Polarized Raman and Infrared Spectra of [$^1H_4$]- and [$^2H_4$]Pyridazines

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The polarized Raman and infrared spectra of [$^1H_4$]- and [$^2H_4$]pyridazines were studied. Assignments of the normal vibrations made by previous workers were reexamined on the basis of polarization behavior of the Raman and infrared bands and also through the normal coordinate calculation, and reasonable assignments are presented.

Although the vibrational spectra of aromatic azines such as pyridine, pyrimidine, and pyrazine have been studied by many workers, few informations are available for the normal vibrations of pyridazine. Vibrational analyses of the Raman and infrared spectra of pyridazine were made by Ito et al.[1)] and Lord et al.[2)] on the basis of intercomparison with the normal vibrations of benzene, pyridine, and diazines, and by Stidham and Tucci[3)] on the basis of the isotopic effect on the vibrational frequencies. Their vibrational assignments, however, are not consistent with each other. Especially for the assignments of the non-totally symmetric vibrations, there are many discrepancies in the vibrational modes and frequencies. Therefore, definite experimental evidences are needed for the reasonable assignments of the normal vibrations.

In this work, vibrational assignments for [$^1H_4$]- and [$^2H_4$]pyridazines are reexamined through measurements of the polarization behavior of the Raman and infrared spectra and also through the normal coordinate calculation and reliable assignments of the normal vibrations are given.

Experimental

Material. [$^2H_4$]Pyridazine was synthesized by the exchange reaction of [$^1H_4$]pyridazine, which was obtained from Aldrich Chemical Company, with D_2O and NaOD. Isotopic purity of the product was determined by the nuclear magnetic resonance measurement. The samples used for the experiment were purified by repeated distillation under reduced pressure.

Optical Measurements. Polarization measurement of the Raman spectrum was made in liquid 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. [$^1H_4$]- and [$^2H_4$]Pyridazines crystalize at −8 °C. Although single crystals of the sample could be easily obtained by the Bridgman method, samples with rectangular shape needed for the quantitative observation of the polarized Raman spectrum could not be prepared because pyridazine is quite volatile and hygroscopic and the crystal surface became opaque and deliquesced immediately after the crystal was cut off with a razor blade. Thus the polarized Raman spectrum was observed in the following way. Single crystals were grown in capillary glass tubes of 3 mm in diameter having a sharp conical end by the Bridgman method and a well grown single crystal was selected. The extinction directions of the crystal were determined under the polarized light. The direction of crystal growth which was along the capillary tube was found to be one of the extinction directions. Determination of another extinction direction was made by rotating the capillary tube, which was supported horizontally, around the crystal growth direction under the light polarized perpendicular to the capillary tube. The extinction direction thus detected was more clearly confirmed by tilting the capillary tube from the horizontal orientation. These two extinction directions will be referred to as *u* and *v* axes, respectively. The *w* axis is taken to be perpendicular to both the *u* and *v* axes. These procedures were carried out in a box where the temperature was kept at −12 °C. The crystal specimen was held in a Raman sample cell kept at −12 °C in such a way that the *u* axis of the crystal 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 observation was made with two crystal orientations. In the first orientation the *v* axis and in the second the *w* axis were directed parallel to the propagation direction of the laser beam, respectively. Thus the *uu*, *uv*, and *uw* polarized Raman spectra were obtained, where the first letter refers to the direction of polarization of the excitation laser beam and the latter to that of the scattering light.

The infrared spectrum was observed in vapor and single crystal phases with a Hitachi Infrared Spectrophotometer Model 345. Preparation of the single crystal sample and the method of measurement of the polarized infrared spectrum are exactly the same as those described previously.[4)]

Normal Coordinate Calculation

The normal coordinate calculations for [$^1H_4$]- and [$^2H_4$]pyridazines were performed through the standard GF matrix method with a FACOM M-200 computer at the Computer Center of Fukuoka University. The molecular structure of [$^1H_4$]pyridazine was taken from the data determined by Almenningen et al.[5)] The F matrix elements for the in-plane and out-of-plane vibrations were evaluated with the potential fields of an improved modification of the Urey–Bradley and valence force fields, respectively, as described previously.[4,6,7)] Values of the force constants for the in-plane and out-of-plane vibrations are given in Tables 1 and 2, respectively. The notations of the force constants are the same as those described previously.[4,6,7)] Calculated vibrational frequencies and modes are listed in Tables 3 and 4, respectively.

