Vibrational Spectra and Thermodynamic Functions of 2-Methoxypyridine and 2-Methoxy-d_3-pyridine

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The infrared spectra in the liquid state (4000—50 cm^{-1}) and in the vapor phase (4000—400 cm^{-1}) and the polarized laser Raman spectra in the liquid state have been measured for 2-methoxypyridine and 2-methoxy-d_3-pyridine. Essentially complete assignments of the observed frequencies are presented. Ideal gas state thermodynamic functions of the molecules are also calculated in the temperature range 200—1500 K.

In continuation of the earlier work on the vibrational analysis of a few substituted pyridine molecules,$^{1-4)}$ the investigation has now been extended to 2-methoxypyridine and 2-methoxy-d_3-pyridine. The infrared spectrum of 2-methoxypyridine in solution or in the pure liquid state was reported by Katritzky and Hands,$^{5)}$ Katritzky and Coats,$^{6)}$ and Spinner and White$^{7)}$ in a limited range, and a partial assignment of only a few bands was given. The earlier work on the simple Raman spectrum of 2-methoxypyridine relate to that of Spinner and White.$^{7)}$ There is however no previous study on the vibrational spectra of the deuterated species, 2-methoxy-d_3-pyridine.

The present investigation was undertaken with a view to making a detailed study of the infrared spectra of 2-methoxypyridine and 2-methoxy-d_3-pyridine in the liquid and vapor phases and the polarized Raman spectra of the two molecules in the liquid state. Assignments of the observed frequencies based on the infrared band contours, state of polarization of the Raman lines and comparison with the assignments for related molecules$^{8-12)}$ are given. The ideal gas state thermodynamic functions of the molecules are also calculated on the basis of these assignments.

Experimental

Chemically pure sample of 2-methoxypyridine, used in this experiment, was obtained from Aldrich Chemical Company, U. S. A. and purified by fractional distillation. A sample of 2-methoxy-d_3-pyridine of 98 at.% isotopic purity was supplied by Merck Sharp and Dohme, Canada Ltd., and used as received.

The infrared spectra of the samples in the liquid and vapor states in the range 4000—400 cm^{-1} were recorded on a Carl-Zeiss Specord IR 75 spectrophotometer. The calibration of the instrument was checked by a polystyrene film run immediately after each record. The gas-phase spectra were taken at different temperatures using a 9 cm heated gas cell equipped with KBr windows. A Perkin-Elmer model 180 spectrophotometer and a DIGILAB FTS-15B Fourier Transform interferometer were employed to scan the far infrared spectra of the pure liquid samples in the region 500—50 cm^{-1}. The Raman spectra were measured on a Cary 82 laser Raman spectrophotometer using 488.0 nm (200 mW) line of an argon ion laser as the excitation source. Polarization measurements were made by the method described elsewhere.$^{4)}$

Results and Discussion

The frequencies observed in the infrared and Raman spectra of the two molecules, their approximate intensities and probable assignments are given in Table 3. The calculated values of the thermodynamic functions are listed in Tables 4 and 5. Assuming C_s symmetry for both the molecules, the thirty-nine normal vibrations, which are active both in the infrared and Raman spectra, are divided over the irreducible representation as follows:

$$\Gamma = 26a' + 13a''$$

The a′ modes should give rise to polarized Raman lines, whilst the depolarized lines are associated with the a″ modes.

Taking the ring as a planar regular hexagon, the principal moments of inertia of 2-methoxypyridine and 2-methoxy-d_3-pyridine molecules and the asymmetry parameters $\kappa=(2B-A-C)/(A-C)$ and $\rho^*=(A-C)/B$, where A, B, and C are the rotational constants, have been calculated (Table 1) with the following geometry on the assumption that the 2-methoxypyridine molecules exist in the cis (synperiplanar) conformation (Fig. 1).

$$r(\text{C–C}) = r(\text{C–N}) = 1.397\,\text{Å},\ r(\text{C–H}) = 1.084\,\text{Å},$$

$$\angle\text{CCC} = \angle\text{CCN} = \angle\text{CCO} = 120°,$$

and for OCH$_3$ group : r(C–H)$=$1.0936 Å, r(C–O)$=$1.426 Å, $\angle$COC$=$109.47°, and all other angles are tetrahedral (109.47°). The values of relative atomic masses recommended by IUPAC$^{13)}$ were used in the calculation.

