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Study of the Vibrational Spectra and Determination of Thermodynamic Functions of 2-Pyridone and 2-Pyridone-*N*-*d*

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The infrared spectra in the polycrystalline state (4000—50 cm^{-1}), in melt and in solution and the Raman spectra in the solid state and in melt of the substances have been studied for 2-pyridone and 2-pyridone-*N*-*d*. A vibrational assignment of the observed frequencies is given. Ideal gas state thermodynamic functions of the two isotopic molecules based on the observed fundamental frequencies have been determined in the temperature range 200—1500 K.

Continuing the earlier investigations on the vibrational spectra of substituted pyridines[1—4] the infrared and Raman spectra of 2-pyridone and 2-pyridone-*N*-*d* have been reported. The infrared spectrum of 2-pyridone in the solid state or in solution was measured by Gibson et al.,[5] Mason,[6] Katritzky and Jones,[7] and Albert and Spinner[8] in a limited range, and only a few bands were assigned. The incomplete simple Raman spectrum of 2-pyridone in aqueous solution was reported by Albert and Spinner.[8] No polarization of the Raman lines was studied previously. It also appears that there is no earlier report on the infrared and Raman spectra of 2-pyridone-*N*-*d*.

The present investigation was aimed at making a detailed study of the infrared and Raman spectra of 2-pyridone and 2-pyridone-*N*-*d* in the polycrystalline, liquid and solution phases. Assignments of the observed vibrational frequencies based on the polarization of the Raman lines and also on the comparison with the assignments proposed for the related molecules[4,9—12] are presented. The ideal gas state thermodynamic functions of the two isotopic molecules have been determined on the basis of the assigned fundamental frequencies.

Experimental

2-pyridone was supplied by Schuchardt, Germany. The compound was purified by repeated sublimation under reduced pressure. A sample of 2-pyridone-*N*-*d* was prepared by the exchange reaction of 2-pyridinol with D_2O. The final product used in the experiment was collected after four such

Table 1. Observed Fundamental Frequencies of 2-Pyridone and 2-Pyridone-*N*-*d*

2-Pyridone					2-Pyridone-*N*-*d*				Assignment
Infrared/cm^{-1}			Raman/cm^{-1}		Infrared/cm^{-1}			Raman/cm^{-1}	
Nujol or HCB mull	Melt	Solution[a)]	Pellet	Melt	Nujol or HCB mull	Melt	Solution[a)]	Pellet	
3197 (mw)					3197 (mw)				$\nu_6+\nu_8$ (A′)
		3134 (ms)							$\nu_6+\nu_{10}$ (A′)
		3116 (ms)							$\nu_6+2\nu_{26}$ (A′)
		3085 (ms)	3090 (5)	3091 (p)				3096 (4) 3085 (4)	ν_2 (a′) and ν_3 (a′), 20b, 2
		3028 (ms)	3042 (1)	3040 (p)				3043 (2)	ν_4 (a′) and ν_5 (a′), 20a, 7b
2982 (ms)		2977 (ms)			2982 (ms)				$\nu_9+\nu_{10}$ (A′)
2942 (ms)					2942 (ms)				$3\nu_{23}$ (A″)
2873 (ms)		2886 (w)			2873 (ms)				$\nu_{10}+\nu_{11}$ (A′)
2842 (ms)		2862 (w)			2843 (ms)				$2\nu_{11}$ (A′)
~2817 (ms)		2826 (w)			2814 (ms)				$\nu_{10}+\nu_{12}$ (A′)
2785 (ms)		2795 (w)			2783 (ms)				$\nu_6+\nu_{14}$ (A′)
2677 (w)					2673 (w)				$\nu_{11}+\nu_{13}$ (A′)
2602 (w)					2612 (w)				$\nu_{10}+\nu_{14}$ (A′)
2549 (w)									$\nu_{10}+\nu_{22}$ (A″)
2527 (w)					2537 (w)				$\nu_9+\nu_{17}$ (A′)
2462 (mw)					2459 (mw)				$\nu_9+\nu_{24}$ (A″)
					2282 (s)				ν_1 (a′), N–D Stretching
					2230 (s)				$\nu_7+\nu_{22}+\nu_{27}$ (A′)
1978 (w)					1978 (w)				$2\nu_{17}$ (A′)
1850 (mw)		1866 (w)			1841 (w)				$2\nu_{24}$ (A′)
1815 (w)		1835 (w)			1806 (w)				$\nu_{15}+\nu_{26}$ (A″) $\nu_{25}+2\nu_{27}$ (A″)

