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The Raman Active Intra- and Intermolecular Vibrations of [$^1H_{10}$]- and [$^2H_{10}$]*p*-Xylenes

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Synopsis. Assignment of the Raman active normal vibrations of [$^1H_{10}$]- and [$^2H_{10}$]*p*-xylenes was made through the vibrational analysis of the polarized Raman spectra. Assignment of the low-frequency Raman bands to the rotational intermolecular vibrations of the crystals was also discussed.

For the study of the pressure effect on the Raman spectrum of *p*-xylene the reliable assignment of both the intra- and intermolecular vibrations is necessary. Although the assignment of the intramolecular vibrations of [$^1H_{10}$]*p*-xylene was studied by several workers,[1,2] no study was made on the intermolecular vibrations. In this work the assignment of the normal vibrations of [$^1H_{10}$]*p*-xylene given by earlier workers is reinvestigated and the intermolecular vibrations of the [$^1H_{10}$]- and [$^2H_{10}$]xylene crystals are studied through the observation of the polarization behavior of the Raman bands and also through the study of the isotopic effect on the vibrational frequency.

Experimental

Material. [$^1H_{10}$]- and [$^2H_{10}$]*p*-xylenes, obtained from Nakalai Chemical Company and MSD Isotopes, respectively, were purified by repeated distillation under reduced pressure.

Optical Measurement. The polarized Raman spectrum was observed in a single crystal grown in a capillary glass tube of about 3 mm in diameter with a Jeol 400 T Laser Raman Spectrophotometer changing temperature from 5 to −80 °C in the same method as described previously.[3] The direction of the crystal growth was found to be one of the crystal axes and another crystal axis was found by rotating the crystal specimen around the crystal growth direction under the polarized light. The former and latter crystal axes are tentatively referred to as the *u* and *v* axes, respectively, because it could not be determined easily which of the crystal *a*, *b*, and *c* axes corresponds to the former or latter axis. The *w* axis was taken to be perpendicular to both the *u* and *v* axes. The polarized *uu*, *uv*, and *uw* Raman spectra were observed in the same manner as described previously.[3]

Results and Discussion

Intramolecular Vibrations. The normal coordinate calculations of [$^1H_{10}$]- and [$^2H_{10}$]*p*-xylenes were performed through the GF matrix method with a FACOM M-200 computer at Computer Center of Fukuoka University. The geometric parameters of the molecule were taken from the data determined by Koningsveld and Berg.[4] The force constants used for the calculation of the normal vibrations are listed in Table 1. The notation of the force constants is the same as that described in the previous papers.[3,5,6] The calculated frequencies and modes are given in Table 2. The *x* axis is taken to be perpendicular to the molecular plane and the *y* and *z* axes are in the plane with the *z* axis passing through the methyl groups.

Table 1. Force Constants for the In-Plane and Out-of-Plane Vibrations

$K_{C'-C}$	5.2 hN m^{-1}	$F_{C\cdots H}$	0.4 hN m^{-1}
K_{C-C}	5.0	$F_{C'\cdots H'}$	0.25
$K_{C'-C''}$	3.0	$F_{H'\cdots H'}$	0.1
K_{C-H}	4.5	ρ	0.3
$K_{C''-H'}$	4.5	f^{o}_{rr}	0.06 aN m rad^{-2}
$H_{CC'C}$	0.4	$Q_{C'-C}$	0.23
$H_{C'CC}$	0.42	Q_{C-C}	0.2
$H_{C''C'C}$	0.15	$Q_{C''-C'}$	0.1
$H_{C'CH}$	0.18	$q^{o}_{C'-C,C-C}$	−0.05
H_{CCH}	0.18	$q^{m}_{C'-C,C-C}$	0.02
$H_{C'C''H'}$	0.15	P_{H}	0.31
$H_{H'C''H'}$	0.42	$P_{C''}$	0.38
$F_{C'\cdots C}$	0.6	$p^{o}_{H,H}$	0.04
$F_{C\cdots C}$	0.4	$p^{m}_{H,H}$	−0.04
$F_{C''-C}$	0.6	t^{o}_{H}	−0.05
$F_{C'\cdots H}$	0.4	t^{m}_{H}	0.02

C′ is the carbon atom bonded to the methyl group, and C″ and H′ are the carbon and hydrogen atoms of the methyl group, respectively.

