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Temperature Effect on the Depolarization Degree of the Raman Active Totally Symmetric Vibrations of Some Benzene Derivatives Belonging to Point Groups D_{6h} and D_{3h}

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The temperature effect on the depolarization degree of the Raman bands of the totally symmetric vibrations of some benzene derivatives belonging to point groups D_{6h} and D_{3h} was studied. In these molecules a direct field due to incident light gives rise to an intrinsic depolarization, and an indirect field causes by dipoles induced in the surrounding molecules by the incident light gives rise to depolarization due to intermolecular interactions. It was observed that although the depolarization degree increases with increasing temperature for all vibrational modes, the relationship between the temperature and depolarization degree is different, depending on the vibrational modes as well as the substituents. These observations are qualitatively explained by a change in the intermolecular interaction due to thermal fluctuations of the intermolecular distance caused by molecular vibrations.

The principal elements of the Raman polarizability have been determined by various workers[1—4] through measurements of the depolarization degree of the rotational Raman bands for small linear and symmetric (or nearly symmetric) top molecules in gas phase, where the principal elements of the Raman polarizability can be definitely determined owing to the symmetry of the molecular vibrations. Ebata et al.[5] measured the depolarization degree of the ν_1 Raman band of jet-cooled benzene using a highly sensitive observation method by a stimulated Raman pumping technique, and determined the relative values of the principal elements of the Raman polarizability of benzene. Shimizu et al.[6] determined the relative values of the principal elements of the Raman polarizability of some totally symmetric vibrations of naphthalene and maleic anhydride through analyses of the intensity of the polarized Raman bands in single crystals. They discussed the relation between the relative values of the principal elements of the Raman polarizability and vibrational modes.

Hyodo and Fujiyama[7] proposed a detailed theoretical model for the value of the depolarization degree of the ν_1 vibrational Raman band of carbon tetrachloride, which was measured to be 0.0039, although the value is expected to be zero according to the symmetry of the vibrational mode. Their model is based on the idea that a molecule is subjected to the direct field of the exciting light, and also to an indirect field caused by dipoles induced in the surrounding molecules by the field of the incident light. The fluctuations of the strength and the direction of the indirect field due of the thermal motion of molecules cause finite depolarized scattering. Ikawa and Whalley[8] studied the pressure effect on the depolarization degree of the ν_1 band of carbon tetrachloride in the range of 0—0.11 GPa, and showed that the theoretical treatment given by Hyodo and Fujiyama is able to explain well the observed results.

In this work the depolarization degree of the totally symmetric vibrations of various benzene derivatives belonging to point groups D_{6h} and D_{3h} are measured at various temperatures, and the effects of temperature and substituent on the depolarization degree are studied.

Experimental

Material. [$^1H_6$]Benzene (C_6H_6, 5.5 °C) and [$^2H_6$]benzene (C_6D_6, 6.8 °C) obtained from Nacalai Tesque, benzene-1,3,5-d_3 ($C_6H_3D_3$, 6.0 °C) and 1,3,5-trichloro-2,4,6-trifluorobenzene ($C_6Cl_3F_3$, 63 °C) from Aldrich, hexafluorobenzene (C_6F_6, 5 °C), 1,3,5-trifluorobenzene ($C_6H_3F_3$, −5.5 °C), 1,3,5-trichlorobenzene ($C_6H_3Cl_3$, 64 °C), and 1,3,5-tribromobenzene ($C_6H_3Br_3$, 123 °C) obtained from Tokyo Kasei Organic Chemicals, and 1,3,5-trimethylbenzene ($C_6H_3(CH_3)_3$, −45 °C) from Kanto Chemicals were purified by repeated vacuum distillations or zone refining of about 100 passages. The numbers in parentheses refer to the melting point at ambient pressure.

Optical Measurement. The depolarization degree of the Raman bands in liquid or molten state was measured in a rectangular cell by a backscattering observation method with a JEOL 400T Laser Raman Spectrophotometer. The samples were excited with the 514.5 nm line from an Ar^+ ion laser of Spectra Physics 168B. The optical alignment was set in such a way that the depolarization

degree of the totally symmetric ν_1 Raman band of liquid carbon tetrachloride became as small as possible, as described previously.[6] The value of the depolarization degree measured for the ν_1 band of carbon tetrachloride in this work is 0.008, while the most reliable value reported at present is 0.0039 at room temperature.[9]

The temperature effect on the depolarization degree was measured with a temperature-control cell system of JEOL Model RS-VTC 41. The depolarization degree of the ν_1 band of carbon tetrachloride measured with this cell system was ranged from 0.025 to 0.035 at room temperature. The fact that the observed values of the depolarization degree are larger than the values obtained with a rectangular cell is considered to be due to the difference of the optical cell system, that is, the shape of the cell and the numbers of the optical windows.

