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Polarized Raman and Infrared Spectra of 2-Chloro- and 2-Bromopyrimidines

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The polarized Raman and infrared spectra of 2-chloro- and 2-bromopyrimidines were studied. Assignments of the normal vibrations for these molecules were made on the basis of polarization behaviors of the Raman and infrared bands and also through the normal coordinate calculation.

The infrared spectrum of 2-chloropyrimidine was first observed by Short and Thompson[1)] and Lafaix and Lebas.[2)] Sarma[3)] remeasured the infrared spectrum of this molecule and gave assignment for the in-plane vibrations based on the normal coordinate calculation. Allenstein *et al.*[4)] studied the infrared and Raman spectra of 2-fluoro-, 2-chloro-, 2-bromo-, and 2-iodopyrimidines and gave assignments for the normal vibrations of these molecules. Their assignments were not made on the basis of enough experimental evidences and no reasonable vibrational analysis of the phosphorescence spectrum of 2-chloropyrimidine, which shows the characteristic vibrational structure due to the Cl atom, can be made using their assignments.

In this paper, the assignments for the normal vibrations of 2-chloro- and 2-bromopyrimidines are reexamined through measurements of polarization behaviors of the Raman and infrared spectra.

Experimental

Material. 2-Chloro- and 2-bromopyrimidines were synthesized from 2-aminopyrimidine by means of the diazo reaction. The crude products were recrystallized from isopentane and then purified by repeated vacuum distillations. The final purification was made by zone-refining of about 100 passages.

Optical Measurement. Polarization measurement of the Raman spectrum was made in molten and single crystal phases with a JEOL 400 T Laser Raman Spectrophotometer. The sample was excited with the 514.5 nm line from an Ar^+ ion laser. A well grown single crystal of 2-chloropyrimidine was obtained by the Bridgman method. Then a cubic sample of about 5 mm^3 was cut off, where the cleavage plane was selected as one of the planes of the cube and each edge of the cube was cut along the crystallographic axis with a polarization microscope. A block of single crystal of 2-bromopyrimidine could not be obtained because this molecule was decomposed by heating over many hours in the Bridgman furnace. Thus a single crystal of this molecule was grown in a capillary glass tube of about 70 mm in length and 3 mm in diameter having a sharp conical end by heating for about three hours in the Bridgman furnace. The method of measurement of the polarized Raman spectrum was exactly the same as that described previously.[5)]

The infrared spectrum was observed in molten and single crystal phases with a Hitachi Infrared Spectrophotometer Model 345. The preparation of the single crystal sample and the method of measurement of the polarized infrared spectrum are exactly the same as those described previously.[6,7)]

Normal Coordinate Calculation

A normal coordinate calculation was performed through the standard ***GF*** matrix method with a FACOM M-200 computer at the Computer Center of Kyushu University. The geometrical parameters of the 2-chloropyrimidine molecule were taken from the data determined by Furberg *et al.*[8)] The molecular structure of 2-bromopyrimidine was assumed to be identical with that of 2-chloropyrimidine except for the C–Br bond, whose distance was assumed to be 0.185 nm. The ***F*** matrix elements for the in-plane vibrations were evaluated with the potential fields of an improved modification of the Urey-Bradley force field.[5,6,7)] The potential field is given by

$$\begin{aligned} V = V_{\mathrm{UB}} &+ \rho\{\Sigma(\Delta R,\Delta R)_o - \Sigma(\Delta R,\Delta R)_m + \Sigma(\Delta R,\Delta R)_p\} \\ &+ \Sigma k^o(\Delta r,\Delta r) + \Sigma k^m(\Delta r,\Delta r) + \Sigma k^m(\Delta R,\Delta R) \\ &+ \Sigma h^m(\Delta R,\Delta\alpha) + \Sigma h^m(\Delta R,\Delta\beta) + \Sigma f^o(\Delta\alpha,\Delta\alpha), \end{aligned}$$

where the symbols such as V_{UB} are the same as those used in the previous papers.[5,6,7)] The symbols given for the atoms and internal coordinates and the molecular axes are illustrated in Fig. 1. For the out-of-plane vibrations the valence force field and the ϕ type torsional coordinates were used. The notations of the force constants Q, q, P, p, and t are the same as those given by Whiffen.[9)]

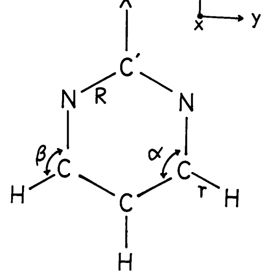

Fig. 1. Symbols given for the atoms and internal coordinates.