The crystal structure of [$^1H_{10}$]*p*-xylene was studied by Koningsveld and Berg.[4] They showed that [$^1H_{10}$]*p*-xylene crystallizes in the monoclinic system of space group C_{2h}^2 with two molecules in the unit cell and no phase transition takes places between 273 and 110 K. No factor group splitting was observed in the Raman bands caused by the intramolecular vibrations and thus the relationship between the Raman tensors for the free molecule and the crystal was derived on the basis of the simplified oriented gas model. The calculation of the Raman tensors was made for two orientations of the monoclinic crystal in the same way as described previously[3,7] and the result is given in Table 3, where the *c*′ and *a*′ axes were taken to be normal to the *ab* and *bc* planes, respectively. The table indicates that (1) the calculations made for the cases I and II give almost equal result for the polarization behavior of the Raman bands, (2) the Raman bands caused by the b_{1g} and b_{3g} vibrations could be observed strongly in the *aa* and *c*′*c*′ (*a*′*a*′ and *cc*) spectra and hardly observed in the *bb* and *ac*′ (*bb* and *a*′*c*) spectra, and (3) the b_{2g} vibrational Raman bands could be observed strongly in the *bb* (*bb*) spectrum and hardly in

Table 2. The Raman Active Normal Vibrations of $[^1H_{10}]$- and $[^2H_{10}]$*p*-Xylenes

		$[^1H_{10}]$*p*-Xylene					$[^2H_{10}]$*p*-Xylene			
		Raman			Calcd	G.V.[a)]	Raman			Calcd
		$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}
		cry	liq	cry			cry	liq	cry	
a_g	ν_2	3056	p		3051	3054	2260	p		2247
	ν_{8a}	1620	p		1620	1618	1598	p		1602
	ϕ-CH_3 str[b)]	1205	p		1199	1205	1218	p		1226
	ν_{9a}	1183	p		1173	1183	877	p		850
	ν_1	829	p		840	829	772	p		787
	ν_{6a}	457	p		461	459	430	p		426
b_{1g}	ν_{10a}	842	dp	uv uw	855	810	660	dp	uv uw	668
	ϕ-CH_3 tor[b)]				275					198
b_{2g}	ν_5	930	dp	uu	915	934	819	dp	uu	821
	ν_4	700	dp	uu	690	702	575	dp	uu	568
	CH_3 wag[b)]	312	dp	uu	302	313	289	dp	uu	280
b_{3g}	ν_{7b}	3030	dp	uv uw	3018	3030	2230	dp	uv uw	2225
	ν_{8b}	1587	dp	uv uw	1596	1581	1578	dp	uv uw	1574
	ν_3	1311	dp	uv uw	1306	1313	1005	dp	uv uw	1006
	ν_{6b}	644	dp	uv uw	658	645	625	dp	uv uw	630
	ν_{9b}	383	dp	uv uw	388	386	333	dp	uv uw	335

a) Taken from Ref. 2. b) H is replaced by D in $[^2H_{10}]$*p*-xylene.

Table 3. Squares of Relative Values of the Elements of the Raman Tensor for *p*-Xylene Crystal

		b_{1g}	b_{2g}	b_{3g}
Case I	$(A_{aa})^2$	0.46	0.27	0.53
	$(A_{bb})^2$	0.00	0.99	0.00
	$(A_{c'c'})^2$	0.45	0.22	0.54
	$(A_{ab})^2$	0.25	0.00	0.22
	$(A_{ac'})^2$	0.00	0.24	0.00
	$(A_{bc'})^2$	0.28	0.00	0.24
Case II	$(A_{a'a'})^2$	0.51	0.19	0.44
	$(A_{bb})^2$	0.00	0.99	0.00
	$(A_{cc})^2$	0.50	0.32	0.53
	$(A_{a'b})^2$	0.27	0.00	0.28
	$(A_{a'c})^2$	0.00	0.24	0.00
	$(A_{bc})^2$	0.23	0.00	0.23

the *ab* and *bc'* (*a'b* and *bc*) spectra. The spectral notations outside and inside the parentheses are referred to as the polarized spectra for the cases I and II, respectively.