Results and Discussion

In theoretical treatments proposed by Hyodo and Fujiyama[7] and Ikawa and Whalley[8] the depolarization degree is related to the mean-square value of the off-diagonal elements of the Raman tensor due to the local field applied to the molecule. That is, the depolarization degree is proportional to the product of the mean-square amplitude (l^2) of the fluctuation of the intermolecular distance and the mean-square gradient of the local field. Since the latter decreases as the negative eighth power of the intermolecular distance (d), the nearest neighbors give the dominant contribution to the depolarization. The depolarization degree (ρ-value) is, therefore, given by

$$\rho = Al^2/d^8,$$

where A is a constant. They calculated the value of l^2/d^8 as a function of pressure and showed the following result. Although the value of l^2 decreases and the value of $1/d^8$ increases with increasing pressure, the effect of pressure on l^2 remarkably dominates the effect on $1/d^8$. As a result, the value of l^2/d^8 decreases with increasing pressure. Their treatment well explains the observed pressure effect on the ρ-value of the ν_1 vibration of CCl_4.

In order to ascertain the applicability of the model given by Hyodo and Fujiyama, and Ikawa and Whalley, the ρ-values of the totally symmetric vibrations of some benzene derivatives belonging to the point group D_{6h} and D_{3h} were measured at various temperatures. A group theoretical consideration indicates that the relation $\alpha'_{xx}=\alpha'_{yy}=\alpha'_{zz}$ does not hold for these molecules, where α' is the Raman polarizability, and, therefore the ρ-value is affected by both the direct and indirect fields caused by the incident light. The change in the ρ-value with temperature is mainly due to the intermolecular interaction caused by the indirect field.

The assignments of the totally symmetric vibrations of C_6H_6, C_6D_6, and $C_6H_3D_3$ were taken from data given by Pietila et al.[10] and Ozkabak and Goodman.[11] The assignment for C_6F_6 was taken from Delbouille[12] and Suzuki et al.[13] and the assignments for $C_6H_3Cl_3$ and $C_6H_3Br_3$ from Sakamoto et al.[14] The assignments for $C_6H_3F_3$, $C_6H_3(CH_3)_3$, and $C_6Cl_3F_3$ were made in this work through vibrational analyses of the Raman and infrared spectra and a normal coordinate calculation. The force constants used in this work

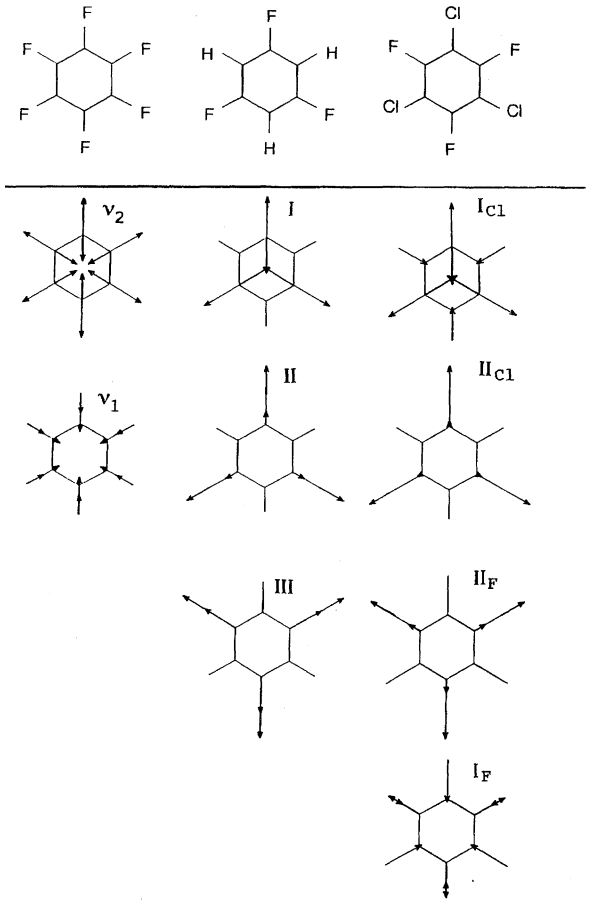

Fig. 1. Totally symmetric vibrational modes of hexafluorobenzene, 1,3,5-trifluorobenzene, and 1,3,5-trichloro-2,4,6-trifluorobenzene.

