Pressure Effect on Inter- and Intramolecular Vibrations of the *p*-Xylene Crystals

Fumio Shimizu, Kazumasa Yoshikai, Hiroshi Kawano,† Yoshinori Nibu, Hiroko Shimada,* and Ryoichi Shimada††

Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-80
†Ohori Senior High School Affiliated with Fukuoka University, Ropponmatsu, Chuo-ku, Fukuoka 810
††Department of General Education, Fukuoka Institute of Technology, Wajiro-Higashi, Higashi-ku, Fukuoka 811-02

(Received October 18, 1995)

The Raman active inter- and intramolecular vibrations of the [$^1H_{10}$]- and [$^2H_{10}$]*p*-xylene crystals were studied under various pressures between 1 atm and 7.5 GPa. The pressure effect of the frequency of the Raman bands due to the intermolecular vibrations indicates that the coupling between the intramolecular torsional vibration of the methyl group and the intermolecular rotational vibrations takes place under about 1 and 2.5 GPa in the [$^1H_{10}$]- and [$^2H_{10}$]*p*-xylene crystals, respectively. The calculated pressure-induced frequency shift of the intramolecular vibrations explains fairly well the observed frequency shifts and supports the conclusion given in the previous work that the contribution of the first-order differential of the intermolecular potential to the pressure-induced frequency shift is vanishingly small when the potential is well approximated.

The study of the temperature effect on the low-frequency Raman bands of the four deuterated *p*-xylene crystals showed that the low-frequency Raman spectra of the *p*-xylene crystals, where two methyl groups are CH_3, gave essentially the same spectral structure under various temperatures between 0 °C and 77 K, while the low-frequency Raman spectra of the *p*-xylene crystals, where two methyl groups are CD_3, gave very complex structure below −80 °C.[1] The complex spectral structure observed for the *p*-xylene crystals having two CD_3 groups was attributed to the coupling of the intermolecular rotational vibrations with the intramolecular CD_3 torsional vibration.[1]

In this work the Raman bands due to the inter- and intramolecular vibrations of the [$^1H_{10}$]- and [$^2H_{10}$]*p*-xylene crystals are studied under various pressures from 1 atm to 7.5 GPa and the pressure-induced coupling of the inter- and intramolecular vibrations and the pressure-induced frequency shift of the intramolecular vibrations are discussed.

Experimental

Material. [$^1H_{10}$]- and [$^2H_{10}$]*p*-xylenes were obtained from Tokyo Kasei Chemical Co. and MSD Isotopes, respectively. The samples were purified by repeated distillations under reduced pressure.

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 7.5 GPa at 300 K by the backscattering observation method. The 514.5, 496.5, 488.0, and 476.5 nm beams from an Ar^+ ion laser of Spectra Physics 168B were used for the excitation. A diamond anvil cell obtained from Toshiba Tungaloy Co. was used for the measurement of the Raman spectrum under high pressure. The experimental methods are exactly the same as those described previously.[2] The pressure inside the gasket hole was determined by measuring the wavelength shift of the R_1 fluorescence line at 694.2 nm emitted from the ruby chips using the equation proposed by Mao et al.[3] 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 ruby.

Results and Discussion

Pressure Effect on the Intermolecular Vibrations. The crystal structure of *p*-xylene belongs to the space group C_{2h}^2 with two molecules in the unit cell[4] and the six rotational intermolecular vibrations are distributed among the A_g and B_g symmetry species as $3A_g+3B_g$. The assignment of the Raman active intermolecular vibrations of the *p*-xylene crystals and the temperature effect on the intermolecular vibrations were studied in the previous work.[1] The *x* axis is taken perpendicular to the molecular plane and the *y* and *z* axes in the plane with the *z* axis passing through the methyl groups.

