Pressure Effect on the Inter- and Intramolecular Vibrations of Hexachlorobenzene Crystal

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The effect of pressure on the Raman active inter- and intramolecular vibrations of the hexachlorobenzene crystal was studied under hydrostatic pressure up to 5.5 GPa. The Raman frequencies of the inter- and intramolecular vibrations increased monotonically and some bands due to the degenerate intramolecular vibrations were resolved into doublets with increasing pressure. The pressure-induced frequency shift and factor group splitting of the bands due to the intramolecular vibrations were calculated using an intermolecular potential of the atom–atom type. These results show that (1) no phase transition takes place in the crystal under pressure up to 5.5 GPa, (2) the observed pressure-induced frequency shift is mainly caused by the repulsive force between chlorine atoms belonging to the adjacent molecules, and (3) the observed splitting of the bands due to the degenerate intramolecular vibrations is caused by the different intermolecular force acting to the a and b vibrational modes.

Thiéry and Léger,[1] Ellenson and Nicol,[2] and Adams and Appleby[3] studied the Raman spectrum of the benzene crystal under high pressure and found the phase transitions of the crystal at 1.4, 4, 11, and 24 GPa by observing abrupt changes of the spectral structure and the vibrational frequency shift induced by pressure. A number of theoretical studies were made on the frequency shift and the factor group splitting of the intramolecular vibrations induced by the intermolecular force.[4—7]

Bates et al.[8] studied the inter- and intramolecular vibrations of the hexachlorobenzene crystal by measuring the polarization behavior of the Raman and infrared spectra. We observed the temperature effect on the Raman active intermolecular vibrations of the hexachlorobenzene crystal and showed that no phase transition takes place in the temperature range from 300 to 77 K under 1 atm.[9]

In this work, the effect of pressure on the Raman active inter- and intramolecular vibrations of the hexachlorobenzene crystal is observed and the phase transition and the pressure-induced frequency shift of the intramolecular vibrations are discussed.

Experimental

Material. Hexachlorobenzene obtained from Tokyo Kasei Co. was purified by zone refining of about 100 passages.

Optical Measurement. The Raman-active inter- and intramolecular vibrations were measured with a JEOL 400T laser Raman spectrophotometer under various pressures from 1 atm (1×10^{-4} GPa) to 5.5 GPa at 300 K by the backscattering observation method. The 514.5, 488.0, and 476.5 nm beams from an Ar^+ ion laser were used for the excitation. A diamond anvil cell obtained from Toshiba Tungaloy Co. was used for measurement of the Raman spectrum under high pressure. The sample and ruby chips suspended in cedar wood oil were held in a sample hole made in the stainless steel gasket. The pressure inside the sample hole was determined by measuring the wavelength shift of the fluorescence line at 694.2 nm (R_1 line) emitted from ruby chips using the equation proposed by Mao et al.[10] The pressure was confirmed to be hydrostatic by observing the shapes of the R_1 and R_2 (692.7 nm) lines emitted from ruby.

Theoretical Treatment of Pressure Effect on the Intramolecular Vibrations

The frequency shift and the factor group splitting of the intramolecular vibrations induced by the intermolecular interaction with other molecules are given by[4—7]

$$\Delta\bar{\nu}_{\text{shift}} = \frac{1}{8\pi^2 c^2 \bar{\nu}_{Qn}} \sum_i \sum_j \left(\frac{\partial^2 V_{ij}}{\partial r_{ij}^2}\right)\left(\frac{\partial r_{ij}}{\partial Q_n}\right)^2 \quad (1)$$

and

$$\Delta\bar{\nu}_{\text{splitting}} = \frac{1}{4\pi^2 c^2 \bar{\nu}_{Qn}} \sum_i \sum_j \left(\frac{\partial^2 V_{ij}}{\partial r_{ij}^2}\right)\left(\frac{\partial r_{ij}}{\partial Q_{n_\mu}}\right)\left(\frac{\partial r_{ij}}{\partial Q_{n_\nu}}\right) \quad (2)$$