Table 1. (Continued)

2-Pyridone					2-Pyridone-*N*-*d*				Assignment
Infrared/cm^{-1}			Raman/cm^{-1}		Infrared/cm^{-1}			Raman/cm^{-1}	
Nujol or HCB mull	Melt	Solution[a)]	Pellet	Melt	Nujol or HCB mull	Melt	Solution[a)]	Pellet	
1766 (w)		1766 (w)			1758 (w)				$\nu_{23}+\nu_{25}$ (A′)
1683 (ms)		1676 (ms)			1683 (ms)		1650 (sh)	1663 (1)	$2\nu_{26}+\nu_{30}$ (A″)
1643 (vs)	1663 (vs)	1659 (vs)	1654 (3)	1680	1637 (vs)	1661 (vs)	1645 (vs)	1645 (1)	ν_6 (a′), C=O Stretching
1608 (vs)	1605 (vs)	1619 (s)	1610 (3)	1599 (p)					ν_7 (a′), N–H in-plane deformation.
1567 (s)			1567 (5)		1560 (s)			1574 (6)	ν_8 (a′), 8a
1537 (s)	1538 (s)	1543 (ms)	1543 (11)	1539 (p)	1531 (s)	1538 (s)	1563 (vs)	1532 (22)	ν_9 (a′), 8b
1453 (s)	1465 (ms)	1472 (ms)	1458 (9)	1459 (p)	1450 (s)	1468 (ms)	1454 (mw)	1451 (5)	ν_{10} (a′), 19a
1433 (s)	1430 (ms)	1442 (ms)	1434 (1)	1427 (p)	1433 (s)	1432 (s)			ν_{11} (a′), 19b
	1370 (mw)	1375 (w)	1366 (9)	1369 (p)		1371 (w)	1385 (mw)	1388 (2)	ν_{12} (a′), 14
1305 (w)	1305 (w)				1307 (mw)	1308 (s)	1307 (mw)	1310 (29)	$\nu_{25}+\nu_{27}$ (A′)
1239 (ms)	1239 (ms)	1248 (s)	1244 (45)	1248 (p)	1239 (ms)	1240 (ms)	1248 (ms)	1242 (15)	ν_{13} (a′), 3
1230 (sh)		1237 (sh)	1234 (sh)		1231 (ms)		1236 (sh)	1235 (88)	$\nu_{16}+\nu_{30}$ (A″)
1217 (sh)	1216 (s)	1214 (sh)	1219 (7)		1217 (sh)	1216 (ms)	1214 (sh)		$\nu_{17}+\nu_{30}$ (A″)
1173 (mw)			1174 (3)		1170 (mw)			1172 (4)	$\nu_{25}+\nu_{29}$ (A′)
1156 (ms)	1155 (s)	1154 (s)	1159 (1)	1157 (p)	1156 (s)	1151 (s)	1158 (s)	1151 (10)	ν_{14} (a′), 9a
1149 (sh)			1148 (3)		1143 (sh)				
1099 (ms)	1093 (ms)	1097 (ms)	1099 (3)	1096 ρ=0.77	1098 (mw)	1094 (mw)	1096 (w)		ν_{15} (a′) and ν_{22} (a″), 15 and N–H out-of-plane deformation
					1031 (mw)	1026 (mw)	1036 (mw)	1031 (2)	ν_7 (a′), N–D in-plane deformation