The intramolecular torsional vibration of the CH_3 group in the [$^1H_{10}$]*p*-xylene crystals was assigned to the Raman band observed around 140 cm^{-1} and the torsional vibration of the CD_3 group in the [$^2H_{10}$]*p*-xylene crystals was expected to be located around 100 cm^{-1} from the relative values of the moments of inertia of the CH_3 and CD_3 groups.[1] The symmetry species of the Raman active intramolecular torsional vibration of the methyl group is b_{1g} in the molecule (D_{2h} point group) and A_g and B_g in the crystal (C_{2h}^2 space group with two molecules in the unit cell).

The Raman spectra of the $[^{1}\mathrm{H}_{10}]$- and $[^{2}\mathrm{H}_{10}]$*p*-xylene crystals observed under various pressures in the intermolecular vibrational region are shown in Fig. 1 and the observed frequency-pressure curves are shown in Figs. 2 and 3. The frequencies of the Raman bands observed under various pressures are given in Table 1. The Raman spectra of the $[^{1}\mathrm{H}_{10}]$- and $[^{2}\mathrm{H}_{10}]$*p*-xylene crystals observed under 1 atm consist of three bands I, II, and III. The bands I, II, and III were mainly ascribed to the rotational intermolecular vibrations about the *x*, *z*, and *y* axes belonging to the symmetry species B_g, A_g, and A_g, respectively, which are referred to as $\mathrm{R_x}(B_g)$, $\mathrm{R_z}(A_g)$, and $\mathrm{R_y}(A_g)$ vibrations, respectively.[1] The spectral structures of the $[^{1}\mathrm{H}_{10}]$- and $[^{2}\mathrm{H}_{10}]$*p*-xylene crystals are unchanged with increasing pressure upto about 2.2 and 0.8 GPa, respectively. The spectral structure of the $[^{1}\mathrm{H}_{10}]$*p*-xylene crystals becomes complex by increasing pressure from about 2.5 to 7.5 GPa and the five bands are clearly resolved. The spectral structure of the $[^{2}\mathrm{H}_{10}]$*p*-xylene crystals also becomes complex with increasing pressure from 1 to 6 GPa and the five bands are clearly resolved in the spectra, but the spectral structure becomes simple again under above 6 GPa and only three

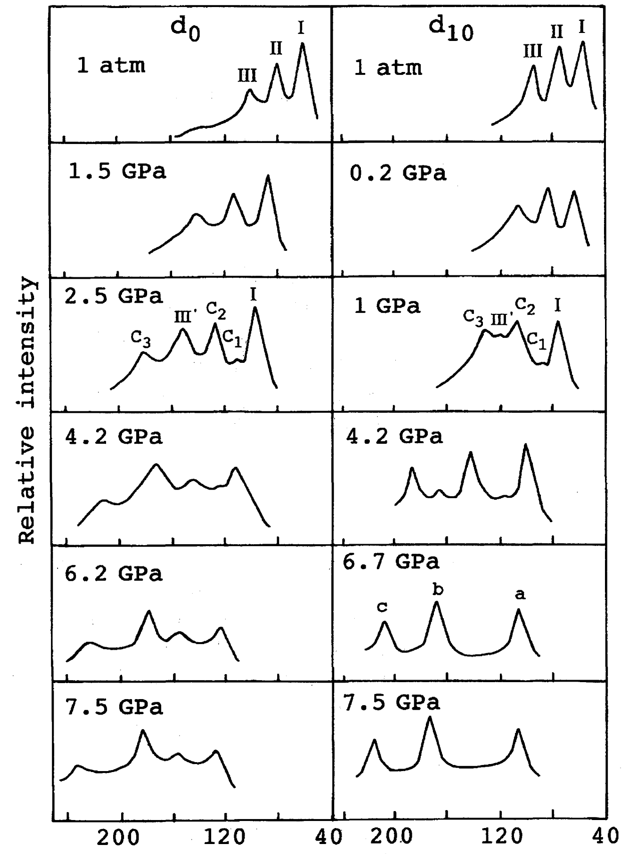

Fig. 1. The low-frequency Raman spectra of the $[^{1}\mathrm{H}_{10}]$- and $[^{2}\mathrm{H}_{10}]$*p*-xylene crystals observed under various pressures.