Making use of the results given in Table 1, the PR separations of the vapor-phase band envelopes in the infrared spectra have been calculated at T=323 K by the method of Seth-Paul and Dijkstra$^{14)}$ and compared with the observed values (Table 2). While the normal

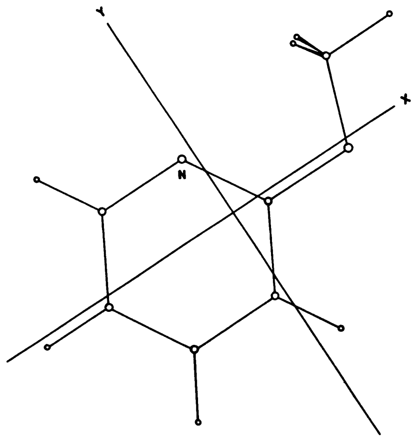

Fig. 1. Cis conformation of 2-methoxypyridine.

TABLE 1. PRINCIPAL MOMENTS OF INERTIA AND ASYMMETRY PARAMETERS FOR 2-METHOXYPYRIDINE AND 2-METHOXY-d_3-PYRIDINE

Molecule	$\frac{I_x}{10^{-47}\ \mathrm{kg\ m^2}}$	$\frac{I_y}{10^{-47}\ \mathrm{kg\ m^2}}$	$\frac{I_z}{10^{-47}\ \mathrm{kg\ m^2}}$	κ	ρ^*
2-Methoxypyridine	169.272	519.530	683.467	−0.7922	2.3091
2-Methoxy-d_3-pyridine	175.661	564.214	729.175	−0.8144	2.4382

The z axis is perpendicular to the plane of the ring.

TABLE 2. PR SEPARATIONS IN THE INFRARED VAPOR-PHASE BAND ENVELOPES

Band type	2-Methoxypyridine PR separation ν/cm^{-1}		2-Methoxy-d_3-pyridine PR separation ν/cm^{-1}	
	Calcd	Obsd	Calcd	Obsd
A (||)	11.1	11.0, 11.5, 11.0, 11.0, 11.5, 11.5, 13.0, 12.0	10.7	11.0, 11.0, 11.0, 11.0, 11.5, 10.0, 10.0, 11.5, 11.0, 11.0
B (⊥)	9.1	10.5, 10.0	8.8	—
C (⊥)	16.7	18.0, 17.5, 18.0	16.1	≈18.0, 17.0, ≈17.0

modes of species a″ will have a contour of type-C with strong *Q* branch, the a′ modes will give rise to A- or B-contours or contours of the hybrid type-AB depending on the directions of the oscillating dipoles.

Species a′. The polarized Raman lines observed at 3013, 3062, 3072, and 3094 cm^{-1} in the case of 2-methoxypyridine and 3021, 3066, and 3078 cm^{-1} and the infrared band at 3088 cm^{-1} in 2-methoxy-d_3-pyridine are readily assigned to the C–H stretching vibrations. The Raman spectra of the two molecules show polarized lines at 1602 and 1572 cm^{-1}, and 1599 and 1571 cm^{-1} respectively; these are assigned to the C–C stretching modes of the highest energy. The infrared bands observed at 1481, 1419, and 1312 cm^{-1} and 1472, 1433, and 1316 cm^{-1} in 2-methoxypyridine and its deuterio analog respectively show type-A vapor-phase contours, and are attributed to the next ring stretching modes. The highly intense and polarized Raman shifts at 988 and 984 cm^{-1} observed in the spectra of the two molecules may be confidently assigned to the ring breathing mode.

