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Out-of-Plane Vibrations of [$^1H_5$]- and [$^2H_5$]Pyridines

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Synopsis. Assignments of the out-of-plane normal vibrations of [$^1H_5$]- and [$^2H_5$]pyridines were reexamined based on the polarization behavior of the Raman bands and also through the normal coordinate calculation.

The normal vibrations of [$^1H_5$]- and [$^2H_5$]pyridines have been studied by many workers. Very recently Wong and Colson reviewed the previous works and reexamined the assignments of the normal vibrations of [$^1H_5$]- and [$^2H_5$]pyridines through the analysis of the high resolution FT-IR spectra.[1] There are, however, some ambiguous arguments in the assignments for the out-of-plane vibrations. They assigned the a_2 vibrations empirically using weak Raman, infrared(combination) and fluorescence bands and their assignments for the b_1 vibrations are reliable only for the infrared bands showing clear rotational band contour in vapor. Therefore, definite experimental evidences are needed for the reasonable assignments for the a_2 and b_1 vibrations.

In this paper the authors intend to give the most reliable assignments for the out-of-plane vibrations of [$^1H_5$]- and [$^2H_5$]pyridines through the analysis of the polarized Raman spectra in single crystals and the normal coordinate calculations.

Experimental

Materials. [$^1H_5$]- and [$^2H_5$]pyridines, obtained from Nakarai Chemical Company and Commissariat a l'Energie Atomique, respectively, were purified by repeated distillation under reduced pressure.

Optical Measurement. The polarized Raman spectrum was observed in a single crystal with a JEOL 400 T Laser Raman Spectrophotometer at −45 °C. Although a block of single crystal of the sample could be obtained by the Bridgman method, a cubic crystal sample could not be cut off because the crystal is very hygroscopic and also melts by pressing with a razor blade even in a Dry Ice box. Thus a single crystal was grown in a capillary glass tube of about 3 mm in diameter and 70 mm in length having a sharp conical end by cooling gradually in a Mini Subzero Tabai MC-81 Refrigerator. The direction of the crystal growth was found to be one of the crystal axis and other two crystal axes were found by rotating the crystal specimen around the crystal growth direction under the polarized light. The crystal growth direction and other two crystal axes thus determined are referred to as u, v, and w axes, respectively. The polarized Raman spectrum was observed in the following two crystal orientations. The u axis was directed parallel to the polarization direction of the excitation laser beam. The v and w axes were directed parallel to the propagation direction of the laser beam in the first and second crystal orientations, respectively. The Raman scattering was observed at right angles with the excitation light beam. Thus the uu, uv, and uw polarized Raman spectra were obtained, where the first letter refers to the direction of the polarization of the excitation light and the latter to that of the scattering light. The sample was excited with the 514.5 nm line from an Ar$^+$ ion laser.

Results and Discussion

A normal coordinate calculation for pyridine was performed through the standard GF matrix methods 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 Bak et al.[2] The force constants used for the calculation of the out-of-plane vibrations are listed in Table 1. The notation of Q, q, P, p, and t are the same as those used by Whiffen.[3] The calculated frequencies and modes are given in Table 2.

The crystal structure of pyridine was studied by Mootz and Wussow.[4] Pyridine crystalizes in the orthorhombic system of the space group C_{2v}^9 with sixteen molecules in the unit cell. No factor group splitting was observed in the Raman bands of the molecular vibrations and therefore the relationship between the Raman tensors for the free molecule and the crystal was derived based on the simplified oriented gas model. The Raman tensors were calculated in the same way as described previously[5,6] and the results are given in Table 3. This table suggests that (1) the a_2 vibrations can be observed strongly in the aa, bb, and cc spectra while the b_1 and b_2 vibrations strongly in the ab, ac, and bc spectra and (2) if the crystal growth direction is along the crystal a or b axis, the b_1 and b_2 vibrations show different polarization behavior in the uv and uw spectra while if the direction is along the c axis, these vibrations show the same polarization behavior. The polarized Raman spectra of [$^1H_5$]- and [$^2H_5$]pyridines are shown in Figs. 1 and 2, respectively. These figures show that the depolarized Raman bands in liquid show two different types of polarization behavior in single crystals, that is, the relative intensity of the bands belonging to the first type is strong in the uu spectrum and very weak in the uv and uw spectra and

Table 1. Force Constants for Out-of-Plane Vibrations

Q_{C-N}	0.22	q^o	−0.06	p^m	−0.03
Q_{C-C}	0.2	q^m	0.01	t^o	−0.02
P_H	0.30	P^o	0.03	t^m	−0.02

in aNmrad^{-2}(=mdyn Arad^{-2}) units.