1009 (ms)		1007 (ms)	1013 (7)	1011 (p)	1007 (mw)	1010 (sh)	1006 (w)		ν_{16} (a′), 18a
993 (mw)	992 (s)	990 (s)	991 (2)	996 (p)	992 (mw)	985 (s)	989 (s)	994 (2)	ν_{17} (a′), 1
981 (s)		982 (sh)	982 (3)		982 (s)		980 (s)	984 (8)	ν_{23} (a″), 17a
926 (ms)		923 (ms)			934 (s)	930 (mw)	916 (ms)	933 (2)	ν_{24} (a″), 5
864 (w)			854 (5)		865 (mw)		857 (ms)	855 (3)	$\nu_{28}+\nu_{29}$ (A′)
								842 (9)	
845 (w)	851 (mw)	843 (mw)	844 (39)	847 (p)	845 (w)	849 (ms)	844 (sh)	833 (61)	ν_{18} (a′), 12
835 (w)			835 (11)	831	832 (w)			825 (12)	$\nu_{19}+\nu_{30}$ (A″)
780 (vs)	769 (s)	768 (vs)	784 (3)		782 (vs)	771 (s)	783 (vs)	782 (2)	ν_{25} (a″), 10b
731 (s)	723 (ms)	724 (s)			731 (ms)	726 (ms)	724 (ms)		ν_{26} (a″), 4
					667 (ms)		682 (ms)		ν_{22} (a″), N–D out-of-plane deformation
609 (mw)	611 (mw)	612 (w)	614 (4)	617 (p)	612 (mw)	610 (mw)	610 (mw)	615 (5)	ν_{19} (a′), 6b
559 (ms)	557 (ms)	559 (s)	561 (9)	555 (p) ρ=0.61	556 (ms)	555 (ms)	558 (s)	557 (10)	ν_{20} (a′) and ν_{21} (a′) C=O in-plane bending and 6a
553 (ms)			552 (3)		548 (ms)			548 (5)	
525 (s)	511 (ms)	513 (ms)	526 (3)		522 (s)	510 (mw)	508 (ms)	525 (2)	ν_{27} (a″), 11
473 (s)	487 (mw)	495 (s)			471 (s)	488 (sh)	491 (s)		ν_{28} (a″), C=O out-of-plane deformation
449 (mw)	455 (mw)	454 (mw)	450 (1)	464 (p)	443 (mw)	456 (mw)	454 (mw)	445 (1)	$2\nu_{30}$ (A′)
392 (mw)			393 (4)	393 (dp)	392 (ms)			389 (6)	ν_{29} (a″), 16a
228 (sh)					228 (sh)				$\nu_{16}-\nu_{25}$ (A″)
220 (ms)			221 (3)		220 (ms)			221 (3)	ν_{30} (a″), 16b
			208 (5)					209 (5)	$\nu_{10}-\nu_{13}$ (A′)
142 (ms)			142 (23)	141 (ms)	141 (ms)			142 (22)	Lattice mode
128 (sh)			125 (41)		129 (sh)			124 (44)	
								112 (34)	
101 (ms)			101 (47)		101 (ms)			102 (50)	
86 (mw)			86 (67)		86 (mw)			87 (84)	
68 (mw)			65 (100)					65 (110)	
			35 (100)					35 (100)	