The two components of the planar ring deformation mode are little affected by substitution in the present cases, and identified with the polarized Raman lines at 622 and 602 cm^{-1}, and 620 and 577 cm^{-1} in the case of the two molecules respectively. The three substituent-sensitive modes belonging to the a′ class may be represented by the polarized Raman lines at 1289, 811, and 254 cm^{-1} in 2-methoxypyridine and 1292, 786, and 232 cm^{-1} in 2-methoxy-d_3-pyridine. The remaining a′ modes that can be derived from pyridine may be assigned to the polarized Raman lines observed at 1256, 1143, 1098, and 1044 cm^{-1}, and 1257, 1144, 1075, and 1042 cm^{-1} in the case of the normal and deuterated molecules respectively.

Species a″. The infrared bands at 781, 738, and 526 cm^{-1} in 2-methoxypyridine and 779, 737, and 524 cm^{-1} in the deuterio analog show conclusively type-C vapor-phase contours, and are assigned as a″ fundamentals. Similarly, the infrared spectra of the two molecules show absorptions of medium strength at 862 and 861 cm^{-1} respectively which appear to have type-C structures with prominent central maxima in the gas-phase spectra. These are assigned to the a″ mode involving principally out-of-plane bending motions of the ring H atoms. The remaining fundamentals belonging to the a″ species may be identified with the weak or moderately intense infrared bands at 957, 827, 412, and 116 cm^{-1} in 2-methoxypyridine and 957, 837, 415, and 130 cm^{-1} in 2-methoxy-d_3-pyridine in agreement with the assignments proposed for other monosubstituted pyridines.[4,9,10)]

The Internal Vibrations of the Methoxyl Group. There would appear twelve additional modes of vibration arising from the internal motions of the methoxyl group. The moderately intense infrared band at 2980 cm^{-1} appears to have type-C band contour in the gas-phase spectrum, while the Raman line at 2944 cm^{-1} is very strong and highly polarized. These are assigned to the a″ and a′ CH$_3$ asymmetric stretching modes respectively. Both of these frequencies are shifted to 2241 and 2263 cm^{-1} on OCH$_3$ deuteration. Again the infrared vapor-phase band contour of the 2241 cm^{-1} band shows a sharp central maximum characteristic of a type-C band, and its Raman counterpart is depolarized. It is, therefore, assigned to the a″ component of the CD$_3$ asymmetric stretching mode, while the *a*′ component may be identified with the polarized Raman line at 2263 cm^{-1}. The frequency at 2209 cm^{-1} appearing with comparable intensity both in the infrared and the Raman spectra may be explained as the overtone $2\times 1101=2202$ cm^{-1} (A′) enhanced by Fermi-resonance interaction with the fundamental at 2263 cm^{-1}. But the situation is complicated by the appearance of three polarized Raman lines of almost equal intensity at 2870, 2850, and 2828 cm^{-1} each having a counterpart in the infrared spectrum of 2-methoxypyridine. Since there occurs an infrared band at 2823 cm^{-1} in the deuterated species corresponding to the 2828 cm^{-1} frequency of the normal molecule, it must be assigned as a combination

