Normal Vibrations of 4-Methyl- and 4-Methyl-d_3-pyridines

Kazumasa Yoshikai, Toshikazu Hieida, Yoshinori Nibu, Hiroko Shimada,* and Ryoichi Shimada†
Department of Chemistry, Faculty of Science, Fukuoka University,
Jonan-ku, Fukuoka 814-01
†Department of Chemistry, Faculty of Science, Kyushu University,
33, Hakozaki, Higashi-ku, Fukuoka 812

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Synopsis. Assignment of the normal vibrations of 4-methylpyridine was made through the vibrational analyses of the Raman and infrared spectra and also through the normal coordinate calculation. The assignment was confirmed by the study made on 4-methyl-d_3-pyridine.

Calvé et al.[1] studied the intermolecular vibrations of 4-methylpyridine in crystal through the analyses of the low-frequency Raman and far-infrared bands at various temperatures from 276.8 (melting point) to 5 K. They found that the crystal has three phases and discussed on the molecular dynamics determining the phase transitions. We are investigating how the intermolecular forces and the phase transitions affect the inter- and intramolecular vibrations of 4-methylpyridine through the study of pressure and temperature effects on the Raman spectrum. For this study, the reliable assignment of the normal vibrations and the calculation of the L_x vector for each mode have to be made. Some studies have been made on the normal vibrations of 4-methylpyridine,[2–3] but the reliable assignment based on enough experimental evidence has not been made. In this paper, the assignment of the normal vibrations of 4-methyl- and 4-methyl-d_3-pyridines was discussed on the basis of the polarization behavior of the Raman and infrared bands and through the normal coordinate calculation.

Experimental

Material. 4-Methyl-d_3-pyridine (4-CD_3-pyridine) was synthesized by the reaction of 4-methylpyridine (4-CH_3-pyridine) and D_2O with DCl at 100 °C. Isotopic purity of the product was determined by the NMR measurement. The samples were purified by repeated vacuum distillations.

Optical Measurements. The Raman spectra were observed in liquid (at 25 °C) and single crystal (at −10 °C) with a JEOL 400 T Laser Raman Spectrophotometer exciting the sample with the 514.5 nm line from an Ar-ion laser. A single crystal was grown in a capillary glass tube in a cooling cell system of JEOL Model RS-VTC 41 and the sample was held in such a way that the crystal growth direction was directed parallel to the polarization direction of the excitation laser beam and the Raman scattering was observed at right angles with the laser beam. The method of measurement of the polarized Raman spectrum was the same as that described previously.[4] The spectra polarized parallel and perpendicular to the polarization direction of the excitation beam are referred to as // and ⊥ spectra, respectively. The rotational band contour of the infrared bands was observed in vapor.

Results and Discussion

A normal coordinate calculation was performed through the standard GF matrix method with a FACOM M-780/10s computer at the Computer Center of Fukuoka University. The structual parameters of the pyridine ring and the methyl group were assumed to be the same as those given by Bak et al.[5] and Keidel and Bauer,[6] respectively. The F matrix elements for the in-plane and out-of-plane vibrations were the same as those used for pyridine[7] and dimethylpyridine.[8] Values of the force constants and the calculated frequencies and modes are given in Tables 1 and 2, respectively. The symbols given for the atoms and internal coordinates are shown in Fig. 1.

The polarized Raman spectra of 4-CH_3- and 4-CD_3-pyridines in single crystal are shown in Fig. 2. Only a qualitative discussion on the polarization behavior of the Raman bands in single crystal could be made because sufficient crystal data needed for the calculation of the Raman tensor are not available. The depolarized Raman bands in liquid show two types of polarization behavior in single crystal. In the first type (type I), the relative intensity of the band observed in the ⊥ spectrum is much stronger than that in the // spec-

Table 1. Force Constants for the In-Plane and Out-of-Plane Vibrations of 4-Methylpyridine

$K_{N\text{-}C}$	5.6 hN m^{-1}	$H_{C''C'H'}$	0.27 hN m^{-1}	$f^{o}_{\beta\beta}$	−0.05 aN m rad^{-2}
$K_{C\text{-}C}$	4.8	$H_{H'C'H'}$	0.39	Q_{NC}	0.22
$K_{C\text{-}C''}$	5.0	$F_{C\cdots C}$	0.6	Q_{CC}	0.2
$K_{C''\text{-}C'}$	3.0	$F_{N\cdots C}$	0.5	$Q_{CC''}$	0.23
$K_{C\text{-}H}$	4.5	$F_{C\cdots C''}$	0.6	$Q_{C''C'}$	0.1
$K_{C'\text{-}H'}$	4.5	$F_{N\cdots H}$	0.6	$P_{C'}$	0.35
H_{CNC}	0.4	$F_{C\cdots H}$	0.4	P_{H}	0.3
H_{NCC}	0.4	$F_{C\cdots C'}$	0.5	$q^{o\,a)}$	−0.06
$H_{CCC''}$	0.55	$F_{C''\cdots H'}$	0.32	$q^{m\,a)}$	0.01
$H_{CC''C}$	0.45	$F_{H'\cdots H'}$	0.1	p^{o}_{H}	0.03
H_{NCH}	0.3	ρ	0.38	p^{m}_{H}	−0.03
H_{CCH}	0.18	f^{o}_{rr}	0.06	t^{o}_{H}	−0.02
$H_{CC''C'}$	0.2	f^{m}_{rr}	−0.04	t^{m}_{H}	−0.02

a) Interaction terms involving the torsional coordinates in the pyridine ring.

