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High-pressure Raman study of liquid and crystalline C_2H_2

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Raman spectra were measured for liquid (0–0.7 GPa), crystalline cubic (0.7–0.9 GPa), and orthorhombic (0.9–3.5 GPa) phases in C_2H_2 at room temperature. For the orthorhombic phase, the high-pressure behavior of the librational and internal vibrations was obtained in a wide pressure range. The frequencies of all the librational modes increased monotonically with pressure, while those of the internal modes showed a variety of frequency shifts depending on vibrational mode. These high-pressure data will be of great use for the construction of theoretical models for the intermolecular interactions in crystalline C_2H_2 .

INTRODUCTION

Acetylene, a linear molecule with a carbon–carbon triple bond, has two molecular–crystalline phases at low temperatures. The phase stable below 133 K has the $Cmca$ orthorhombic structure.¹ In the bc plane, adjacent molecules form a planar T-shaped configuration with an anomalously small intermolecular distance between the hydrogen and the triple bond. The other phase stable between 133 and 191 K has the $Pa3$ cubic structure,² in which the molecules are oriented in the directions parallel to the body diagonals of the cubic lattice at the face-centered sites.

The intermolecular interactions in crystalline C_2H_2 have recently attracted much theoretical interest. The simple atom–atom potentials, successfully applied to other hydrocarbon crystals, cannot satisfactorily account for the static and dynamical properties of crystalline C_2H_2 .³ Several workers introduced, additionally, electrostatic interactions represented by electric charges localized on the atoms or by multipoles distributed on the molecule.^{4,5} The intermolecular potentials consisting of atom–atom and electrostatic interactions were shown to be applicable to the cubic structure but not to the orthorhombic one. Marchi and Righini⁶ demonstrated that an intermolecular potential, which explicitly included a hydrogen bond between the C–H and triple bonds in the T-shaped configuration, was able to reproduce the lattice vibrational properties of the orthorhombic phase.

The phase study of C_2H_2 by Raman scattering⁷ revealed that two high pressure crystalline phases appeared at room temperature in correspondence with the two known low temperature phases.^{8,9} The cubic and orthorhombic phases were found to be stable in the pressure ranges of 0.7–0.9 and 0.9–3.5 GPa, respectively. Above 3.5 GPa solid state polymerization was induced. Following the preliminary phase study, we made detailed Raman measurements on the high-pressure phases to investigate the vibrational properties of crystalline C_2H_2 as a function of pressure.

The purpose of this paper is to present the Raman frequency shifts with pressure measured for the internal and librational vibrations in liquid and crystalline C_2H_2 at room temperature. The frequency shifts obtained for the orthorhombic phase in a wide pressure range will be discussed in relation to the intermolecular interactions in the T-shaped configuration.

EXPERIMENTAL

A wedge-driven diamond cell¹⁰ was employed for high-pressure Raman measurements. Acetylene gas of 99.9999% purity, commercially obtained from Koatsu-Gas Kogyo Ltd. (Osaka), was condensed in the cell being cooled in a liquid nitrogen chamber. After solidified gas was enclosed in a small hole (diameter, 0.3 mm; depth, 0.2 mm) drilled in a metal gasket between opposed anvils, the cell was warmed up to room temperature for measurements. A single crystal of the cubic phase was grown in the liquid phase by carefully tuning the pressure across the solidification pressure of 0.7 GPa. A polycrystal of the orthorhombic phase consisting of several domains, each having a diameter of a few hundred microns, was obtained by keeping the pressure just above the cubic–orthorhombic transition pressure for several hours. The 530.9 and 647.1 nm lines of a Kr^+ ion laser were used for excitation at power levels below a few tens of milliwatts. The laser power was much reduced to a few milliwatts in measurements of the orthorhombic phase at pressures above 3 GPa. Incident light with excess power quickly induced polymerization at the focusing point on the sample surface. Spectra were taken with a Spex 1403 double monochromator in the photon counting method. Pressures were determined using the ruby fluorescence scale.¹¹

RESULTS

Internal modes

An isolated C_2H_2 molecule has three Raman-active internal modes; C–H stretching (ν_1), C–C stretching (ν_2), and C–C–H bending mode (ν_4). The low temperature Raman experiments^{8,9} have shown that each mode splits into several branches on crystallization into the cubic or orthorhombic phase owing to crystal field effects.

