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High-pressure Raman study of a one-dimensional hydrogen-bonded crystal of cyanoacetylene

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At room temperature, cyanoacetylene undergoes a liquid–solid transition at 70 ± 30 MPa and further a polymerization reaction at 1.5 GPa. Raman spectra indicates that the crystal structure of the high-pressure phase is isomorphic with the monoclinic low-temperature structure ($P2_1/m$, $Z = 2$), in which linear cyanoacetylene molecules are joined with CH NC hydrogen bonds to form infinite one-dimensional chains. The internal stretching frequency of the C–H proton donor decreases wtih increasing pressure, while that of the $C{\equiv}N$ proton acceptor increases. The librational modes associated with the rotational motions of the rigid molecules show large shifts to higher frequencies with pressure. The observed frequency shifts are attributed to the strengthening of the $CH\cdots NC$ hydrogen bond in the one-dimensional molecular chain.

INTRODUCTION

High-pressure behavior of hydrogen bonds in molecular solids has been an attractive subject in chemistry and physics. Hydrogen bonding, one of the fundamental bonding forces, plays an important role in construction of stable molecular arrangements in a condensed form. Typical groups contributing as a proton donor are those of O–H, N–H, and C–H. For the molecular solids containing these donor groups, high-pressure spectroscopic studies have been made in order to investigate pressure effects on the bonding nature. There have been reports on high-pressure Raman studies of water[1] and alcohols[2] with O–H groups and amins[3] with N–H groups. In these hydrogen-bonded solids, the large frequency shifts of the lattice and molecular vibrations associated with the hydrogen bonds were observed, indicating the strengthening of the bonding forces at high pressures.

Cyanoacetylene, $H{-}C{\equiv}C{-}C{\equiv}N$, is a linear molecule with $C{\equiv}C$ and $C{\equiv}N$ triple bonds.[4,5] The molecules tend to join each other linearly with the $CH\cdots NC$ hydrogen bonds. The formation of linear polymers in the liquid phase was confirmed by dielectric constant measurements.[6] The crystal structure of the low temperature phase appearing below 278 K at atmospheric pressure was determined by x-ray diffraction to be a monoclinic structure ($P2_1/m$) with two molecules in the unit cell.[7] The molecules are joined with the hydrogen bonds into linear infinite chains, which are nearly close packed. In the sequential transitions from the gas to liquid and to solid at low temperatures, the C–H stretching mode shows a discontinuous decrease in frequency by several tens of wave numbers at each transition.[8] These experimental results demonstrate the role of the $CH\cdots NC$ hydrogen bond in the formation of the linear molecular chains. The hydrogen bond in cyanoacetylene has also been studied theoretically. The hydrogen-bond energies of the complexes[9] and the proton affinity of the monomer[10] were calculated by *ab initio* molecular orbital theory.

We have made Raman study of cyanoacetylene to investigate phase transitions and vibrational properties under pressure. Raman measurements revealed that cyanoacety-

lene underwent a liquid–solid transition at 70 MPa and further a solid-state reaction at pressures above 1.5 GPa. No structural transformation occurred in the molecular crystalline phase. In this paper, the Raman spectra of the high-pressure crystalline phase are presented and the observed Raman frequencies are discussed in relation to changes in the hydrogen bond.

EXPERIMENTAL

Cyanoacetylene of 97% purity (Nakarai Chemicals Ltd. Kyoto) was used for high-pressure measurements without further purification. Cyanoacetylene is a colorless and transparent liquid at atmospheric pressure and room temperature. The liquid phase exists for a narrow temperature range from 278 to 315.5 K. Because of being chemically reactive and highly volatile, the sample was handled in a solid form below a melting temperature of 278 K. High-pressure Raman measurements were made with a gasketed diamond anvil cell. A frozen sample was charged in a small hole 0.4 mm in diameter drilled in a metal gasket of Inconel X-750 approximately 0.2 mm thick, which had been preindented from an original thickness of 0.33 mm. The pressure was determined on the basis of the ruby fluorescence scale.[11] A detailed description on the diamond cell and sample loading technique has been reported elsewhere.[12]

Raman spectra were measured in forward scattering geometry. The 530.9 nm line of a krypton-ion laser (Spectra Physics model 171) was used as an excitation source. The incident beam was focused to a fine spot approximately 0.06 mm in diameter on the sample. Cyanoacetylene was so chemically reactive that the sample surface immediately turned black by radiation of the excitation light even with moderate powers of several tens of milliwatts. The input power was reduced step by step until no damage was confirmed on the radiated surface. Eventually the excitation laser was operated at extremely low power levels of 0.5–1.0 mW input. Instead of the 530.9 nm line we also tried the 647.1 nm line for which exciting light with much power was able to be put in the sample without radiation damages.

