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The Vibrational Spectra and Thermodynamic Functions of 2,3-Dichloropyridine

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The infrared spectrum in the vapor, liquid, solution, and solid phases and the laser Raman spectrum in the liquid state have been measured for 2,3-dichloropyridine. A complete vibrational assignment is given. Ideal gas state thermodynamic functions of the molecule are computed over the temperature range 200—1500 K.

The infrared spectrum of 2,3-dichloropyridine in solutions was measured by Green *et al.*,[1)] and a vibrational assignment based on comparison with the related molecules was given. For evaluation of the thermodynamic properties, a precise knowledge of the fundamental frequencies is necessary. A study of the vapor-phase infrared spectrum and the polarized Raman spectrum is essential for an accurate vibrational assignment of the observed frequencies. There is, however, no previous report on the Raman and vapor-phase infrared spectra of this molecule. In extension of the previous work on the vibrational spectra of some substituted pyridines,[2—5)] the infrared spectrum of 2,3-dichloropyridine in the vapor, liquid, solution and solid phases and the Raman spectrum in the liquid state have been studied in details in this work. The present measurements suggest some changes in the previous assignments.[1)]

The present paper gives an essentially complete assignment of the observed frequencies based on the contours of the vapor-phase infrared bands, the state of polarization of the Raman lines and comparison with the assignments proposed for related molecules.[4—10)] It also includes the ideal gas state thermodynamic functions of the molecule calculated on the basis of the present assignment.

Experimental

Pure sample of 2,3-dichloropyridine obtained from Schuchardt, Germany was purified by repeated sublimation under vacuum.

The Raman spectrum of the compound in the liquid state just above the melting point was recorded on a Cary 82 laser Raman spectrophotometer. The spectrum was excited by the 514.5 nm line (200 mW) of an argon ion laser. The polarization measurement was carried out by the method described previously.[5)] The infrared spectrum in the region 4000—400 cm^{-1} in the vapor state, in nujol mull or polycrystalline film, in liquid film prepared from the melt of the substance and in solution in CCl_4 or CS_2 was measured using a Carl-Zeiss Specord IR 75 spectrophotometer after the calibration of the instrument had been checked by a polystyrene film run. A 9 cm heated gas cell equipped with KBr windows was used to record the vapor-phase spectrum. The far infrared spectrum in nujol mull in the region 500—30 cm^{-1} was obtained using a Perkin-Elmer Model 180 spectrophotometer.

Results and Discussion

The observed infrared and Raman frequencies of 2,3-dichloropyridine together with their approximate intensities and assignments are given in Table 3. The fundamental frequencies are collected in Table 4. Table 5 shows the calculated values of the thermodynamic quantities of the molecule over the temperature range 200—1500 K. The variations of these thermodynamic functions with temperature are represented graphically in Figs. 2 and 3.

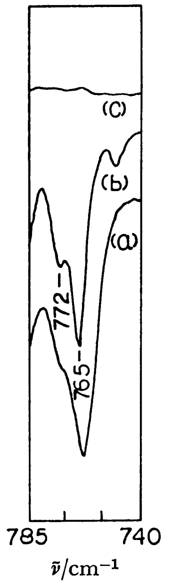

Fig. 1. Infrared spectrum of 2,3-dichloropyridine showing 772 and 765 cm^{-1} bands. a): Thin film (melt), (b): solution in CS_2, (c): pure CS_2.

The 2,3-dichloropyridine molecule belongs to the point group C_s and its twenty seven normal vibrations, which are active both in the Raman and infrared spectra, are distributed over the two symmetry species as

$$19a' + 8a''.$$

The a′ modes should be polarized and the a″ modes depolarized in the Raman spectrum. The principal moments of inertia of 2,3-dichloropyridine molecule and the asymmetry parameters $\kappa=\dfrac{2B-A-C}{A-C}$ and $\rho^*=\dfrac{A-C}{B}$, where A, B, and C are rotational constants, have been calculated (Table 1) with the following interatomic distances and bond angles assuming that the ring is a planar regular hexagon:

r(C–C) = r(C–N) = 1.397 Å, r(C–H) = 1.084 Å, r(C–Cl) = 1.717 Å,

∠CCC = ∠CCN = ∠CCH = ∠CCl = 120°,

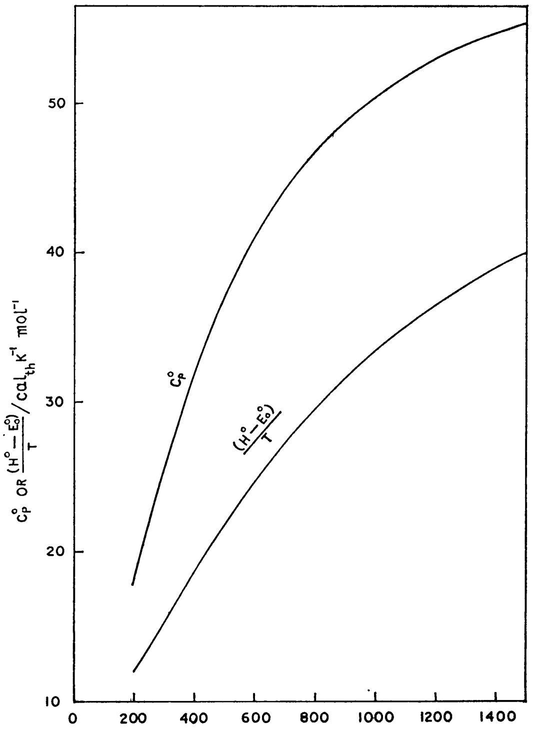

Fig. 2. Variation of heat capacity and enthalpy of 2,3-dichloropyridine with absolute temperature.

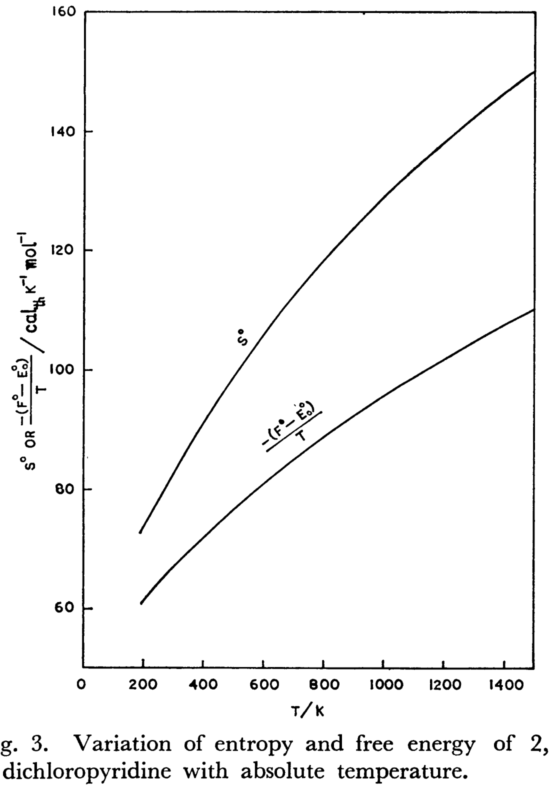

Fig. 3. Variation of entropy and free energy of 2,3-dichloropyridine with absolute temperature.

Table 1. Principal moments of inertia[a] and the asymmetry parameters for 2,3-dichloropyridine

$I_x/10^{-47}$ kg m^2	$I_y/10^{-47}$ kg m^2	$I_z/10^{-47}$ kg m^2	κ	ρ^*
424.003	601.068	1025.070	−0.0048	0.8312

a) The z-axis is perpendicular to the plane of the ring.

Table 2. PR separations in the infrared vapor-phase band envelopes

Band type	PR separation $\tilde{\nu}$/cm^{-1} Calcd	Obsd
A (∥)	10.7	10.0, 10.0
B (⊥)	8.1	8.0, 8.0, 8.0, 8.0
C (⊥)	16.1	16.0, 17.0

and by using the relative atomic masses recommended by IUPAC.[11] The PR separations of band envelopes in the vapor-phase infrared spectrum have been calculated at T=346 K by the method of Seth-Paul and Dijkstra,[12] and are included in Table 2 along with the observed separations.

The infrared bands belonging to the species a″ should show C-contour with a PQR structure showing a sharp strong Q maximum but ill-defined P and R branches,[13] while those of species a′ will have A- or B- contour or contours of the hybrid type-AB.