TABLE 3. OBSERVED FUNDAMENTAL FREQUENCIES AND ASSIGNMENTS FOR 2-METHOXYPYRIDINE AND 2-METHOXY-d_3-PYRIDINE

2-Methoxypyridine			2-Methoxy-d_3-pyridine			
Infrared ν/cm^{-1}		Raman ν/cm^{-1}	Infrared ν/cm^{-1}		Raman ν/cm^{-1}	Assignment
Liquid	Vapor	Liquid	Liquid	Vapor	Liquid	
3095 (sh)	3107	3094 (sh)	3088 (sh)	3107		ν_1 (a′), 20b
3077 (mw)	3086	3072 (9) p	3077 (mw)	3084	3078 (sh) p	ν_2 (a′), 2
3058 (mw)	3060	3062 (sh) p	3057 (mw)	3061	3066 (10) p	ν_3 (a′), 20a
3014 (ms)	3023 3021 3012	3013 (2) p	3018 (mw)	3032	3021 (1) p	ν_4 (a′), 7b
2980 (ms)	2985		2241 (ms)	2248	2241 (0)dp	ν_{27} (a″), –CH_3 or –CD_3 asymmetric stretching
2945 (ms)	2960	2944 (8) p	2263 (ms)	2276 2271 A 2265	2263 (1) p	ν_5 (a′), –CH_3 or CD_3 asymmetric stretching
2849 (w)	2847	2850 (2) p	2075 (ms)	2090 2085 A 2079	2075 (4) p	ν_6 (a′), –CH_3 or –CD_3 symmetric stretching
1605 (s)	1613.5 1608.0 1602.0	1602 (1) p	1599 (vs)	1600	1599 (1) p	ν_7 (a′), 8a
1573 (s)	1573	1572 (3) p	1571 (s)	1572	1571 (2) p	ν_8 (a′), 8b
1481 (vs)	1491 1486 A 1480	1480 (0)	1472 (vs)	1481 1475 A 1470	1473 (0) p	ν_9 (a′), 19a
1464(mw)†	1466	1464 (0) dp	1049 (mw)	1048	1051 (sh) p	ν_{10} (a′) and ν_{28} (a″), –CH_3 or –CD_3 asymmetric deformation
1444 (s)	1452.0 1446.0 A 1440.5	1444 (2) p	1101 (vs)	1118 1113 A 1107	1100 (1) p	ν_{11} (a′), –CH_3 or –CD_3 symmetric deformation
1419 (vs)	1428 1422 A 1417	1419 (0)	1433 (vs)	1443.5 1438.0 A 1432.0	1434 (1) p	ν_{12} (a′), 19b
1312 (s)	1319 1314 A 1308	1310 (5) p	1316 (vs)	1325 1321 A 1315	1316 (5) p	ν_{13} (a′), 14
1289 (vs)	1296.0 1290.0 A 1284.5	1289 (4) p	1291 (vs)	1300 1295 A 1290	1292 (2) p	ν_{14} (a′), –C–OCH_3 or –C–OCD_3 stretching, 13
1252 (ms)	1260	1256 (2) p	1251 (mw)		1257 (2) p	ν_{15} (a′), 3
1143 (ms)	1147.5 1142.0 A 1136.0	1143 (1) p	1144 (ms)	1146.5 1141.0 A 1135.0	1144 (1) p	ν_{16} (a′), 9a
1098 (w)		1098 (2) p	1075 (w)		1075 (0) p	ν_{17} (a′), 15
			1040 (ms)	1044 1038 A 1033	1042 (3) p	ν_{18} (a′), 18a
1044 (s)	1049 1044 A 1036	1044 (5) p	894 (mw)		897 (0) dp	ν_{29} (a″), –CH_3 or –CD_3 out-of-plane rocking
1022 (s)	1024	1022 (1) p	996 (s)	997	997 (sh)	ν_{19} (a′), –O–CH_3 or –O–CD_3 stretching
988 (ms)	995.0 984.5 B	988 (10) p	983 (s)	981	984 (8) p	ν_{20} (a′), 1
957 (w)	955		957 (ms)	955		ν_{30} (a″), 17a
862 (mw)	≈869 861 ≈851		861 (mw)	862		ν_{31} (a″), 5
827 (mw)	832	828 (0)	837 (mw)	835		ν_{32} (a″), 10a
			802 (sh)		786 (5) p	ν_{21} (a′), 12
811 (ms)	818 813 807	811 (8) p	642 (mw)	642		ν_{22} (a′), –CH_3 or CD_3 in-plane-rocking

Table 3. (Continued)

2-Methoxypyridine			2-Methoxy-d_3-pyridine			
Infrared ν/cm^{-1}		Raman ν/cm^{-1}	Infrared ν/cm^{-1}		Raman ν/cm^{-1}	Assignment
Liquid	Vapor	Liquid	Liquid	Vapor	Liquid	
781 (s)	790 782 C 772	783 (0) dp	779 (s)	≈789 780 C ≈771		ν_{33} (a″), 10b
738 (ms)	744.5 737.0 C 727.0	729 (0)	737 (ms)	744 736 C 727		ν_{34} (a″), 4
621 (mw)	619	622 (1) p	618 (mw)	612	620 (1) p	ν_{23} (a′), 6b
601 (ms)	604 600 A 592	602 (1) p	575 (ms)	580 577 A 569	577 (1) p	ν_{24} (a′), 6a
526 (ms)	530 522 C 512	528 (0)dp	525 (mw)	≈527 520 C ≈510	527 (0) dp	ν_{35} (a″), 11
455 (mw)	458 448 B	457 (3) p	438 (mw)		440 (2) p	ν_{25} (a′), ∠COC deformation
412 (mw)			415 (mw)*		414 (0) dp?	ν_{36} (a″), 16a
256 (mw)		254 (0) p	240 (mw)*		232 (1) p	ν_{26} (a′), 18b
237 (sh)		234 (1) dp	234 (sh)*			ν_{37} (a″), ∠COC deformation
116 (mw)			130 (mw)*			ν_{39} (a″), 16b