High-pressure Raman spectra of the internal modes obtained for the liquid, cubic, and orthorhombic phases at 295 K are shown in Fig. 1. The ν_1 and ν_2 peaks were observed in the liquid phase. In the cubic phase, only the ν_2 peak was observed. The other peaks of the two phases could not be found in the spectral regions expected from the Raman spectra reported for the low temperature phases. They were probably buried in the background attributed to emission from the diamonds. Two ν_1 , two ν_2 , and three ν_4 peaks were

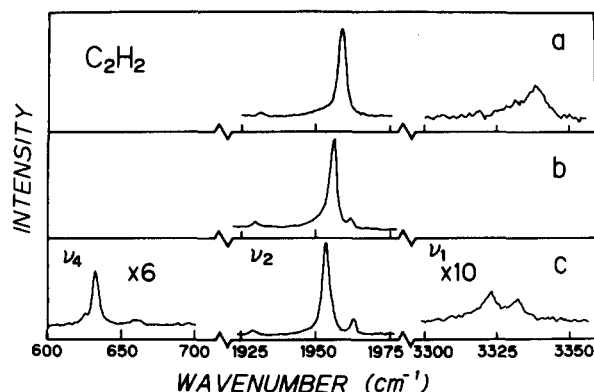


FIG. 1. Raman spectra of internal modes observed for the liquid phase at 0.4 GPa (a), the cubic phase at 0.8 GPa (b), and the orthorhombic phase at 3.2 GPa (c).

observed for the orthorhombic phase, which are consistent with those reported for the low temperature phase. A weak peak around 1930 cm^{-1} seen in each spectrum of the ν_2 mode was interpreted as an isotope effect of carbon.

The frequency shifts of internal vibrations are plotted as a function of pressure in Fig. 2. The strong peak of the ν_2 stretching mode showed a discontinuous decrease in frequency by about 3 cm^{-1} on the liquid–cubic phase transition at 0.7 GPa and again on the cubic–orthorhombic phase transition at 0.9 GPa. Similar downward shifts of the ν_2 peak have been found in the sequential phase transitions, the liquid to cubic and further to orthorhombic phases, realized at low temperatures and normal pressure. In this case, each transition is accompanied by decrease in frequency by about 5 cm^{-1} .

The pressure dependence of the internal frequencies was obtained for the orthorhombic phase in the pressure range of 0.9–3.5 GPa. In the ν_1 and ν_2 stretching vibrations, the frequencies of the A_g mode shifted little with pressure, while those of the B_{3g} mode increased by a few wave numbers. Consequently, the splittings between the A_g and B_{3g} peaks

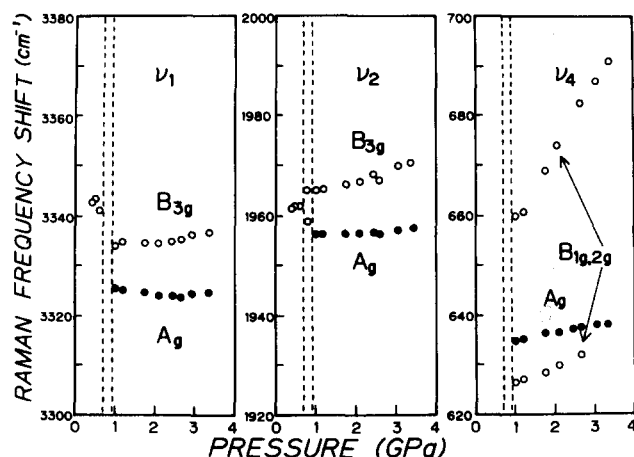


FIG. 2. Pressure shifts of internal Raman frequencies obtained for the liquid and crystalline C_2H_2 . Two broken lines drawn in each figure indicate separations between the liquid and cubic phases at 0.7 GPa and the cubic and orthorhombic phases at 0.9 GPa.

widened monotonically with rising pressure. Striking features of frequency shifts were observed in the ν_4 bending mode region. One branch, having the highest frequency among three, showed a very large shift to higher frequency, which was comparable to those observed for the lattice modes as described later. This peak is due to the out-of-plane bending motion, assigned to either B_{1g} or B_{2g} symmetry. The hydrogen atom moves in the plane perpendicular to the plane formed by the triple bonds of the nearest-neighbor molecules. By contrast, the in-plane A_g bending mode showed a weak dependence on pressure.