respectively, where Q_n and $\bar{\nu}_{Qn}$ are the n-th normal coordinate and its unperturbed vibrational frequency, respectively, r_{ij} is the interatomic distance between atoms i and j belonging to molecules μ and ν, respectively, and V_{ij} is the potential energy of the atom–atom type due to the intermolecular interaction between two molecules. The V_{ij} expressed by[6,7,11]

$$2V_{ij} = [-Ar_{ij}^{-6} + B\exp(-Cr_{ij}) + q_i q_j e^2 r_{ij}^{-1}] \quad (3)$$

was used, where A, B, and C are parameters, and q_i and q_j are the electric charges on the atoms i and j, respectively. The parameters were taken from those given by Spackman[11] and the charge was evaluated by the CNDO MO calculation. The three terms in Eq. 3 represent the dispersive, repulsive, and electrostatic energies, respectively. The term $\partial r_{ij}/\partial Q_n$ in Eqs. 1 and 2 is represented as

$$\partial r_{ij}/\partial Q_n = (\partial r_{ij}/\partial \boldsymbol{r}_i)(\partial \boldsymbol{r}_i/\partial Q_n). \quad (4)$$

Therefore, in order to calculate the frequency shift and the factor group splitting from Eqs. 1 and 2, the three terms, $\partial^2 V_{ij}/\partial r_{ij}^2$, $\partial r_{ij}/\partial \boldsymbol{r}_i$, and $\partial \boldsymbol{r}_i/\partial Q_n$, must be evaluated. The first term was calculated using Eq. 3 and the second term was approximated by $\cos\phi_i$, where ϕ_i is the angle between the displacement vector $\boldsymbol{r}_i$ of the atom i in the normal vibration and the vector of the interatomic distance $\boldsymbol{r}_{ij}$, since r_i is very small compared to r_{ij}.[7,8] The last term corresponds to the Lx vector of the n-th normal vibration and was obtained by the normal coordinate calculation. The molecular geometry and molecular orientation in the crystal were assumed to keep unchanged under application of pressure and the atom–atom distance between two molecules was evaluated assuming isotropic compressibility.

The frequency shift and the factor group splitting were calculated as a function of the distance between the centers of gravity of the two adjacent molecules (intermolecular distance). The intermolecular distance r and r_0 at pressures p and zero, respectively, are related to the compressibility V/V_0, that is, $(r/r_0)^3 = V/V_0$, where V and V_0 are the relative volumes of the hexachlorobenzene molecule occupying at pressures p and zero, respectively.[12] The value of V/V_0 for the hexachlorobenzene crystal was given by Vaidya and Kennedy.[13] In this manner the intermolecular distance can be converted into pressure and thus, the values of the frequency shift and the factor group splitting induced by pressure can be obtained.

Results and Discussion

Pressure Effect on the Intermolecular Vibrations. Hexachlorobenzene crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell.[14] The Raman spectra of the hexachlorobenzene crystal in the intermolecular vibrational region observed under various pressures at 300 K are shown in Fig. 1. The six intermolecular vibrational Raman bands were observed at 20, 23, 37, 43, 52, and 55 cm^{-1} under 1 atm, which were assigned to the intermolecular vibrations of Ag, Bg, Bg, Ag, Bg, and Ag species, respectively.[9] The pressure dependence of the Raman frequency, which will be called as frequency–pressure curve hereafter, is shown in Fig. 2. The Raman band becomes slightly broader and the frequency increases monotonically with increasing pressure. The monotonous pressure–frequency curve and the unchanged spectral structure suggest that the phase transition does not take place in the hexachlorobenzene crystal under high pressure up to about 5.5 GPa.

The relative frequency shift, $(\overline{\nu}_{p\ \mathrm{GPa}} - \overline{\nu}_{1\ \mathrm{atm}})/\overline{\nu}_{1\ \mathrm{atm}}$, was calculated under various pressures for the intermolecular vibrational bands observed at 20, 37, and 52 cm^{-1} under 1 atm and the result is given in Fig. 3. In this figure the relative frequency shift for the inter-