Table 2. Normal Vibrations of 4-Methyl- and 4-Methyl-d_3-pyridines

Sym Spec	Mode	4-Methylpyridine					4-Methyl-d_3-pyridine				Pyridine[a]
		Akyüz[b]	This work				This work				
			Raman		IR	Calcd	Raman		IR	Calcd	
		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol	Pol	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol	Pol	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}
		liq	cry	liq cry	vap		cry	liq cry	vap		
a_1	ν_2	3051	3052	p		3052	3055[c]	p		3052	3055
	ν_{20a}	3051	2995	p		3012	2990[c]	p		3012	3005
	ν_{8a}	1606	1610	p	A	1619	1610	p	A	1619	1580
	ν_{19a}	1497	1500[c]	p		1536	1500[c]	p	A	1536	1484
	ϕ-CH_3 str[d]	1212	1241	p	A	1231	1246	p		1258	
	ν_{9a}	1221	1225	p		1196	1223	p		1197	1216
	ν_{18a}	1071	1073	p		1065	1060	p		1061	1070
	ν_1	996	999	p	A	1007	995	p	A	1006	990
	ν_{12}	803	807	p	A	797	780	p		765	1030
	ν_{6a}	516	518	p		533	496	p		505	602
b_2	ν_{20b}	3070	3070[e]			3074	3070[e]			3074	3080
	ν_{7b}	3034	3035	dp I		3033	3035[c]	dp		3033	3035
	ν_{8b}	1565	1567	dp I	B	1594	1555	dp I	B	1591	1572
	ν_{19b}	1413	1417	dp I	B	1426	1415	dp I	B	1428	1438
	ν_3	1280	1347	dp I		1353	1347	dp I		1349	1355
	ν_{14}	1360	1230	I		1227	1225	dp I		1224	1220
	ν_{18b}	1094				1069				1068	1045
	ν_{6b}	671	670	dp I		670	670	dp I		666	650
	CH_3 bend[d]	344	351	dp I		343	312	dp I		309	
a_2	ν_{17a}	971				993				993	975
	ν_{10a}	874	885	dp II		896	880	dp II		896	882
	ν_{16a}	383	380	dp II		378				377	377
	ϕ-CH_3 tor[d]					235				170	
b_1	ν_5	874	873	dp I		867	850	dp I		834	878
	ν_{11}	803	795[e]		C	805	795	dp I	C	793	715
	ν_4	727	730	dp I	C	742	705	dp I	C	725	755
	ν_{16b}	487	488	dp I	C	469	463	dp I	C	449	408
	CH_3 wag[d]	214	210	dp I		217	200	dp I		204	
Characteristic vibrations of CH_3 group[d]											
a_1	C–H str	2983	2945[c]	p		2976	2215[c]	p		2209	
	C–H str	2923	2925	p		2929	2135[c]	p		2103	
	CH_3 sym def	1381	1393	p		1414	1073	p		1081	
b_2	C–H str	2964	2960[c]	dp		2977	2235[c]	dp		2212	
	CH_3 deg def	1454	1460	dp		1435				1031	
	CH_3 rock		970	I		974				767	
b_1	CH_3 deg def	1454	1460	dp		1433				1030	
	CH_3 rock	1041	1050	I		1031	900	dp I	C	880	

a) See Refs. 7 and 9. b) See Ref. 3. c) Observed in liquid phase. d) H is replaced by D in 4-methyl-d_3-pyridine. e) Observed in the infrared spectrum.

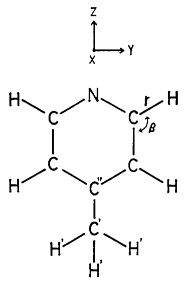

Fig. 1. Symbols for the atoms and internal coordinates of the 4-methylpyridine molecule.

trum, and in the second type (type II) the Raman band was detected only in the // spectrum. The moments of inertia calculated for the 4-CH_3- and 4-CD_3-pyridine molecules suggest that the infrared bands belonging to symmetry species a_1, b_2, and b_1 show the A, B, and C band contours, respectively, in both molecules. The observed Raman and infrared bands were classified into each symmetry species according to their polarization behavior and the mode of the normal vibrations was determined through the normal coordinate calculation.