Table 1. Force Constants of the In-plane Vibrations for Trisubstituted Benzene Derivatives Belonging to D_{3h} Point Group

	TFB[a]	TClB[a]	TBrB[a]	TClFB[a]	TCH_3B[a]
$K_{C'-C}$[b]	5.0	5.0	5.0	5.0	5.0
$K_{C'-X}$[c]	4.5	2.5	2.2	4.5(2.5)[d]	3.0
K_{C-H}	4.6	4.6	4.6		4.6
$H_{CC'C}$[b]	0.4	0.25	0.2	0.25	0.4
$H_{C'CC'}$[b]	0.3	0.3	0.3	0.4	0.3
$H_{C'CH}$[b]	0.2	0.2	0.2		0.2
$H_{CC'X}$[b]	0.2	0.35	0.3	0.35	0.15
$F_{C'\cdots C'}$[b]	0.5	0.5	0.5	0.5	0.5
$F_{C\cdots C}$	0.5	0.5	0.5	0.5	0.5
$F_{C\cdots X}$	0.9	0.5	0.4	0.9(0.5)[d]	0.6
$F_{C\cdots H}$	0.46	0.46	0.46		0.46
ρ	0.25	0.25	0.25	0.25	0.25

(in hNm^{-1}=mdyn $Å^{-1}$ units)

a) TFB, TClB, TBrB, TClFB, and TCH_3B refer to 1,3,5-fluoro-, 1,3,5-trichloro, 1,3,5-tribromo-, 1,3,5-trichloro-2,4,6-trifluoro-, and 1,3,5-trimethylbenzenes, respectively. b) C′ and C refer to the carbon atoms located at 1,3,5 and 2,4,6 positions, respectively. c) X refers to fluorine, chlorine, bromine, and methyl group. d) The values inside and outside the parentheses refer to the values for the chlorine and fluorine atoms, respectively.

Table 2. Values of Depolarization Degree for the Totally Symmetric Vibrations of C_6H_6, C_6D_6, and C_6F_6 Obtained with the Rectangular Cell System

Molecule	Mode	Vibrational frequency		Depol. degree
		Obsd	Calcd	
		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	ρ
C_6H_6	ν_1	993	993	0.014
	ν_2	3071	3077	0.12
C_6D_6	ν_1	944	944	0.014
	ν_2	2293	2289	0.11
C_6F_6	ν_1	562	587	0.031
	ν_2	1491	1470	0.07

are given in Table 1.

The calculated vibrational modes of the totally symmetric vibrations of C_6F_6, $C_6H_3F_3$, $C_6Cl_3F_3$ are shown in Fig. 1. In $C_6H_3F_3$ the mode involving the C–F stretching vibration is referred to as mode I, and the ring modes involving displacements of the F and H atoms to modes II and III, respectively. In order to distinguish the displacements of the F and Cl atoms in $C_6Cl_3F_3$ the subscripts of F and Cl are marked. The same notations of modes I, II, and III are used for the vibrational modes of the other molecules belonging to point group D_{3h}.