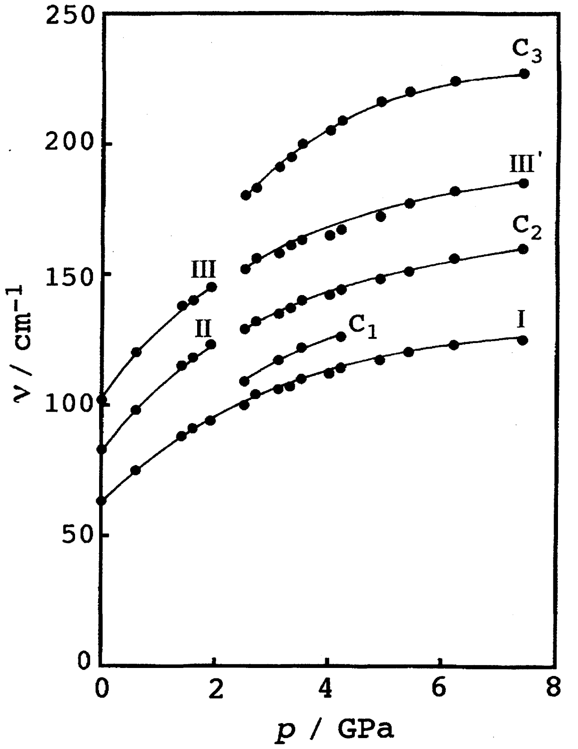

Fig. 2. Pressure effect on the frequencies of the Raman bands of the $[^{1}\mathrm{H}_{10}]$*p*-xylene crystal in the intermolecular vibrational region.

Table 1. Vibrational Frequencies of the $[^{1}\mathrm{H}_{10}]$- and $[^{2}\mathrm{H}_{10}]$*p*-Xylene Crystals under Various Pressures in the Intermolecular Vibrational Region

	$[^{1}\mathrm{H}_{10}]$*p*-Xylene				$[^{2}\mathrm{H}_{10}]$*p*-Xylene				Assignment
Band	1 atm	2.5 GPa	4.2 GPa	7.5 GPa	1 atm	1 GPa	4.5 GPa	7.5 GPa	
	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	
I	63	100	114	125	57	75	100		$\mathrm{R_x}(B_g)$
$\mathrm{C_1}$		109	126			86			Coupling
II	83				76				$\mathrm{R_z}(A_g)$
$\mathrm{C_2}$		129	144	160		102	146		Coupling
III	102				94				$\mathrm{R_y}(A_g)$
III′		152	167	185		118	165		$\mathrm{R_z}(B_g)$
$\mathrm{C_3}$		180	209	227		130	187		Coupling
a								113	
b								178	
c								218	

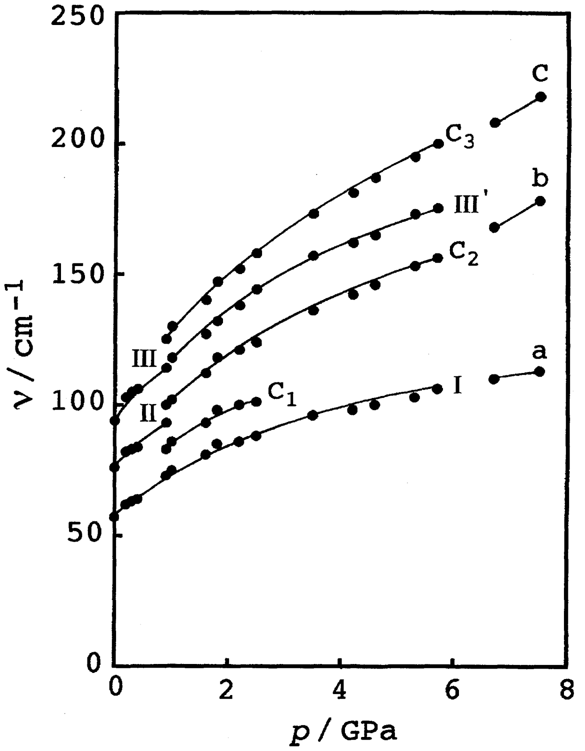

Fig. 3. Pressure effect on the frequencies of the Raman bands of the $[^2H_{10}]p$-xylene crystal in the intermolecular vibrational region.

