Pressure Effect on the Inter- and Intramolecular Vibrations of 1,2,4,5-Tetrachlorobenzene Crystal

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The effect of pressure on the frequencies and band structures of the Raman active inter- and intramolecular vibrations of the 1,2,4,5-tetrachlorobenzene crystal was studied under hydrostatic pressures upto 4 GPa at 300 K in a gasketed diamond anvil cell. Changes of the Raman frequencies and band structures of the vibrations suggest that the phase transition takes place under about 0.7 GPa. The frequency shift of the intramolecular vibrations induced by pressure was calculated using an intermolecular potential of the atom–atom type based on the two-site molecular exciton theory. The calculation shows that the observed pressure-induced frequency shift is mainly caused by the repulsive force between the chlorine atoms belonging to the adjacent molecules.

Dean et al.[1)] and Herbstein[2)] studied the crystal structure of 1,2,4,5-tetrachlorobenzene by the X-ray diffraction and showed that the crystal undergoes phase transition from the β to α phases at 188 K under 1 atm. D'Alessio and Bonadeo[3)] and White and Eckhardt[4)] studied the lattice vibrations of the crystal through the observation of the polarization behavior of the Raman spectrum. Very recently, Shimada et al.[5)] observed the temperature effect on the Raman bands due to lattice vibrations and confirmed the phase transition. Halac et al.,[6)] Bonadeo et al.,[7)] and Jongenelis et al.[8)] carried out the calculation of the lattice dynamics and discussed the crystal stability and the phonon frequency.

Scherer[9)] and Scherer and Evans[10)] gave the assignment of the normal vibrations of 1,2,4,5-tetrachlorobenzene through the analyses of the Raman and infrared spectra and also through the normal coordinate calculation. Very recently Shimada et al.[11)] reinvestigated the assignment of the normal vibrations based on the polarization behavior of the Raman and infrared bands.

A number of experimental and theoretical studies were made on the phase transition of the benzene crystal through the observation[12,13)] and calculation[14)] of the inter- and intramolecular vibrations of the crystal under high pressure. Adams and Ekejiuba[15)] studied the phase transition of dihalogenobenzene crystals through the observation of the low-frequency region of the Raman spectra of the crystals under high pressure. A number of theoretical studies were also made on the frequency shift of the intramolecular vibrations induced by intermolecular forces.[16—19)]

In this work, the Raman active inter- and intramolecular vibrations of the 1,2,4,5-tetrachlorobenzene crystal are studied under high pressure and the phase transition and the pressure-induced intramolecular vibrational frequency shift are discussed.

Experimental

Materials. 1,2,4,5-Tetrachlorobenzene obtained from Nacalai Tesque, Inc. was purified by zone-refining of about 100 passages.

Optical Measurement. The Raman spectra of the inter- and intramolecular vibrations were measured with a JEOL 400T laser Raman spectrophotometer under various pressures from 1 atm (1×10^{-4} GPa) to 4 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 thickness from the table to culet of the diamond of 0.16 carats is 2.0 mm and the diameters of the table and culet are 1.7 and 0.6 mm, respectively. A stainless steel gasket with thickness of 0.3 mm and area of 5×5 mm^2 was placed between the culets of the two opposed diamonds. A hole with diameter of 0.3 mm was made in the center of the gasket and the sample and ruby chips suspended in cedar wood oil were held in the hole. The pressure inside the gasket hole was determined by measuring the wavelength shift of the $\mathrm{R_1}$ fluorescence line at 694.2 nm emitted from the ruby chips using the equation proposed by Mao et al.[20)] The pressure inside the hole was confirmed to be hydrostatic by observing the shapes of the $\mathrm{R_1}$ and $\mathrm{R_2}$ (692.7 nm) fluorescence lines emitted from ruby.

