Bull. Chem. Soc. Jpn., 58, 1321—1322 (1985)

Polarized Raman and Infrared Spectra of Tetramethyl-d_{12}-pyrazine

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(Received November 12, 1984)

Synopsis. Assignments of the normal vibrations of tetramethyl-d_{12}-pyrazine were made based on the polarization behavior of the Raman and infrared bands and also on the normal coordinate calculation. The result ascertains the assignments of the normal vibrations given previously for tetramethylpyrazine.

Very recently we gave assignments of the normal vibrations for tetramethylpyrazine.$^{1)}$ In order to confirm the results, tetramethyl-d_{12}-pyrazine was synthesized and the normal vibrations were studied.

Experimental

Material. Tetramethyl-d_{12}-pyrazine(TMP-d_{12}) was synthesized by the reaction of tetramethylpyrazine (TMP-d_0) and D_2O with DCl. Isotopic purity of the product was determined by the nuclear magnetic resonance measurement.

Optical Measurements. The apparatus and methods used for the measurements of the polarized Raman and infrared spectra of TMP-d_{12} single crystals were exactly the same as those described previously.$^{1)}$

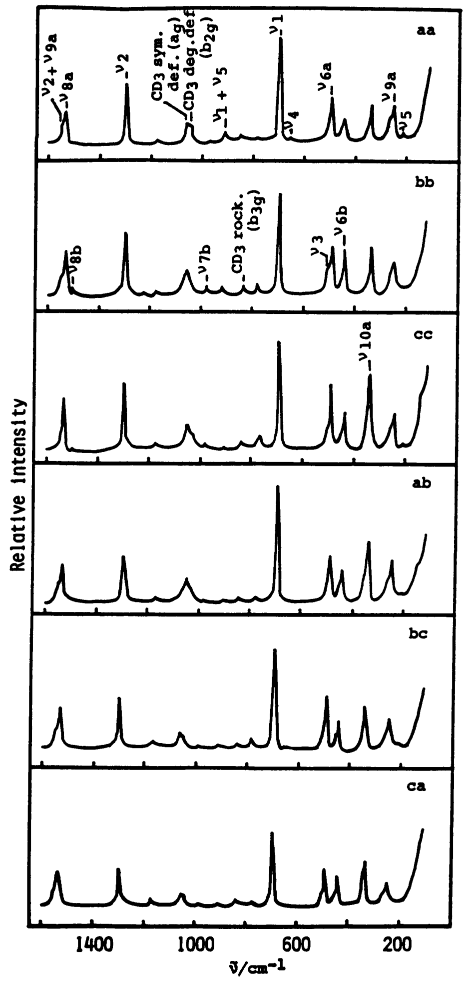

Fig. 1. Polarized Raman spectrum of tetramethyl-d_{12}-pyrazine.
The first letter in ab spectrum *etc.* refers to the direction of polarization of the excitation light and the second to that of the scattering light.

Results and Discussion

The polarized Raman and infrared spectra of TMP-d_{12} single crystals are shown in Figs. 1 and 2. The polarization behavior of the Raman and infrared bands, and the rotational envelope of the infrared bands of TMP-d_{12} belonging to the same symmetry species are expected to be the same as those of TMP-d_0, because both molecules have the same molecular and crystal structures, and the nearly equal moments of inertia. The potential field and the force constants used for the normal coordinate calculation of TMP-d_{12} were taken to be exactly the same as those used in TMP-d_0 and the calculated vibrational frequencies