bands were clearly observed. These three bands are referred to as the bands a, b, and c, respectively. The spectra observed under pressures from about 1 to 6 GPa in the $[^2H_{10}]p$-xylene crystals show exactly the same structure as the spectra observed at temperatures below −80 °C,[1)] except for the intensity of the band C_2. Therefore, it can be considered that the bands I, C_1, C_2, III′, and C_3 observed under pressures from about 1 to 6 GPa correspond to the bands I, C_1, C_2, III′, and C_3 observed at low temperatures, respectively.

The molecules in crystal and the atoms in molecule are bonded by the van der Waals and the covalent forces, respectively, and therefore, the intermolecular vibrations suffer from environmental effects, such as temperature and pressure, more strongly than the intramolecular vibrations. Thus, the large pressure-induced frequency shift of the intermolecular vibrations compared with the pressure-induced frequency shift of the CD_3 torsional vibration brings the frequencies of the intermolecular vibrations to closer to the frequency of the CD_3 torsional vibration. As the result the coupling of intermolecular rotational vibrations with the intramolecular torsional vibrations of the CD_3 groups takes place under 1 GPa. The bands suffered from the coupling are referred to as the bands C_1, C_2, and C_3, respectively, (see Fig. 1) as referred previously.[1)] As increasing pressure from 6 GPa, the frequency of the rotational intermolecular vibrations becomes to separate again from the frequency of the torsional vibration of the CD_3 group and the coupling of the intermolecular vibrations with the torsional vibrations of the CD_3 groups vanishes. Thus, the complex spectral structure becomes simple again above 6 GPa. The observed three bands a, b, and c may correspond to the bands, I, II, and III, respectively.

The spectra consisting of five bands observed under above 2.5 GPa in the $[^1H_{10}]p$-xylene crystals also indicate that the intermolecular rotational vibrations couple with the intramolecular torsional vibration of the CH_3 group. The pressure-induced frequency shift is much larger than the temperature-induced frequency shift and therefore, the frequency of the rotational intermolecular vibrations can approach to the frequency of the intramolecular torsional vibrations of the CH_3 group with increasing pressure. This is the reason why the coupling of the inter- and intramolecular vibrations in the $[^1H_{10}]p$-xylene crystals could not be recognized in the observation of the temperature effect on the intermolecular vibrations.[1)]

In the p-xylene crystals the axis concerned with the $R_z(A_g)$ intermolecular rotational vibration coincides with the axis concerned with the methyl torsional vibrations. The rotational oscillations about the same axis may cause the coupling of the inter- and intramolecular vibrations. This may be supported by the observations in the tetramethylpyrazine crystals, where any axis of the intermolecular rotational vibration does not coincide with the axis of the methyl torsional vibration, that no coupling of the inter- and intramolecular vibrations could be recognized by the temperature[5)] and