Theoretical Treatment of the Pressure Effect on the Intramolecular Vibrations

The frequency shift of the intramolecular vibrations induced by the intermolecular interaction with neighboring molecules is given by[16—19)]

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

according to the two-site molecular exciton theory, where Q_n and $\overline{\nu}_{Qn}$ 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 the two adjacent molecules, and V_{ij} is the potential of the atom–atom type due to the intermolecular interaction between two molecules. The potential expressed by[18,19)]

$$2V_{ij} = -Ar_{ij}^{-6} + B\ \exp\left(-Cr_{ij}\right) + q_iq_je^2r_{ij}^{-1} \qquad (2)$$

was used, where A, B, and C are parameters for which the values given by Bonadeo and D'Alessio[21] and by Reynolds et al.[22] were used, and q_i and q_j are the electronic charges on the atoms i and j, which were evaluated by the CNDO MO calculation. The three terms in Eq. 2 represent the dispersive, repulsive, and electrostatic energies, respectively. The term $\partial r_{ij}/\partial Q_n$ in Eq. 1 is represented as

$$\begin{aligned}\partial r_{ij}/\partial Q_n = (\partial r_{ij}/\partial \boldsymbol{r}_i)(\partial \boldsymbol{r}_i/\partial Q_n) = (\partial r_{ij}/\partial x_i)(\partial x_i/\partial Q_n) \\ + (\partial r_{ij}/\partial y_i)(\partial y_i/\partial Q_n) + (\partial r_{ij}/\partial z_i)(\partial z_i/\partial Q_n).\end{aligned}$$

Therefore, in order to calculate the frequency shift by Eq. 1, the three terms of $\partial^2 V_{ij}/\partial r_{ij}^2$, $\partial \boldsymbol{r}_i/\partial Q_n$, and $\partial r_{ij}/\partial \boldsymbol{r}_i$ must be evaluated. The first term was calculated using Eq. 2 and the second term, which corresponds to the Lx vector of the n-th normal vibration, was obtained from the normal coordinate calculation. Since the variation of the interatomic distance r_{ij} caused by the infinitesimal displacement $\boldsymbol{r}_i$ of the atom i due to normal vibration is very small, the last term was approximated by $\cos \phi_i$,[18] where ϕ_i is the angle between the displacement coordinate $\boldsymbol{r}_i$ and the direction of the interatomic distance r_{ij}, and can be obtained from the normal coordinate calculation. The molecular geometry and the molecular orientation in crystal were assumed to keep unchanged under application of high pressure and the atom–atom distance between two molecules was evaluated by assuming isotropic compressibility. The frequency shift was first calculated as a function of the distance between the centers of gravity of the two adjacent molecules (intermolecular distance). The intermolecular distances r and r_0 under pressures p and zero, respectively, can be related to the compressibility V/V_0 according to the relation[23]

$$(r/r_0)^3 = V/V_0,$$

where V and V_0 are the relative volume of the 1,2,4,5-tetrachlorobenzene molecule occupying under pressures p and zero, respectively. The values of compressibility were given for various molecular crystals under various pressures by Vaidya and Kennedy.[24] Thus the intermolecular distance can be converted into pressure and therefore, the relation between the frequency shift and pressure can be obtained.

Results and Discussion

Pressure Effect on Intermolecular Vibrations. The crystal structure of 1,2,4,5-tetrachlorobenzene in the β phase belongs to the monoclinic space group $P2_1/a$ with two molecules in the unit cell at 300 K.[1,2] At 188 K the crystal undergoes the phase transition to the α phase, where the crystal belongs to the triclinic space group $P\bar{1}$ with two molecules in the unit cell. According to the group theory the six rotational intermolecular vibrations are Raman active in both the β and α phases and these six vibrations are classified into symmetry species A_g and B_g, three vibrations belonging to each species. The frequencies and the assignment for the rotational intermolecular vibrations in the β and α phases are given by earlier workers.[3—5]

The Raman spectra of the 1,2,4,5-tetrachlorobenzene crystal in the intermolecular vibrational region observed under various pressures up to 4 GPa at 300 K are shown in Fig. 1. The spectra observed under 0.1 and 0.6 GPa consist of five bands and show the same spectral structure as that observed under 1 atm at 300 K, where the crystal exists in the β phase.[3—5] In the Raman spectrum observed under 0.7 GPa, some new weak bands are observed in addition to the five bands and spectral structure is quite complex. In the spectra observed under 0.8, 1.0, and 4.0 GPa only five bands are observed again and the spectral structure is the same as that observed under 1 atm at 77 K, where the crystal exists in the α phase.[3—5] Therefore, the bands observed under lower and higher pressures than 0.7 GPa can be ascribed to the rotational intermolecular vibrations in the β and α phases, respectively. The frequencies observed under various pressures at 300 K are given in Table 1 and the relationship between the observed frequencies and pressure, which will be called as the frequency–pressure curve hereafter, is shown in Fig. 2. This figure shows that (1) the frequency increases monotonically and continuously with increasing pressure from 1 atm (10^{-4} GPa) to about 0.7 GPa, (2) the discontinuity of the frequency occurs under about