However, obtained spectra were not satisfactory in quality compared with those obtained for the 530.9 nm line. The scattered light was collected in the forward direction. The spectra were recorded with a Spex double monochromator (model 1403) with photon-counting detection. Twenty repeated measurements were accumulated to obtain a spectrum of good quality. The spectral resolution was about 4 cm^{-1}. All measurements were made at 295 K.

RESULTS AND DISCUSSION

Liquid cyanoacetylene crystalized at 70 ± 30 MPa. A single crystal of the high-pressure phase was prepared simply by controlling the pressure on the sample. The liquid abruptly transformed into a polycrystal when the pressure increased beyong the crystallization pressure. The pressure was then released to the equilibrium crystallization pressure and kept until all but one grain melted. A remaining single crytal first grew along one particular direction of the crystal with a slight advance of the diamond anvils. When the growing faces at the both sides of the long-and-narrow crystal reached the gasket wall, the crystal began to widen to fill the whole gasket hole. By comparison of the Raman spectrum of the high-pressure phase with that reported for the low-temperature phase,[13] the crystal structure of the high-pressure phase was shown to be identical to that of the low-temperature phase, i.e., a monoclinic structure belonging to the $P2_1/m$ space group with $Z = 2$. In addition, the crystal axis initially grown was shown to correspond with the a axis of the monoclinic lattice by polarization Raman measurements. The Raman Spectra of the crystalline phase were measured at pressures up to 1.5 GPa. At this pressure the transparent crystal gradually turned black. The Raman spectrum of the reaction product indicated the formation of conjugated linear polymers by a solid-state reaction.[14]

A typical Raman spectrum measured for the high-pressure monoclinic crystal is shown in Fig. 1. Two strong peaks observed around 100 cm^{-1} are due to the rotational motions of molecules, R_{xy} librational modes. Three peaks due to the translational motions of molecular chains, two T_{xy} and one T_z modes, should be observed additionally in the lower frequency region. Either peak was not resolved in the spectra measured with polarized or depolarized excitation light. These translational peaks are thought to be obscured by background scattering. Two doublet peaks appearing at 200 and 500 cm^{-1} are due to the bending vibrations of C–C≡C (ν_7) and C–C≡N (ν_6), respectively. The C–C–H bending peak was not observed. Four peaks observed in the frequency region from 800 to 3400 cm^{-1} arise from the internal stretching vibrations: the C–C (ν_4), C≡C (ν_3), C≡N (ν_2), and C–H (ν_1) stretching peaks in the order of increasing frequency.

Raman spectra showed different peak profiles depending on the orientation of a single crystal prepared in the diamond cell. According to the symmetry correlation diagram for the monoclinic structure, each of the rotational (R_{xy}) and bending modes (ν_6, ν_7) splits into two Raman and two IR active modes.[13] For a particular crystal orientation, these three modes have happened to be observed as singlet peaks instead of doublet peaks. Figure 2 shows the Raman spectra
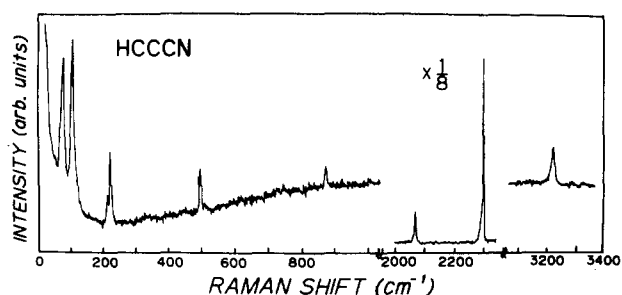
of these three peaks recorded for two crystals with different orientations. In the upper spectrum each Raman band shows a doublet structure in agreement with the predictions based on the correlation diagram. On the other hand, three singlet peaks are observed in the lower spectrum; their counterpart peaks all disappear. The missing peaks were unable to be observed for depolarized excitation light. These results indicate that the librational and bending modes with the vibrational motions in the plane perpendicular to the anvil face are undetectable for the forward scattering geometry employed in the present measurement. The observed singlet peaks are attributed to the librational and bending vibrations in the plane parallel to the anvil face.