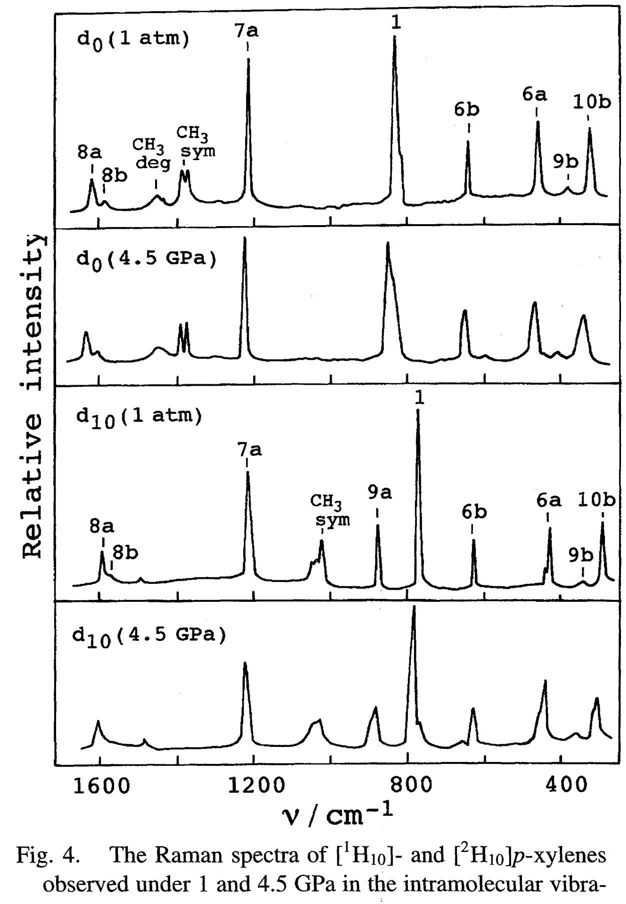

Fig. 4. The Raman spectra of $[^1H_{10}]$- and $[^2H_{10}]p$-xylenes observed under 1 and 4.5 GPa in the intramolecular vibrational region.

pressure[6] effects on the intermolecular vibrations.

The band III′, which is located at the shoulder of the band III, was assigned to the rotational intermolecular vibration about the z axis belonging to the symmetry species B_g, ($R_z(B_g)$ vibration).[1] The band III′ can be detected clearly after the coupling of the inter- and intramolecular vibrations takes place because the strong band III suffers from the coupling and departs from the band III′. The pressure-induced frequency shift of the bands I, II, III, and III′ observed in the [$^1H_{10}$]- and [$^2H_{10}$]p-xylene crystals are all well explained by the isotopic effect on the frequency of the rotational intermolecular vibrations.

The coupling between the inter- and intramolecular vibrations of the symmetry species B_g was not detected in this work. The assignment given for the observed low frequency Raman bands are shown in Figs. 1, 2, 3, and Table 1.

Pressure Effect on the Intramolecular Vibrations. The Raman spectra of [$^1H_{10}$]- and [$^2H_{10}$]p-xylenes observed under various pressures are shown in Fig. 4. The spectra under various pressures are essentially the same as the spectra observed under 1 atm except for the blue shift of the bands with increasing pressure. The bands observed at 316(283), 390(333), 458(428), 645(622), 829(763), (870), 1202(1217), 1371, 1382(1033), 1579(1582), and 1615(1597) cm^{-1} under 1 atm were assigned to the ν_{10b} (methyl wagging), ν_{9b} (methyl bending), ν_{6a} (ring deformation), ν_{6b} (ring deformation), ν_1 (ring breathing), ν_{9a} (methyl bending), ν_{7a} (ring-methyl stretching), methyl symmetric deformation (b_{3g}), methyl symmetric deformation (a_g), ν_{8b} (ring deformation), and ν_{8a} (ring deformation) vibrations, respectively.[7] The frequencies inside and outside of the parentheses are refered to as the frequencies of [$^2H_{10}$]- and [$^1H_{10}$]p-xylenes, respectively. These bands are clearly resolved under high pressures up to 5 GPa.

The observed pressure-frequency curves for these vibrations are shown in Figs. 5 and 6 for [$^1H_{10}$]- and [$^2H_{10}$]p-xylenes, respectively, where the pressure-induced frequency shifts, $\Delta\tilde{\nu} = \tilde{\nu}_{p\ \mathrm{GPa}} - \tilde{\nu}_{1\ \mathrm{atm}}$, are plotted in the ordinates. This