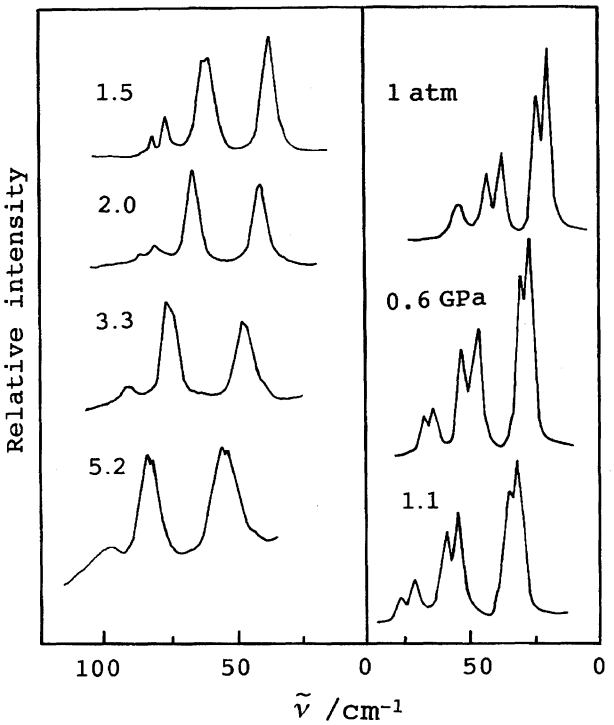

Fig. 1. The Raman spectra of the hexachlorobenzene crystal in the intermolecular vibrational region observed under various pressures at 300 K. 0 GPa corresponds to 10^{-4} GPa (1 atm).

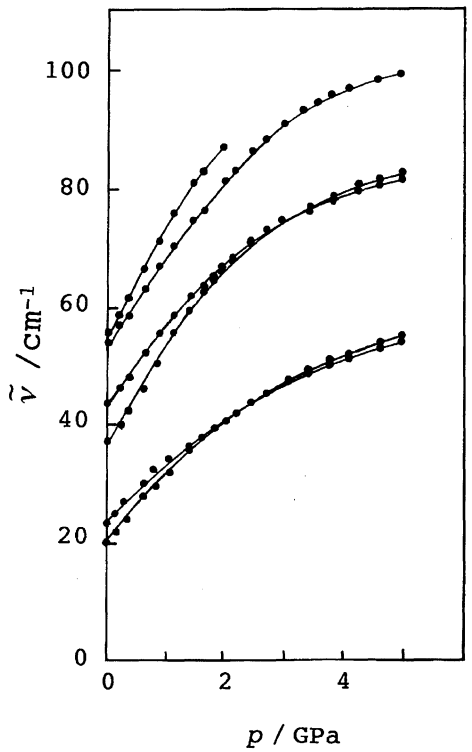

Fig. 2. Pressure effect on the intermolecular vibrational frequencies of the Raman bands of the hexachlorobenzene crystal observed at 300 K.

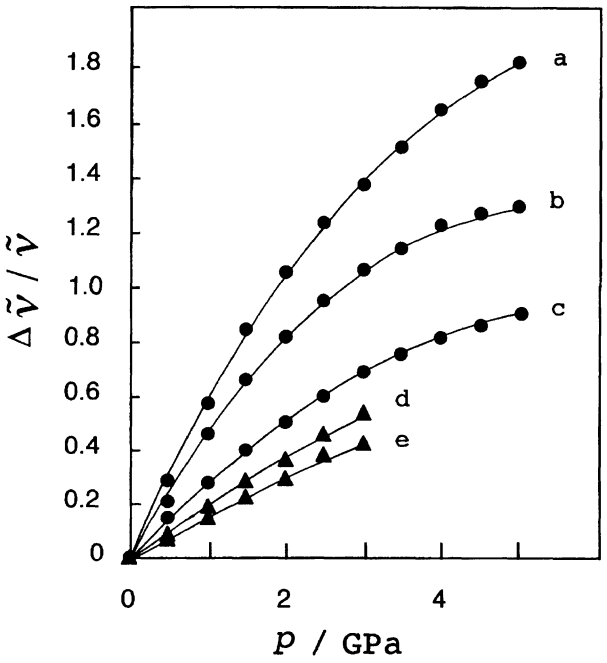

Fig. 3. Pressure effect on the relative frequency shift, $(\overline{\nu}_{p\ \mathrm{GPa}}-\overline{\nu}_{1\ \mathrm{atm}})/\overline{\nu}_{1\ \mathrm{atm}}=\Delta\overline{\nu}/\overline{\nu}$, of the intermolecular vibrations observed at 300 K. a, b, and c refer to the relative frequency shift for the 20, 37, and 52 cm^{-1} bands observed under 1 atm in the hexachlorobenzene crystal, respectively, and d and e for the 84 and 60 cm^{-1} bands observed under 1 atm in the phase I of the benzene crystal, respectively.