Species a′. There are expected three frequencies in the C–H stretching region, and the polarized Raman lines at 3068 and 3054 cm^{-1} are assigned to these modes. The Raman shifts at 1562, 1552, 1436, 1398, and 1031 cm^{-1} are observed to be polarized; these are unambiguously identified as a′ fundamentals arising essentially from the stretching of the C–C (C–N) bonds. The infrared band at 1125 cm^{-1} shows type-B contour in the gas-phase spectrum, its Raman counterpart located at 1126 cm^{-1} being polarized. This may be attributed to the a′ mode involving stretching of the C–Cl bonds in agreement with the similar assignment proposed in the case of *o*-dichlorobenzene.[6]

A moderately intense infrared band has now been observed at 772 cm^{-1} which was not reported by the previous investigators[1] probably due to lack of proper resolution. In the present investigation the 772 cm^{-1} band is appearing as a shoulder on the higher wavenumber side of the 765 cm^{-1} band in the pure liquid state. The band is, however, clearly resolved in solution in CS$_2$ (Fig. 1). Though its Raman counterpart is not observed, it has been tentatively assigned as the a′ fundamental corresponding to the substituent-sensitive mode 12.[2,9] The infrared band at 517 cm^{-1} (present value) was assigned previously[1] to the a″ species. But the corresponding Raman line observed at 506 cm^{-1} appears to be polarized; it must therefore be assigned as an a′ fundamental. The observed frequency difference between the infrared band and the Raman shift may be due to the fact that the infrared band at 517 cm^{-1} is sharp, while the Raman line is weak and broad having its maximum at about 506 cm^{-1}. Moreover, its position is somewhat influenced by the neighbouring strong Raman line at 477 cm^{-1}. The remaining a′ fundamentals are identified with the polarized Raman lines at 1215, 1159, 1062, 652, 477, and 204 cm^{-1} and the infrared bands at 1298 and 763 cm^{-1} in agreement with the previous assignment.[1]