Table 1. Force Constants for In-Plane Vibrations

$K_{\text{N-N}}$	5.5	$F_{\text{N}\cdots\text{C}}$	0.6
$K_{\text{N-C}}$	5.3	$F_{\text{C}\cdots\text{C}}$	0.8
$K_{\text{C-C}}$	4.5	$F_{\text{N}\cdots\text{H}}$	0.55
$K_{\text{C-H}}$	4.6	$F_{\text{C}\cdots\text{H}}$	0.45
H_{CNN}	0.5	k^{o}_{rr}	0.05
H_{NCC}	0.35	k^{m}_{rr}	−0.05
H_{CCC}	0.4	k^{m}_{RR}	−0.1
H_{NCH}	0.2	$f^{\text{o}}_{\beta\beta}$	0.12
H_{CCH}	0.27	ρ	0.37

Force consatants denoted by K, H, F, ρ, and k are given in hN m^{-1} (=mdyn/Å) and f in aNmrad^{-2} (=mdynÅ/rad^2) units. R refers to the N–N, C–N and C–C bonds, r to the C–H bond and β to the ∠NCH and ∠CCH. Superscripts o and m refer to ortho and meta, respectively.

Table 2. Force Constants for Out-of-Plane Vibrations

$Q_{\text{N-N}}$	0.17	q^{m}	0.01
$Q_{\text{N-C}}$	0.19	p^{o}	0.06
$Q_{\text{C-C}}$	0.21	p^{m}	−0.06
P_{H}	0.33	t^{o}_{N} a)	−0.03
q^{o}_{N} a)	−0.04	t^{o}_{C} a)	−0.02
q^{o}_{C} a)	−0.03	t^{m}	−0.01

Force constants are given in aNmrad^{-2} (=mdynÅ/rad^2) units. a) Subscript N indicates that the force constants are concerned with the torsional coordinates involving the C–N and N–N bonds and subscript C the C–C bond. Superscripts o and m refer to ortho and meta, respectively.

Results and Discussion

The relative intensities of the Raman bands in the polarized Raman spectrum are governed by the orientation of the molecules in crystal, that is, the relative intensities depend on the direction cosines between the molecular and crystal axes in the oriented gas model approximation. Therefore, the molecular vibrations belonging to the same symmetry species should show the same polarization behavior in the polarized Raman spectrum observed with a certain crystal orientation with respect to the polarization directions of the excitation and scattering lights. If the crystal structure is known, the relative intensities of the bands can be calculated from the direction cosines between the crystal and molecular axes and thus, the observed polarization behavior of the Raman bands gives a quantitative justification for the assignments of the normal vibrations. Even if the crystal structure is unknown, the polarized Raman spectrum can be observed along the extinction directions. The extinction axes of the crystal coincide with the crystal axes in general and thus the observed polarization behavior of the Raman bands gives a qualitative information for the classification of the observed Raman bands into a certain symmetry species. We applied this experimental procedure for the assignments of the normal vibrations of halosubstituted pyrimidines[8] and pyridine[9] and obtained satisfactory results.