Lattice modes

Librational lattice spectra were obtained for the orthorhombic phase but not for the cubic one. The librational frequencies of the cubic phase were estimated to be less than 70 cm^{-1} from those reported for the low temperature phase. Librational peaks were probably buried in the tail of Rayleigh scattering extending to about 100 cm^{-1} .

Figure 3 shows the librational spectra of the orthorhombic phase taken at various pressures. Three librational peaks, A_g , B_{1g} , and B_{2g} were observed as expected from the results of the low temperature experiments. At 1.0 GPa a strong peak composed of the overlapping A_g and B_{1g} peaks and a weak B_{2g} peak were located at 90 and 200 cm^{-1} , respectively. With increasing pressure, a shoulder peak appeared on the high frequency side of the strong peak. The intensity ratio of the shoulder to strong peak was about 1:2. In the low temperature orthorhombic phase, the B_{1g} peak is observed as a shoulder peak on the low frequency side of the strong A_g peak. The peak intensity of the B_{1g} mode is about half of that of the A_g peak. We, therefore, assigned the shoulder peak appearing at higher pressures as the B_{1g} mode.

Pressure shifts of the librational vibrations are shown in

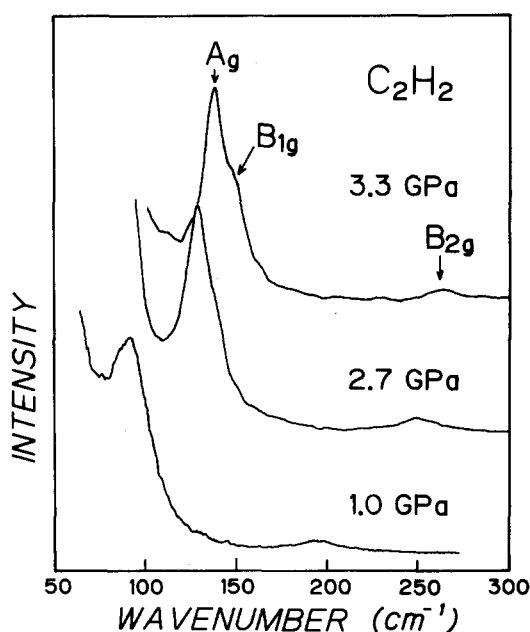


FIG. 3. Raman spectra of librational modes observed for the orthorhombic C_2H_2 at high pressures.

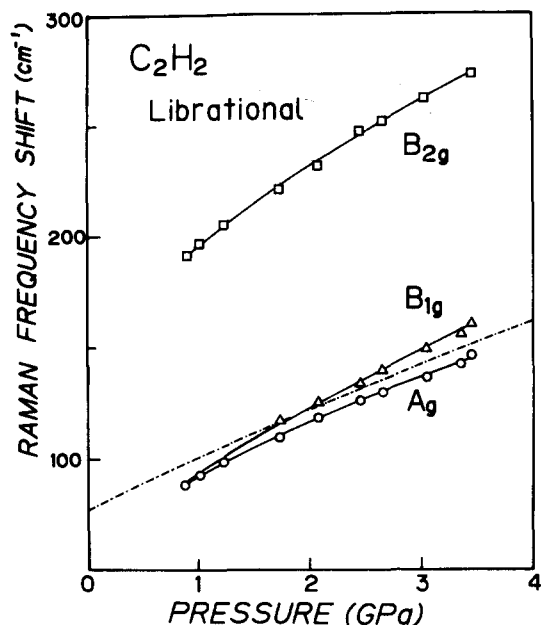


FIG. 4. Pressure shifts of librational Raman frequencies obtained for the orthorhombic C₂H₂. An alternate long and short dash line shows frequencies calculated for the A_g mode at 0 K.¹²

Fig. 4. Each frequency increased rapidly with pressure. The fitting of frequencies to a quadratic expression in terms of pressure gave the following results:

$$\nu_{A_g} = 64.2 + 29.8P - 1.8P^2,$$

$$\nu_{B_{1g}} = 56.7 + 37.9P - 2.4P^2,$$

and

$$\nu_{B_{2g}} = 153.9 + 44.5P - 2.9P^2,$$

where ν is in cm⁻¹ and P in GPa. As seen in the internal bending mode, the out-of-plane B_{1g} mode showed a stronger

pressure dependence than the in-plane A_g mode. The frequencies calculated by LeSar for the A_g symmetric mode¹² are in good agreement with the experimental results.