The polarized Raman spectra of $[^1H_{10}]$- and $[^2H_{10}]$*p*-xylenes in the intramolecular vibrational regions are shown in Figs. 1 and 2, respectively. The figures show that the non-totally symmetric Raman bands, which are depolarized in liquid, give two different types of polarization behavior, that is, (1) the relative intensity of the bands belonging to the first type is strong in the *uu* spectrum and extremely weak in the *uv* and *uw* spectra and (2) the relative intensity of the second type bands is nearly equal in the *uv* and *uw* spectra and extremely weak in the *uu* spectrum. Comparison of the observed polarization behavior with the values given in Table 3 indicates that (1) the first type bands can be ascribed to the b_{2g} vibrations, (2) the second ones to the b_{1g} and/or b_{3g} vibrations, and (3) the *u* axis corresponds to the crystal *b* axis. The vibrational mode is determined through the normal coordinate calculation.

The assignment given for the Raman active vibrations of $[^1H_{10}]$- and $[^2H_{10}]$*p*-xylenes is given in Figs. 1 and 2, and Table 2. The assignment given for $[^1H_{10}]$*p*-xylene is the same as that given by earlier workers except for the b_{1g} vibration. Although earlier workers assigned the Raman band at 810 cm^{-1} to the ν_{10a} vibration of b_{1g} species, this band is polarized in liquid and splits into two bands at 812 and 807 cm^{-1} in single crystal. The 812 cm^{-1} band showed neither the first nor the second polarization behavior and was observed in all the *uu*, *uv*, and *uw* spectra. Therefore this band was assigned to the a_g vibration ($2\times\nu_{16a}$). The 807 cm^{-1} band showed the first type polarization and was assigned to the methyl rocking vibration of species b_{2g} on the basis of the calculation. The band observed at 842 cm^{-1} was assigned to the ν_{10a} vibration because this band showed the second type polarization in single crystal. The reliability of the assignment given for the normal vibrations of $[^1H_{10}]$*p*-xylene was conformed by the consistency of the isotopic effect on the normal vibrations of $[^2H_{10}]$*p*-xylene.

The normal coordinate calculation indicates that (1) the ϕ-CH_3 (and ϕ-CD_3) stretching vibration mixes with the ν_1 and ν_{6a} vibrations and (2) the D bending ν_{9a} and D wagging ν_5 vibrations mix with the ν_1 and ν_4 vibrations, respectively, in $[^2H_{10}]$*p*-xylene. These vibrational mixings could be confirmed by the experimental facts that (1) the frequencies of the ν_1 and ν_{6a} vibrations of $[^1H_{10}]$- and $[^2H_{10}]$*p*-xylenes decrease largely from those of $[^1H_6]$- and $[^2H_6]$benzenes, respectively, (2) especially the frequency decrease of the ν_1 vibration of $[^2H_{10}]$*p*-xylene is prominent, and (3) the frequency of the ν_4 vibration of $[^2H_{10}]$*p*-xylene decreases largely from that of $[^1H_{10}]$*p*-xylene.

Intermolecular Vibrations. The crystal structure of *p*-xylene belongs to space group C_{2h}^2 with two molecules

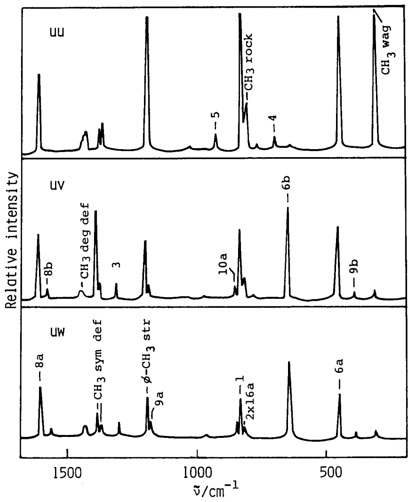

Fig. 1. Polarized Raman spectra of $[^1H_{10}]p$-xylene in single crystal.