The a axis of the monoclinic lattice, which is parallel to the molecular chain axis, was determined from polarized Raman spectra. Figure 3 shows Raman spectra in the frequency region of the C≡C and C≡N stretching vibrations. The upper spectrum was measured with the incident light polarized parallel to the crystal axis initially grown. The C≡C and C≡N stretching peaks are observed at 2066 and 2271 cm^{-1}, respectively. Both peaks completely disappear in the lower spectrum measured with the polarized light rotated by 90 deg from the initial orientation. These two modes are associated with the stretching motions of atoms in the

FIG. 1. A typical Raman spectrum of crystalline cyanoacetylene measured at 0.60 GPa.
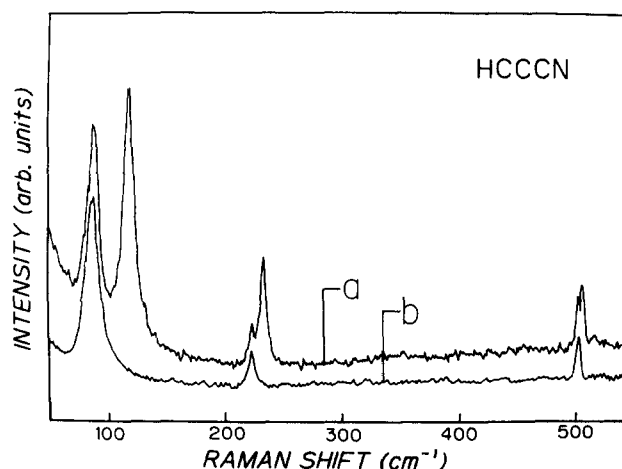

FIG. 2. Raman spectra of the librational and bending peaks of crystalline cyanoacetylene measured for crystals with different orientations. Singlet or doublet peaks are observed depending on the crystal orientation.
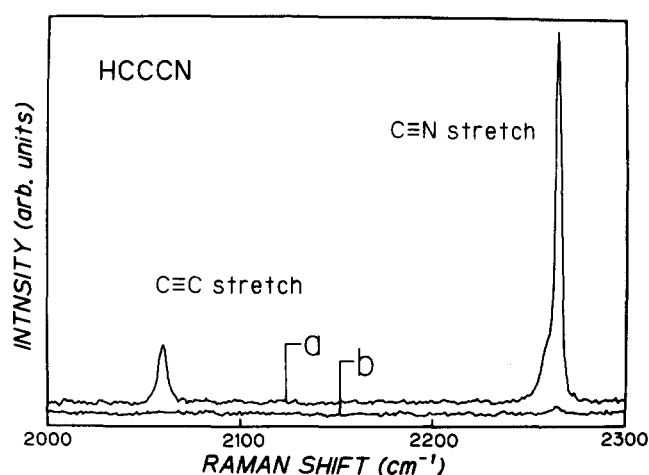
FIG. 3. Raman spectra of the C≡C and C≡N stretching modes of crystalline cyanoacetylene measured at 0.6 GPa with excitation light polarized (a) parallel and (b) perpendicular to the molecular chain axis.

molecular axis, being inactive for the perpendicularly polarized light. Thus, the microscope and polarization Raman measurements showed that cyanoacetylene crystals grow preferably along the molecular chain axis, i.e., the *a* axis of the monoclinic lattice. The Raman spectra of the crystalline phase were measured with the excitation light polarized parallel to the *a* axis. With this optical geometry, good spectra were satisfactorily obtained.