The peak assignments of the librational modes can be reexamined using the observed frequency shifts. The weak peak, having the highest frequency among the observed three peaks, was first assumed to be an overtone of the A_g mode by Ito *et al.*,⁸ since its frequency was just twice as much as that of the A_g mode in the low temperature phase. Anderson *et al.*⁹ pointed out that this peak was a lattice fundamental rather than a second-order feature judging from the clear sharpening of the band at low temperatures. They reassigned the peak as an out-of-plane B_{2g} mode. The frequency-pressure relations obtained by the present experiments clearly indicate that the weak peak has no relation to an overtone of the A_g mode. Hence, we follow the peak assignments given by Anderson *et al.* in this paper.

The Raman-active internal and librational frequencies obtained for the liquid, cubic, and orthorhombic phases at typical pressures are summarized in Table I together with those for the corresponding low temperature phases.

DISCUSSION AND CONCLUSION

We discuss the pressure dependence of the Raman frequencies observed for the orthorhombic phase in relation to the intermolecular interactions. According to Marchi and Righini⁶ the intermolecular potential in the orthorhombic structure are satisfactorily represented by three terms; atom-atom, electrostatic, and a hydrogen-bond interaction. The former two are long range interactions commonly included in the potentials for the cubic and orthorhombic structures. The hydrogen bond is a short range interaction arising from the singular T-shaped configuration of the two adjacent molecules in the orthorhombic structure. Ap-

TABLE I. Raman frequencies (cm⁻¹) of liquid and crystalline C₂H₂ at high pressures and 295 K. Data of the liquid and low temperature crystals are also listed for comparison.

	Liquid internal modes		Cubic			Orthorhombic						Assignment ^{b,c}
	198 K ^a	0.41 GPa	150 K ^b	173 K ^c	0.77 GPa	4.2 K ^c	30 K ^b	77 K ^c	1.2 GPa	2.1 GPa	3.4 GPa	
ν_4	625			626		628	628.5	626	627.3	630.0		B_{1g} or B_{2g}
						639	638.5	637	635.3	636.5	638	A_g
						660	659.5	656	660.8	674	691	B_{1g} or B_{2g}
ν_2		1934	1929.5		19.33.1	1926	1926.5	1927	1931.8	1933.3	1936.0	C^{13}
	1961	1961.6	1956.5	1956	1959.0	1951	1951.5	1948	1956.3	1956.5	1957.8	A_g
			1961.5	1960	1965.1	1962	1960.5	1959	1965.3	1967.0	1970.5	B_{3g}
ν_1			3329.5	3324		3315	3314.5	3314	3325	3324	3324	A_g
	3341	3342.8	3335	3332		3324	3232.5	3324	3334	3334	3337	B_{3g}
Librational modes												
				22		86	84	82		126	156	B_{1g}
			28.5	23		88	87.5	85	98.8	119	143	A_g
			65	67		177	174.5	171	204.8	232	268	B_{2g}

^a Reference 13.

^b Reference 9.

^c Reference 8.

proach of the neighboring molecules with pressure are, thus, expected to cause larger changes in the hydrogen bond than in the atom-atom or electrostatic interactions. The frequency shifts observed for the internal and librational vibrations are thought to be mainly attributed to changes in the hydrogen bond.

The monotonical increase in splitting observed for the internal ν_2 stretching mode suggests that the hydrogen bond is strengthened as the adjacent molecules approach each other with increasing pressure. Ito *et al.*⁸ first pointed out the possibility that the large splitting in the ν_2 mode was due to the hydrogen bond. The observed splitting in the low temperature orthorhombic phase was twice as large as that in the low temperature cubic phase. In addition, the intermolecular distance between hydrogen and carbon atoms in the T-shaped configuration was estimated to be about 2.74 Å, which is very short in comparison with those usually encountered in the organic crystals. They, therefore, concluded that the hydrogen-bond interaction was the main origin of the large splitting. At high pressures the doublet peaks of the stretching mode showed similar behavior. The splitting widened by a factor of 2 at the cubic-orthorhombic transition, at which the molecules oriented in the directions of the body diagonals of the cubic unit cell rotated to form planar T-shaped configurations in the *bc* plane of the orthorhombic unit cell. On further compression, the splitting increased gradually. This is due to the increase in the hydrogen-bond interaction.