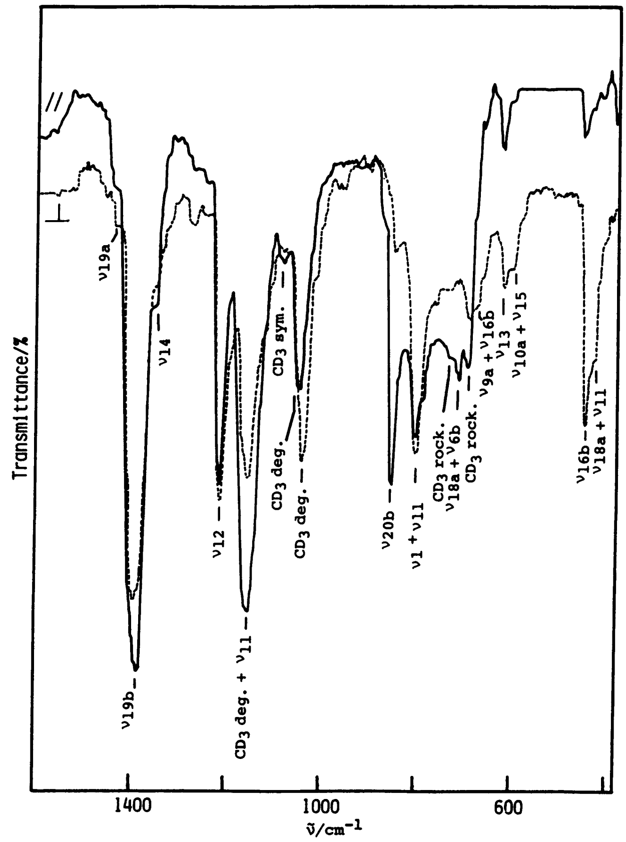

Fig. 2. Polarized infrared sectrum of tetramethyl-d_{12}-pyrazine.
// and ⊥ spectra refer to the infrared spectra measured with the incident light polarized parallel and perpendicular to the crystal growth direction. Polarization behaviors are classified into three types. The relative intensities of the // and ⊥ bands are the following; $I_{//}\approx I_{\perp}$ for type-I, $I_{//}>I_{\perp}$ for type-II, and $I_{//}<I_{\perp}$ for type-III.

TABLE 1. NORMAL VIBRATIONS OF TETRAMETHYL-d_{12}-PYRAZINE

Symmetry species	Mode	Obsd $\tilde{\nu}$/cm^{-1}	Calcd $\tilde{\nu}$/cm^{-1}
a$_g$	ν_{8a} Ring	1533	1534
	ν_2 ϕ-CD$_3$ str.	1296	1296
	ν_1 Ring	695	692
	ν_{6a} Ring	489	491
	ν_{9a} CD$_3$ bend.	247	235
b$_{1u}$	ν_{19a} Ring	1435	1440
	ν_{12} Ring	1210	1204
	ν_{13} ϕ-CD$_3$ str.	615	600
	ν_{18a} CD$_3$ bend.	270$^{a)}$	278
b$_{3g}$	ν_{8b} Ring	1507	1518
	ν_{7b} ϕ-CD$_3$ str.	970	970
	ν_3 CD$_3$ bend.	503	501
	ν_{6b} Ring	439	426
b$_{2u}$	ν_{19b} Ring	1390	1404
	ν_{14} Ring	1337	1323
	ν_{20b} ϕ-CD$_3$ str.	840	820
	ν_{15} CD$_3$ bend.	250$^{a)}$	245
b$_{2g}$	ν_4 Ring	667	657
	ν_5 CD$_3$ wag.	215	214
	ϕ-CD$_3$ tor.		80
b$_{3u}$	ν_{16b} Ring	445	454
	ν_{11} CD$_3$ wag.	110$^{a)}$	117
	ϕ-CD$_3$ tor.		138
b$_{1g}$	ν_{10a} CD$_3$ wag.	340	346
	ϕ-CD$_3$ tor.	160	158
a$_u$	ν_{16a} Ring		502
	ν_{17a} CD$_3$ wag.		189
	ϕ-CD$_3$ tor.		68
	Characteristic vibrations of CD$_3$ group		
a$_g$	Antisym. C–D str.	2155	2185
	Sym. C–D str.	2050	2020
	CD$_3$ sym. def.	1055	1043
b$_{1u}$	Antisym. C–D str.	2210	2233
	CD$_3$ rock.	733	737
b$_{3g}$	Antisym. C–D str.	2210	2233
	CD$_3$ rock.	840	837
b$_{2u}$	Antisym. C–D str.	2235	2233
	Sym. C–D str.	2040	2020
	CD$_3$ Sym. def.	1080	1088
	CD$_3$ deg. def.	1045	1040
	CD$_3$ rock.	690	692
b$_{2g}$	CD$_3$ deg. deg.	1040	1038
b$_{3u}$	CD$_3$ deg. def.	1040	1038

a) Frequencies were estimated from combination bands.

