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Pressure Effect on Phase Transitions in Hexamethylbenzene Crystals

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The pressure effect on the phase transitions in hexamethylbenzene and hexa(methyl-d_3)benzene crystals was studied compared with the temperature effect on the phase transitions. The transition from phase II to phase III of hexa(methyl-d_3)benzene crystal takes place under lower pressure than that for hexamethylbenzene crystal. The change in the spectral structure due to the intermolecular vibrations caused by an increase in the pressure indicates that the marked interaction between the intermolecular rotational vibration and the intramolecular methyl torsional vibration of hexa(methyl-d_3)-benzene crystal takes place under lower pressure than that for hexamethylbenzene crystal. These facts suggest that the intramolecular methyl torsional vibration plays an important role for the II-to-III phase transition in hexamethylbenzene crystals.

Fujiwara et al.[1)] showed that hexa(methyl-d_3)benzene crystal undergoes a phase transition from phase II to phase III at 132.4 K through a measurement of the thermodynamic properties of the crystal, while hexamethylbenzene crystal undergoes a phase transition at 117 K.[2,3)] They pointed out that the observed marked isotopic effect on the temperature-inducing phase transition could be attributed to a difference in the methyl torsional vibration. Spaght et al.[4)] showed that hexamethylbenzene crystal undergoes a phase transition from phase I to phase II at 383 K. The crystal phases are referred to as phases I, II, and III downwards from the melting temperature. The crystal structures for phases I, II, and III were determined by Watanabe et al.,[5)] Brockway and Robertson,[6)] and Cellotti et al.,[7)] respectively.

Shimizu et al.[8)] observed the Raman spectra due to the intermolecular rotational vibrations of p-xylene and p-di(methyl-d_3)benzene crystals at various temperatures and found that the spectra show almost the same structure down to about -80 °C, while the spectral structures of two crystals become quite different below -80 °C. They[9)] also observed the same spectral behavior for the intermolecular rotational vibrations when the pressure is increased. They attributed the changes in the spectral structures caused by changes of the temperature and pressure to an interaction between the intramolecular methyl torsional and the intermolecular rotational vibrations. The change in the spectral structure of p-di(methy-d_3)benzene crystal caused by the interaction takes place at higher temperature and under lower pressure than those for p-xylene. Maehara et al.[10)] showed that such isotopic effects on the intermolecular vibrations are not observed in tetramethylpyrazine and tetra(methyl-d_3)pyrazine crystals, where the torsional axes of the methyl torsional vibrations do not coincide with the rotational axes of the intermolecular rotational vibrations.

The assignment of the Raman bands due to the inter- and intramolecular vibrations of hexamethylbenzene crystal was studied by Fujiwara et al.[1)] and Shimada et al.[11)]

In this work, the temperature effect on the intermolecular vibrations of hexamethylbenzene and hexa(methyl-d_3)benzene crystals was reinvestigated in detail at various temperatures between 420 and 77 K. The pressure effects on the inter- and intramolecular vibrations were also studied. The isotopic effects on the intermolecular vibrations of hexamethylbenzene and hexa(methyl-d_3)benzene crystals are discussed based on the interaction between the inter- and intramolecular vibrations.

Experimental

Material. Hexamethylbenzene (HMB-d_0), obtained from Tokyo Kasei Organic Chemicals, was purified by zone refining of about 100 passages. Hexa(methyl-d_3)benzene (HMB-d_{18}) of 98% purity, obtained from CDN Isotopes, was used without further purification. Samples were powdered as finely as possible with a mortar and pestle.

Optical Measurement. The Raman spectra of HMB-d_0 and HMB-d_{18} crystals due to the inter- and intramolecular vibrations were measured with a JEOL 400T laser Raman spectrophotometer and Bio-Rad FT-Raman II NBR-9001 at various temperatures under 1 atm and under various pressures from 1 atm (1×10^{-4} GPa) to 3 GPa at room temperature by the backscattering observation method. The 514.5, 488.0, and 476.5 nm beams from an Ar^+ ion laser of Spectra Physics Model 168B and 1064 nm beam from a Nd : YAG laser of Spectra Physics Model T10-106C were used for the excitation. Polarization measurement showed that the powder sample gave unpolarized Raman bands.