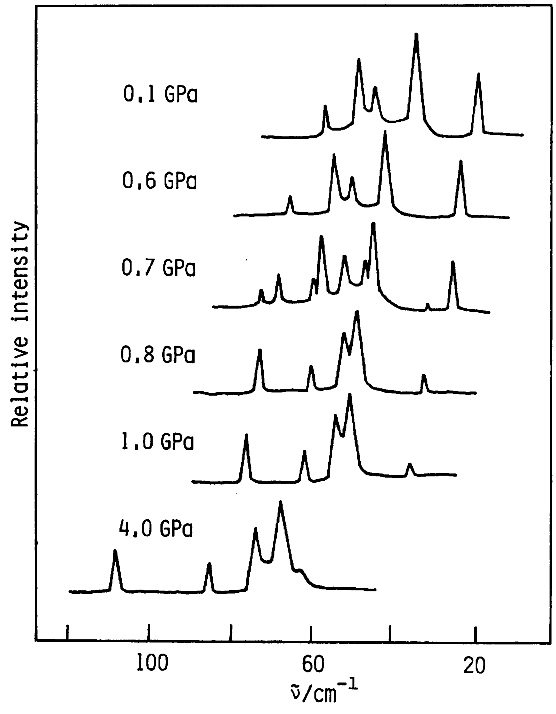

Fig. 1. The Raman spectra of the 1,2,4,5-tetrachlorobenzene crystal in the intermolecular vibrational region observed under various pressures at 300 K. 0 GPa corresponds to 10^{-4} GPa (1 atm).

Table 1. Raman Frequencies of Intermolecular Vibrations of 1,2,4,5-Tetrachlorobenzene Crystal

β Phase				α Phase			
1 atm[a]	0.1 GPa	0.6 GPa	0.7 GPa	0.7 GPa	0.8 GPa	1.0 GPa	4.0 GPa
$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$
20	21	26	27	33	34	36	64
35.5	36	44	46	48	50	51	68
45	46	51	53	53	54	55	75
49	50	57	59	61	62	63	86
57.5	58	68	70	74	75	77	109

a) Taken from Ref. 4.

Table 2. Calculated and Observed Frequency Shifts of the Raman Active Intramolecular Vibrations of 1,2,4,5-Tetrachlorobenzene

Phase	Mode	Calculated frequency shift								$\tilde{\nu}_{0.7\,\mathrm{GPa}}-\tilde{\nu}_{1\,\mathrm{atm}}$	
		1 atm				0.7 GPa				Calcd	Obsd
		Repul.	Disp.	E.S.	Total	Repul.	Disp.	E.S.	Total		
		$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$
β	9a	50.1	−21.6	0.0	28.5	79.6	−31.0	0.0	48.6	20.1	12
	10b	10.1	−6.8	0.4	3.7	13.1	−7.8	0.4	5.7	2.0	8
	7a	22.2	−8.3	0.0	13.9	34.1	−11.3	0.0	22.8	8.9	5
	6a	19.2	−10.1	−0.1	9.0	27.9	−13.7	−0.1	14.1	5.1	3
	1	25.0	−14.0	−0.1	10.9	40.3	−21.5	−0.1	18.7	7.8	4
		0.7 GPa				4.0 GPa				$\tilde{\nu}_{4.0\,\mathrm{GPa}}-\tilde{\nu}_{0.7\,\mathrm{GPa}}$	
α	9a	14.0	−7.9	0.1	6.2	42.3	−16.4	0.0	25.9	19.7	13
	10b	20.3	−11.6	0.3	9.0	49.5	−22.7	0.4	27.2	18.2	21
	7a	5.1	−2.3	−0.1	2.7	13.8	−4.2	−0.1	9.5	6.8	8
	6a	5.5	−2.7	0.0	2.8	13.0	−4.4	0.0	8.6	5.8	7
	1	6.4	−4.4	−0.1	1.9	20.4	−11.3	−0.1	9.0	7.1	7