a) Solution in CS_2, CH_2Cl_2, CCl_4, or D_2O.

exchanges.

The infrared spectra of 2-pyridone and 2-pyridone-*N-d* in the range 4000—400 cm^{-1} were measured on a Carl-Zeiss Specord IR 75 spectrometer in the polycrystalline state as nujol or hexachlorobutadiene (HCB) mull, in the liquid state just above the melting point and in solutions in different solvents, e.g., CCl_4, CS_2, CH_2Cl_2, and D_2O. The far infrared spectra of the two compounds in the region 500—50 cm^{-1} were recorded in nujol mull on a Perkin-Elmer Model 180 spectrophotometer.

The Raman spectra were obtained in the polycrystalline state in the case of both the molecules and also in the melt of the substance in the case of 2-pyridone using a Spex 1403 Ramalog spectrometer and the 514.5 nm line as the exciting wavelength from a Spectra Physics argon ion laser. The polarization of the Raman lines of 2-pyridone was also measured using an analyser and a scrambler as described elsewhere.[1)]

Results and Discussion

The observed infrared frequencies and Raman shifts of the two isotopic molecules, their approximate relative intensities and probable assignments are given in Table 1. Tables 2 and 3 list the calculated values of the thermodynamic functions. In Fig. 1 is reproduced the laser Raman spectrum of 2-pyridone-*N-d* in the polycrystalline state.

Assuming the amide form for 2-pyridone[6,8,13,14)] and 2-pyridone-*N-d* the two isotopic molecules belong to the point group C_s and the thirty normal modes of vibration, which are active both in the infrared and Raman

Table 2. Thermodynamic Functions of 2-Pyridone[a,b)]

Temp	C_p°	$(H^\circ-E_0^\circ)/T$	S°	$-(F^\circ-E_0^\circ)/T$
K	cal_{th} K^{-1} mol^{-1}	cal_{th} K^{-1} mol^{-1}	cal_{th} K^{-1} mol^{-1}	cal_{th} K^{-1} mol^{-1}
200	15.04	10.13	66.15	56.03
250	18.63	11.46	69.88	58.42
273.15	20.32	12.14	71.61	59.47
298.15	22.15	12.91	73.47	60.56
300	22.29	12.96	73.60	60.64
400	29.19	16.17	80.98	64.81
500	35.03	19.38	88.14	68.76
600	39.77	22.40	94.96	72.57
700	43.61	25.16	101.40	76.23
800	46.75	27.67	107.40	79.76
900	49.35	29.94	113.10	83.15
1000	51.54	31.99	118.40	86.41
1100	53.39	33.86	123.40	89.55
1200	54.97	35.55	128.10	92.57
1300	56.31	37.10	132.60	95.48
1400	57.48	38.51	136.80	98.28
1500	58.48	39.81	140.80	101.00

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

Table 3. Thermodynamic Functions of 2-Pyridone-*N-d*[a,b)]

Temp	C_p°	$(H^\circ-E_0^\circ)/T$	S°	$-(F^\circ-E_0^\circ)/T$
K	cal_{th} K^{-1} mol^{-1}	cal_{th} K^{-1} mol^{-1}	cal_{th} K^{-1} mol^{-1}	cal_{th} K^{-1} mol^{-1}
200	15.48	10.22	66.36	56.14
250	19.34	11.66	70.23	58.57
273.15	21.16	12.38	72.02	59.64
298.15	23.09	13.20	73.95	60.76
300	23.23	13.26	74.10	60.84
400	30.38	16.67	81.79	65.12
500	36.29	20.03	89.22	69.20
600	41.03	23.15	96.27	73.13
700	44.84	25.98	102.90	76.91
800	47.95	28.54	109.10	80.55
900	50.50	30.84	114.90	84.05
1000	52.63	32.92	120.30	87.41
1100	54.42	34.80	125.40	90.64
1200	55.93	36.50	130.20	93.74
1300	57.22	38.04	134.80	96.72
1400	58.32	39.45	139.00	99.59
1500	59.26	40.74	143.10	102.40

