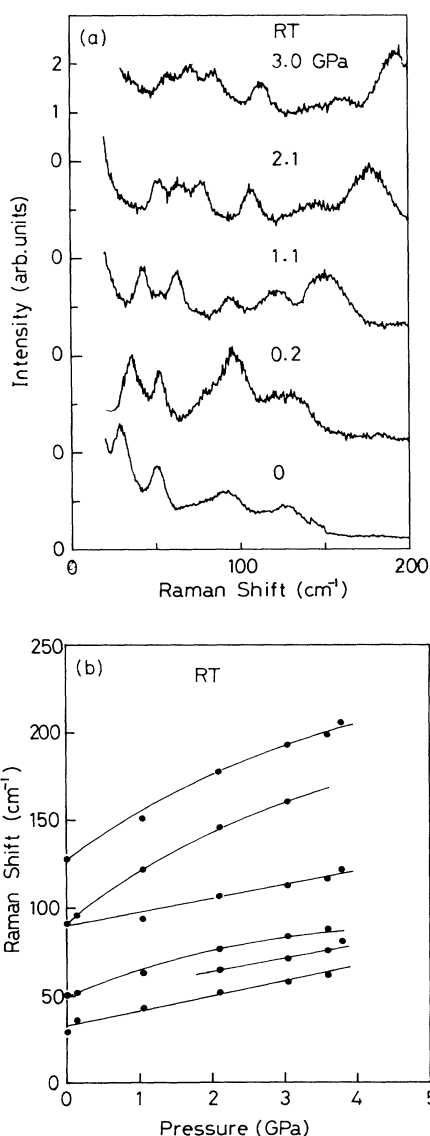

FIG. 5. Pressure dependence of lattice modes in acetanilide: (a) Raman spectra of lattice modes observed under various pressures at room temperature. (b) Pressure dependence of Raman shifts of lattice modes in at room temperature.

TABLE I. Mode assignment of amide-I phonons in acetanilide.

	Raman	IR	Assignment(D_{2h})
M_1	1665 cm^{-1}		A_g
M_2		1666 cm^{-1}	B_{2u}
M_3	1679 cm^{-1}		B_{1g}
M_4			B_{2u}
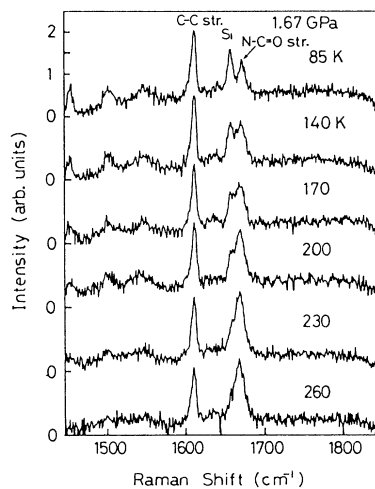
FIG. 6. Raman spectra due to amide-I (N—C═O stretching) and C—C stretching modes in acetanilide at various temperatures under 0, 0.71, 1.67, and 3.45 GPa.

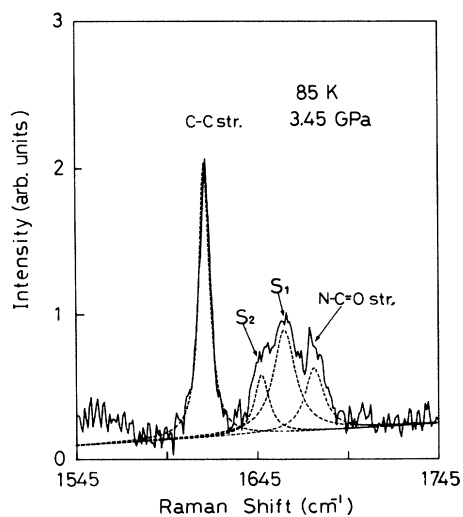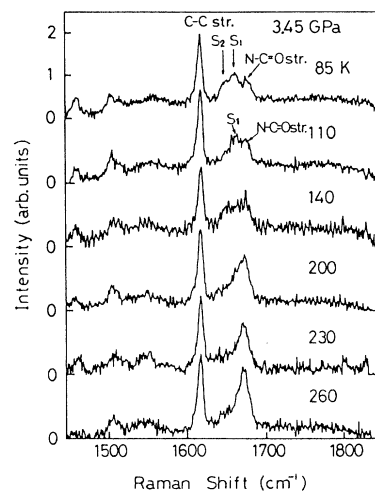FIG. 7. Raman spectra due to amide-I (N—C═O stretching) and C—C stretching modes in acetanilide under various pressures at 85 K.