Results and Discussion

The force constants used for the in-plane and out-of-plane vibrations of 2-chloro- and 2-bromopyrimidines are listed in Tables 1 and 2, respectively. These values are consistent with the force constants given for pyrimidine.[10] The calculated frequencies and modes of the normal vibrations are given in Table 5.

Table 1. Force constants for in-plane vibrations

$K_{\mathrm{C-N}}$	5.90	
$K_{\mathrm{C-C}}$	4.65	
$K_{\mathrm{C-H}}$	4.46	
$K_{\mathrm{C-X}}$	2.07[a)]	1.75[b)]
H_{NCN}	0.75	
H_{NCC}	0.52	
H_{CNC}	0.40	
H_{CCC}	0.20	
H_{HCN}	0.19	
H_{XCN}	0.10[a)]	0.08[b)]
H_{HCC}	0.19	
$F_{\mathrm{C\cdots N\cdots C}}$	0.52	
$F_{\mathrm{N\cdots C\cdots X}}$	1.08[a)]	0.92[b)]
$F_{\mathrm{N\cdots C\cdots N}}$	0.80	
$F_{\mathrm{N\cdots C\cdots C}}$	0.51	
$F_{\mathrm{N\cdots C\cdots H}}$	0.68	
$F_{\mathrm{C\cdots C\cdots C}}$	0.80	
$F_{\mathrm{C\cdots C\cdots H}}$	0.49	
ρ	0.26	
$k^{o}_{(\mathrm{H},\mathrm{H})}$	0.06	
$k^{m}_{(\mathrm{H},\mathrm{H})}$	−0.07	
$k^{m}_{(R,R)}$	−0.10	
$h^{m}_{(R,\alpha_{\mathrm{H}})}$	−0.05	
$h^{m}_{(R,\beta_{\mathrm{X}})}$	−0.06	
$h^{m}_{(R,\beta_{\mathrm{H}})}$	0.11	
$f^{o}_{(\alpha,\alpha)}$	0.08	

Force constants denoted by K, H, F, ρ, and k are given in J/dm^2 (=mdyn/Å) units, and those denoted by h and f are in pJ/dm rad (=mdyn/rad) and aJ/rad^2 (=mdyn Å/rad^2) units, respectively. a) X is Cl atom. b) X is Br atom.

Table 2. Force constants for out-of-plane vibrations

$Q_{\mathrm{C'-N}}$	0.17	
$Q_{\mathrm{C-N}}$	0.18	
$Q_{\mathrm{C-C}}$	0.20	
q^{o}	−0.06	
q^{m}	0.03	
P_{X}	0.36[a)]	0.37[b)]
P_{H}	0.34	
p^{o}	0.07	
$p^{m}_{\mathrm{H},\mathrm{X}}$	−0.02	
$P^{m}_{\mathrm{H},\mathrm{H}}$	−0.07	
p^{p}	0.02	
$t^{o}_{\mathrm{C'-N},\mathrm{X}}$	−0.01	
$t^{o}_{\mathrm{C-N},\mathrm{H}}$	−0.02	
$t^{o}_{\mathrm{C-C},\mathrm{H}}$	−0.02	

Force constants are given in aJ/rad^2 (=mdyn Å/rad^2) units. a) X is Cl atom. b) X is Br atom.