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

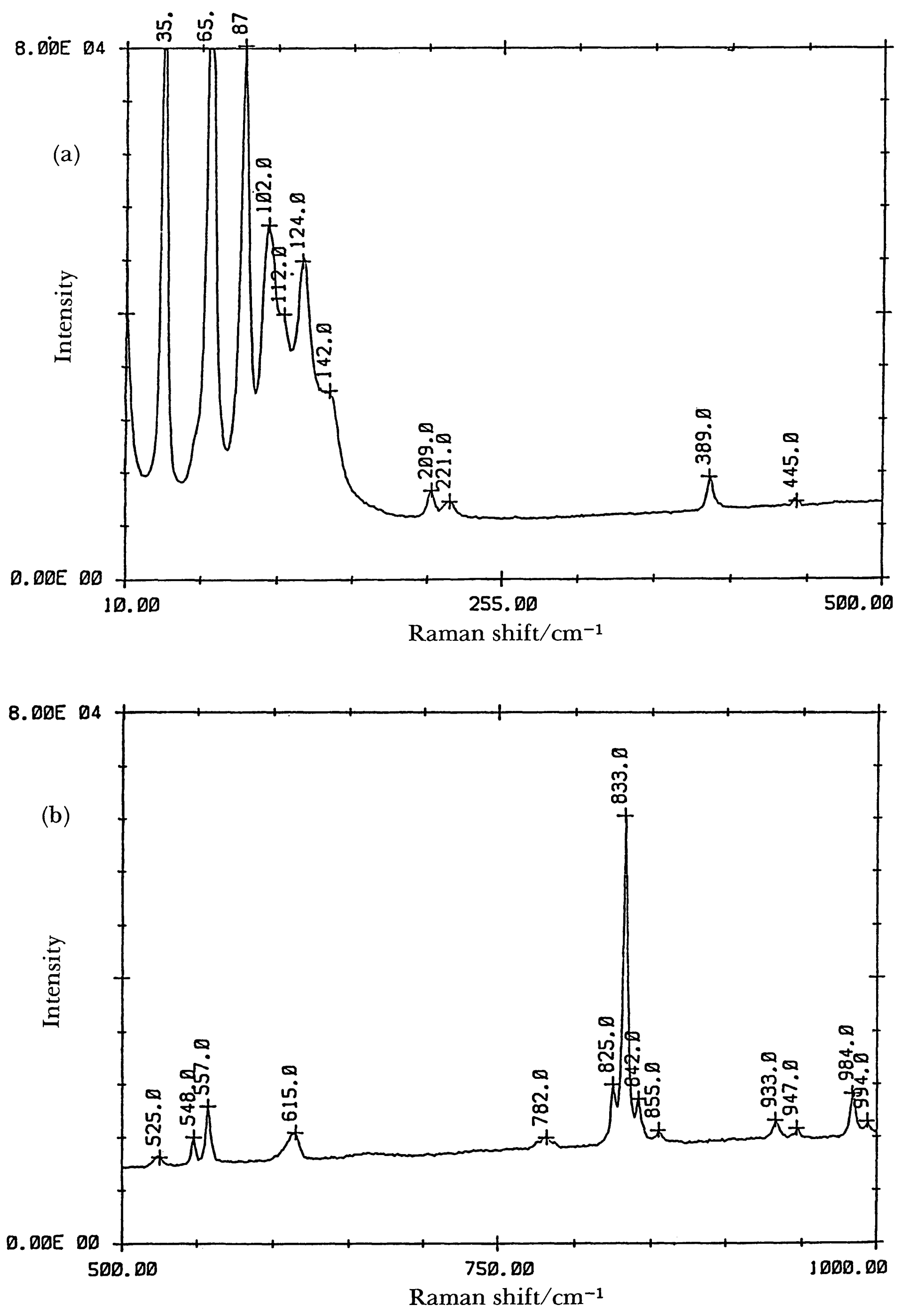
spectra, are distributed among the symmetry species as follows:

$$\Gamma = 21\ a' + 9a''$$

The species a′ gives polarized Raman lines and the species a″ depolarized Raman lines.

Species a′. The polarized Raman lines at 3091 and 3040 cm^{-1} in the case of 2-pyridone and the Raman shifts observed at 3096, 3085, and 3043 cm^{-1} in the case of 2-pyridone-*N-d* are assigned to the four C–H stretching modes. The infrared spectra of both the isotopic molecules in the liquid state show absorption at 1538 cm^{-1}, but in the polycrystalline state it is split up into two components. The Raman counterpart behaves similarly. These are attributed to both the components of the highest C–C stretching mode. The remaining ring stretching modes are identified with the polarized Raman lines at 1459, 1427, 1369, and 996 cm^{-1} in 2-pyridone and the Raman shifts observed at 1451, 1388, 994 cm^{-1} and the infrared band at 1433 cm^{-1} in 2-pyridone-*N-d*. The Raman spectrum of 2-pyridone gives polarized lines at 1248, 1157, and 1011 cm^{-1} and the infrared spectrum shows absorption of medium strength at 1099 cm^{-1}, while in the deuterated compound the Raman lines at 1242 and 1151 cm^{-1} and the infrared bands at 1098 and 1007 cm^{-1} are observed. These are assigned to the four C–H in-plane deformation modes.