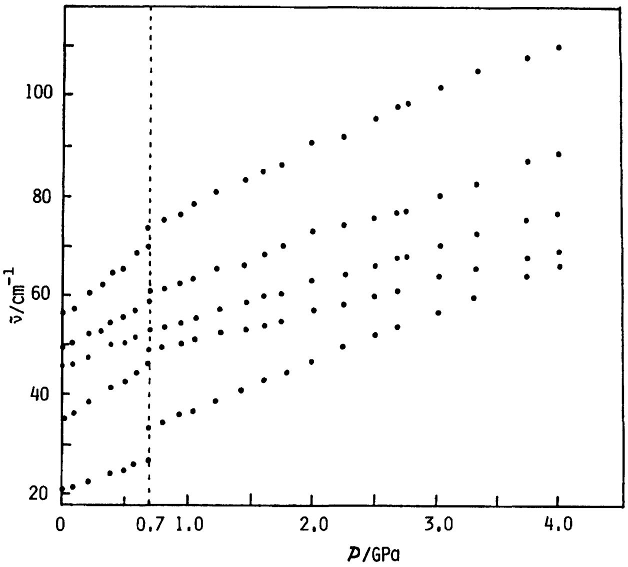

Fig. 2. Pressure effect on the intermolecular vibrational frequencies of the Raman bands of the 1,2,4,5-tetrachlorobenzene crystal observed at 300 K.

0.7 GPa, and (3) the frequency increases monotonically again with increasing pressure from about 0.7 to 4 GPa. Thus, the complex spectral structure observed under 0.7 GPa can be ascribed to the overlapping of the intermolecular vibrational bands in the β and α phases. These results indicate that (1) the 1,2,4,5-tetrachlorobenzene crystal undergoes the phase transition from β to α phases under about 0.7 GPa, (2) the crystal under 0.7 GPa coexists in the β and α phases in this experiment, and (3) no phase transition takes place under pressures from 0.7 to 4 GPa.

Pressure Effect on Intramolecular Vibrations of 1,2,4,5-Tetrachlorobenzene. The Raman spectra observed under various pressures are shown in Fig. 3. The Raman bands observed at 188, 227, 349, 684, and 1163 cm^{-1} under 1 atm in the intramolecular vibrational region are assigned to the intramolecular ν_{9a}, ν_{10b}, ν_{7a}, ν_{6a}, and ν_1 vibrations, respectively.[11] These five bands are clearly observed under high pressure up to 4 GPa. The observed frequency–pressure curves for these vibrations are shown in Figs. 4 and 5, where the differences of the pressure-induced frequency shifts, $\Delta\tilde{\nu}=\tilde{\nu}_{p\,\mathrm{GPa}}-\tilde{\nu}_{1\,\mathrm{atm}}$ in the β phase and $\Delta\tilde{\nu}=\tilde{\nu}_{p\,\mathrm{GPa}}-\tilde{\nu}_{0.7\,\mathrm{GPa}}$ in the α phase are plotted in the ordinates. This figure shows that (1) in the β phase the observed frequency shift increases monotonically with increasing pressure at the rate of 7—23 cm^{-1}/GPa depending on the vibrational modes up to about 0.5 GPa, while the

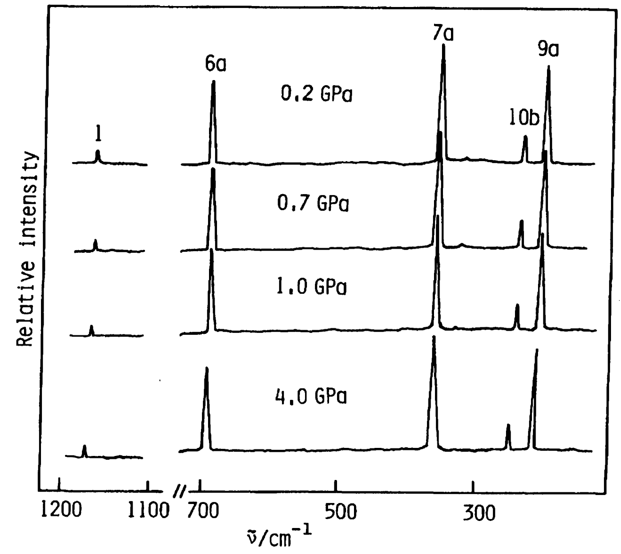

Fig. 3. The Raman spectra of the 1,2,4,5-tetrachlorobenzene crystal in the intramolecular vibrational region observed under various pressures at 300 K.