A cryostat of OXFORD DN1704 was used for measuring the Raman spectra at various temperatures, and a diamond anvil cell obtained from Toshiba Tungaloy Co. was used for measuring the Raman spectrum under high pressure. The method of observation of the Raman spectrum under high pressure was exactly the same as that described previously.[9,10] The powder sample and ruby chips suspended in cedar-wood oil were held in a hole made in the center of the stainless-steel gasket. The gasket was placed between the culets of two opposed diamond anvils, and pressure was generated by turning the driving screw attached to the plates, which support the diamond anvils. The pressure inside the gasket hole was measured by the wavelength shift of the R_1 fluorescence line at 694.2 nm emitted from ruby chips, using the equation proposed by Mao et al.[12] The pressure inside the hole was confirmed to be hydrostatic by observing the shapes of the R_1 and R_2 (692.7 nm) fluorescence lines emitted from the ruby.

Results and Discussion

Temperature Effect on the Intermolecular Vibrations. The low-frequency Raman bands of HMB-d_0 and HMB-d_{18} crystals in phase II observed at various temperatures between 300 and 77 K are shown in Fig. 1, and the curves of the temperature dependence on the vibrational frequency (temperature–frequency curves) are given in Fig. 2. Figure 1 indicates that the Raman spectra of HMB-d_0 and HMB-d_{18} crystals observed at 300 K consist of two bands (bands a and b). Bands a and b for HMB-d_0 were assigned to intermolecular rotational vibrations about the z and x (and/or y) axes in phase II, respectively.[1,11] The z axis was taken perpendicular to the molecular plane, and x and y axes were in the molecular plane with the x axis passing through the C–CH_3 (or C–CD_3) bonds. Since the frequency of the intermolecular rotational vibration is inversely proportional to the square root of the moment of inertia I, the square root of the relative moments of inertia about the x, y, and z axes for HMB-d_0 and HMB-d_{18} was calculated. The calculated values of the square root of $(I_{\mathrm{HMB}\text{-}d_{18}}/I_{\mathrm{HMB}\text{-}d_0})$ for x and y axes are 1.11, and the value for z axis is 1.10. The values of the observed relative frequency, $\tilde{\nu}_{\mathrm{HMB}\text{-}d_0}/\tilde{\nu}_{\mathrm{HMB}\text{-}d_{18}}$, are 1.1 for bands a and b. The isotopic effect indicates that bands a and b are assigned reasonably to the intermolecular rotational vibrations.

The spectral structure of HMB-d_0 crystal remains unchanged along with a decrease in the temperature down to about 105 K, while at temperatures below about 100 K the spectrum consists of three bands a, h, and i. The intensity of band a decreases with decreasing temperature.

Band h was assigned to the intermolecular rotational vibration, and band i to the intramolecular torsional vibration of the methyl groups in phase III for HMB-d_0 crystal.[1,11] The value of the observed relative frequency, $\tilde{\nu}_{\mathrm{HMB}\text{-}d_0}/\tilde{\nu}_{\mathrm{HMB}\text{-}d_{18}}$, for band h was 1.1. The calculated value of the square root of $(I_{\mathrm{CD}_3}/I_{\mathrm{CH}_3})$ for the methyl torsional vibration was 1.41,