Polarized Raman lines are observed at 847, 617, and 555 cm^{-1} in 2-pyridone while its deuterated analogue



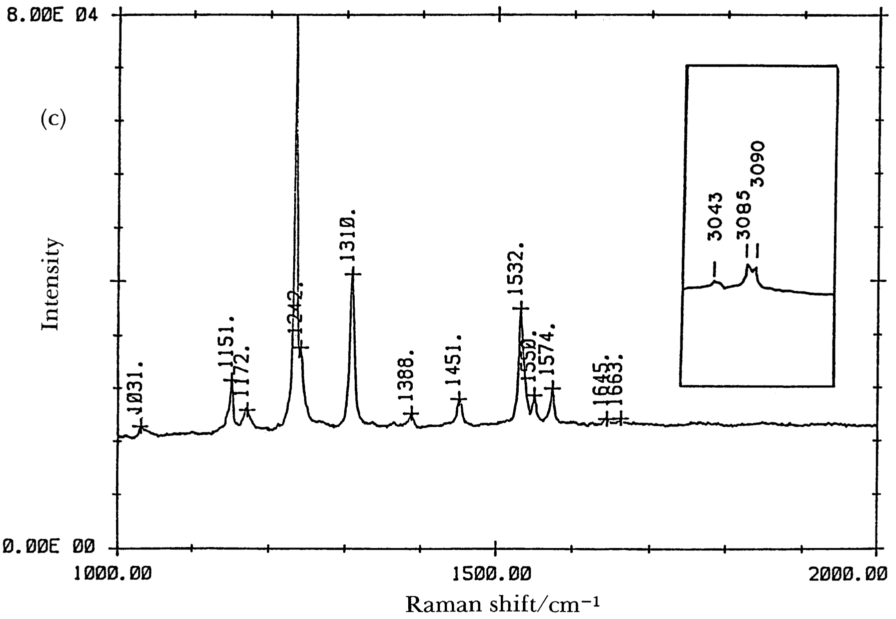


Fig. 1. (a), (b), and (c). Laser Raman spectrum of 2-pyridone-*N*-*d* in the polycrystalline state.

shows Raman shifts at 833, 615, and 548 cm^{-1}. These may be unambiguouly identified with the modes being derived primarily from the planar ring deformation.

Species a″. A depolarized Raman line is observed at 393 cm^{-1} in 2-pyridone in the liquid state, while the corresponding Raman shift is observed at 389 cm^{-1} in the case of 2-pyridone-*N*-*d*. This may be associated with one component of the nonplanar ring angle deformation, the other component being substituent sensitive may be identified with the infrared band of medium intensity observed at 220 cm^{-1} in the case of both the isotopic molecules. The other fundamental frequencies belonging to a″ class may be assigned to the infrared bands at 981, 926, 780, 731, and 525 cm^{-1} in 2-pyridone and 982, 934, 782, 731, and 522 cm^{-1} in 2-pyridone-*N*-*d*. These assignments are in close agreement with those proposed for other monosubstituted pyridines.[1,3,4,9,10)]

The Internal Vibrations of the NH and CO Group. If the molecule of 2-pyridone exists in the amide form[15)] due to tautomerism, it should exhibit the N–H stretching band near 3400 cm^{-1} in the infrared spectrum. Since there is strong intermolecular hydrogen bonding which exists not only in the crystalline state[16)] but also in the liquid and solution phases (as evident from the