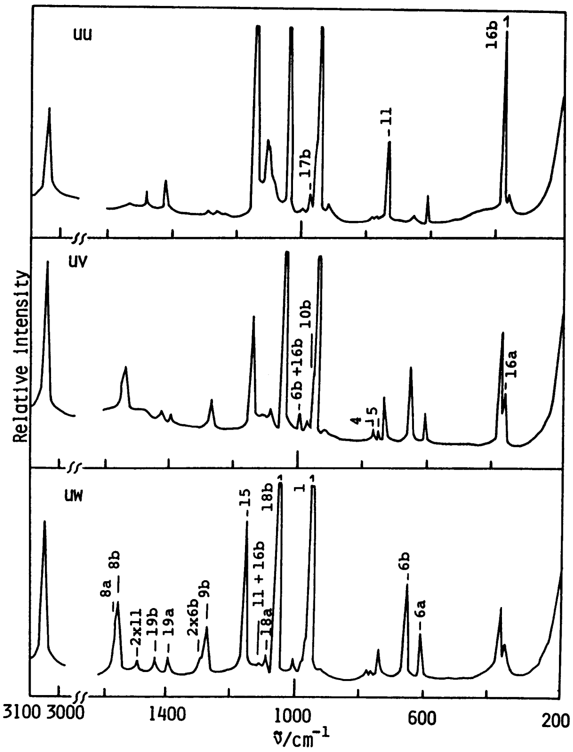

Fig. 1. Polarized Raman spectrum of [^{1}H$_4$]pyridazine single crystal.

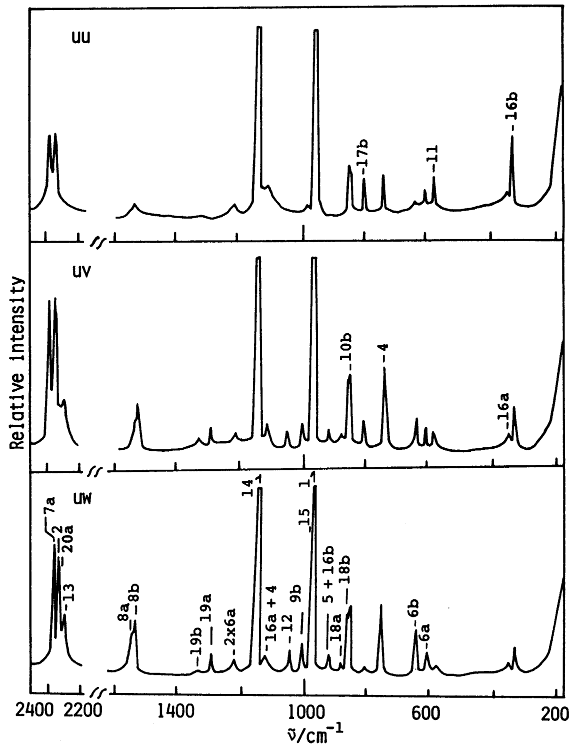

Fig. 2. Polarized Raman spectrum of [^{2}H$_4$]pyridazine single crystal.

The polarized Raman and infrared spectra of [^{1}H$_4$]- and [^{2}H$_4$]pyridazines observed in single crystals are shown in Figs. 1, 2, 3, and 4, respectively. The nontotally symmetric vibrational bands in the polarized Raman spectrum of a single crystal can be classified

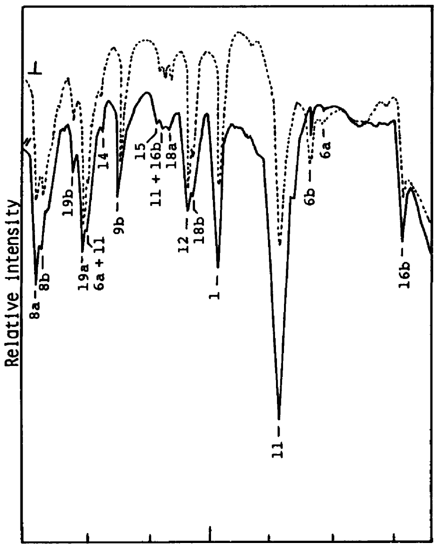

Fig. 3. Polarized infrared spectrum of [$^1H_4$]pyridazine single crystal.

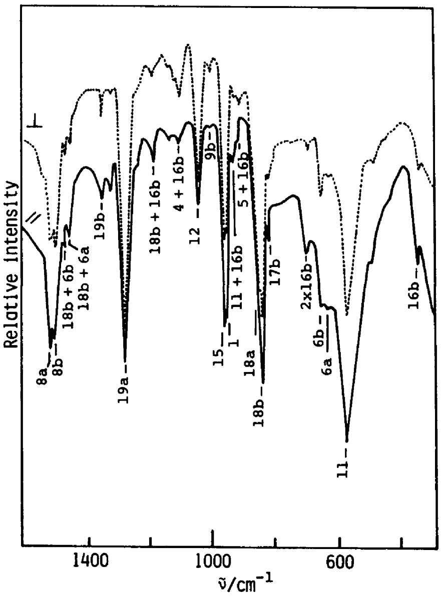

Fig. 4. Polarized infrared spectrum of [$^2H_4$]pyridazine single crystal.