The depolarization measurement of the Raman spectra for

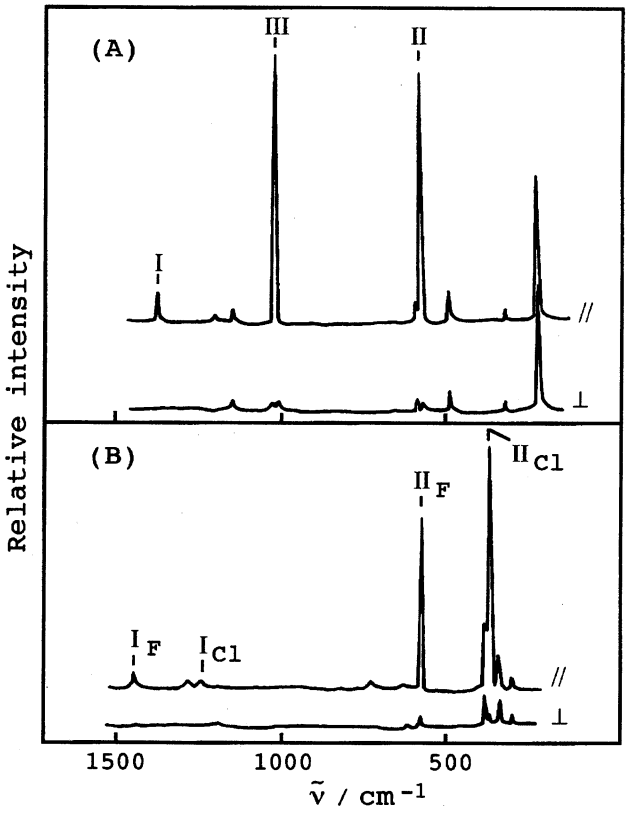

Fig. 2. Polarized Raman spectra of 1,3,5-trifluorobenzene (A) and 1,3,5-trichloro-2,4,6-trifluorobenzene (B) in liquid.

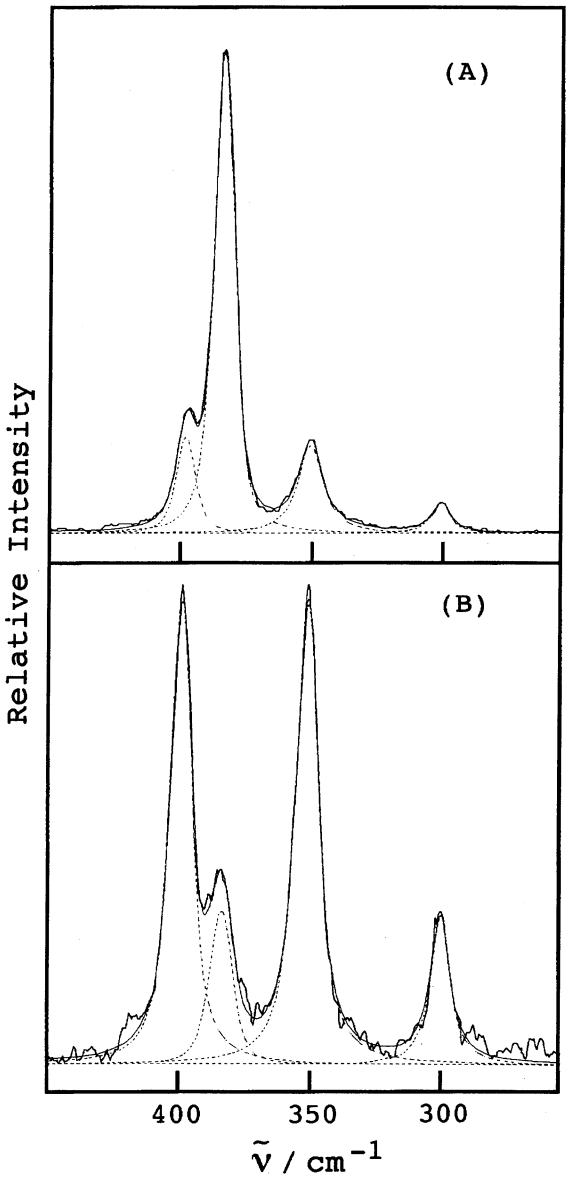

Fig. 3. Curve fitting result for the //(A) and ⊥ (B) polarized components of the Raman bands observed around 250—450 cm^{-1} for 1,3,5-trichloro-2,4,6-trifluorobenzene. The decomposed bands are shown by - - - curves. The composed and observed bands are by the fine and heavy — curves, respectively.

$C_6H_3F_3$ and $C_6Cl_3F_3$ are shown in Fig. 2 and the assignments of the bands are given in the figure. The intensity of the bands due to modes II and III is strong, while the intensity for mode I is very weak for all molecules belonging to point group D_{3h}. The curve-fitting method was made using the Voigt function for a reasonable evaluation of the intensity of the band overlapped with other bands, and the result obtained for $C_6Cl_3F_3$ is shown in Fig. 3 as an example. The ρ-values thus obtained using the rectangular cell are given in Tables 2 and 3, where the values for the liquid samples were measured at 25 °C and those for the solid samples in molten state at temperatures above the melting point by 2—3 °C.