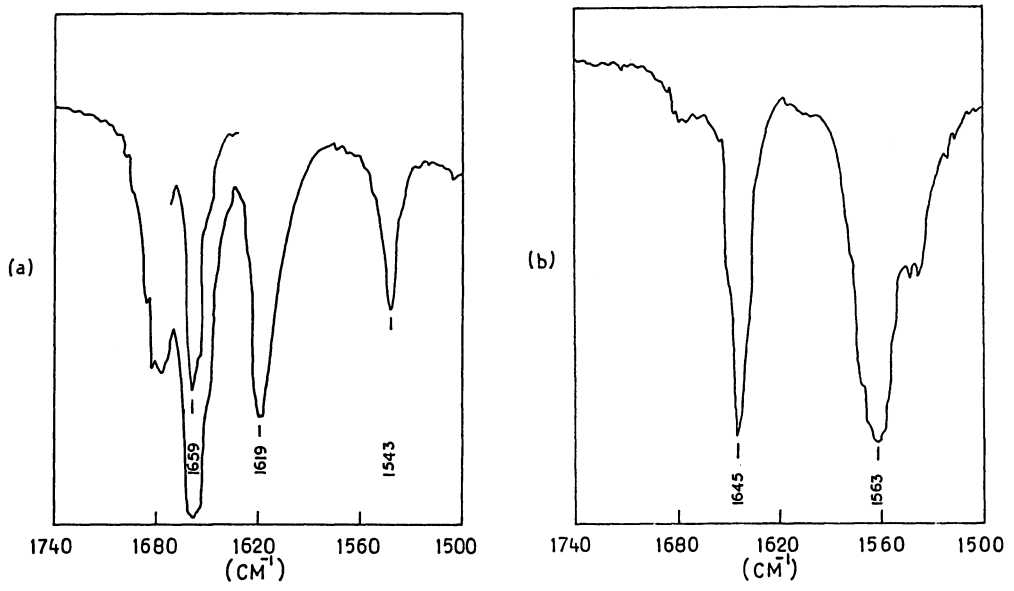


Fig. 2. Portions of the infrared spectra of (a) 2-pyridone in methylene chloride, and (b) 2-pyridone-*N*-*d* in D_2O.

spectrum) the N–H stretching frequency may decrease to about 3200 cm^{-1} and it is, therefore, probably submerged in the broad absorption region covering the range 3300—2500 cm^{-1}, and as such this frequency cannot be located with certainty. Mason[6] reported the N–H stretching band at 3404 cm^{-1} in a very dilute solution in CCl$_4$ and at 3198 cm^{-1} in the solid state in the case of 2-pyridone. The present study shows that the infrared band at 3197 cm^{-1} (present value) persists in solid 2-pyridone-*N-d*. So the band at 3197 cm^{-1} cannot be assigned to the N–H stretching mode. But in the case of 2-pyridone-*N-d* a strong infrared band is observed at 2282 cm^{-1} which is absent in the spectrum of the normal 2-pyridone molecule. It is, therefore, assigned to the N–D stretching mode.

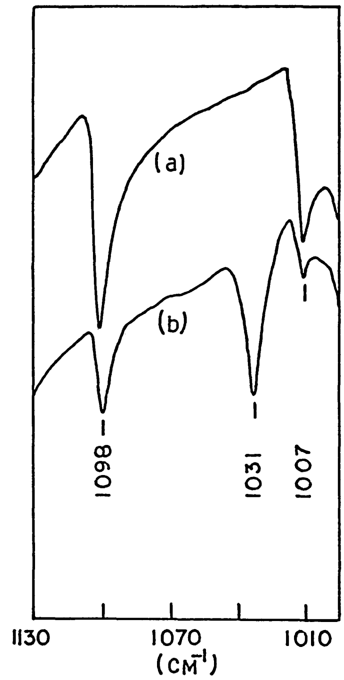


Fig. 3. Portions of the infrared spectra of (a) 2-pyridone in nujol, and (b) 2-pyridone-*N-d* in nujol.