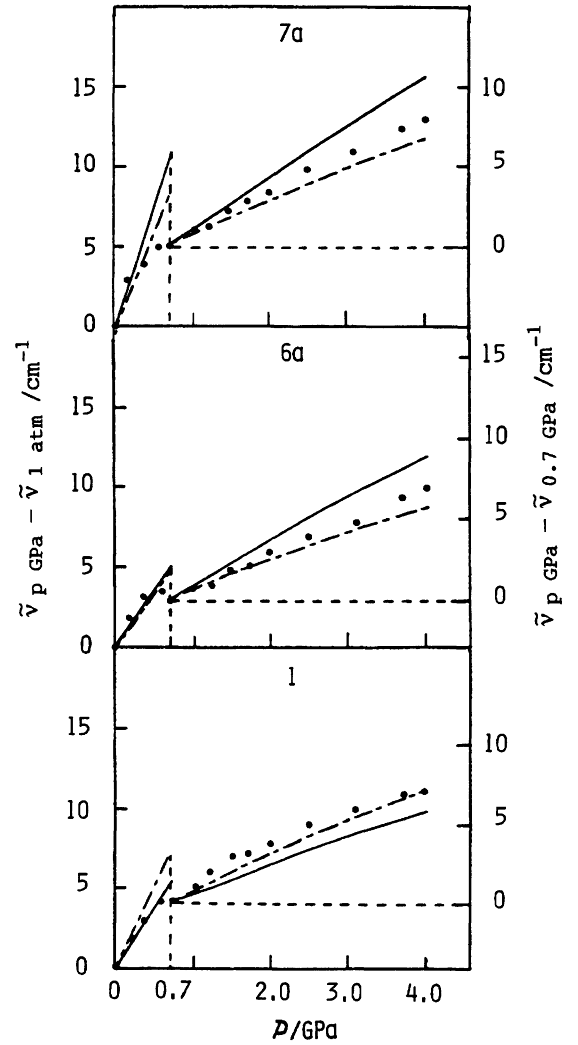

Fig. 4. Pressure effect on the ν_{7a}, ν_{6a}, and ν_1 vibrational frequencies of the 1,2,4,5-tetrachlorobenzene crystal. The observed (····) and calculated (–·–, —) frequency shifts, $\Delta\tilde{\nu}=\Delta\tilde{\nu}_{p\,\mathrm{GPa}}-\Delta\tilde{\nu}_{1\,\mathrm{atm}}$ in the β phase and $\Delta\tilde{\nu}=\Delta\tilde{\nu}_{p\,\mathrm{GPa}}-\Delta\tilde{\nu}_{0.7\,\mathrm{GPa}}$ in the α phase, are plotted in the ordinate. The values in the left and right sides of the ordinate are for the β and α phases, respectively. –·– and — are obtained using parameters given by Bonadeo and D'Alessio and by Reynolds et al., respectively.

rate of the observed frequency shift decreases abruptly from about 0.5 to 0.7 GPa for all vibrational modes, (2) in the α phase the observed frequency shift increases monotonically again at the rate of 2—6 cm^{-1}/GPa from about 0.7 to 4 GPa depending on the vibrational modes, and (3) the observed frequency shift is large for the ν_{9a} and ν_{10b} vibrations compared with the other ν_{7a}, ν_{6a}, and ν_1 vibrations in both the β and α phases.

The frequency shift of the intramolecular vibrations induced by intermolecular interactions with the six neighboring molecules was calculated according to Eq. 1 with changing the intermolecular distance which was converted into pressure as described above. The compressibility of the tetrachlorobenzene crystal was not reported and thus the compressibility was assumed to be the same as that of the hexachlorobenzene crystal.[24] The frequency shifts induced by the repulsive, dispersive, and electrostatic forces calculated for the ν_{9a}, ν_{10b}, ν_{7a}, ν_{6a}, and ν_1 vibrations under 1 atm and 0.7 GPa in the β phase and those under 0.7 and 4.0 GPa in the α phase are given in Table 2. The values given in this table are obtained using the parameters in Eq. 2 given by Bonadeo and D'Alessio.[21] The calculated frequency–pressure curves are shown in Figs. 4 and 5, where the dotted broken and solid lines are obtained using the parameters given by Bonadeo and D'Alessio[21] and by Reynolds et al,[22] respectively. In the β phase the calculated frequency shift increases almost linearly with increasing pressure up to 0.7 GPa at the rate of 7—23 cm^{-1}/GPa, whose value is almost equal to the observed value upto about 0.5 GPa for the ν_{9a}, ν_{7a}, ν_{6a}, and ν_1 vibrations. Since the observed frequency shift becomes small abruptly when pressure approaches to 0.7 GPa as described above, the discrepancy of the observed and calculated frequency shifts is found from pressure of about 0.5 GPa and this discrepancy becomes large as increasing pressure upto 0.7 GPa. This large discrepancy may be due to the fact that the assumptions such as isotropic compressibility and unchanged molecular orientation under application of pressure made in this calculation are not adequate under pressure near 0.7 GPa, where the phase transition is taking place. The calculated frequency shift for the ν_{10b} vibration in the β phase is smaller than the observed shift unlike the ν_{9a}, ν_{7a}, ν_{6a}, and ν_1 vibrations. The reason for which is now in question.