The polarized Raman and infrared spectra of 2-chloro- and 2-bromopyrimidines observed in single crystals are shown in Figs. 2, 3, 4, and 5, respectively. The infrared spectra measured with incident lights polarized parallel and perpendicular to the crystal growth direction, which was determined to be one of the crystallographic axes for both molecules, are referred to as // and ⊥ spectra and drawn with the solid and dotted lines, respectively. The polarized Raman spectrum of 2-chloropyrimidine single crystal was denoted by two characters such as uv. The first letter refers to the direction of polarization of the excitation light and the latter to that of the scattering light. Since the crystallographic analysis for the cleavage plane of 2-chloropyrimidine single crystal was not reported yet, the crystal growth direction was tentatively taken to the *u* axis and the direction perpendicular to it in the cleavage plane was taken to the *v* axis. The *w* axis was taken to the direction perpendicular to both the *u* and *v* axes. A single crystal of 2-bromopyrimidine grown in a capillary tube was held in a capillary cell system of JEOL Model RS-VTC41 in such a way that both the crystal growth direction and other one of the crystallographic axes make right angle to the excitation light beam polarized along the crystal growth direction. The scat-

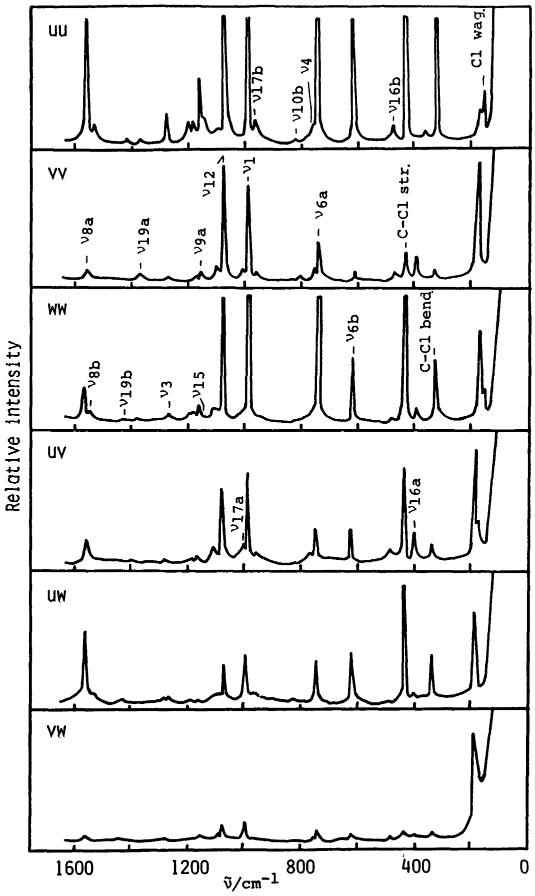

Fig. 2. Polarized Raman spectra of 2-chloropyrimidine single crystal.

tering light was observed from the direction perpendicular to the excitation light beam. The Raman spectra polarized parallel and perpendicular to the crystal growth direction are referred to as // and ⊥ spectra, respectively.

2-Chloropyrimidine. The non-totally symmetric Raman bands in the polarized single crystal Raman spectrum can be classified into three types based on their polarization behaviors as can be seen in Fig. 2. The relative intensity of each band belonging to the first type is strong in the uu spectrum and medium in the ww and uw spectra and weak in other spectra. The relative intensity of each second type band is weak in the uu, uv, and vv spectra and very weak in other spectra. The third type bands are observed with weak intensity in the uv and vv spectra and very weakly in other spectra. These three types of polarization behaviors are referred to as types A, B, and C, respectively.

The polarized infrared bands can be classified into three types I, II, and III based on their polarization behaviors as can be seen in Fig. 3. The bands belonging to the first type mainly constitute the // spectrum, that is, the bands are polarized nearly along the crystal growth direction. The intensity of each second type band in the // spectrum is nearly twice as strong as that in the ⊥ spectrum. The third type bands mainly constitute the ⊥ spectrum, that is, the bands are polarized exclusively perpendicular to the crystal growth direction.