into three types of polarization behavior as can be seen in Figs. 1 and 2. The intensity relationship of the polarized Raman bands belonging to the first type is $I_{uw}>I_{uv}\gg I_{uu}$, the second type $I_{uu}>I_{uv}>I_{uw}$ and the third type $I_{uv}>I_{uw}>I_{uu}$. These three types of polarization behavior are referred to as types α, β, and γ, respectively. The polarized infrared spectra measured with the incident lights polarized parallel and perpendicular to the crystal growth direction are referred to as // and ⊥ spectra and drawn with the solid and dotted lines, respectively. The infrared bands in crystal can be classified into three types I, II, and III based on their polarization behavior. The intensity relationship of the bands belonging to the first type is $I_{/\!/}\simeq I_{\perp}$, the second and third types $I_{/\!/}>I_{\perp}$ and $I_{/\!/}<I_{\perp}$, respectively.

The moments of inertia calculated from the molecular structure suggest that the infrared bands belonging to a_1, b_2, and b_1 symmetry species show A, B, and C band contour in [$^1H_4$]pyridazine and B, A, and C contour in [$^2H_4$]pyridazine, respectively. Therefore, each Raman and infrared bands can be experimentally classified into a certain symmetric species based on the polarization behavior observed in crystal phase together with the band contour in vapor phase. The determination of the vibrational modes can be made based on the normal coordinate calculation.

[$^1H_4$]Pyridazine. a_1 Species: Strongly polarized Raman bands observed at 3070, 3053, 1441, 1352, 1150, 1063, and 963 cm^{-1} in liquid phase can be straightforwardly assigned to the totally symmetric ν_{7a}, ν_2, ν_{19b}, ν_{14}, ν_{15}, ν_{18b}, and ν_1 vibrations, respectively, by referring the normal coordinate calculation. The infrared band corresponding to the ν_1 vibration shows A band contour in vapor and the type I polarization in crystal. Infrared bands at 1555 and 632 cm^{-1} show the type I polarization in crystal and therefore these bands were assigned to the ν_{8a} and ν_{6a} vibrations, respectively, although the corresponding Raman band at 1570 cm^{-1} seems to be depolarized in liquid due to overlapping of a band assigned to the ν_{8b} vibration and the corresponding Raman band at 622 cm^{-1} is very slightly polarized in liquid.

b_2 Species: Infrared bands observed at 1408, 1283, 1058, and 663 cm^{-1} show B band contour in vapor and therefore can be assigned to the b_2 vibrations. Thus these bands were assigned to the ν_{19a}, ν_{9b}, ν_{12}, and ν_{6b} vibrations, respectively. The corresponding infrared and Raman bands observed in crystal show the type III and type α polarization, respectively. Raman bands at 3080, 3041, 1564, and 1113 cm^{-1} show also the type α polarization in crystal and the corresponding infrared bands show the type III polarization in crystal. Therefore, these bands were assigned to the ν_{20a}, ν_{13}, ν_{8b}, and ν_{18a} vibrations, respectively.

b_1 Species: Infrared bands at 760 and 372 cm^{-1} show C band contour in vapor and hence these bands were assigned to the ν_{11} and ν_{16b} vibrations of b_1 species, respectively. The corresponding infrared and Raman bands observed in crystal show the type II and type β polarization, respectively. A Raman band at 986 cm^{-1} shows the type β polarization in crystal and thus this band was assigned to the ν_{17b} vibration.

a_2 Species: Depolarized Raman bands at 786, 775, and 363 cm^{-1} in liquid show the type γ polarization in crystal and therefore these bands were assigned to the ν_4, ν_5, and ν_{16a} vibrations of a_2 species, respectively, because the Raman bands showing the types α and β polarization in crystal were already assigned to the bands belonging to the b_2 and b_1 vibrations, respectively. A Raman band at 970 cm^{-1} which was not clearly