The temperature effect on the ρ-values of the ν_1 and ν_2

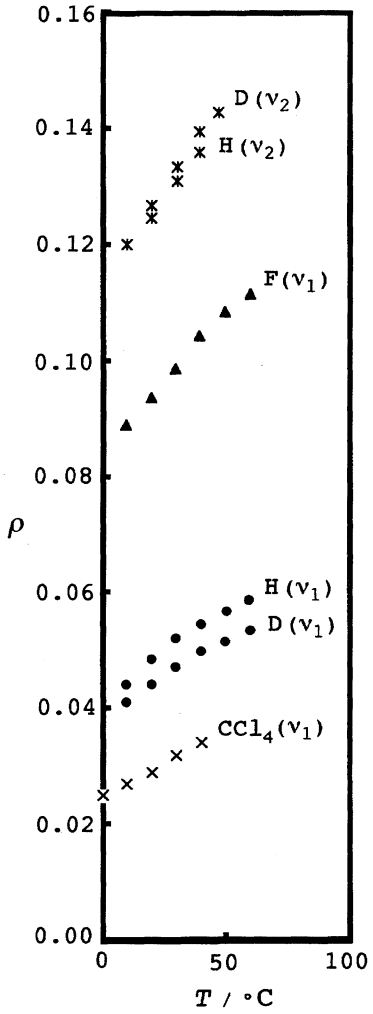

Fig. 4. Temperature effect on the ρ-values of the ν_1 and ν_2 vibrational bands of [$^1H_6$]benzene (H) and [$^2H_6$]benzene (D), and the effect on the ρ-value of the ν_1 band of carbon tetrachloride (CCl_4) and hexafluorobenzene (F) observed with the temperature control cell system.

Table 3. Values of Depolarization Degree for the Totally Symmetric Vibrations of $C_6H_3D_3$, $C_6H_3F_3$, $C_6H_3Cl_3$, $C_6H_3Br_3$, $C_6Cl_3F_3$, and $C_6H_3(CH_3)_3$ Obtained with the Rectangular Cell System

Molecule	Mode	Vibrational frequency		Depol. degree
		Obsd	Calcd	
		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	ρ
$C_6H_3D_3$ [a]	II	951	951	0.016
	III	1004	1004	0.025
	C–D str	2280	2283	0.15
	C–H str	3052	3067	0.15
$C_6H_3F_3$ [a]	II	580	576	0.028
	III	1012	1038	0.022
	I	1354	1378	0.02
	C–H str	3095	3083	0.15
$C_6H_3Cl_3$ [a]	II	376	350	0.049
	III	997	997	0.035
	I	1148	1173	0.053
	C–H str	3083	3082	0.20
$C_6H_3Br_3$ [a]	II	230	221	0.09
	III	987	985	0.043
	I	1118	1131	0.050
	C–H str	3075	3093	0.20
$C_6Cl_3F_3$ [b]	II_{Cl} [c]	385	357	0.045
	II_F [c]	586	581	0.050
	I_F [c]	1410	1394	0.040
	I_{Cl} [c]	1225	1225	
$C_6H_3(CH_3)_3$ [a]	II	577	587	0.029
	III	997	1002	0.035
	I	1300	1309	0.041
	C–H str (ring)	3032	3047	0.15

a) 1,3,5-Trisubstituted benzene. b) 1,3,5-Trichloro-2,4,6-trifluorobenzene. c) Subscripts F and Cl indicate the modes involving the displacement of F and Cl atoms, respectively.

vibrational bands of C_6H_6 and C_6D_6 and the ν_1 band of C_6F_6 is shown in Fig. 4, together with the effect on the ν_1 band of CCl_4. The temperature effect on the ρ-values of the bands due to modes II and III for $C_6H_3D_3$, $C_6H_3F_3$, $C_6H_3(CH_3)_3$, and $C_6H_3Cl_3$ is shown in Figs. 5 and 6, respectively. The temperature effect on mode I bands could not be measured because of the very weak intensity of the bands.