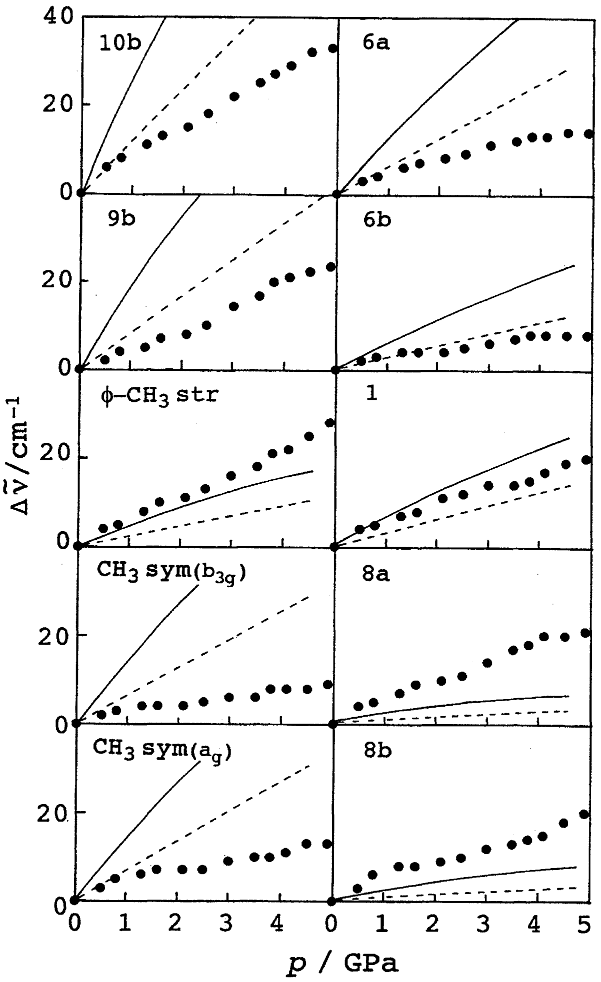

Fig. 5. The observed (····) and calculated (——, - - -) pressure effects on the frequencies of the ν_{10b}, ν_{9b}, ν_{6a}, ν_{6b}, ν_1, ν_{8a}, ν_{8b}, ϕ-CH$_3$ stretching, and CH$_3$ symmetric deformation vibrations of [$^1H_{10}$]p-xylene. —— and - - - were obtained using parameters given by the Spackman, and Bonadeo and D'Alessio, respectively.

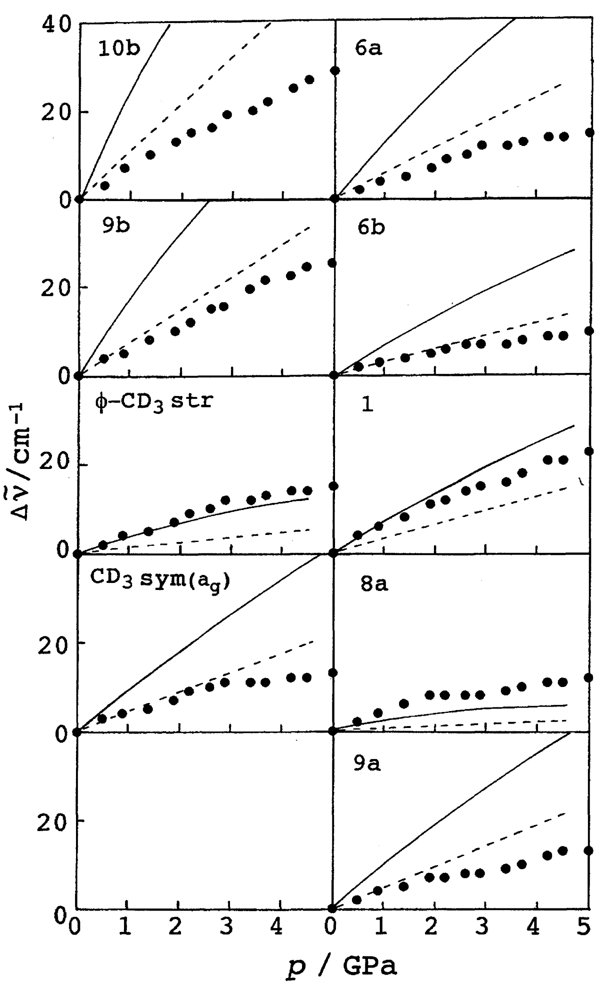

Fig. 6. The observed (····) and calculated (——, - - -) pressure effects on the frequencies of the ν_{10b}, ν_{9b}, ν_{6a}, ν_{6b}, ν_1, ν_{8a}, ν_{9a}, ϕ-CD$_3$ stretching, and CD$_3$ symmetric deformation vibrations of [$^2H_{10}$]p-xylene. —— and - - - were obtained using parameters given by the Spackman, and Bonadeo and D'Alessio, respectively.

figure shows that the observed frequency shift increases monotonically with increasing pressure at the rate of 2—10 cm^{-1}/GPa depending on the vibrational modes.