Furberg *et al.*[8] analyzed the crystal structure of 2-chloropyrimidine and showed that the molecule crystallizes in the orthorhombic space group D_{2h}^{15}, where the molecular x axis orients nearly parallel to the crystal b axis and the z axis orients roughly parallel to the c axis although it leans somewhat toward the a axis. Therefore, the transition moments of the molecular vibrations belonging to the b_1 and a_1 symmetry species are expected to direct nearly along the crystal b and roughly along the c axes, respectively.

a_1 Species: Strongly polarized Raman bands observed at 437, 754, 990, 1078, 1163, 1380, 1561, 3010, and 3045 cm^{-1} in molten phase are straightforwardly assigned to the totally symmetric C–Cl stretching, ν_{6a}, ν_1, ν_{12}, ν_{9a}, ν_{19a}, ν_{8a}, ν_{13}, and ν_2 vibrations, respectively, on referring to the normal vibrations of pyrimidine[11–14] and other chlorinated pyrimidines,[6] and also based on the normal coordinate calculation. The corresponding single crystal infrared bands showed type I polarization behavior. This observation suggests that the crystal growth direction tends toward the crystal c axis.

b_2 Species: Infrared bands observed at 332, 626, 1154, 1277, 1384, 1425, 1540, and 3080 cm^{-1} in the single crystal spectrum showed type II polarization behavior and the corresponding single crystal Raman bands showed type A polarization behavior. These bands were assigned to the Cl bending, ν_{6b}, ν_{15}, ν_3, ν_{14}, ν_{19b}, ν_{8b}, and ν_{7b} vibrations, respectively, because higher frequencies of this band group are too much high to be assigned to the out-of-plane vibrations.

b_1 Species: Infrared bands observed at 477, 767, and 815 cm^{-1} in the single crystal spectrum showed type III polarization behavior and the corresponding crystal Raman bands showed type B polarization. These bands were assigned to the ν_{16b}, ν_4, and ν_{10b} vibrations, respectively. A Raman band observed at 960 cm^{-1} in single crystal showed type B polarization behavior and thus this band was assigned to the ν_{17b} vibration. A depolarized Raman band observed at 175 cm^{-1} in molten phase splits into two bands at 178 and 188 cm^{-1} in single crystal. The former band is clearly resolved in the uu, uv, and ww spectra while the latter is observed strongly in all spectra except for the uu. Therefore, the 178 cm^{-1} band was assigned to the Cl wagging vibration of b_1 species. The 188 cm^{-1} band may be ascribed to a lattice vibration.

a_2 Species: Raman bands observed at 405 and 1005 cm^{-1} showed type C polarization behavior in single crystal and no corresponding infrared bands could be observed. Therefore, these bands were assigned to the ν_{16a} and ν_{17a} vibrations, respectively.

The Raman bands observed at 330 and 437 cm^{-1} in molten phase, which were assigned to the Cl bending and C–Cl stretching vibrations, respectively, split into doublets separated by about 3 cm^{-1} in the Raman spec-

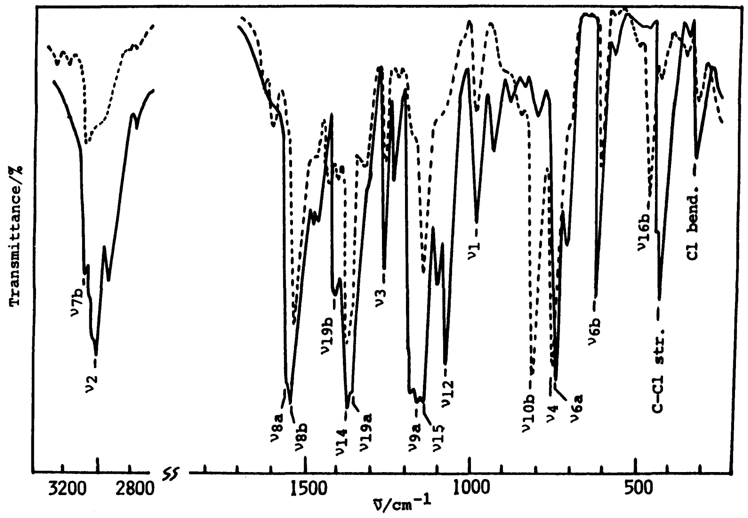

Fig. 3. Polarized infrared spectrum of 2-chloropyrimidine single crystal.

trum observed in solid phase under high resolution. The intensity ratio of the lower and higher frequency bands is about 1/3 for both bands. These splittings are ascribed to the isotopic shift, that is, the lower frequency band is due to the ^{37}Cl atom and the higher to the ^{35}Cl atom.