First, the temperature effect on the ρ-value measured with the temperature control cell system is discussed. Figs. 4, 5, and 6 indicate that (1) the ρ-values increase monotonously with increasing temperature, (2) the slope of the curve for the ρ-value versus temperature (ρ–T curve) is different depending on the molecules and vibrational modes, and (3) the slope of the ρ–T curve becomes slightly gentle with increasing temperature for all cases. Figure 4 shows that the slope of the ρ–T curve for the ν_1 vibration of C_6F_6 is much steeper than those for the ν_1 vibrations of C_6H_6 and C_6D_6. Figure 5 shows that the slopes of the ρ–T curves for the mode II of $C_6H_3D_3$, $C_6H_3F_3$, $C_6H_3(CH_3)_3$, and $C_6H_3Cl_3$ are quite different. The slopes for $C_6H_3D_3$ and $C_6H_3(CH_3)_3$ are approximately equal to the slopes for the ν_1 vibrations of C_6H_6 and C_6D_6, and the slope for $C_6H_3F_3$ is almost equal to the slope for the ν_1 vibration of C_6F_6. The slope for $C_6H_3Cl_3$ is slightly more gentle than that of $C_6H_3F_3$, but steeper than those of $C_6H_3D_3$ and $C_6H_3(CH_3)_3$. Figure 6 shows that the slopes of the ρ–T curves for mode III of these molecules are almost equal to each other, and that the slopes are approximately equal to the slopes for the ν_1 vibration of C_6H_6 and C_6D_6.

It is expected that the value of $1/d^8$ decreases and the value of l^2 increases with increasing temperature because the values of d and l increase with temperature. The observation that the ρ-values of all the observed vibrational bands increase monotonously with increasing temperature leads to the following conclusion. Since the temperature effect on the value of l^2 dominates the temperature effect on $1/d^8$, the slope of the curve for l^2/d^8 versus temperature (l^2/d^8–T curve) increases with increasing temperature. The observed

variation of the ρ-value with increasing temperature well corresponds to the observed variation of the ρ-value with decreasing pressure, as can be seen for the ν_1 vibration of CCl_4.[8]

These observed facts suggest that the temperature effect on the ρ-value depends mainly on the displacement of the atom involved in the vibrational mode. The most remarkable temperature effect was observed for the vibrational mode involving the displacement of the F atom. The intermolecular distance of D···D in C_6D_6 liquid may not be so different from that in $C_6H_3D_3$ liquid. The same may be true for the intermolecular distances of F···F in C_6F_6 and $C_6H_3F_3$ liquids. The intermolecular distance H···H in C_6H_6 crystal and the intermolecular distance F···F in C_6F_6 crystal were both calculated to be about 2.8 Å. Therefore, it could be expected that the $1/d^8$–T curves for C_6H_6, C_6D_6, $C_6H_3D_3$, C_6F_6, and $C_6H_3F_3$ liquids show approximately the same behavior. The slopes of the ρ–T curves for the ν_1 vibration of C_6F_6 and mode II of $C_6H_3F_3$ are much steeper than the slopes of the curves for the ν_1 vibration of C_6H_6 and mode III of $C_6H_3F_3$. This observation suggests that the contribution of l^2 from the intermolecular F···F distance to the slope of the ρ–T curve is much greater than that of l^2 based on the intermolecular H···H distance. The observation also shows that the temperature effect on the ρ-value of the band of mode III involving the displacement of the H atom in $C_6H_3X_3$, where X refers to D, CH_3, F, or Cl, is almost the same as that of the band of the ν_1 vibration of C_6H_6. Therefore, it can be concluded that the contribution of l^2 caused by vibrations involving the displacement of a certain atom to the ρ–T curve is almost equal for all molecules studied in this work.

The observed fact that the slope of the ρ–T curve for mode II of $C_6H_3Cl_3$ is slightly gentle compared with that for mode II of $C_6H_3F_3$ may indicate that the temperature effect on the l^2 value for $C_6H_3Cl_3$ is smaller than that of $C_6H_3F_3$, since the intermolecular Cl···Cl distance is expected to be larger than the F···F distance.

These observed results indicate that the model proposed for the depolarization degree by Hyodo and Fujiyama is quite reasonable and certain to explain the effect of an intermolecular interaction on the depolarization degree of the Raman band.