TABLE 3. OBSERVED VIBRATIONAL FREQUENCIES AND ASSIGNMENTS FOR 2,3-DICHLOROPYRIDINE

Infrared, $\tilde{\nu}$/cm^{-1}				Raman, $\tilde{\nu}$/cm^{-1}	Assignment
Nujol mull	Melt	Solution	Vapor	Melt	
3058 (ms)*	3063 (ms)	3064 (ms)	3067	3068 (53) p	ν_1 and ν_2 (a′, a′)
3044 (ms)*	3053 (ms)	3054 (ms)		3054 (49) p	ν_3 (a′)
1970 (mw)		1943 (w)			$2\times\nu_{20}$ (A′)
1930 (mw)		1906 (w)			$\nu_{20}+\nu_{21}$ (A′)
1896 (w)		1867 (w)			$2\times\nu_{21}$ (A′)
		1812 (w)			$\nu_{10}+\nu_{16}$ (A′)
		1764 (w)			$\nu_{20}+\nu_{22}$ (A′)
1754 (w)		1730 (w)			$\nu_{21}+\nu_{22}$ (A′)
		1694 (w)			$\nu_{20}+\nu_{23}$ (A′)
		1639 (w)			$\nu_{11}+\nu_{17}$ (A′)
1577 (sh)	1576 (sh)	1576 (sh)			$\nu_{12}+\nu_{17}$ (A′)
1575 (ms)	1570 (sh)	1571 (sh)			$\nu_{22}+\nu_{14}$ (A″)
1561 (s)	1559 (s)	1560 (s)	1563	1562 (18) p	ν_4 (a′)
1553 (s)	1553 (sh)	1554 (sh)	1556	1552 (12) p	ν_5 (a′)
≈1437 (ms)	1434 (ms)	1435 (ms)	1443 1435 B	1436 (4) p	ν_6 (a′)
1425 (mw)	1419 (w)	1421 (sh)	1420		$\nu_{14}+\nu_{16}$ (A′)
1408 (sh)	1412 (sh)	1410 (sh)			$\nu_{15}+\nu_{16}$ (A′)
1398 (vs)	1396 (vs)	1398 (vs)	1405 1401 A 1395	1398 (4) p	ν_7 (a′)
1386 (sh)	1385 (sh)	1386 (sh)			$\nu_{13}+\nu_{25}$ (A″)
1302 (w)	1298 (w)	1300 (w)			ν_8 (a′)
≈1247 (w)	1253 (w)	1251 (w)			$\nu_{14}+\nu_{18}$ (A′)
1235 (w)	1237 (w)	1237 (w)			$\nu_{15}+\nu_{18}$ (A′)
1213 (w)	1211 (mw)	1211 (mw)		1215 (4) p	ν_9 (a′)
1190 (ms)	1192 (ms)	1192 (mw)	≈1200	1194 (3) p	$\nu_{21}+\nu_{26}$ (A′)
1160 (vs)	1159 (vs)	1158 (vs)	1170 1165 A 1160	1159 (37) p	ν_{10} (a′)
1131 (ms) 1123 (ms)	1125 (ms)	1125 (ms)	1130 1122 B	1126 (5) $\rho=0.68$	ν_{11} (a′)
≈1115 (sh)	≈1116 (sh)	1118 (sh)			$\nu_{16}+\nu_{18}$ (A′) $\nu_{15}+\nu_{25}$ (A″)
1078 (w)	1077 (w)	1077 (w)			$\nu_{23}+\nu_{25}$ (A′)
1059 (mw)	1061 (ms)	1061 (ms)	1068 1060 B	1062 (100) p	ν_{12} (a′)
			1045		$\nu_{22}+\nu_{26}$ (A′)
		1037 (sh)	1038		$2\times\nu_{17}$ (A′)
1031 (vs)	1032 (vs)	1032 (vs)	1031	1031 (21) p	ν_{13} (a′)
≈1004 (w)	1003 (w)	1004 (w)			$\nu_{16}+\nu_{25}$ (A″)
988 (mw)	972 (mw)	971 (mw)	971		ν_{20} (a″)
951 (w)	934 (w)	934 (w)			ν_{21} (a″)
803 (vs) 794 (sh)	797 (vs)	793 (vs)	799 792 C 782		ν_{22} (a″)
≈769 (sh)	≈771 (sh)	772 (mw)			ν_{14} (a′)
760 (ms)	763 (ms)	765 (ms)	770		ν_{15} (a′)
723 (s)	726 (s)	726 (s)	736 730 C 720		ν_{23} (a″)
656 (s) 649 (s)	651 (s)	651 (s)	654 646 B	652 (68) p	ν_{16} (a′)
516 (mw)	517 (w)	515 (w)		506 (5) p	ν_{17} (a′)

TABLE 3. (Continued)

Infrared, $\tilde{\nu}$/cm^{-1}				Raman, $\tilde{\nu}$/cm^{-1}	Assignment
Nujol mull	Melt	Solution	Vapor	Melt	
475 (ms)	475 (ms)	474 (ms)	474	477 (53) p	ν_{18} (a′)
443 (w)					$\nu_{26}+\nu_{19}$ (A″) $\nu_{22}-\nu_{25}$ (A′)
426 (ms)				428 (9) dp	ν_{24} (a″)
351 (ms)				353 (4) dp	ν_{25} (a″)
250 (ms) 246 (ms)				255 (8) dp	ν_{26} (a″)
202 (w)				204 (17) p	ν_{19} (a′)
153 (ms)				142 (24) dp	ν_{27} (a″)
56 (ms)					Lattice mode
38 (s)					

* Frequency observed in solid thin film. (s) = strong, (m) = medium, (w) = weak, (v) = very, (sh) = shoulder, p = polarized, dp = depolarized.