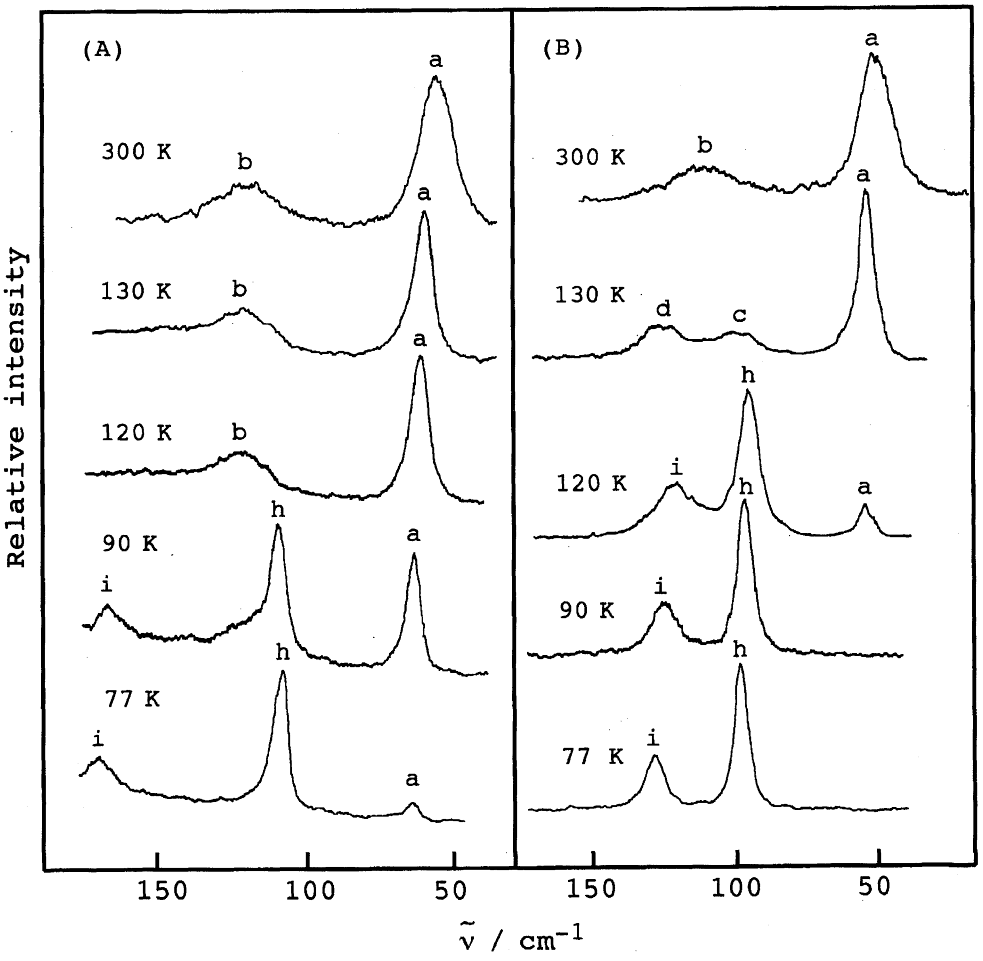

Fig. 1. The Raman spectra of hexamethylbenzene (A) and hexa(methyl-d_3)benzene (B) crystals in the intermolecular vibrational region observed at various temperatures between 300 and 77 K under 1 atm.

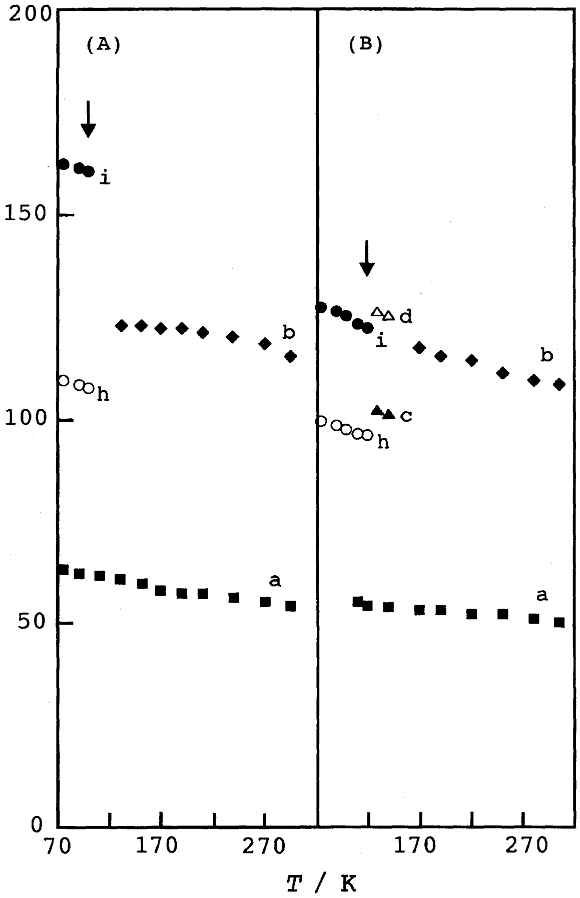

Fig. 2. Temperature–frequency curves for the Raman bands of hexamethylbenzene (A) and hexa(methyl-d_3)benzene (B) crystals in the intermolecular vibrational region observed at various temperatures between 77 and 300 K under 1 atm.

and the value of the observed relative frequency of band i, ($\tilde{\nu}_{\text{HMB-}d_0}/\tilde{\nu}_{\text{HMB-}d_{18}}$), was 1.3. Thus, the assignments given for bands h and i are reasonably recognized by the isotopic effects.

The behavior of the change in the spectral structure of HMB-d_{18} crystal caused by a decrease in temperature becomes different from that of HMB-d_0 below about 140 K. As can be seen in Figs. 1 and 2, bands c and d are resolved in the spectra observed at temperatures between about 140 and 125 K, and bands a, h, and i are observed below about 120 K. Band a can not be observed below about 100 K in HMB-d_{18} crystal.