Table 2. Out-of-Plane Vibrations of [$^1H_5$]- and [$^2H_5$]Pyridines

Sym. spec.	Mode	[$^1H_5$]pyridine WC[a)] Infrared $\tilde{\nu}$/cm^{-1}	Pol Vapor	This work Raman $\tilde{\nu}$/cm^{-1}	Pol Crystal	Calcd $\tilde{\nu}$/cm^{-1}	[$^2H_5$]pyridine WC[a)] Infrared $\tilde{\nu}$/cm^{-1}	Pol Vapor	This work Raman $\tilde{\nu}$/cm^{-1}	Pol Crystal	Calcd $\tilde{\nu}$/cm^{-1}
	ν_{17a}	980[b)]		975	uu	966	815[b)]		813	uu	797
a_2	ν_{10a}	880[c)]		882	uu	868	690[b)]		688	uu	678
	ν_{16a}	373		377	uu	370	318.0		323	uu	319
	ν_{17b}	1007		952	uv uw	958	828.3		820	uv uw	814
	ν_5	936.6	C	878	uv uw	860	765.3	C	763	uv uw	746
b_1	ν_4	744.0	C	755	uv uw	754	630.8		627	uv uw	610
	ν_{11}	700.3	C	715	uv uw	728	525.8	C	528	uv uw	535
	ν_{16b}	403.3	C	408	uv uw	391	367.6		362	uv uw	349

a) Taken from Ref. 1. b) Taken from H. D. Stidham and D. P. DiLella, *J. Raman Spectrosc.*, **9**, 90 (1980), *ibid.*, **9**, 247 (1980). c) Taken from Y. Mochizuki, K. Kaya, and M. Ito, *J. Chem. Phys.*, **69**, 935 (1978).

Table 3 Squared Values of the Elements of the Derived Polarizability Tensors

	b_2	b_1	a_2
$(A_{aa})^2$	0.02	0.02	0.47
$(A_{bb})^2$	0.01	0.04	0.47
$(A_{cc})^2$	0.004	0.004	0.98
$(A_{ab})^2$	0.41	0.54	0.01
$(A_{ac})^2$	0.30	0.22	0.01
$(A_{bc})^2$	0.27	0.21	0.01

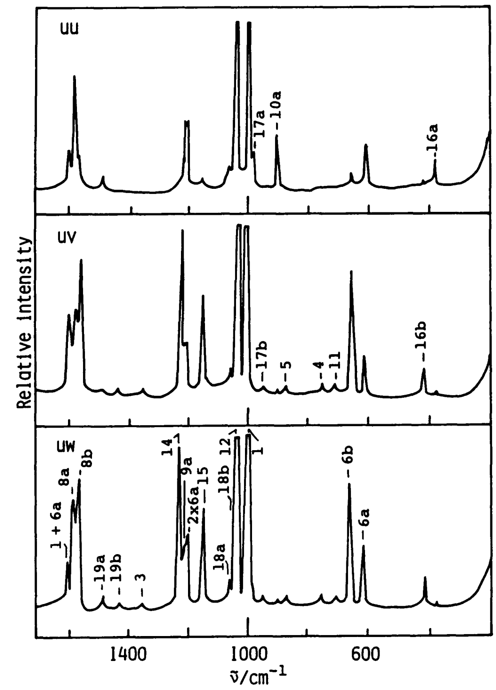

Fig. 1. Polarized Raman spectrum of [$^1H_5$]pyridine single crystal.