FIG. 8. Raman spectra of amide-I modes (N—C═O stretching) under 3.45 GPa at 85 K. Solid and dashed lines denote observed and decomposed spectrum, respectively.
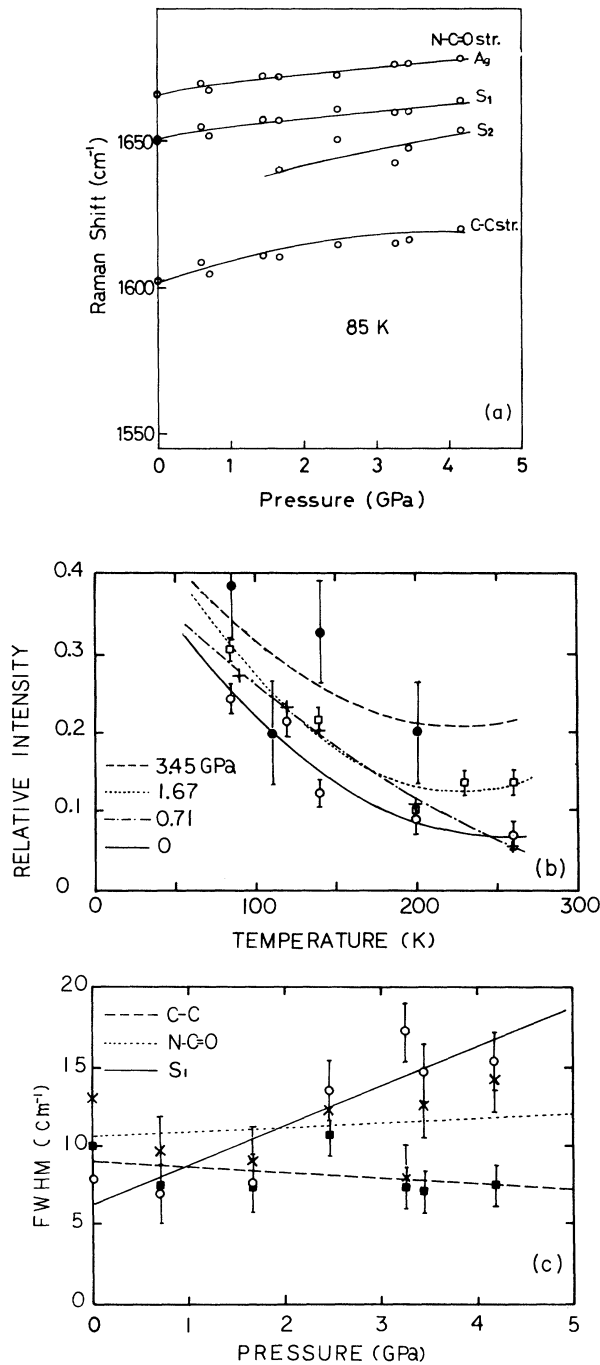
FIG. 9. Result of deconvolution analysis for spectra in Fig. 6: (a) Pressure dependences of Raman shifts of amide-I (N—C= O stretching), S_1 and S_2 bands. (b) Temperature dependence of integrated Raman intensity associated with S_1 band under various pressures. Open circles, crosses, open squares, and solid circles denote 0, 0.71, 1.67, and 3.45 GPa, respectively. The intensity is given relative to that of C—C stretching mode. Respective curves are obtained from least-squares fits taking into account power series up to order 2. (c) Pressure dependence of line width associated with C—C stretching, amide-I (N—C=O stretching) and S_1 bands, which are denoted by solid squares, crosses, and open circles, respectively. Respective lines are obtained from least-squares fits.
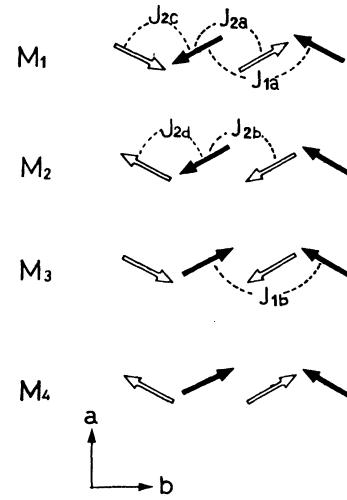