In the α phase the calculated frequency shift increases monotonically with increasing pressure for the ν_{9a}, ν_{10b},

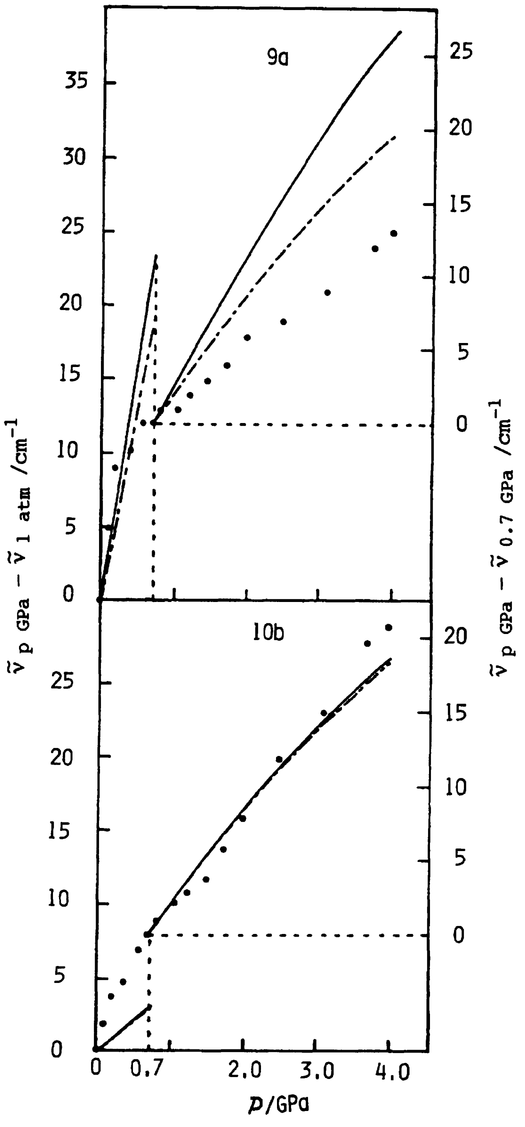

Fig. 5. Pressure effect on the ν_{9a} and ν_{10b} vibrational frequencies of the 1,2,4,5-tetrachlorobenzene crystal.

ν_{7a}, ν_{6a}, and ν_1 vibrations and the agreement between the calculated and observed shifts is fairly well for the all vibrations. This agreement is more excellent if the values of parameters given by Bonadeo and D'Alessio[21] are used rather than the values by Reynolds et al.[22] The monotonical increase of the frequency shift in the α phase suggests that no phase transition takes place under pressures from 0.7 to 4 GPa as described in the intermolecular vibrations.

The calculation also shows that (1) the contribution to the frequency shift decreases drastically in the order of the repulsive, dispersive, and electrostatic forces for all vibrations and (2) the repulsive force between the chlorine atoms belonging to different molecules gives the largest contribution to the frequency shift.

In conclusion the pressure effect on the Raman bands due to the inter- and intramolecular vibrations of the 1,2,4,5-tetrachlorobenzene crystal indicates that (1) the crystal undergoes the phase transition from the β to α phases under the pressure of about 0.7 GPa, (2) the values of the parameters for the potential of the intermolecular interaction given by Bonadeo and D'Alessio[21] give fairly good agreement between the calculated and observed frequency shifts induced by pressure, and (3) the frequency shift is mainly induced by the distance-sensitive steep potential due to the short-range intermolecular repulsive force between chlorine atoms.

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