The pressure behavior of the internal bending modes may be another experimental result related to the hydrogen bond. The frequencies of the out-of-plane B_{1g} and B_{2g} modes shifted to the high frequency at rates much higher than that of the in-plane A_g mode. The in-plane mode is associated with bending motions in which the hydrogen atoms move along the triple bonds of the nearest-neighbor molecules; the out-of-plane mode is associated with bending motions in which the hydrogen atoms move perpendicular to the plane containing the triple bonds. The marked difference in frequency shift between the two modes suggests that the hydrogen bond in the T-shaped configuration has directional character. In general, the hydrogen bond is thought to consist of two bonding natures; a directional covalent bond and non-directional coulombic force. For the formation of a covalent-like bond with directional character in the planar T-shaped configuration, the in-plane bending motions of hydrogen is preferable to the out-of plane motions. The directional character in the hydrogen bond resulted in the frequency shifts strongly dependent on the vibrational plane of the hydrogen atom.

With the librational vibrations, the stronger pressure dependence was observed for the out-of-plane B_{1g} mode rather than for the in-plane A_g mode as in the internal bending vibrations. The role of the hydrogen bond in the libra-

tional vibrations was shown by Marchi and Righini⁶ in their theoretical calculations of the lattice frequencies of the orthorhombic phase. They obtained good agreements between the calculated and experimental results when the hydrogen bond was taken into account explicitly in the intermolecular interactions. The effect of the inclusion of the hydrogen bond was to increase the librational frequencies by a significant amount. Its contribution was a little larger for the B_{1g} mode than for the A_g mode. It is, therefore, expected that changes with pressure in the hydrogen bond cause a larger frequency shift in the B_{1g} mode than in the A_g mode. The frequency shifts experimentally obtained were consistent with this expectation.

The high-pressure Raman data will be of great use for theoretical investigations of the intermolecular interactions in crystalline C_2H_2 . The potential models have been refined so that calculated results reproduce consistently the vibrational and structural properties obtained by the low temperature experiments. In the comparison of calculated results with experimental ones, the lattice frequencies have exclusively been employed; no attention has been paid to the internal frequencies. The observed frequency shifts indicate that the internal vibrations are affected significantly by pressure as well as the librational vibrations. In particular, the mode-dependent behavior found in the internal vibrations is expected to contribute to an understanding of the hydrogen bond singularly formed in the T-shaped configuration.

For further advances in the study of the intermolecular interactions, structural data on the high-pressure cubic and orthorhombic phases is required. X-ray diffraction measurements on these crystalline phases are in progress in our laboratory.

¹G. J. H. van Nes and F. van Bolhuis, *Acta Crystallogr. Sect. B* **35**, 2580 (1979).

²H. K. Koski and E. Sandor, *Acta Crystallogr. Sect. B* **31**, 350 (1975).

³G. Filippini, C. M. Gramaccioli, and M. Simonetta, *J. Chem. Phys.* **73**, 1376 (1980).

⁴Z. Gamba and H. Bonadeo, *J. Chem. Phys.* **76**, 6215 (1982).

⁵M. L. Klein and I. R. MacDonald, *Chem. Phys. Lett.* **80**, 76 (1981).

⁶M. Marchi and R. Righini, *Chem. Phys.* **94**, 465 (1985).

⁷K. Aoki, Y. Kakudate, S. Usuba, M. Yoshida, K. Tanaka, and S. Fujiwara, *Solid State Commun.* **64**, 1329 (1987).

⁸M. Ito, T. Yokoyama, and M. Suzuki, *Spectrochim. Acta Part A* **26**, 695 (1970).

⁹A. Anderson, B. Andrews, and B. H. Torrie, *J. Raman Spectrosc.* **16**, 202 (1985).

¹⁰K. Aoki, Y. Kakudate, S. Usuba, K. Tanaka, and S. Fujiwara, *Jpn. J. Appl. Phys.* **26**, 95 (1987).

¹¹H. K. Mao, P. M. Bell, J. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).

¹²R. LeSar, *J. Chem. Phys.* **86**, 1485 (1987).

¹³G. Glockler and M. M. Renfrew, *J. Chem. Phys.* **6**, 340 (1938).