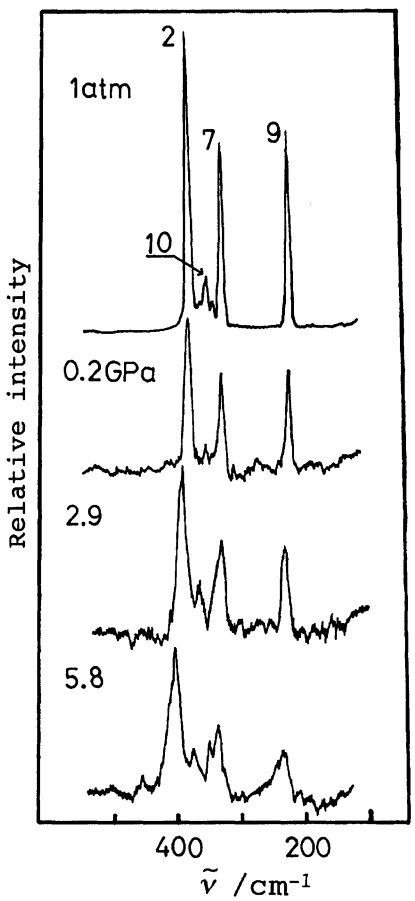

Fig. 4. The Raman spectra of the hexachlorobenzene crystal in the intramolecular vibrational region observed under various pressures at 300 K.

molecular vibrational bands of the benzene crystal observed at 60 and 84 cm^{-1} under 1 atm is also given. Figure 3 indicates that the relative frequency shift is larger in the hexachlorobenzene crystal than in the benzene crystal, that is, the intermolecular vibrations are more strongly affected by pressure in the hexachlorobenzene crystal than in the benzene crystal. This fact suggests that the chlorine atom gives significant contribution to the frequency shift.

Pressure Effect on the Intramolecular Vibrations. The Raman bands observed at 220, 323, 345, 373, 1227, and 1523 cm^{-1} under 1 atm at 300 K were assigned to the intramolecular ν_9, ν_7, ν_{10}, ν_2, ν_1, and ν_8 vibrations, respectively.[8] The first four bands were clearly resolved under high pressure up to about 5.5 GPa, although the last two weak bands become broader with increasing pressure and could not be resolved clearly under high pressure. The Raman spectra observed under various pressures and the frequency–pressure curves for the first four bands are shown in Figs. 4 and 5, respectively. In Fig. 5 the difference of the pressure-induced frequency shift, $\Delta\overline{\nu}=\overline{\nu}_{p\ \mathrm{GPa}}-\overline{\nu}_{1\ \mathrm{atm}}$, is plotted against pressure. The observed relative frequency shift, $\Delta\overline{\nu}/\overline{\nu}_{1\ \mathrm{atm}}$, under various pressures is shown in Fig. 6, together with that for the ν_1 and ν_9 bands in the benzene crystal.

These figures show that (1) the Raman bands assigned to the ν_2 and ν_{10} vibrations shift to the higher frequency side monotonically as increasing pressure, (2) the Raman bands assigned to the ν_7 and ν_9 vibrations shift to the higher frequency side monotonically with increasing pressure and the splitting of the band into doublet is clearly resolved in these bands under pressure over about 3 and 4 GPa, respectively, (3) the splitting of the ν_9 and ν_7 vibrational bands increases gradually with pressure and the values of the splitting are 9 and 4 cm^{-1} under 4.5 GPa, respectively, while the splitting is not detected for the degenerate ν_{10} vibration, (4) the relative frequency shift is larger in the hexachlorobenzene crystal than in the benzene crystal as in the case of the intermolecular vibrations, and (5) the relative frequency shift is much small in the intramolecular vibrations compared with that in the intermolecular vibrations.