(s)=strong, (m)=medium, (w)=weak, (v)=very, (sh)=shoulder, p=polarized, dp=depolarized.

*: Frequency observed in polycrystalline thin film at liquid nitrogen temperature.

†: Frequency observed in CCl_4 solution.

band. Of the remaining two frequencies, the 2850 cm^{-1} band is taken as the CH_3 symmetric stretching fundamental on the basis of the observed fact that a sharp band is usually occurs at about 2835 cm^{-1} when a methoxyl group is attached to the aromatic ring,[8,15–17] while the 2870 cm^{-1} band may be explained as the overtone 2×1444=2888 cm^{-1} (A′) in Fermi-resonance[18] with the fundamental at 2850 cm^{-1}. These are shifted to 2124, 2105, and 2075 cm^{-1} on OCH_3 deuteration. Of these, the 2105 cm^{-1} band being weak must be explained as a combination tone. The polarized Raman line at 2075 cm^{-1} and its infrared counterpart at the same frequency showing type-A contour in the gas-phase spectrum are more intense, and may be reasonably assigned to the CD_3 symmetric stretching mode, while the 2124 cm^{-1} frequency appearing with smaller intensity both in the infrared and Raman spectra may be interpreted as the overtone 2×1049=2098 cm^{-1} (A′) or the combination band 1101+996=2097 cm^{-1} (A′) in Fermi-resonance with the 2075 cm^{-1} fundamental.

A moderately intense polarized Raman line at 1444 cm^{-1} with a strong infrared counterpart at the same frequency is observed in 2-methoxypyridine, but it is absent in the Raman spectrum of the deuterio analog, though an infrared band with much reduced intensity appears at 1451 cm^{-1}. It is also known that the CH_3 symmetric deformation frequency being somewhat sensitive to the electronegativity of the attached oxygen atom in OCH_3 group, shifts to higher frequency[15] as a result of changes in the HCO bending force constant.[19] These observations lead the 1444 cm^{-1} band to be assigned to the CH_3 symmetric deformation mode, while the 1451 cm^{-1} band in 2-methoxy-d_3-pyridine may be attributed to the combination 802+642=1444 cm^{-1} (A′). The Raman line at 1464 cm^{-1} with its infrared counterpart of medium intensity is assigned to both the components of the CH_3 asymmetric deformation mode.

There appear two polarized Raman lines of almost equal strength at 1100 and 1051 cm^{-1} on OCH_3 deuteration. The infrared band at 1101 cm^{-1} showing type-A contour is very strong, while the band at 1049 cm^{-1} is comparatively weak. The former is therefore assigned to the CD_3 symmetric bending vibration and the latter to the CD_3 asymmetric bending mode in agreement with the assignments proposed for similar molecules.[20–23]

It is found that the 1044 and 811 cm^{-1} bands observed in the infrared and Raman spectra of 2-methoxypyridine, which are already assigned to the a′ fundamentals, decrease appreciably in intensity showing a small shift to lower frequency on OCH_3 deuteration. This may be taken as an evidence that two different fundamentals are overlapping at each of these positions. This frequency range being appropriate for CH_3 rocking modes, the bands at 1044 and 811 cm^{-1} are again assigned to the out-of-plane and in-plane CH_3 rocking modes respectively in agreement with the assignments for other molecules.[9,20,23,24] There appear two additional bands at 894 and 642 cm^{-1} in the infrared spectrum of 2-methoxy-d_3-pyridine. The corresponding Raman shift at 897 cm^{-1} being completely depolarized, is assigned to the CD_3 out-of-plane rocking mode, while the frequency at 642 cm^{-1} may be identified with the CD_3 in-plane rocking mode. The fundamental associated with the torsional mode remains unidentified in the present cases.