The Raman frequencies obtained for the liquid and crystalline phase are summarized in Table I. The corresponding frequencies of the liquid[15] and solid[13] at atmospheric pressure are also given for comparison. Peak assignments were based on those reported by Nolin *et al.*[13]

Librational frequencies obtained by five independent experimental runs are plotted together in Fig. 4. The ob-

served frequencies are described by a quadratic expression in terms of pressure,

$$\nu_{R_{xy}} = \begin{cases} 78.0 + 31P - 2.2P^2 \\ 103.8 + 40P - 8.5P^2 \end{cases},$$

where ν is in cm^{-1} and P in GPa. These librational modes are associated with the rotational motions of the rigid molecules which are joined with the hydrogen bonds. Their vibrational frequencies are predominantly determined by the strength of the hydrogen bond. Hence, the observed large increases in frequencies can be attributed to the strengthening of the hydrogen bond at high pressure. Similar pressure behavior of librational frequencies has been found in crystalline acetylene.[16] Acetylene molecules form a planar T-shaped configuration with the hydrogen bond between the terminal hydrogen atom and the C≡C triple bond. The librational vibrations showed frequency shifts with pressure coefficients of 30–45 cm^{-1}/GPa. These values are comparable with those obtained for cyanoacetylene crystal.

The frequency variations of the internal modes with pressure are plotted in Fig. 5. Most of them are pressure insensitive. Among them the stretching mode of the C–H proton donor displays characteristic pressure behavior, showing a shift to a lower frequency. The other internal modes, including the stretching mode of the C≡N proton acceptor, show shifts to higher frequencies. The stretching frequencies of the hydrogen-bonded C–H and C≡N groups are given by quadratic expressions

$$\nu_1 = 3218 - 14P + 2.3P^2 \quad \text{for C–H}$$

and

$$\nu_2 = 2268 + 5P - 2.2P^2 \quad \text{for C≡N},$$

where ν is in cm^{-1} and P in GPa. The opposite shifts of the C–H and C≡N stretching frequencies is experimental evidence for the strengthening of the hydrogen bond in the molecular chain under pressure.

Similar frequency shifts of the stretching vibrations of

TABLE I. Summary of Raman frequencies (cm^{-1}) of liquid and crystalline cyanoacetylene.

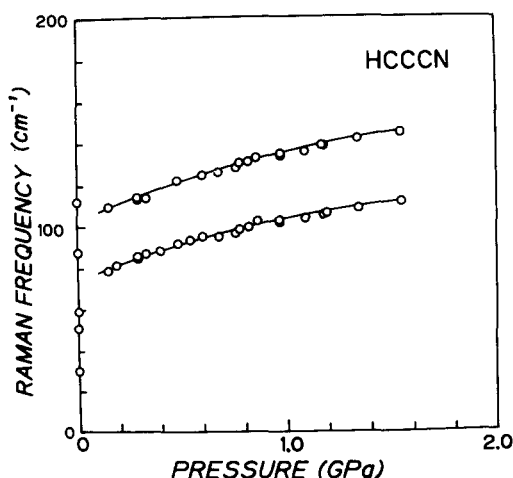| Liquid		Crystal			
1 atm, R.T.[b]	70 MPa, 295 K	1 atm, 77 K[a]	0.68 GPa, 295 K	1.54 GPa, 295 K	Assignments[a]
		30			Translation (T_z)
		51			Translations (T_{xv})
		59			
		88	95	112	*Librations*
		112	126	145	
230	230	227	231	232	ν_7, C–C≡C bend
		236	240	244	
502	505	507	508	509	ν_6, C–C≡N bend
		511	513	515	
684		749			ν_5, C–C–H bend
		763			
877	877	883	889	894	ν_4, C–C stretch
2070	2071	2066	2066	2068	ν_3, C≡C stretch
2270	2266	2267	2271	2275	ν_2, C≡N stretch
3256		3209	3210	3202	ν_1, C–H stretch

[a] Reference 15.
[b] Reference 13.