Bands c and d can be assigned to bands arising from an interaction of the intermolecular rotational vibration with the intramolecular torsional vibration of the CD_3 groups in HMB-d_{18} crystal just as the case of *p*-di(methyl-d_3)benzene crystal.[8] The frequency of the intermolecular vibrations shifts to the higher frequency side when the temperature is decreased, and, thus, the frequency of the intermolecular rotational vibration about the x axis approaches the frequency of the torsional vibration of the CD_3 groups at about 140 K in HMB-d_{18} crystal. As a result, a remarkable interaction takes place between the intermolecular rotational vibration and the intramolecular torsional vibration of the CD_3 groups in HMB-d_{18} crystal. On the other hand, the frequency of the intramolecular torsional vibration of the CH_3 groups is fairly separated from the frequency of the intermolecular rotational vibration about the x axis at 140 K, therefore, no interaction between the inter- and intramolecular vibrations takes place in HMB-d_0 crystal at 140 K. This is the reason why the spectral structure of HMB-d_{18} crystal differs from the spectral structure of HMB-d_0 crystal at 130 K, as shown in Fig. 1. In HMB-d_0 crystal band b is very broad, and no obvious interaction between the inter- and intramolecular vibrations was detected down to 105 K.

Figure 2 shows that band h is observed below about 120 and 100 K in HMB-d_{18} and HMB-d_0 crystals, respectively. This interesting observation indicates that the transition from phase II to phase III in HMB-d_{18} crystal takes place at a higher temperature than that in HMB-d_0 crystal. The observed fact that the inter- and intramolecular vibrational interaction as well as the transition from phase II to phase III take place at a higher temperature in HMB-d_{18} crystal than in HMB-d_0 crystal suggests that the intramolecular methyl torsional vibration plays an important role in the phase transition from II to III, just as pointed out by Fujiwara et al.[1] The temperature of the phase transition from II to III observed in this work is slightly different from that obtained through an analysis of the thermodynamic properties of crystals.[1—3]

The Raman spectra observed at above 300 K are essentially the same as the spectra observed at 300 K in both HMB-d_{18} and HMB-d_0 crystals, except for a broadening of the bands and a shift to the lower frequency side with increasing temperature. The temperature–frequency curve for the intermolecular vibrations of HMB-d_0 and HMB-d_{18} crystals between 420 to 300 K are given in Fig. 3. As can be seen in Fig. 3, the frequency increases discontinuously at about 380 K with decreasing temperature for both HMB-d_0 and HMB-d_{18} crystals. This discontinuity agrees well with the result obtained for the change in the molecular volume of HMB-d_0 at 383 K by Chihara and Seki.[13] They attributed the change in the molecular volume to the transition from phase I to phase II of crystal. The observed result that the transition from phase I to phase II takes place at almost the same temperature in HMB-d_0 and HMB-d_{18} crystals indicates that the methyl torsional vibrations do not take part in the I–II phase transition. The frequencies of the Raman bands observed at various temperatures are given in Table 1.

Pressure Effect on the Intermolecular Vibrations. The Raman spectra of HMB-d_0 and HMB-d_{18} crystals observed under various pressures in the intermolecular vibrational region are shown in Fig. 4, and the observed pressure–frequency curves are shown in Fig. 5. The Raman bands become very weak and diffuse with increasing pressure, and the emission band arising from an Ar^+ laser becomes observable in the spectrum. Therefore, the reasonable frequency of the individual band was evaluated by a curve-fitting method using the Voight function. The results obtained under 1.6 and 2.0 GPa for HMB-d_0 crystal and 1.1 and 1.6 GPa for HMB-d_{18} crystals are shown in Fig. 6. In Fig. 6 the band marked