FIG. 10. Schematic illustration of amide-I modes in acetanilide. Solid and open arrows denote vibrational dipole moments (N—C=O stretching) of molecules in the plane $c/4$ and in the $3c/4$, respectively. J_{1a} and J_{1b} indicate intrachain dipole-dipole interactions. J_{2a}, J_{2b}, J_{2c}, and J_{2d} indicate interchain dipole-dipole interactions.

ergy due to the lattice deformation around the localized state and the energy reduction caused by the interaction between the amide-I mode and lattice modes. Thus, the optical excitation energy of the self-trapped state is given by[5]

$$\omega_s = \omega_o - (\Delta_1 - 2J_{1a}) \ , \tag{1}$$

where ω_o is the frequency of the amide-I phonon at zone center (A_g mode) and Δ_1 is the energy gain owing to the self-trapping. Assuming that the S_1 band observed at 1650 cm^{-1} is due to excitation of the self-trapped state, we obtain $\Delta_1 = 23$ cm^{-1} at 298 K and $\Delta_1 = 18$ cm^{-1} at 6 K from Eq. (1) by taking the change in J_{1a} into account. The magnitude of Δ_1 is reduced upon monotonically upon cooling with a temperature coefficient of -0.017 ± 0.007 cm^{-1}/K.

Provided that a single optical phonon (lattice mode) couples with the amide-I phonon, the expression for Δ_1 is given by[5]

$$\Delta_1 = \tfrac{1}{2}\chi^2/(M\Omega^2) \ , \tag{2}$$

where χ is the coupling constant between the amide-I and the optical phonon. Quantities Ω and M are the frequency and the reduced mass of the optical phonon, respectively. The Raman shifts of lattice phonons are raised monotonically upon cooling as indicated in Fig. 4. Using Eq. (2) and the averaged temperature coefficients of the Raman shifts of lattice phonons, we obtain the temperature coefficient of Δ_1 to be -0.027 ± 0.005 cm^{-1}/K under the assumption that χ remains unchanged upon cooling. This value thus obtained agrees with that estimated by using Eq. (1) within experimental accuracy.

Quantity Δ_1 is also reduced under hydrostatic pressure because of the increase in the frequencies of the lattice

modes. Using Eq. (2) and the averaged pressure coefficients for lattice modes, we obtain a pressure coefficient for Δ_1 of -8 ± 1 cm^{-1}/GPa at room temperature. Although we have never investigated pressure dependence of lattice modes at low temperatures, it is expected that Δ_1 is reduced by pressure at low temperatures. Our experiment shows that the energy difference between the amide-I phonon (A_g mode) and the S_1 bands does not change appreciably under pressure up to 4 GPa at 85 K. This result implies that the magnitude of J_{1a} also decreases to leave Δ_1-2J_{1a} nearly constant under pressure. We obtain the pressure coefficient of J_{1a} to be -4 ± 0.5 cm^{-1}/GPa under assumption that $d\Delta_1/dP=-8\pm1$ cm^{-1}/GPa at 85 K. The coefficient thus estimated is consistent with the result, $dJ_{1a}/dP=-3.5\pm0.8$ cm^{-1}, obtained in the previous section.