The pressure-induced frequency shift of the intramolecular vibrations was calculated for the ν_{10b}, ν_{9b}, ν_{6a}, ν_{6b}, ν_1, ν_{9a}, ν_{7a}, methyl symmetric deformation of a_g and b_{3g} species, ν_{8b}, and ν_{8a} vibrations under various pressures from 1 atm to 4.5 GPa considering the contribution from the neighboring sixteen molecules in the same procedure as described previously.[2,8] The parameters of the intermolecular potential were taken from the data given by Spackman[9] and Bonadeo and D'Alessio.[10] The molecular geometry and the molecular orientation in crystals were assumed to keep unchanged under application of high pressure. The values of compressibility were not available for the *p*-xylene crystals and thus the values given for the dichlorobenzene crystals[11] were used. The calculated pressure-induced frequency shifts are shown in Figs. 5 and 6 together with the observed shifts. The straight and dashed frequency–pressure curves in Figs. 5 and 6 are obtained using the parameters given by Spackman[9] and Bonadeo and D'Alessio,[10] respectively.

The calculated frequency–pressure curves obtained by Bonadeo and D'Alessio's parameters give more well agreement than the curves by Spackman's parameters. The calculated pressure-induced frequency shifts obtained by Bonadeo and D'Alessio's parameters are given in Table 2. The agreement of the observed and calculated frequency shifts is rather poor for the vibrations related to the displacements of the methyl groups. This may be due to the fact that the orientation of the hydrogen atoms of the methyl groups assumed in

Table 2. Vibrational Frequencies of [$^1H_{10}$]- and [$^2H_{10}$]*p*-Xylenes under Various Pressures in the Intramolecular Vibrational Region

Vibrational mode	[$^1H_{10}$]*p*-Xylene				[$^2H_{10}$]*p*-Xylene			
	1 atm	4.5 GPa	$\tilde{\nu}_{4.5\ \mathrm{GPa}}-\tilde{\nu}_{1\ \mathrm{atm}}$		1 atm	4.5 GPa	$\tilde{\nu}_{4.5\ \mathrm{GPa}}-\tilde{\nu}_{1\ \mathrm{atm}}$	
	Obsd	Obsd	Obsd	Calcd	Obsd	Obsd	Obsd	Calcd
	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}
ν_{10b}(CH$_3$wag)[a)]	316	348	32	58	283	310	27	50
ν_{9b}(CH$_3$bend)[a)]	390	414	24	38	333	357	24	34
ν_{6a}(ring)	458	472	14	28	428	442	14	28
ν_{6b}(ring)	645	653	8	12	622	631	9	14
ν_1(ring)	829	848	19	13	763	784	21	15
ν_{7a}(ϕ-CH$_3$str)[a)]	1202	1227	25	9	1217	1241	24	6
CH$_3$sym(b_{3g})[a)]	1371	1379	8	28				
CH$_3$sym(a_g)[a)]	1382	1395	13	31	1033	1045	12	20
ν_{8b}(ring)	1579	1597	18	3	1582			2
ν_{8a}(ring)	1615	1635	20	2	1597	1608	11	1
ν_{9a}(CH$_3$bend)[a)]					870	883	13	21

a) H is replaced by D in the [$^2H_{10}$]*p*-xylene crystal.