The frequency shift and the factor group splitting of the intramolecular vibrations caused by the intermolecular interaction with the eight neighboring molecules were calculated according to Eqs. 1 and 2 with changing the intermolecular distance which was converted into pressure as described above. The calculation was carried out upto 4.5 GPa, since the compressibility of

Table 1. Calculated and Observed Pressure-Induced Frequency Shifts of the Raman Active Intramolecular Vibrations of the Hexachlorobenzene Crystal

Mode	Calculated frequency shift								Frequency shift		Splitting of a and b modes	
	$\bar{\nu}_{1\ atm}$				$\bar{\nu}_{4.5\ GPa}$				$\bar{\nu}_{4.5\ GPa}-\bar{\nu}_{1\ atm}$		$\bar{\nu}_{4.5\ GPa}-\bar{\nu}_{1\ atm}$	
	Repul. $\bar{\nu}/cm^{-1}$	Disp. $\bar{\nu}/cm^{-1}$	E.S. $\bar{\nu}/cm^{-1}$	Total $\bar{\nu}/cm^{-1}$	Repul. $\bar{\nu}/cm^{-1}$	Disp. $\bar{\nu}/cm^{-1}$	E.S. $\bar{\nu}/cm^{-1}$	Total $\bar{\nu}/cm^{-1}$	Calcd $\bar{\nu}/cm^{-1}$	Obsd $\bar{\nu}/cm^{-1}$	Calcd $\bar{\nu}/cm^{-1}$	Obsd $\bar{\nu}/cm^{-1}$
9a	6.3	−1.7	0.1	4.7	31.6	−4.5	0.1	27.2	22.5	16	9.0	4
9b	4.7	−1.3	0.1	3.5	20.0	−3.1	0.1	17.0	13.5	12		
7a	3.1	−1.1	0.0	2.0	11.4	−2.1	0.0	9.3	7.3	9	19.5	9
7b	7.1	−1.7	0.0	5.4	36.6	−4.4	0.0	32.2	26.8	18		
10a	26.7	−8.7	0.4	18.4	53.7	−13.9	0.5	40.3	21.9	19	1.4	0
10b	25.1	−8.1	0.4	17.4	50.3	−12.8	0.4	37.9	20.5	19		
2	4.4	−1.1	0.0	3.3	21.1	−2.7	0.0	18.4	15.1	20		

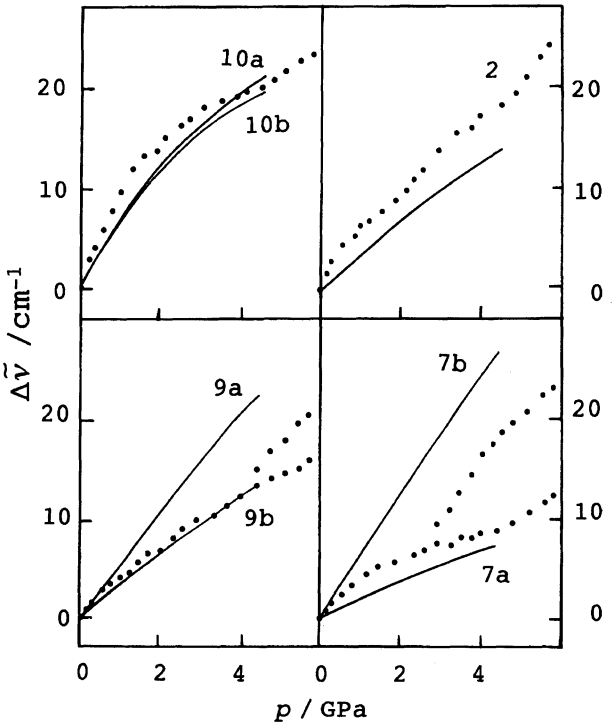

Fig. 5. The observed (···) and calculated (—) pressure effects on the ν_{10}, ν_9, ν_2, and ν_7 vibrational frequencies of the hexachlorobenzene crystal. The difference of the frequency shift, $\Delta\bar{\nu}=\bar{\nu}_{p\ GPa}-\bar{\nu}_{1\ atm}$, is plotted against pressure.