Table 3. Normal Vibrations of [$^1H_4$]Pyridazine

Sym spec	Mode	Stidham[a)]	This work						
			Raman			Infrared			Calcd
		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}
				liq	cry		vap	cry	
a$_1$	ν_{7a}	3064	3070	p					3083
	ν_2	3052	3053	p					3077
	ν_{8a}	1572	1570	dp?		1555		I	1573
	ν_{19b}	1417	1441	p		1440		I	1453
	ν_{14}	1347	1352	p		1340		I	1355
	ν_{15}	1063	1150	p		1153		I	1122
	ν_{18b}	1150	1063	p		1055		I	1058
	ν_1	964	963	p		960	A	I	973
	ν_{6a}	630	622	dp?		632		I	631
b$_2$	ν_{20a}	3056	3080	dp	α				3097
	ν_{13}	3085	3041	dp	α				3040
	ν_{8b}	1556	1564	dp	α	1540		III	1587
	ν_{19a}	1450	1401	dp	α	1408	B	III	1424
	ν_{9b}	1283	1287	dp	α	1283	B	III	1286
	ν_{18a}	1129	1113	dp	α	1112		III	1110
	ν_{12}	1032	1052	dp	α	1058	B	III	1049
	ν_{6b}	667	660	dp	α	663	B	III	656
b$_1$	ν_{17b}	842	986	dp	β				982
	ν_{11}	760	755	dp	β	760	C	II	777
	ν_{16b}	370	370	dp	β	372	C	II	374
a$_2$	ν_{10b}	861	970		γ				958
	ν_4	753	786	dp	γ				788
	ν_5	938	775	dp	γ				774
	ν_{16a}	410	363	dp	γ				371

a) H. D. Stidham and J. V. Tucci, *Spectrochim. Acta,* **23A**, 2233 (1967).

resolved in liquid shows the type γ polarization in crystal and thus this band was assigned to the ν_{10b} vibration.

The normal vibrations thus assigned are summarized in Table 3 together with those given by Stidham and Tucci.[3)] Stidham and Tucci assigned the infrared band observed at 1417 cm^{-1} to the a$_1$ vibration but this band shows B band contour in vapor and the type III polarization in crystal. Thus this band should be assigned to the b$_2$ vibration. They also assigned the Raman bands observed at 1450, 1129, and 1032 cm^{-1} to the b$_2$ vibrations but the first two bands are polarized in liquid and the last shows a$_2$ polarization behavior in crystal. Therefore, the bands observed at 1417, 1450, 1129, and 1032 cm^{-1} by them were assigned to the ν_{19a}, ν_{19b}, $\nu_{11}+\nu_{16b}$, and $\nu_{6b}+\nu_{16b}$ vibrations, respectively. They observed a weak Raman band at 938 cm^{-1} and assigned to the a$_2$ vibration. This band, however, shows neither b$_2$, b$_1$, nor a$_2$ polarization behavior in crystal and thus we assigned it to the $\nu_{8a}-\nu_{6a}$ vibration. Stidham and Tucci observed very weak Raman bands at 753, 861, 842, and 410 cm^{-1} and assigned those to the out-of-plane vibrations but these bands could not be clearly observed in this work.

[$^2H_4$]Pyridazine. a$_1$ Species: Strongly polarized Raman bands observed at 2295, 2276, 1318, 1130, 965, 946, 835, and 600 cm^{-1} can be assigned to the ν_{7a}, ν_2, ν_{19b}, ν_{14}, ν_{15}, ν_1, ν_{18b}, and ν_{6a} vibrations, respectively. The corresponding infrared bands show the type I polarization in crystal. An infrared band at 1515 cm^{-1} shows the type I polarization in crystal and hence this band was assigned to the ν_{8a} vibration, although the corresponding Raman band at 1532 cm^{-1} seems to be depolarized in liquid due to overlapping of a band assigned to the ν_{8b} vibration.

b$_2$ Species: Infrared bands observed at 1268 and 1035 cm^{-1} show A band contour in vapor and the type III polarization in crystal, and the corresponding Raman bands show the type α polarization in crystal. Therefore, these bands were assigned to the ν_{19a} and ν_{12} vibrations, respectively. Raman bands observed at 2272, 2247, 1525, 980, 865, and 639 cm^{-1} show the type α polarization in crystal and the corresponding infrared bands show the type III polarization in crystal. Therefore these bands were assigned to the ν_{20a}, ν_{13}, ν_{8b}, ν_{9b}, ν_{18a}, and ν_{6b} vibrations, respectively.