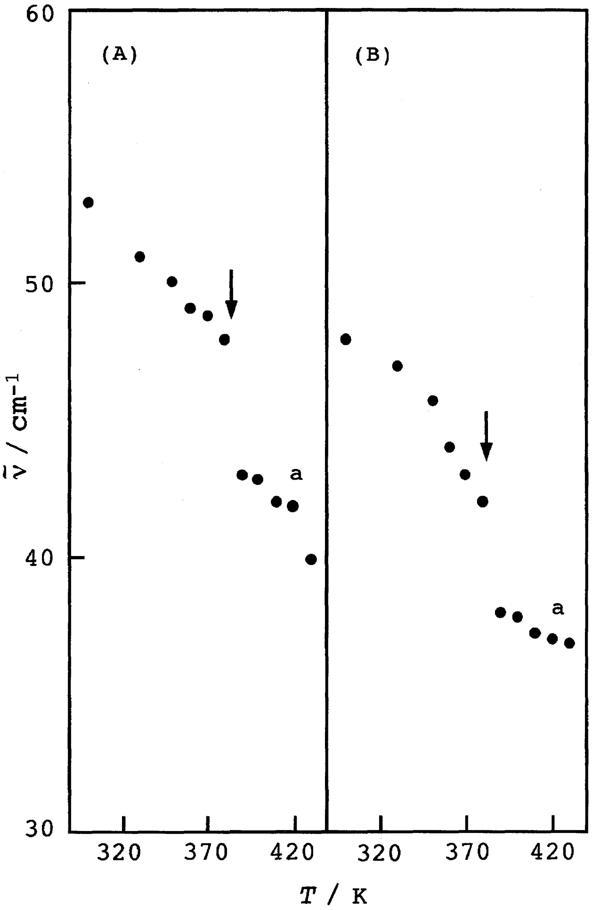

Fig. 3. Temperature–frequency curves for the Raman bands of hexamethylbenzene (A) and hexa(methyl-d_3)benzene (B) crystals in the intermolecular vibrational region observed at various temperatures between 300 and 430 K under 1 atm.

Table 1. Raman Frequencies of the Intermolecular Vibrations of Hexamethylbenzene Crystals

	HMB-d_0				HMB-d_{18}					
	$\tilde{\nu}$/cm^{-1}				$\tilde{\nu}$/cm^{-1}					
T/K	a[a]	b	h	i	a	b	c	d	h	i
380	48	112			41	104				
300	53	116			49	108				
130	61	122			54		102	126		
120	61	122			54				96	122
90	62		107	165					98	126
77	63		108	168					99	128

	HMB-d_0			HMB-d_{18}				
	$\tilde{\nu}$/cm^{-1}			$\tilde{\nu}$/cm^{-1}				
P/GPa	a	b	h	a	b	c	d	h
1 atm	53	116		49	108			
0.5	67	137		63	130			
0.7	72	142		68		120	140	
1.1	83	150		80				130
1.6	84		150	82				140

a) For the marks of the bands a, b, c, d, h, and i, see the spectral bands shown in Fig. 1.

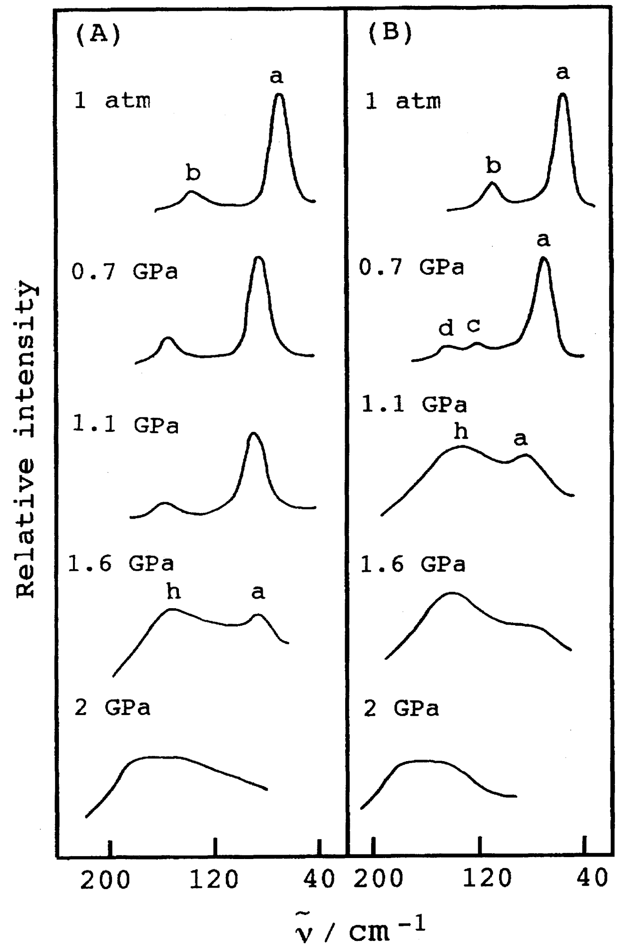

Fig. 4. The Raman spectra of hexamethylbenzene (A) and hexa(methyl-d_3)benzene (B) crystals in the intermolecular vibrational region observed under various pressures at room temperature.

by $*$ is the emission band accompanying the 488.0 nm oscillation of the Ar$^+$ ion. The spectra observed under 1.1, 1.6, and 2 GPa for HMB-d_{18} crystal and under 1.6 and 2 GPa for HMB-d_0 crystal were simulated based on the curve-fitting method, and the spectra shown in Fig. 4 correspond to the spectra after eliminating the emission band. The frequencies of the Raman bands observed under various pressures are given in Table 1. The Raman spectra of HMB-d_0 and HMB-d_{18} crystals observed under 1 atm consist of two bands a and b. The behavior of the change in the spectral structures with an increase in pressure quite closely resembles that for the case of decreasing temperature.