The Raman intensity of the Stokes process yields to the excitation probability of the self-trapped state. Provided that S_1 band corresponds to the zero-phonon line, the excitation probability depends linearly both on the Franck-Condon factor and on the occupation probability of the ground state of the self-trapped state. The Franck-Condon factor of the optical transition to the self-trapped state is given by

$$F=\exp[-\Delta_1/(\hbar\Omega)] \, , \tag{3}$$

where we assume that an optical lattice mode is coupled with the amide-I phonon. The value of F at atmospheric pressure is estimated to range from 0.5 to 0.9 depending on the type of optical mode. The occupation probability of the ground state is given by

$$P=1-\exp(-\hbar\Omega/kT) \, . \tag{4}$$

Hydrostatic pressure affects on both quantities F and P through the frequency of the lattice mode. Quantity FP is plotted in Fig. 11 as a function of temperature under various frequencies of the lattice mode. In this calculation, we have assumed the optical phonon observed at 130 cm^{-1} under atmospheric pressure is coupled with the amide-I excitation. Comparing the experimental result shown in Fig. 9(b) with this calculation, we find that the pressure dependence of the Raman intensity of the S_1 band can be interpreted semiquantitatively in terms of the self-trapped model by taking the change in frequency of the lattice mode into account.

The line width depends on the life time of excitation states. As shown in Fig. 9(c), the linewidth of the S_1 band has the same order as those of other conventional bands due to the N—C$=$O and C—C stretching modes. This feature is consistent with the result of a dynamical test showing directly that the life time of the S_1 band is almost the same as a vibrational line in a molecular crystal.[11] According to our result indicated in Fig. 9(c), the linewidth of the S_1 band increases with increasing pressure; it becomes about three times as large as that under atmospheric pressure if pressure increases up to 5 GPa, while those of the N—C$=$O and C—C stretching modes
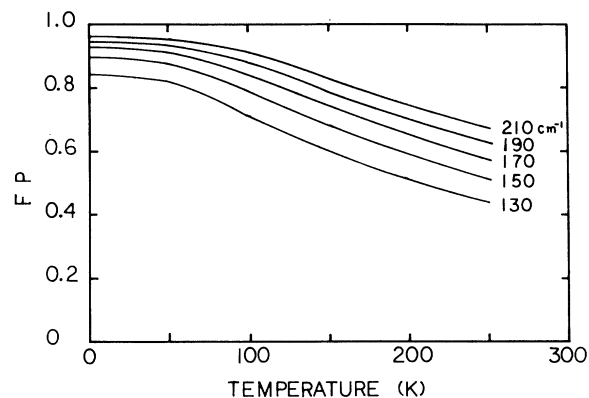

FIG. 11. Temperature dependence of quantity FC calculated from Eqs. (3) and (4) for various values of the frequency of the lattice mode observed at 130 cm^{-1} under ambient condition. In this figure 150, 170, 190, and 210 cm^{-1} correspond to 0.8, 1.6, 2.8, and 3.7 GPa, respectively.

remain nearly unchanged. This feature suggests that the dynamical property of the S_1 band is different from that of a conventional vibration in a molecular system. According to the dynamical measurement, the origin of the S_1 band is interpreted in terms of nondegenerate hydrogen-atom configurations.[11] In order to verify this model, knowledge of the N—H stretching and of the N—H bending vibrations are desired. At present, we can not exclude the possibility.

V. CONCLUSIONS

We have measured Raman-scattering spectra due to low-frequency lattice phonons, amide-I phonons, and the 1650-cm^{-1} band in crystalline acetanilide under hydrostatic pressure up to 4 GPa at temperatures in the range 80–300 K. The intrachain dipole-dipole interaction associated with the amide-I vibration is obtained to be 3.5 cm^{-1} under ambient condition from the energy splitting between the A_g and B_{1g} modes of the amide-I phonon. The pressure dependences of the Raman shift and the intensity of the 1650-cm^{-1} band are analyzed under assumption of the self-trapped model in which a single lattice mode at 130 cm^{-1} interacts with the amide-I excitation. The experimental results are interpreted semiquantitatively by taking into account the observed changes in frequency of lattice modes and in magnitude of intrachain dipole-dipole interaction. It is required to improve the signal-to-noise ratio of the Raman spectrum under high pressure at low temperature for analysis based on the self-trapped model in which a band of 10–20 optical phonons and/or acoustic phonons interact with the amide-I excitation.

In addition to the 1650-cm^{-1} band, a band is observed at about 30 cm^{-1} below the amide-I phonon (A_g mode) at low temperature in hydrostatic pressure above $\sim$2 GPa. Further studies are required to understand the origin for the band.

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