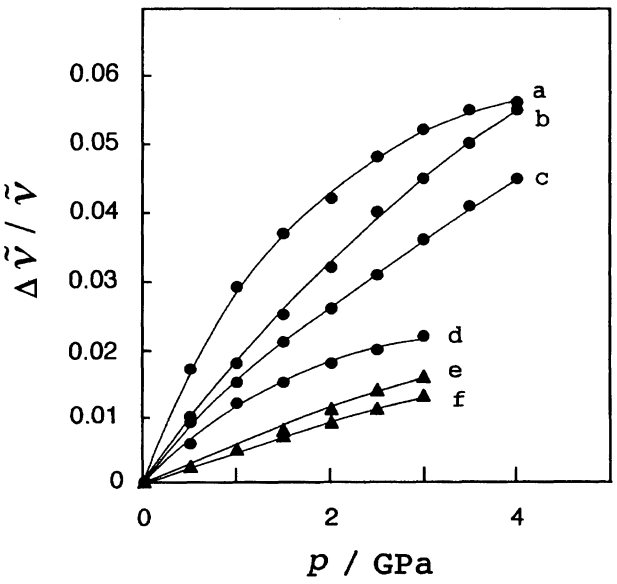

Fig. 6. Pressure effect of the relative frequency shift, $(\bar{\nu}_{p\ GPa}-\bar{\nu}_{1\ atm})/\bar{\nu}_{1\ atm}=\Delta\bar{\nu}/\bar{\nu}$, of the intramolecular vibrations. a, b, c, and d refer to the relative frequency shift for the ν_{10}, ν_9, ν_2, and ν_7 vibrations in the hexachlorobenzene crystal, respectively, and e and f for the ν_9 and ν_1 vibrations in the benzene crystal, respectively.

the hexachlorobenzene crystal was reported under pressure up to 4.5 GPa.[13] The calculated frequency shifts induced by the repulsive, dispersive, and electrostatic forces for the ν_{9a}, ν_{9b}, ν_{7a}, ν_{7b}, ν_{10a}, ν_{10b}, and ν_2 vibrations under 1 atm and 4.5 GPa are given in Table 1 and the calculated frequency–pressure curves are shown in Fig. 5 together with the observed curves.

The calculated results show that (1) the contribution to the frequency shift decreases drastically in the order of the repulsive, dispersive, and electrostatic forces for all vibrations, (2) the largest contribution to the repulsive force is due to the chlorine–chlorine interaction belonging to the different molecules, (3) the intermolecular interaction gives the different frequency shifts for the a and b modes of the degenerate ν_9, ν_7, and ν_{10} vibrations, (4) the difference of the frequency shifts for the a and b vibrational modes at the same pressure, which will be called as the splitting of the a and b modes hereafter, increases with increasing pressure, (5) the degree of the splitting decreases in the order of ν_7, ν_9, and ν_{10} vibrations and the differences of the calculated splitting of the a and b modes under the pressures 1 atm and 4.5 GPa are 19.5, 9.0, and 1.4 cm^{-1} for the ν_7, ν_9, and ν_{10} vibrations, respectively, and (6) the values of the fac-

tor group splitting are the order of about 1/10 of the frequency shifts for the all vibrations.

The calculated value of the splitting for the ν_7, ν_9, and ν_{10} vibrations explains well the reason why the appreciable splitting of the a and b modes was observed for the ν_7 and ν_9 vibrations, while no clear splitting was detected for the ν_{10} vibration.

It is concluded that (1) the phase transition does not take place in the hexachlorobenzene crystal up to about 5.5 GPa, (2) the observed splitting of the degenerate vibrations is caused by the different intermolecular interaction acting to the a and b vibrational modes of the degenerate vibrations but is not by the factor group splitting, and (3) the repulsive force between two chlorine atoms belonging to the different molecules causes the large pressure-induced frequency shift for the inter- and intramolecular vibrations in the hexachlorobenzene crystal. The small relative frequency shift observed in the benzene crystal supports the conclusion that the chlorine–chlorine repulsive force gives the main contribution to the frequency shift in the hexachlorobenzene crystal. The fairly well agreement of the calculated and observed frequency shifts of the intramolecular vibrations indicates that the potential of intermolecular interaction used in this work is fairly adequate.

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