The observed results are summarized as follows. For HMB-d_0 crystal, (1) the spectral structure remained unchanged under pressure from 1 atm to about 1.5 GPa, except for a remarkable broadening of band b above 1.3 GPa, (2) the very broad band h is observed under above 1.6 GPa, and (3) the strongest band a becomes weaker with increasing pressure, and hardly detected above 3 GPa. For HMB-d_{18} crystal, (1) the spectral structure remained unchanged under pressure from 1 atm to about 0.6 GPa, (2) bands c and d are clearly resolved under pressure between 0.7 and 0.9 GPa, (3)

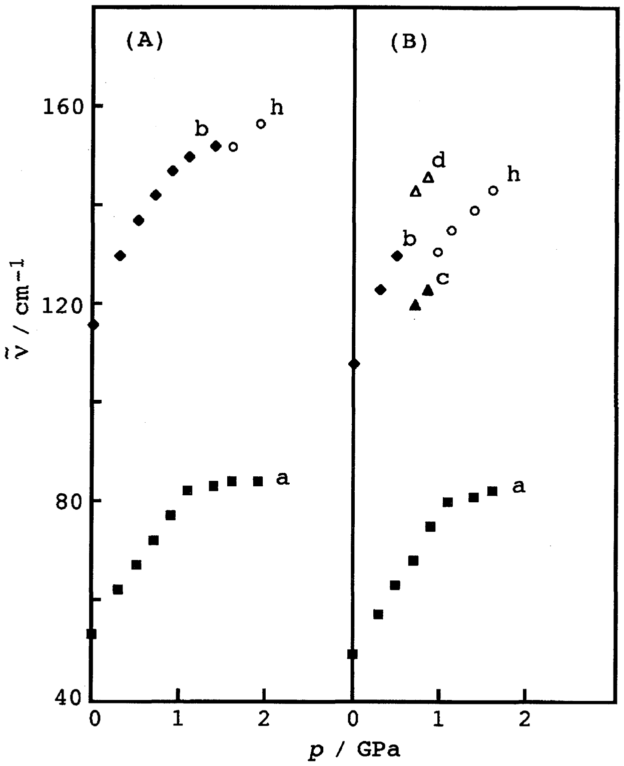

Fig. 5. Pressure–frequency curves for the Raman bands of hexamethylbenzene (A) and hexa(methyl-d_3)benzene (B) crystals in the intermolecular vibrational region observed under various pressures at room temperature.

the very broad band h is observed under above 1 GPa, and (4) the strongest band a becomes weaker with increasing pressure and is hardly detected above 2.2 GPa. A comparison of the spectral structure observed under various pressures with that observed at various temperatures indicates that bands a, b, and h observed under various pressures and temperatures have a one-to-one correspondence to each other in HMB-d_0 crystal. The same discussion can be made for bands a, b, c, d, and h observed in HMB-d_{18} crystal.

The molecules in the crystal and the atoms in the molecule are bonded by the van der Waals and covalent forces, respectively, and therefore, the application of pressure gives a much stronger affect on the intermolecular vibrations than on the intramolecular vibrations. Thus, the frequency of the intermolecular vibrations shifts to the high-frequency side upon the application of pressure, and approaches to the frequency of the CD_3 torsional vibration. As a result, the interaction of the intermolecular rotational vibration with the intramolecular torsional vibration of the CD_3 groups takes place under about 0.7 GPa in HMB-d_{18} crystal. This interaction induces the appearance of bands c and d.

Since the frequency of the CH_3 torsional vibration is higher than the frequency of the CD_3 torsional vibration, the interaction of the inter- and intramolecular vibrations could take place at pressures higher than 0.7 GPa in HMB-d_0 crystal. Band b becomes very broad with increasing pressure, and the interaction of the inter- and intramolecular vibrations could not be detected in HMB-d_0 crystal. The facts that the interaction of the inter- and intramolecular vibrations and the phase