Species a_1: The highly polarized Raman bands in liquid and the infrared bands showing A band contour in vapor can be straightforwardly assigned to the a_1 vibrations. The assignment given for the a_1 vibrations

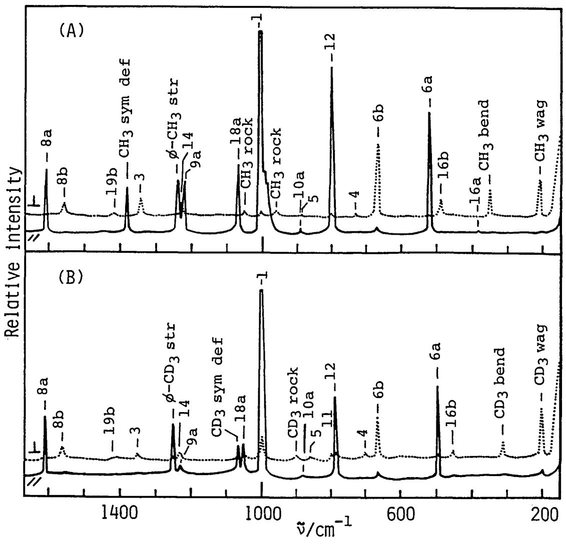

Fig. 2. Polarized Raman spectra of the 4-methyl- (A) and 4-methyl-d_3-pyridine (B) single crystals.

in this work is the same as that given by the earlier workers except for the ν_{20a}, ϕ-CH_3 stretching, and ν_{9a} vibrations. The Raman bands observed at 1212 and 1221 cm^{-1} in liquid shift to 1225 and 1241 cm^{-1} in crystal, respsctively. These bands were assigned to the ν_{9a} and ϕ-CH_3 stretching vibrations in this work, although the earlier workers assigned them to the ϕ-CH_3 stretching and ν_{9a} vibrations, respectively. The normal coordinate calculation indicates that the vibrational frequency of the ϕ-CD_3 stretching vibration is slightly higher than that of the ϕ-CH_3 stretching vibration resulting from the mixing between the ϕ-CH_3 (or ϕ-CD_3) stretching and symmetric CH_3 (or CD_3) deformation vibrations, while the frequency of the ν_{9a} vibration is almost equal in both molecules. The Raman bands at 1212 and 1221 cm^{-1} in 4-CH_3-pyridine correspond to the Raman bands of 4-CD_3-pyridine observed at 1215 and 1236 cm^{-1} in liquid, respectively. The 1221 cm^{-1} band shifts to the higher frequency side by deuterium substitution, while the 1212 cm^{-1} band is almost unchanged. This observation indicates that the assignment given for the ϕ-CH_3 stretching and ν_{9a} vibrations in this work is reasonable. The highly polarized Raman band of 4-CH_3-pyridine observed at 2995 cm^{-1} in liquid was assigned to the ν_{20a} vibration according to the calculation.

Species b_2: The infrared bands showing B band contour in vapor can be assigned definitely to the b_2 vibrations. The corresponding Raman bands observed in single crystal showed the type I polarization. The assignment given for the b_2 vibrations in this work is the same as that given by the earlier workers except for the ν_3 and ν_{14} vibrations. The bands assigned to the ν_3 and ν_{14} vibrations by the earlier workers are extremely weak or hardly detected in the Raman and infrared spectra. The Raman bands observed at 1347 and 1230 cm^{-1} clearly show the type I polarization and therefore these bands were assigned to the ν_3 and ν_{14} vibrations, respectively. The normal coordinate calculation indicates that the ν_{14} mode is hardly affected by methyl substitution and thus the vibrational frequency of this mode should be nearly equal to that of pyridine.

Species b_1: The infrared bands showing C band contour in vapor can be assigned to the b_1 vibrations. The corresponding Raman bands in single crystal showed the type I polarization. The assignment of the b_1 vibrations made in this work is the same as that given by the earlier workers.

Species a_2: The Raman bands showing the type II polarization could be assigned to the a_2 vibrations since the corresponding infrared bands could not be observed. The Raman bands observed at 970 and 873 cm^{-1} were assigned to the a_2 vibrations by the earlier workers, but these bands showed the type I polarization in crystal and therefore these were assingned to the CH_3 rocking (b_2) and ν_5 (b_1) vibrations, respectively. The 885 cm^{-1} band assigned to the ν_{10a} vibration might be the combination band of the ν_{6a} and ν_{16a} vibrations, but extremely weak intensity of the ν_{16a} Raman band denies this possibility. The normal vibrations of 4-CH_3- and 4-CD_3-pyridines thus determined are given in Table 2 and Fig. 2.

The normal coordinate calculation indicates that the ν_{12} and ν_{6a} vibrations mix considerably with the ϕ-CH_3 stretching vibration. This mixing is proved by the experimental fact that the frequencies of the ν_{12} and ν_{6a} vibrations decrease largely from the corresponding vibrations of pyridine. The calculation also shows that the ν_{11} and ν_{16b} vibrations mix with the CH_3 wagging vibration. The fact that the frequencies of the ν_{11} and ν_{16b} vibrations increase from the corresponding vibrations of pyridine justifies the mixing. The same frequency shifts due to the vibrational mixing were also found in the normal vibrations of 4-CD_3-pyridine.

The assignment of the normal vibrations given for 4-CH_3-pyridine is consistent with that given for 4-CD_3-pyridine. We believe that the assignment of the normal vibrations of 4-CH_3-pyridine is reliable and the L_x vectors calculated from the force constants given in Table 1 can be surely used for the study of the pressure and temperature effects on the Raman spectrum of 4-CH_3-pyridine.

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