b$_1$ Species: Infrared bands observed at 562 and 321 cm^{-1} show C band contour in vapor and the type II polarization in crystal. The corresponding Raman bands show the type β polarization in crystal. Hence these bands were assigned to the ν_{11} and ν_{16b} vibrations, respectively. A Raman band observed at 802 cm^{-1} shows the type β polarization in crystal and the corresponding infrared band shows the type II polarization

Table 4. Normal Vibrations of [$^2H_4$]Pyridazine

Sym spec	Mode	Stidham[a)]	This work						
			Raman			Infrared			Calcd
		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}
				liq	cry		vap	cry	
a_1	ν_{7a}	2303	2295	p					2267
	ν_2	2277	2276	p					2262
	ν_{8a}	1545	1532	dp?		1515		I	1505
	ν_{19b}	1270	1318	p		1307		I	1308
	ν_{14}	1203	1130	p					1158
	ν_{15}	835	965	p		950		I	966
	ν_1	950	946	p		945		I	956
	ν_{18b}	894	835	p		833		I	827
	ν_{6a}	608	600	p		610		I	615
b_2	ν_{20a}	2259	2272	dp	α				2274
	ν_{13}	2303	2247	dp	α				2245
	ν_{8b}	1528	1525	dp	α	1505		III	1535
	ν_{19a}	1318	1272	dp	α	1268	A	III	1281
	ν_{12}	973	1032	dp	α	1035	A	III	1023
	ν_{9b}	1038	980	dp	α	983		III	969
	ν_{18a}	853	865	dp	α	860		III	894
	ν_{6b}	642	639	dp	α	633		III	647
b_1	ν_{17b}	710	802	dp	β	800		II	808
	ν_{11}	563	578	dp	β	562	C	II	588
	ν_{16b}	327	330	dp	β	321	C	II	324
a_2	ν_{10b}	727	820	dp	γ				823
	ν_4	686	738	dp	γ				723
	ν_5	766							592
	ν_{16a}	351	347	dp	γ				335

a) H. D. Stidham and J. V. Tucci, *Spectrochim. Acta,* **23A**, 2233 (1967).

in crystal. Therefore this band was assigned to the ν_{17b} vibration.

a_2 Species: Depolarized Raman bands at 820, 738, and 347 cm^{-1} show the type γ polarization in crystal and therefore these bands were assigned to ν_{10b}, ν_4, and ν_{16a} vibrations, respectively. The ν_5 vibrational band could not be resolved in the polarized Raman spectrum.

The normal vibrations of [$^2H_4$]pyridazine thus assigned are summarized in Table 4 together with those given by Stidham and Tucci.[3)] Stidham and Tucci assigned the Raman bands at 1270 and 1318 cm^{-1} to the a_1 and b_2 vibrations, respectively. However the former shows b_2 and the latter a_1 polarization behavior, and thus we assigned these bands to the ν_{19a} and ν_{19b} vibrations, respectively. A polarized Raman band at 1203 cm^{-1} in liquid was assigned the $2\nu_{6a}$ vibration although Stidham and Tucci assigned it to the ν_{14} vibration. A strong and polarized Raman band at 1130 cm^{-1}, which was assigned to the $2\nu_{11}$ vibration by them, was assigned to the ν_{14} vibration in this work. Stidham and Tucci assigned a very weak Raman band at 710 cm^{-1} to the b_1 vibration, but this band shows neither b_2, b_1, nor a_2 polarization behavior in single crystal, and therefore, this band was assigned to the $\nu_{19b}-\nu_{6a}$ vibration. They also assigned very weak Raman bands at 686 and 766 cm^{-1} to the a_2 vibrations, but these bands could not be observed in this work.

Agreements between observed and calculated vibrational frequencies for both [$^1H_4$]- and [$^2H_4$]pyridazines are satisfactory. We believe that the polarization behavior of the Raman and infrared bands gives clear and definite experimental justification for the assignments, and the normal vibrations determined in this work are quite reliable.

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