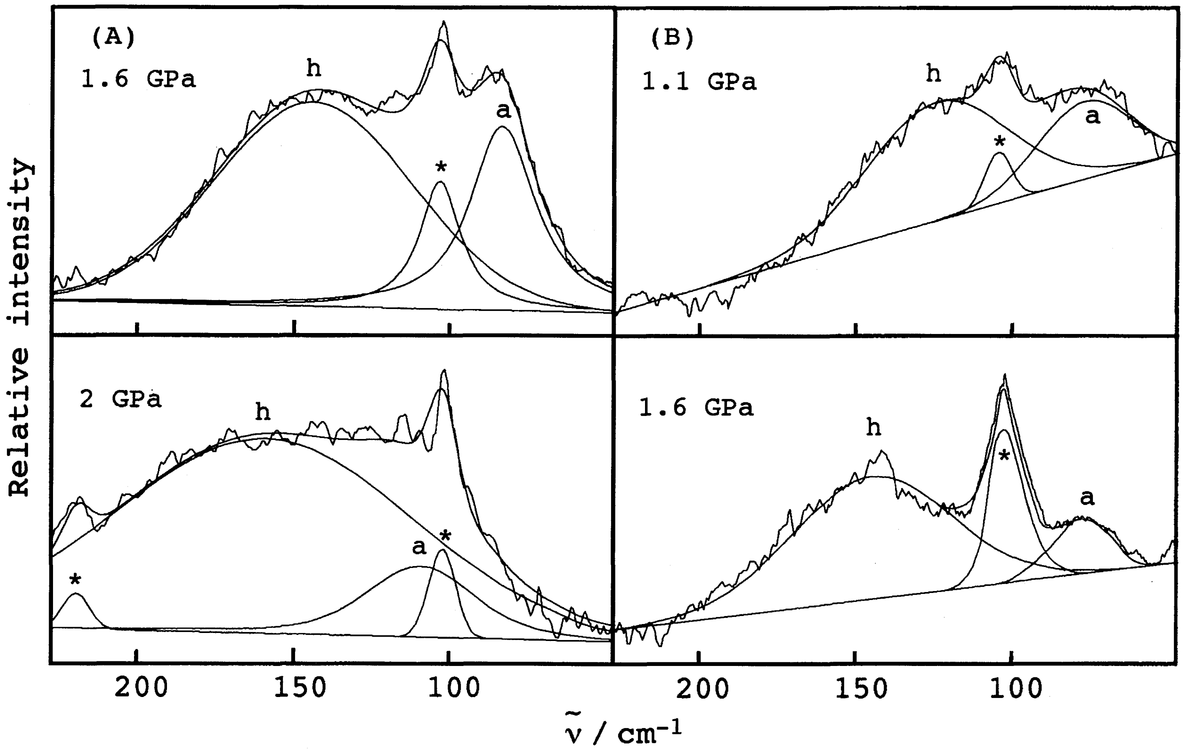

Fig. 6. Simulated Raman bands of hexamethylbenzene (A) and hexa(methyl-d_3)benzene (B) crystals in the intermolecular vibrational region observed under 1.6 and 2 GPa, and 1.1 and 1.6 GPa, respectively, obtained by the curve fitting method. The band marked with * is the emission band.

transition from II to III in HMB-d_{18} crystal take place under a pressure lower than that in HMB-d_0 crystal suggest that the intramolecular methyl torsional vibration plays an important role in the phase transition from II to III, just as pointed out for the temperature effect described above.

The intensity of the spectral bands decreased remarkably and the band width became very broad in phase III compared with those in phase II. Since the intensity and width of the Raman bands due to the intramolecular vibrations in phases II and III showed the ordinary pressure-dependence with increasing pressure as described below, the behaviors observed for the bands due to the intermolecular vibrations are very unique. These unique behaviors might be due to a strong intermolecular interaction of a large number of molecules in the unit cell as well as inter- and intramolecular vibrational interactions in phase III.

The pressure effect on the phase transition from I to II could not be resolved in this work.

Pressure Effect on the Intramolecular Vibrations. The spectral structure observed under various pressures is essentially the same as that observed under 1 atm,[11] except for the ordinary blue shift of the bands and an increase in the band width with increasing pressure, as can be generally seen in molecular crystals.[9,10] The bands observed at 560(512), 455(422), and 361(327) cm^{-1} under 1 atm were assigned to the ν_1(ring breathing), ν_6(ring deformation), and ν_9(methyl bending) vibrations, respectively.[11] The frequencies inside and outside of the parentheses are referred to as the frequencies of HMB-d_{18} and HMB-d_0, respectively. The vibrational frequencies observed under various pressures are given in Table 2.