2-Bromopyrimidine. The depolarized Raman bands observed in molten phase show three different types of polarization behaviors in the single crystal Raman spectrum as can be seen in Fig. 4. The bands belonging to the first type can be observed clearly in the ⊥ spectrum. In the second type, the intensity of the // polarized band is slightly stronger than that of the ⊥ band. In the third type, the intensity of the ⊥ band is stronger than that of the // band. These three types of polarization behaviors are referred to as types A, B, and C, respectively. The polarized infrared bands of 2-bromopyrimidine were also classified into three types I, II, and III based on their polarization behaviors. In the first type, the intensities of the bands in the // and ⊥ spectra are nearly equal. In the second type, the intensity of the // band is stronger than that of the ⊥ band while in the third type, the intensity of the ⊥ band is much stronger than that of the // band.

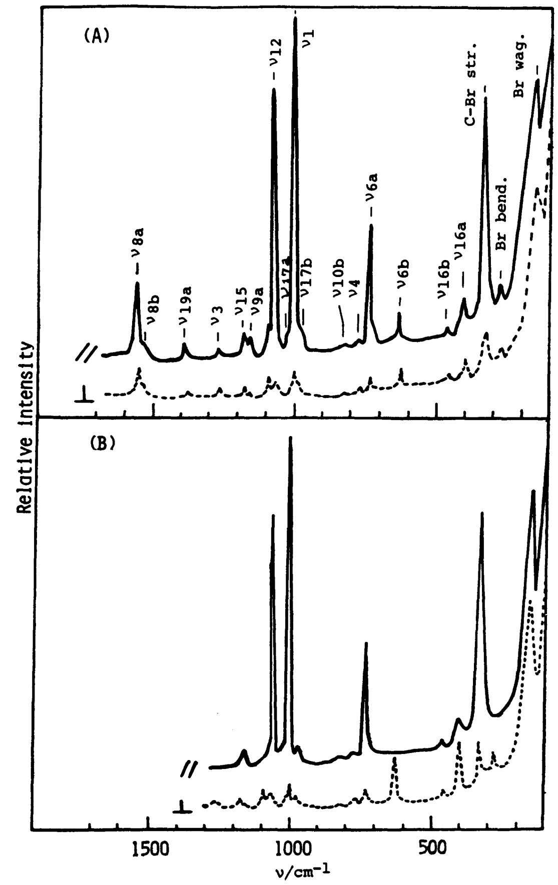

Fig. 4. Raman spectrum of 2-bromopyrimidine. (A): Depolarization behavior measured in moleten phase. (B): Polarization behavior measured in single crystal.

a_1 *Species*: Strongly polarized Raman bands observed at 330, 734, 998, 1074, 1157, 1381, 1559, 3013, and 3050 cm^{-1} in molten phase were straightforwardly assigned to the totally symmetric C–Br stretching, ν_{6a}, ν_1, ν_{12}, ν_{9a}, ν_{19a}, ν_{8a}, ν_{13}, and ν_2 vibrations, respectively on referring to the assignments given for pyrimidine and 2-chloropyrimidine, and also based on the calculation. The corresponding infrared bands showed type I polarization behavior in single crystal.

b_2 *Species*: Infrared bands observed at 276, 630, 1170, 1270, 1367, 1432, 1539, and 3080 cm^{-1} in single crystal showed type II polarization behavior and the corresponding Raman bands showed type A polarization behavior. These bands were assigned to the Br bending, ν_{6b}, ν_{15}, ν_3, ν_{14}, ν_{19b}, ν_{8b}, and ν_{7b} vibrations, respectively.