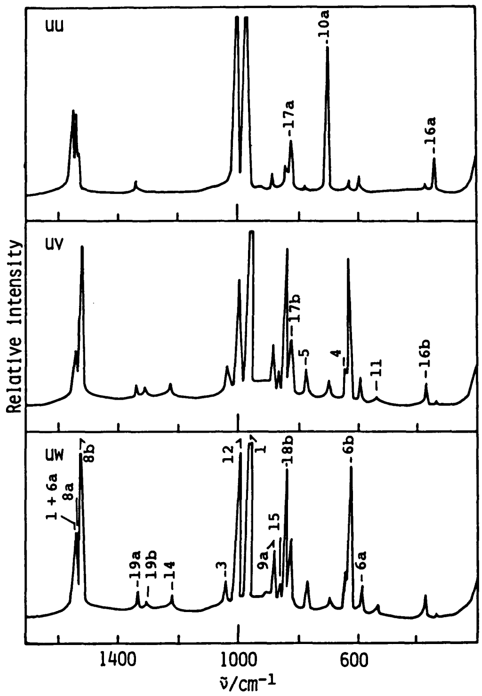

Fig. 2. Polarized Raman spectrum of [$^2H_5$]pyridine single crystal.

the relative intensity of the second type bands is strong in the uv and uw spectra and very weak in the uu spectrum. Comparing the observed relative intensity of the polarized Raman bands with the data given in Table 3, it can be concluded that the first type bands can be assigned to the a_2 vibrations and the second type bands to the b_1 or b_2 vibrations. These figures also show that the second type bands show almost equal polarization behavior in the uv and uw spectra. This observation indicates that the u axis should correspond to the crystal c axis. No infrared bands corresponding to the first type polarized Raman bands could be observed and this fact supports the first type bands being to be assigned to the a_2 vibrations. The vibrational modes were determined based on the normal coordinate calculation.

[$^1H_5$]Pyridine. Depolarized Raman bands observed at 952, 878, 755, 715, and 408 cm^{-1} in liquid show the second type polarization in crystal. Thus these bands can safely be assigned to the ν_{17b}, ν_5, ν_4, ν_{11}, and ν_{16b} vibrations of b_1 species, respectively, because the non-totally symmetric in-plane vibrations except for the ν_{6b} vibration are expected to be observed in the region higher than 1000 cm^{-1} in this molecule. Although Wong and Colson[1)] assigned the frequency of 1007 cm^{-1} to the b_1 vibration, this frequency could not be observed in the polarized Raman spectrum. Depolarized Raman bands at 975, 882, and 377 cm^{-1} in liquid show the first type polarization in crystal and thus these can definitely be assigned to the ν_{17a}, ν_{10a}, and ν_{16a} vibrations of a_2 species, respectively.

[$^2H_5$]Pyridine. Depolarized Raman bands at 763, 627, 528, and 362 cm^{-1} in liquid show the second type polarization in crystal. Thus these bands can be assigned to the ν_5, ν_4, ν_{11}, and ν_{16b} vibrations of b_1 species, respectively. A depolarized and broad Raman band around 820 cm^{-1} in liquid is clearly resolved into two bands at 820 and 813 cm^{-1} in crystal and show the second and first type polarization, respectively. Therefore, the former was assigned to the ν_{17b} vibration. Depolarized Raman bands at 813, 688, and 323 cm^{-1} in liquid show the first type polarization in crystal and thus these can be assigned to the ν_{17a}, ν_{10a}, and ν_{16a} vibrations of a_2 species, respectively. Wong and Colson presented the ν_5 and ν_{10b} modes for the hydrogen wagging vibrations of b_1 species in decreasing order of vibrational frequency, while the normal coordinate calculation used reasonably estimated force constants gives the ν_{17b} and ν_5 modes for these wagging vibrations, respectively.

The polarization behavior of the Raman bands gave clear and definite experimental justification for the assignments of the out-of-plane vibrations. The polarization behavior of the Raman bands also supports the assignments for the in-plane vibrations given by Wong and Colson except for the ν_{18b} vibration of [$^1H_5$]pyridine. Wong and Colson assigned weak infrared bands observed at 705.8 and 1690.9 cm^{-1} to the $\nu_{18b}-\nu_{16a}$ and $\nu_{18b}+\nu_{6a}$ vibrations, respectively, and gave the frequency of 1079 cm^{-1} for the ν_{18b} vibration. A Raman band observed at 1045 cm^{-1} as a shoulder of the strong ν_{12} band shows clearly the second type polarization in single crystal and the frequency is higher than 1000 cm^{-1}. Thus we assigned the frequency of 1045 cm^{-1} to the ν_{18b} vibration of [$^1H_5$]pyridine.

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