Table 3. Contribution of the First-Order Differential Term of the Intermolecular Potential to the Pressure-Induced Frequency Shift of the Intramolecular Vibrations in [$^1H_{10}$]- and [$^2H_{10}$]*p*-Xylenes

Mode	$\Delta\tilde{\nu}_{\mathrm{case\ I}}-\Delta\tilde{\nu}_{\mathrm{case\ II}}$							
	[$^1H_{10}$]*p*-Xylene				[$^2H_{10}$]*p*-Xylene			
	Spackman		B. D.[b)]		Spackman		B. D.	
	2 GPa	4 GPa	2 GPa	4 GPa	2 GPa	4 GPa	2 GPa	4 GPa
	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}
ν_{10b}	3.8	7.6	1.3	2.9	3.4	6.7	1.1	2.6
ν_{9b}	1.0	3.9	0.6	1.4	1.7	3.3	0.5	1.2
ν_{6a}	1.0	3.7	0.6	1.5	1.9	3.8	0.7	1.5
ν_{6b}	0.5	1.8	0.3	0.7	1.0	2.1	0.4	0.8
ν_1	0.5	1.8	0.3	0.7	1.0	2.0	0.4	0.8
ν_{7a}	0.3	1.1	0.2	0.5	0.3	0.6	0.1	0.2
CH$_3$(b_{3g})	0.8	3.0	0.4	1.0				
CH$_3$(a_g)	1.0	3.7	0.6	1.5	1.1	2.3	0.4	0.9
ν_{8b}	0.1	0.3	0.1	0.1				
ν_{8a}	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
ν_{9a}					0.9	1.8	0.4	0.8

a) The first-order differential term of the intermolecular potential is neglected in the case I and the term is involved in the case II.

b) B. D. refers to Bonadeo and D'Alessio.

this work was not adequate. The study of the orientation of the hydrogen atoms of the methyl groups in *p*-xylene crystals under various pressures is waited. The calculated frequency shift is very smaller than the observed shift for the ν_{8b} and ν_{8a} vibrations. The reason for which is now in question.

In the previous work,[8] it was concluded that (1) the contribution of the first-order differential of the intermolecular potential to the frequency shift is vanishingly small if the best choice of the values of the parameters for the intermolecular potential is made, and thus (2) the neglect of the first-order differential term, which was generally made in the calculation of the pressure-induced frequency shift, is reasonable.

In order to conform the conclusion, the difference of the frequency shift defined by $(\Delta\tilde{\nu}_{\text{case I}} - \Delta\tilde{\nu}_{\text{case II}})$ was calculated, where case I means the calculation made with neglecting the first-order differential term and case II with involving the term (see Ref. 8). The calculated values are given in Table 3.

Table 3 indicates that the difference of the frequency shift calculated using the Bonadeo and D'Alessio's parameters is smaller than the difference calculated using the Spackman's parameters. As can be seen in Figs. 5 and 6, the Bonadeo and D'Alessio's parameters give better agreement between the observed and calculated pressure-induced frequency shifts than the Spackman's parameters. These results support the conclusion given in the previous work.

The authors thank the Japan Private School Promotion Foundation for Science Research Promotion Fund.

References

1) F. Shimizu, K. Yoshikai, Y. Nibu, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **68**, 3417 (1995).

2) S. Matsukuma, H. Kawano, Y. Nibu, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **67**, 1588 (1994).

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

4) H. van Koningsveld and A. J. van den Berg, *Acta Crystallogr.*, **42**, 491 (1986).

5) M. Maehara, T. Hieida, Y. Nibu, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **61**, 2579 (1988).

6) M. Maehara and H. Shimada, to be published.

7) S. Nakamura, Y. Sonoda, S. Tominari, Y. Nibu, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **65**, 280 (1992).

8) H. Kawano, M. Maehara, Y. Nibu, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **67**, 2308 (1994).

9) M. A. Spackman, *J. Chem. Phys.*, **85**, 6579 (1986).

10) H. Bonadeo and E. D'Alessio, *Chem. Phys. Lett.*, **19**, 117 (1973).

11) S. N. Vaidya and G. C. Kennedy, *J. Chem. Phys.*, **55**, 987 (1971).