The strong infrared band at 1022 cm^{-1} and the polarized Raman line at 457 cm^{-1} in 2-methoxypyridine shift to 996 and 440 cm^{-1} respectively on OCH_3 deuteration. The former is assigned to the O–CH_3 stretching mode in agreement with the previous assignments,[7,25,26] while the latter may arise from the O–CH_3 in-plane bending vibration.[11] The O–CH_3 out-of-plane bend-

Table 4. Thermodynamic functions of 2-methoxypyridine[a)]

Temperature K	C_p° $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$	$(H^\circ-E_0^\circ)/T$ $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$	S° $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$	$-(F^\circ-E_0^\circ)/T$ $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$
200	19.20	12.92	74.03	61.11
250	23.40	14.59	78.76	64.17
273.15	25.44	15.42	80.92	65.50
298.15	27.65	16.35	83.24	66.89
300	27.82	16.43	83.41	66.99
400	36.31	20.35	92.60	72.25
500	43.54	24.29	101.50	77.21
600	49.44	28.01	109.98	81.98
700	54.23	31.42	117.97	86.55
800	58.17	34.53	125.48	90.95
900	61.46	37.34	132.53	95.19
1000	64.23	39.90	139.15	99.25
1100	66.58	42.22	145.38	103.17
1200	68.58	44.34	151.26	106.93
1300	70.30	46.27	156.82	110.56
1400	71.77	48.04	162.09	114.05
1500	73.04	49.66	167.08	117.42

a) Ideal gas state at standard pressure of 1 atm. 1 $\mathrm{cal_{th}}$=4.184 J.

Table 5. Thermodynamic functions of 2-methoxy-d_3-pyridine[a)]

Temperature K	C_p° $\mathrm{Cal_{th}\ K^{-1}\ mol^{-1}}$	$(H^\circ-E_0^\circ)/T$ $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$	S° $\mathrm{Cal_{th}\ K^{-1}\ mol^{-1}}$	$-(F^\circ-E_0^\circ)/T$ $\mathrm{Cal_{th}\ K^{-1}\ mol^{-1}}$
200	19.82	13.04	75.03	61.99
250	24.42	14.85	79.94	65.09
273.15	26.64	15.75	82.20	66.45
298.15	29.03	16.77	84.63	67.87
300	29.21	16.84	84.81	67.97
400	38.20	21.09	94.48	73.40
500	45.70	25.28	103.84	78.56
600	51.71	29.21	112.72	83.52
700	56.54	32.78	121.07	88.29
800	60.45	36.00	128.88	92.88
900	63.67	38.90	136.19	97.29
1000	66.33	41.52	143.04	101.53
1100	68.55	43.88	149.47	105.60
1200	70.42	46.01	155.51	109.51
1300	72.00	47.95	161.22	113.27
1400	73.35	49.72	166.60	116.89
1500	74.50	51.33	171.70	120.37

a) Ideal gas state at standard pressure of 1 atm. 1 $\mathrm{cal_{th}}$=4.184 J.

ing mode may be represented by the depolarized Raman shift at 234 $\mathrm{cm^{-1}}$ in 2-methoxypyridine.

The Application of the Product Rule. When the Teller-Redlich product rule is applied to the assignments for the a′ species, it is found that the observed ratio is

$$\frac{\pi\nu^{i}}{\pi\nu} = 0.192$$

and the calculated value of this ratio is 0.189.

Since the torsional frequencies are not identified, the product rule cannot be applied to the assignments for the a″ species.

Thermodynamic Functions

The thermodynamic functions of 2-methoxypyridine and 2-methoxy-d_3-pyridine were calculated at several temperatures assuming a rigid rotator, harmonic oscillator approximation and free internal rotation of the methyl group by utilising the fundamental frequencies given in Table 3. The reduced moments of inertia of the CH_3 and CD_3 groups were calculated to be 5.2627×10^{-47} kg m^2 and 10.4120×10^{-47} kg m^2 respectively.

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