The curves for the observed relative frequency shifts defined by $(\tilde{\nu}_{p\ \mathrm{GPa}} - \tilde{\nu}_{1\ \mathrm{atm}})/\tilde{\nu}_{1\ \mathrm{atm}}$ against the applied pressure (pressure-relative frequency shift curve) for these vibrations are shown in Fig. 7, where $\tilde{\nu}_{p\ \mathrm{GPa}}$ and $\tilde{\nu}_{1\ \mathrm{atm}}$ are the vibrational frequencies observed under pressures of p GPa and 1 atm, respectively. This figure shows that (1) the relative frequency shifts increase monotonously with increasing pressure up to 1.5 in HMB-d_0 and up to 0.5 GPa in HMB-d_{18}, (2) discontinuities are detected in the pressure-relative frequency shift curves under about 1.6 GPa in HMB-d_0 and under between 0.5 and 1 GPa in HMB-d_{18}, and (3) the relative frequency shifts increase again monotonously with increasing pressure from 1.6 and 1 GPa in HMB-d_0 and HMB-d_{18}, respectively, at a rate of 2—10 cm^{-1}/GPa, depending on the vibrational modes.

Table 2. Raman Frequencies of the Intramolecular Vibrations of Hexamethylbenzene Crystals

	HMB-d_0			HMB-d_{18}		
	$\tilde{\nu}/\mathrm{cm}^{-1}$			$\tilde{\nu}/\mathrm{cm}^{-1}$		
P/GPa	ν_1	ν_6	ν_9	ν_1	ν_6	ν_9
1 atm	560	455	361	512	422	327
1.1	570	459	374	527	430	334
2.2	583	467	385	538	434	345

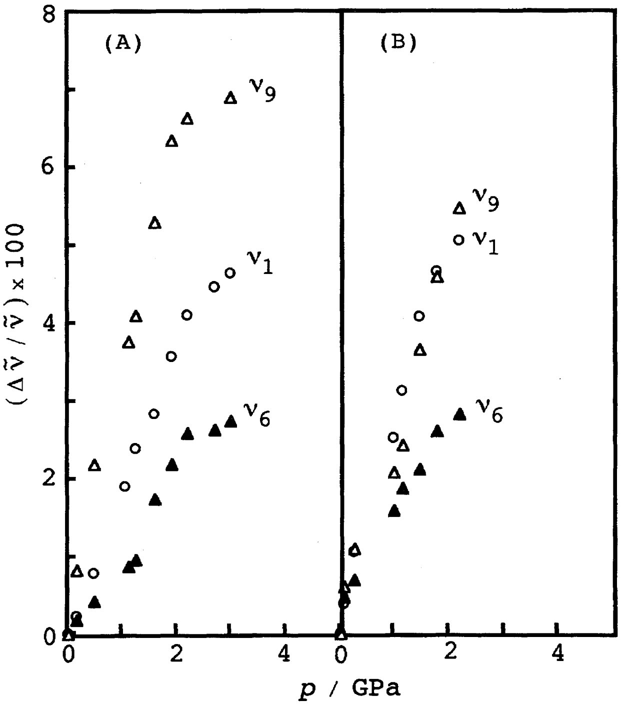

Fig. 7. Pressure–relative frequency shift curve for the intramolecular ν_1, ν_6, and ν_9 vibrations of hexamethylbenzene (A) and hexa(methyl-d_3)benzene (B) observed under various pressures at room temperature. The relative frequency shift is defined by $(\tilde{\nu}_{p\ \mathrm{GPa}} - \tilde{\nu}_{1\ \mathrm{atm}})/\tilde{\nu}_{1\ \mathrm{atm}}$, which is abbreviated by $\Delta\tilde{\nu}/\tilde{\nu}$ in the figure.

The pressure–induced frequency shift is caused by the intermolecular interactions.[9,10] The observed discontinuities in the pressure–relative frequency shift curves indicate that the intermolecular interactions change under about 1.6 GPa in HMB-d_0 crystal and under between 0.5 and 1 GPa in HMB-d_{18} crystal; that is, the phase transition takes place under about 1.6 GPa in HMB-d_0 crystal and between 0.5 and 1 GPa in HMB-d_{18} crystal. The observed discontinuities support the occurrence of a phase transition from II to III in HMB-d_0 and HMB-d_{18} crystals, described in the pressure effect of the intermolecular vibrations.

The observed results for the temperature and pressure effects on the inter- and intramolecular vibrations of HMB-d_0 and HMB-d_{18} crystals are summarized as follows; (1) The interaction between the intermolecular rotational vibration about the x axis and the intramolecular methyl torsional vibration in HMB-d_{18} crystal takes place at higher temperature and under lower pressure than that in HMB-d_0 crystal. (2) The transition from phase II to phase III in HMB-d_{18} crystal takes place at higher temperature and under lower pressure than that in HMB-d_0 crystal. These facts suggest that the intramolecular methyl torsional vibration plays an important role in the transition from phase II to phase III in hexamethylbenzene crystals.

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