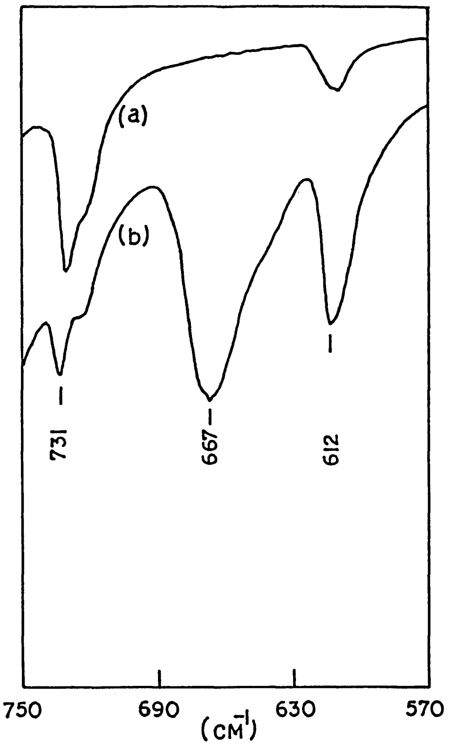


Fig. 4. Portions of the infrared spectra of (a) 2-pyridone in nujol, and (b) 2-pyridone-*N-d* in nujol.

A polarized Raman line at 1599 cm^{-1} with a very strong infrared counterpart at 1605 cm^{-1} is observed in 2-pyridone. This band is found to disappear on N–H deuteration (Fig. 2) and a new band of medium strength at 1031 cm^{-1} is observed in both the infrared (Fig. 3) and Raman spectra of 2-pyridone-*N-d*. The former band must therefore be assigned to the N–H in-plane deformation mode[1] against the previous assignment of this frequency to a C–C stretching mode[7] and the latter (1031 cm^{-1}) to the N–D in-plane bending mode.

It is observed that in 2-pyridone an infrared band of medium intensity at 1099 cm^{-1}, which has already been assigned to a C–H in-plane deformation mode, decreases in intensity on N–H deuteration. This is indicative of the fact that two fundamentals are overlapping at this position. Moreover, the Raman line at the same frequency which appears to be depolarized in 2-pyridone is missing in the Raman spectrum of 2-pyridone-*N-d*. This shows that the band at 1099 cm^{-1} must have some contribution from the N–H out-of-plane deformation mode. On the other hand, an infrared band of medium intensity at 667 cm^{-1} is observed on N–H deuteration (Fig. 4). This band is attributed to the N–D out-of-plane deformation mode.

The highly intense infrared bands at 1643 and 1637 cm^{-1} in 2-pyridone and 2-pyridone-*N-d*, respectively, are assigned to the C=O stretching frequency.[1] The C=O in-plane and out-of-plane deformation frequencies are identified with the observed infrared bands at 559 and 473 cm^{-1} respectively in 2-pyridone and at 556 and 471 cm^{-1} respectively in the case of 2-pyridone-*N-d*.[17]

Teller–Redlich product rule applied to the present assignment gives the following result:

$$\text{For the a}' \text{ species} \quad \Gamma'_{\text{exp}} = \prod_i \frac{\nu_i^{\text{D}}}{\nu_i^{\text{H}}} = 0.445, \quad \Gamma'_{\text{cal}} = 0.510$$

$$\text{For the a}'' \text{ species} \quad \Gamma'_{\text{exp}} = \prod_i \frac{\nu_i^{\text{D}}}{\nu_i^{\text{H}}} = 0.613, \quad \Gamma''_{\text{cal}} = 0.728$$

Thermodynamic Functions: Assuming a rigid rotator and harmonic oscillator approximation ideal gas state thermodynamic functions of 2-pyridone and 2-pyridone-*N-d* have been calculated in the temperature range 200—1500 K using the standard expressions[18] and the wavenumbers of the fundamental frequencies.

Remarks

It is seen from the vibrational analysis given above that the spectral behavior of the two isotopic molecules corroborates to the fact that 2-pyridone and 2-pyridone-*N-d* exist predominantly in the amide form due to tautomerism in the solid, liquid, and solution phases.

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