Ebata et al.[5] obtained the ρ-value of the ν_1 vibration of C_6H_6 to be 0.008 in a jet; this value is attributed to the ρ-value caused by the direct field, because no intermolecular interaction is expected in jets. As described above, the ρ-values of the ν_1 vibrations of CCl_4 and C_6H_6 observed with a rectangular cell at 25 °C are 0.008 and 0.014, respectively, although the most reliable value for the ρ-values of the ν_1 vibrations of CCl_4 is 0.0039 at room temperature.[9] This fact indicates that a reasonable ρ-value, which is caused by both the direct and indirect fields of the ν_1 vibration of C_6H_6 obtained in the ideal experimental conditions, is to be smaller than 0.014. Thus, it can be concluded that the ρ-value of the ν_1 vibration of C_6H_6 caused by the indirect field is smaller than the value caused by the direct field.

Next, the ρ-value obtained with the rectangular cell is

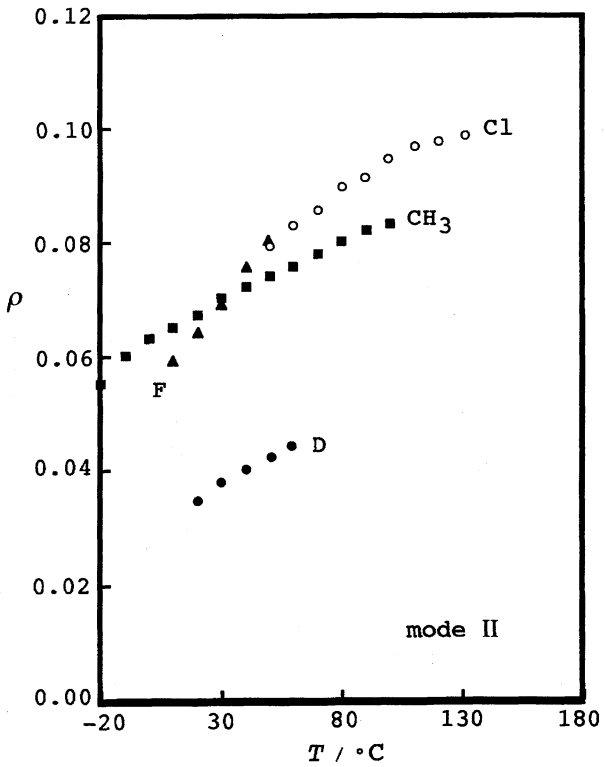

Fig. 5. Temperature effect on the ρ-value of the band due to the mode II for benzene-1,3,5-d_3 (D), 1,3,5-trifluoro- (F), 1,3,5-trimethyl (CH_3), and 1,3,5-trichlorobenzenes (Cl) observed with the temperature control cell system.

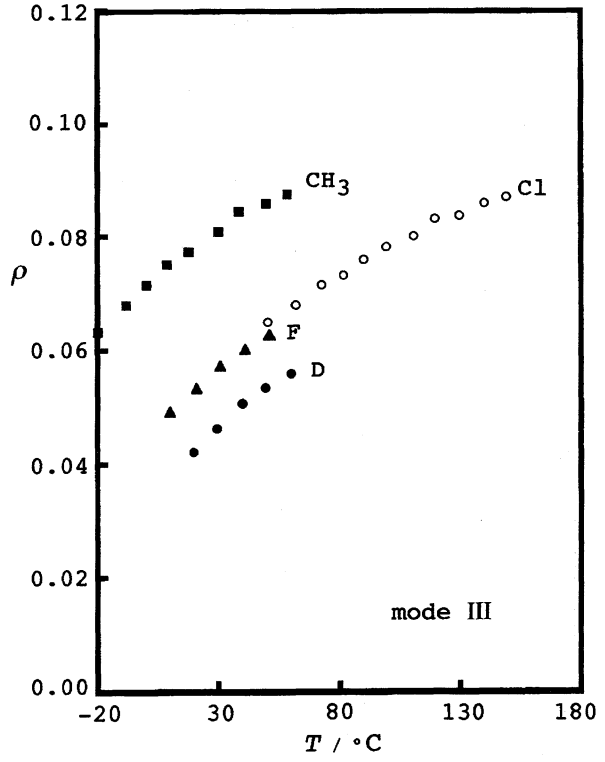

Fig. 6. Temperature effect on the ρ-value of the band due to the mode III for benzene-1,3,5-d_3 (D), 1,3,5-trifluoro- (F), 1,3,5-trimethyl (CH_3), and 1,3,5-trichlorobenzenes (Cl) observed with the temperature control cell system.