b_1 *Species*: Infrared bands observed at 465, 766, 826, and 960 cm^{-1} in single crystal showed type III polarization behavior and the corresponding Raman bands showed type B polarization. These bands were assigned to the ν_{16b}, ν_4, ν_{10b}, and ν_{17b} vibrations, respectively. A Raman band observed at 158 cm^{-1} showed type B polarization behavior and therefore this band was assigned to the Br wagging vibration of b_1 species.

a_2 *Species*: Raman bands observed at 400 and 1002 cm^{-1} showed type C polarization behavior and

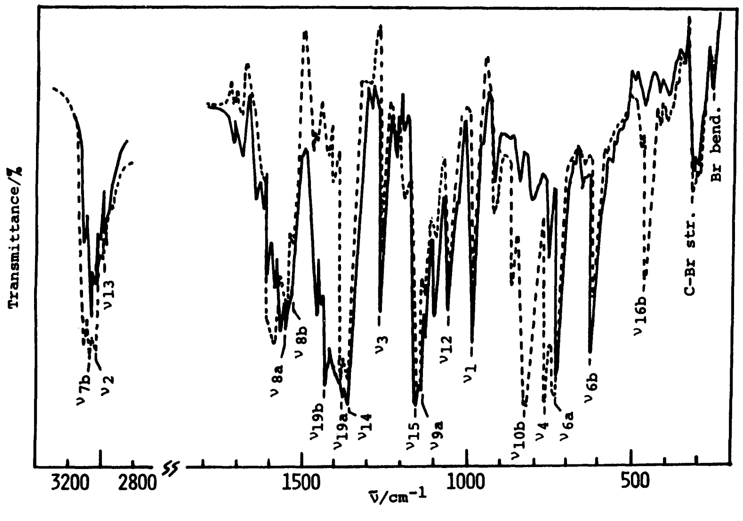

Fig. 5. Polarized infrared spectrum of 2-bromopyrimidine single crystal.

were assigned to the ν_{16a} and ν_{17a} vibrations, respectively. No corresponding infrared bands could be observed.

The isotopic splitting arising from the ^{79}Br and ^{81}Br atoms could not be observed because of small frequency differences due to the isotope. The single crystal infrared spectrum of 2-bromopyrimidine gave different polarization behavior from that of 2-chloropyrimidine. This may be due to different orientations of the two molecules in these single crystals. Detailed vibrational analyses of the Raman and infrared spectra of 2-chloro- and 2-bromopyrimidines are given in Tables 3 and 4, respectively. The normal vibrations are summarized in Table 5.

The assignments of the C–Cl stretching and ν_{6a} vibrations given by Sarma[3] are different from those given by Allenstein *et al.*[4] The normal coordinate calculation shows that the ν_{6a} vibration mixes with the C–X stretching vibration largely in 2-halopyrimidines, and this causes increase of the frequency of the ν_{6a} vibration and decrease of that of the C–X stretching vibration from their normal frequencies. Systematic vibrational analyses of the infrared and Raman spectra of 2-halopyrimidines given by Allenstein *et al.* support this mixing. These facts give the reasoning of assignments made by Allenstein *et al.* and us for the C–X stretching and ν_{6a} vibrations.

Sarma and Allenstein *et al.* assigned the 1169 cm^{-1} band of 2-chloropyrimidine to the ν_{15} vibration and 1158 cm^{-1} of 2-bromopyrimidine to the ν_3 vibration,

Table 3. Vibrational analysis of the Raman and infrared spectra of 2-chloropyrimidine