FIG. 4. Pressure shifts of the librational frequencies of crystalline cyanoacetylene. The data at atmospheric pressure are those measured at 77 K (Ref. 13).
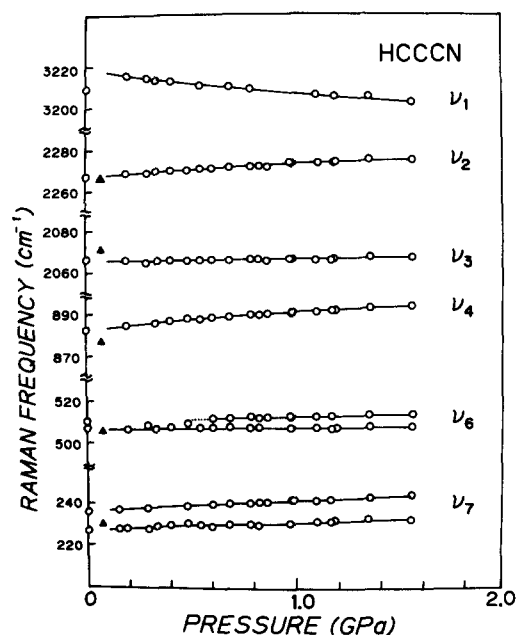
FIG. 5. Pressure shifts of the internal frequencies of liquid (triangles) and crystalline (open circles) cyanoacetylene. The data obtained for the crystalline phase at atmospheric pressure and 77 K (Ref. 13) are plotted together.

proton donor and acceptor have been observed for other hydrogen-bonded molecular solids. In crystalline methanol, for instance, the stretching frequency of the O–H group shows a negative pressure dependence with a coefficient of approximately -15 cm^{-1}/GPa, while that of the O–C group shows a positive dependence with a coefficient of approximately 4 cm^{-1}/GPa.[2] The tendency of the frequency shifts is consistent with that observed for cyanoacetylene crystal. However, the pressure coefficients for the CH$\cdots$NC hydrogen bond are much smaller than those for the O–H$\cdots$O hydrogen bond. This is dominantly due to the one-dimensional feature of cyanoacetylene crystal. The molecules in the chain are connected with the hydrogen bonds, whereas the molecular chains are weakly joined with van der Waals type forces. The applied pressure is expected to act mainly as an external force to move the molecular chains closer. The decrease in the intermolecular distance in the chain might be a little. This small mean pressure effect on the hydrogen bond results in the small pressure shifts of the C–H and C$\equiv$N stretching frequencies.

The relatively large frequency shift of the C–C stretching vibration is an interesting aspect related to the bonding state in the molecule. Microwave absorption[4] and x-ray diffraction studies[7] have shown that the C–C single bond situated between the C$\equiv$C and C$\equiv$N triple bonds has an unusually short length of 1.382 Å. This short distance is explained in terms of resonance between the electronic strctures H–C$\equiv$C–C$\equiv$N and H–C$^+$$=C=C=N^-$. The increase in the ν_4 frequency implies an enhancement in the electronic resonance, in other words, an increase in the degree of double bonding character in the C–C single bond. This consideration leads to a prediction that the Raman frequency of the C–C stretching vibration is also influenced by pressure through the enhanced resonance interactions between the

two electronic structures. On the contrary, the C$\equiv$C stretching frequency hardly showed a frequency shift, remaining unchanged in the whole pressure region measured. Theoretical study of the electronic state of cyanoacetylene is required for understanding the observed pressure dependence of the internal vibrational frequencies.

Intensity variation of Raman peaks was one of our interests concerning with the high-pressure study of cyanoacetylene. Raman intensities of normal modes are given by polarizabilities associated with their normal coordinations. Pressure changes in the electronic state of molecules and crystals affect polarizabilities, causing intensity variations in Raman scattering. In cyanoacetylene crystal, the intensity of the C–H stretching mode is most likely influenced by pressure since it shows the large pressure dependence of the frequency. Unfortunately, Raman spectra of good quality sufficient for intensity comparison were not obtained for the C–H stretching mode. We examined intensity variation for the stretching vibration of the C$\equiv$N proton acceptor instead of the C–H proton donor. The peak intensity, however, showed no significant variation with pressure, suggesting little change in polarizability.

Finally, we emphasize again that cyanoacetylene is one of the ideal substances for studying pressure effects on the hydrogen-bonds. The linear chain structure allows us to treat cyanoacetylene crystal as an one-dimensional system in theoretical calculations. The interactions between the molecular chains could be neglected within the first approximation. It will be, therefore, not difficult to study theoretically the pressure dependent behaviors of the vibrational and electronic properties of cyanoacetylene and compare them with the high-pressure experimental results. Such a comparison will be of great help in understanding the pressure variations in the chemical bonds, in particular, the CH$\cdots$NC hydrogen bond and the resonanced electronic state under pressure.

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