and modes are given in Table 1. Vibrational analyses of the Raman and infrared bands were made in the same way as that described for TMP-d_0.[1]

a$_g$ Species: Strongly polarized Raman bands observed at 1533, 1296, 695, and 489 cm^{-1} in the depolarization measurements in liquid phase were straightforwardly assigned to the totally symmetric ν_{8a}, ν_2 (ϕ-CD$_3$ stretching), ν_1, and ν_{6a} vibrations, respectively. A weak and almost depolarized Raman band observed at 247 cm^{-1} in liquid does not show any polarization behavior corresponding to non-totally symmetric vibrations in single crystal, thus, this band was assigned to the ν_{9a}(CD$_3$ bending) vibration.

b$_{3g}$ Species: Raman bands observed at 1507, 970, 503, and 439 cm^{-1} have stronger intensity in the bb and cc spectra than in other spectra, therefore, these were assigned to the ν_{8b}, ν_{7b} (ϕ-CD$_3$ stretching), ν_3(CD$_3$ bending), and ν_{6b} vibrations, respectively.

b$_{2g}$ Species: Raman bands at 667 and 215 cm^{-1} were found only in the aa and cc spectra with very weak intensity, therefore, these were assigned to the ν_4 and ν_5 (CD$_3$ wagging) vibrations, respectively.

b$_{1g}$ Species: A Raman band observed at 340 cm^{-1} has strong intensity in the cc and ab spectra, thus this was assigned to the ν_{10a} (CD$_3$ wagging) vibration.

b$_{1u}$ Species: Infrared bands observed at 1210 and 615 cm^{-1} showed the B band-type and the type-I polarization, thus, these were assigned to the ν_{12} and ν_{13} (ϕ-CD$_3$ stretching) vibrations, respectively. A weak infrared band observed at 1435 cm^{-1} showing the type-I polarization was assigned to the ν_{19a} vibration. A medium intense infrared band observed at 710 cm^{-1} showed the A band-type and the type-II polarization, therefore, this could be assigned to a combination band of the ν_{6b} (b$_{3g}$) and ν_{18a} (b$_{1u}$) vibrations. This gives frequency of 270 cm^{-1} for the ν_{18a} (CD$_3$ bending) vibration.

b$_{2u}$ Species: A very strong infrared band observed at 1390 cm^{-1} and a medium intense band at 840 cm^{-1} showed the A band-type and the type-II polarization. Therefore, these bands were assigned to the ν_{19b} and ν_{20b} (ϕ-CD$_3$ stretching) vibrations, respectively. A shoulder band observed at 1337 cm^{-1} showing the type-II polarization was assigned to the ν_{14} vibration. A weak infrared band at 595 cm^{-1} showing the type-III polarization could be assigned to a combination band of the ν_{10a} (b$_{1g}$) and ν_{15} (b$_{2u}$) vibrations. This gives frequency of 250 cm^{-1} for the ν_{15} (CD$_3$ bending) vibration.

b$_{3u}$ Species: A medium intense band observed at 445 cm^{-1} showed the C band-type and the type-III polarization, thus, this was assigned to the ν_{16b} vibration. A strong infrared band observed at 1150 cm^{-1} showing the b$_{2u}$ polarization behavior could be assigned to a combination band of the CD$_3$ degenerate deformation (b$_{1g}$) and ν_{11} (b$_{3u}$) vibrations, which is generally observed very strongly in the six-membered aromatics. This assignment gives frequency of 110 cm^{-1} for the ν_{11} (CD$_3$ wagging) vibration. The summary of assignments is given in Table 1.

The calculation indicates that the ν_4 vibration couples with the CD$_3$ rocking vibration in TMP-d_{12}. This was supported by our assignments, which show that the frequency of the ν_4 vibration of TMP-d_{12} is lower than those of pyrazine and TMP-d_0. The calculated frequencies and modes well coincide with the observed frequencies and polarization behavior of the Raman and infrared bands of TMP-d_{12}. This indicates that the assignments given for the normal vibrations of TMP-d_0 are quite reasonable.

References

1) Y. Ishibashi, F. Arakawa, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **56**, 1327 (1983).