discussed. The ρ-values for mode II of $C_6H_3D_3$, $C_6H_3F_3$, $C_6H_3(CH_3)_3$, $C_6H_3Cl_3$, and $C_6H_3Br_3$ are 0.016, 0.028, 0.029, 0.049, and 0.09, respectively, and the ρ-values for mode III of these molecules are 0.027, 0.020, 0.035, 0.035, and 0.043, respectively, where the first three values were obtained at 25 °C, and the last two at 65 and 125 °C, respectively, as can be seen in Table 3. The ρ-values given in Table 3 can not be compared directly with each other because the ρ-value increases with temperature, as described above. Nevertheless, the following conclusions may be derived. (1) The depolarization caused by the indirect field for mode III is approximately equal for the molecules studied in this work, and, thus, the difference of the observed ρ-values for mode III of $C_6H_3D_3$, $C_6H_3F_3$, $C_6H_3(CH_3)_3$, $C_6H_3Cl_3$, and $C_6H_3Br_3$ may be attributed mostly to the intrinsic depolarization caused by the direct field. (2) The depolarization caused by the indirect field for mode II is different depending on the substituents, and, thus, the difference of the observed ρ-values for mode II of these molecules results from the depolarization caused by both the direct and indirect fields.

The ρ-value for the C–H stretching mode of liquid samples is 0.15 at 25 °C, while the ρ-value for solid samples is about 0.2 at temperatures above the melting point by 2—3 °C. The slopes of the ρ–T curves for the ν_2 mode of C_6H_6 and C_6D_6 are much steeper that the slopes of the ρ–T curves for the ν_1 mode, as can be seen in Fig. 4. This observation indicates that the depolarization due to the indirect field is much larger for the ν_2 mode than for the ν_1 mode. Therefore, it can be concluded that the large ρ-value obtained for the C–H (C–D) stretching mode may result considerably from depolarization caused by the indirect filed.

A study of the ρ-value measured in jets is needed because the ρ-value in jets offers valuable information caused by direct field, although we could not measure the ρ-value of the Raman bands in jets with our experimental equipment because of quite weak scattering intensity. The observed results obtained in this work are expected to be very useful for making a detailed theoretical treatment of the ρ-value caused by the indirect field.

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References

1) H. W. Schrötter and H. J. Bernstein, *J. Mol. Spectrosc.*, **12**, 1 (1964).
2) N. J. Bridge and A. D. Buckingham, *Proc. R. Soc. (London) A*, **295**, 334 (1966).
3) G. W. Hills and W. J. Jones, *J. Chem. Soc., Faraday Trans. 2*, **71**, 812 (1975).
4) M. P. Bogaard, A. D. Buckingham, R. K. Pierens, and A. H. White, *J. Chem. Soc., Faraday Trans. 1*, **74**, 3008 (1978).
5) T. Ebata, M. Hamakado, S. Moriyama, Y. Morioka, and M. Ito, *Chem. Phys. Lett.*, **199**, 33 (1992).
6) F. Shimizu, Y. Nibu, T. Osaki, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **68**, 160 (1995).
7) S. Hyodo and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **53**, 2456 (1980).
8) S. Ikawa and E. Whalley, *J. Chem. Phys.*, **89**, 51 (1988).
9) W. F. Murphy, M. W. Evans, and P. Bender, *J. Chem. Phys.*, **47**, 1836 (1967).
10) L. O. Pietilä, B. Mannfors, and K. Palmö, *Spectrochim. Acta, Part A*, **44A**, 141 (1988).
11) A. G. Ozkabak and L. Goodman, *J. Chem. Phys.*, **87**, 2564 (1987).
12) L. Delbouille, *J. Chem. Phys.*, **25**, 182 (1956).
13) Y. Suzuki, R. Shimada, and H. Shimada, *Res. Fukuoka Inst. Tech.*, **29**, 35 (1996).
14) H. Sakamoto, K. Yoshikai, T. Maruyama, Y. Nibu, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **63**, 525 (1990).