Raman				Infrared			
		Pol.					
$\tilde{\nu}$/cm^{-1}	Int.	Liq.	Cry.	$\tilde{\nu}$/cm^{-1}	Int.	Pol. Cry.	Assignment
178 188	m	dp	B				Cl wag.
327$^{a)}$ 330	m	dp	A	332	m	II	Cl bend.
405	w	dp	C				ν_{16a}
434$^{a)}$ 437	s	p		439	s	I	C–Cl str.
480	vw	dp	B	477	m	III	ν_{16b}
				580	w	II	ν_{16a}+Cl wag.
629	m	dp	A	626	s	II	ν_{6b}
				715	m	I	ν_{9a}−C–Cl str.
754	s	p		750	vs	I	ν_{6a}
770	vw	dp	B	767	vs	III	ν_4
807	vw	dp	B	815	vs	III	ν_{10b}
952	vw	p		950	m	I	ν_{6b}+Cl bend.
960	vw		B				ν_{17b}
990	vs	p		988	m	I	ν_1
1005	vw		C				ν_{17a}
1078	vs	p		1080	s	I	ν_{12}
1107	w	p		1102	m	I	ν_{8a}−C–Cl str.
				1154	vs	II	ν_{15}
1163	w	p		1163	vs	I	ν_{9a}
1195	w	p		1192	s	I	ν_{6a}+C–Cl str.
1264	vw	p		1250	m	I	2ν_{6b}
1278	w	dp	A	1277	s	II	ν_3
1380	w	p		1378	vs	I	ν_{19a}
				1384	vs	II	ν_{14}
1425	vw	dp	A	1425	m	II	ν_{19b}
				1433	w	III	2ν_{6b}+Cl wag.
				1468	w	I	ν_{15}+Cl bend.
1544	w	dp	A	1540	s	II	ν_{8b}
1561	m	p		1557	vs	I	ν_{8a}
3010	vw	p		3007	vw	I	ν_{13}
3045	s	p		3040	s	I	ν_2
3078	m	dp		3080	s	II	ν_{7b}
3087	m	p		3088	m	I	2ν_{8b}
3120	m	p		3119	m	I	2ν_{8a}

a) The lower and higher frequency bands are due to ^{37}Cl and ^{35}Cl atoms, respectively.

Table 4. Vibrational analysis of the raman and infrared spectra of 2-bromopyrimdine

Raman				Infrared			
$\tilde{\nu}$/cm^{-1}	Int.	Pol.		$\tilde{\nu}$/cm^{-1}	Int.	Pol. Cry.	Assignment
		Liq.	Cry.				
158	m	dp	B				Br wag.
276	w	dp	A	276	w	II	Br bend.
330	vs	p		325	m	I	C–Br str.
400	w	dp	C				ν_{16a}
462	vw	dp	B	465	s	III	ν_{16b}
623	m	dp	A	630	vs	II	ν_{6b}
734	s	p		740	vs	I	ν_{6a}
765	vw	dp	B	766	vs	III	ν_4
820	vw	dp	B	826	vs	III	ν_{10b}
				875	m	III	ν_{6a}+Br wag.
				923	w	I	$2\nu_{16b}$
960	vw	dp	B	960	vw	III	ν_{17b}
998	vs	p		992	s	I	ν_1
1002	vw	dp	C				ν_{17a}
1074	vs	p		1073	m	I	ν_{12}
1090	w	dp	B				C–Br str.+ν_4
				1105	m	II	ν_{19a}−Br bend.
				1127	m	II	ν_{17a}+Br wag.
1157	w	p		1154	vs	I	ν_{9a}
1170	w	dp		1170	m	II	ν_{15}
				1200	w	III	$\nu_{6a}+\nu_{16b}$
1270	w	dp		1270	s	II	ν_3
				1367	vs	II	ν_{14}
1381	w	p		1378	vs	I	ν_{19a}
				1432	m	II	ν_{19b}
				1460	m	II	$2\nu_{6a}$
				1480	w	I	ν_{15}+C–Br str.
1530	vw	dp		1539	m	II	ν_{8b}
1559	s	p		1551	s	I	ν_{8a}
				1578	m	III	$\nu_{6a}+\nu_{10b}$
				1610	m	III	$\nu_{9a}+\nu_{16b}$
3013	vw	p		3016	w	I	ν_{13}
3050	m	p		3049	s	I	ν_2
3086	m	dp		3080	m	II	ν_{7b}
				3110	m	I	$2\nu_{8a}$

but these bands showed a_1 polarization behavior in the Raman and infrared spectra and hence these bands could not be assigned to the b_2 vibration. Frequencies of 1132 and 1165 cm^{-1} constitute the main progressions in the phosphorescence spectra of pyrimidine[15,16] and 2-chloropyrimidine,[15,17] respectively, and these frequencies are to be assigned to the ν_{9a} vibration. Hence the bands assigned to the ν_{15}, and ν_3 vibrations by Sarma and Allenstein *et al.* should be both assigned to the ν_{9a} vibrations of 2-chloro- and 2-bromopyrimidines.