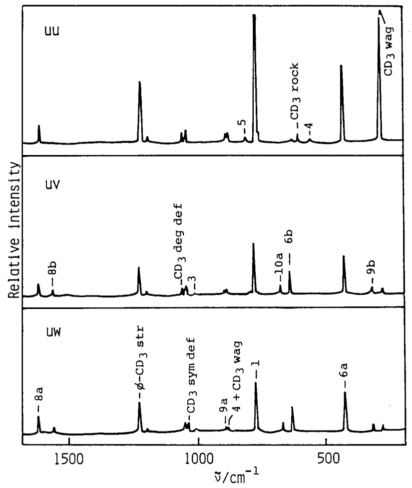

Fig. 2. Polarized Raman spectra of $[^2H_{10}]p$-xylene in single crystal.

in the unit cell and thus the six rotational intermolecular vibrations are distributed among a_g and b_g symmetry species; $3a_g+3b_g$. The polarized Raman spectra of the $[^1H_{10}]$- and $[^2H_{10}]p$-xylenes crystals in the low-frequency region observed at 0 °C are shown in Fig. 3, where the solid and dotted lines correspond to the *uu* and *uv* spectra, respectively. The Raman frequencies increase monotonically with decreasing temperature from 0 to −80 °C although the spectral structure does not change. This observation is consistent with the fact that no phase transition takes place in this temperature region.[4] The *uw* spectrum shows almost equal polarization behavior to that of the *uv* spectrum. Since the *u* axis corresponds to the crystal *b* axis, which is the two fold screw axis in the *p*-xylene crystal, the elements of the Raman tensor *uu* (=*bb*) and *uv* (=*ab* or *bc*) belong to the symmetry species a_g and b_g, respectively. Therefore, the bands observed at 101 (92) and 62 (56) cm^{-1} in the *uu* spectrum, and the bands at 88 (78) and 62 (56) cm^{-1} in the *uv* spectrum could be assigned to the rotational intermolecular vibrations

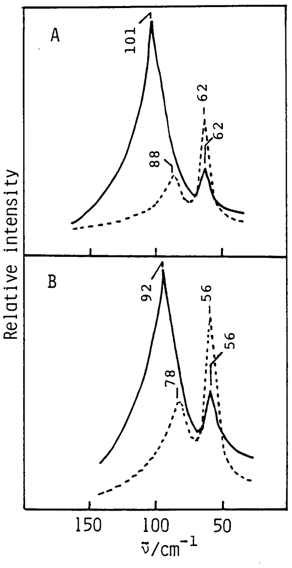

Fig. 3. Polarized Raman spectra of (A) $[^1H_{10}]$- and (B) $[^2H_{10}]$-*p*-xylene in single crystals in low-frequency region.

belonging to the symmetry species a_g and b_g, respectively. The values outside and inside the parentheses are referred to as the Raman frequencies of $[^1H_{10}]$- and $[^2H_{10}]p$-xylenes, respectively. The observation of the 62 (56) cm^{-1} bands in both the *uu* and *uv* spectra may be due to the accidental degeneracy of the a_g and b_g intermolecular vibrations. The isotopic factor of the bands $(\tilde{\nu}[^1H_{10}]/\tilde{\nu}[^2H_{10}])$ is equal to the value of $(I_r[^2H_{10}]/I_r[^1H_{10}])^{1/2}$, where $\tilde{\nu}$ is the Raman frequency and I_r the moment of inertia about the axis r $(r=x, y, z)$, if the Raman bands correspond to the rotational intermolecular vibrations. The calculated isotopic factors are 1.1 for all the rotational intermolecular vibrations around the x, y, and z axes, and the observed isotopic factors are about 1.1 for all the Raman bands. The good agreement of the observed and calculated isotopic factors shows that the assignment of the Raman bands in the low-frequency region to the rotational intermolecular vibrations is reasonable.

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