Allenstein *et al.* assigned the 1270 and 1390 cm^{-1} bands of 2-chloropyrimidine and 1273 and 1385 cm^{-1} bands of 2-bromopyrimidine to the ν_{14} and ν_{19b} vibrations, respectively. These bands showed b_2 polarization behavior. On referring to the normal vibrations of pyrimidine, we assigned these bands to the ν_3 and ν_{14} vibrations, respectively. The normal coordinate calculation also supports these assignments.

Allenstein *et al.* observed a 760 cm^{-1} Raman band as a shoulder of the strong 754 cm^{-1} band and assigned it to the ν_{17a} vibration for 2-chloropyrimidine. We reexamined the observation of a Raman band showing a_2 polarization behavior around this region very carefully but no such a band could be observed. On the other hand, the polarized dark sublevel phosphorescence spectrum of pyrimidine indicates that a 1004 cm^{-1} band shows a_2 polarization behavior and thus this frequency should be assigned to the ν_{17a} vibration.[10] Therefore we assigned the 1005 cm^{-1} band showing a_2 polarization behavior in the Raman spectrum to the ν_{17a} vibration.

The normal coordinate calculation indicates that the ν_{16b} vibration mixes largely with the X wagging vibration. This mixing is supported by the observation that the frequencies of the ν_{16b} vibration for 2-chloro- and 2-bromopyrimidines increase from the frequency of 345 cm^{-1} for the ν_{16b} vibration of pyrimidine.

TABLE 5. NORMAL VIBRATIONS OF 2-CHLORO- AND 2-BROMOPYRIMIDINES

		2-Chloropyrimidine				2-Bromopyrimidine		
	Mode	Sarma[3)]	Allenstein[4)]	This work		Allenstein[4)]	This work	
		$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	Obsd $\tilde{\nu}/\mathrm{cm}^{-1}$	Calcd $\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	Obsd $\tilde{\nu}/\mathrm{cm}^{-1}$	Calcd $\tilde{\nu}/\mathrm{cm}^{-1}$
a_1	C-X str.[a)]	1144	434 441	437	442	329	330	334
	ν_2	3062	3080	3045	3055	3118	3050	3055
	ν_{13}	3033	3050	3010	3006	3044	3013	3006
	ν_{8a}	1559	1555	1561	1563	1558	1559	1164
	ν_{19a}	1382	1370	1380	1389	1378	1381	1386
	ν_{9a}	754	1094	1163	1160	1105	1157	1152
	ν_{12}	1075	1078	1078	1072	1073	1074	1061
	ν_1	988	992	990	1004	989	998	998
	ν_{6a}	434	755	754	747	730 735	734	724
b_2	ν_{7b}	3115	3055	3080	3082	3080	3080	3082
	ν_{8b}	1552	1564	1540	1542	1562	1539	1542
	ν_{19b}	1428 1435	1390	1425	1437	1385	1432	1438
	ν_{14}		1270	1384	1372	1273	1367	1366
	ν_3	1202	1205	1277	1266	1158	1270	1264
	ν_{15}	1166	1169	1154	1158	1093	1170	1156
	X-bend		330	332	333	275	276	280
	ν_{6b}	626	629	626	622	624	630	622
a_2	ν_{17a}		760	1005	994		1002	994
	ν_{16a}		409	405	396	404	400	396
b_1	ν_{17b}		855	960	951	838	960	952
	ν_{10b}		810	815	825	830	826	825
	X wag.		194	178	165	160	158	155
	ν_4		772	767	762	762	766	764
	ν_{16b}		480	477	477	460	465	475

a) X is Cl or Br atom.

We believe that the assignments of the normal vibrations given for 2-chloro- and 2-bromopyrimidines are reliable and quite useful for the reasonable vibrational analysis of the phosphorescence spectrum of 2-chloropyrimidine, which will be reported soon.

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