Combination bands (IR in solution) in the region 4000—2000 cm^{-1}: 3125 (w) (3123 (22) p) $=2\times\nu_4$ (A′), 3117 (w) $=\nu_4+\nu_5$ (A′), 2980 (w) $=\nu_5+\nu_6$ (A′), 2954 (w) $=\nu_4+\nu_7$ (A′), 2867 (vw) $=2\times\nu_6$ (A′), 2831 (vw) $=\nu_6+\nu_7$ (A′), 2813 (w) $=\nu_7+\nu_{15}+\nu_{16}$ (A′), 2793 (w) $=2\times\nu_7$ (A′), 2771 (w) $=\nu_4+\nu_9$ (A′), 2673 (w) $=\nu_5+\nu_{11}$ (A′), 2645 (vw) $=\nu_6+\nu_9$ (A′), 2616 (w) $=\nu_5+\nu_{12}$ (A′), 2555 (w) $=\nu_7+\nu_{10}$ (A′), 2520 (w) $=\nu_7+\nu_{11}$ (A′), 2509 (w) $=\nu_8+\nu_9$ (A′), 2495 (w) $=\nu_6+\nu_{12}$ (A′), 2471 (w) (2472 (3) p) $=\nu_6+\nu_{13}$ (A′), 2428 (w) (2426 (3) p) $=\nu_7+\nu_{13}$ (A′), 2380 (w) $=\nu_9+\nu_{10}$ (A′), 2250 (w) $=2\times\nu_{11}$ (A′), 2186 (w) $=\nu_{10}+\nu_{13}$ (A′), 2090 (vw) $=\nu_{12}+\nu_{13}$ (A′), 2048 (w) $=\nu_7+\nu_{16}$ (A′), 2003 (vw) $=\nu_9+\nu_{22}$ (A″).

TABLE 4. THE FUNDAMENTAL FREQUENCIES FOR 2,3-DICHLOROPYRIDINE

Symmetry species	Mode No.	Fund.	Wavenumber $\tilde{\nu}$/cm^{-1}	Symmetry species	Mode No.	Fund.	Wavenumber $\tilde{\nu}$/cm^{-1}
a′	2	ν_1	3068	a′	7b	ν_{15}	763
	20b	ν_2	3068		6b	ν_{16}	652
	20a	ν_3	3054		6a	ν_{17}	506
	8a	ν_4	1562		9a	ν_{18}	477
	8b	ν_5	1552		18b	ν_{19}	204
	19a	ν_6	1436	a″	17a	ν_{20}	972
	19b	ν_7	1398		5	ν_{21}	934
	14	ν_8	1298				
	3	ν_9	1215		10b	ν_{22}	797
	15	ν_{10}	1159		4	ν_{23}	726
	13	ν_{11}	1126		11	ν_{24}	428
	18a	ν_{12}	1062		16a	ν_{25}	353
	1	ν_{13}	1031		10a	ν_{26}	255
	12	ν_{14}	772		16b	ν_{27}	142

TABLE 5. THERMODYNAMIC FUNCTIONS OF 2,3-DICHLOROPYRIDINE[a)]

Temperature K	C_p° cal$_{th}$ K^{-1} mol^{-1}	$(H^\circ-E_0^\circ)T^{-1}$ cal$_{th}$ K^{-1} mol^{-1}	S° cal$_{th}$ K^{-1} mol^{-1}	$-(F^\circ-E_0^\circ)T^{-1}$ cal$_{th}$ K^{-1} mol^{-1}
200	18.50	12.14	73.40	61.27
250	22.04	13.76	77.91	64.15
273.15	23.68	14.54	79.93	65.40
298.15	25.42	15.38	82.08	66.71
300	25.54	15.44	82.24	66.81
400	31.92	18.78	90.49	71.71
500	37.09	21.95	98.19	76.24
600	41.13	24.82	105.32	80.50
700	44.28	27.39	111.91	84.52
800	46.79	29.66	117.99	88.33
900	48.81	31.68	123.62	91.94
1000	50.47	33.48	128.85	95.38
1100	51.84	35.09	133.73	98.64
1200	52.99	36.53	138.29	101.76
1300	53.97	37.84	142.57	104.74
1400	54.79	39.02	146.60	107.58
1500	55.50	40.10	150.40	110.31

a) Ideal gas state at standard pressure of 1 atm. 1 cal$_{th}$ = 4.184 J.

Species a″. In the earlier work[1] the infrared frequencies at 426 and 351 cm^{-1} (present values) were assigned to the a′ class and the weak infrared band at 443 cm^{-1} to the a″ species. But the Raman spectrum reveals that the corresponding shifts at 428 and 353 cm^{-1} respectively are completely depolarized. They must therefore be assigned as a″ fundamentals arising respectively from the C–H and C–C–C out-of-plane deformations. The 443 cm^{-1} band may be explained as the combination band 250+202=452 cm^{-1} (A″) or the difference band 793−351=442 cm^{-1} (A′).

The infrared bands at 793 and 726 cm^{-1} showing type C contours in the gas phase and the depolarized Raman lines observed at 255 and 142 cm^{-1} are reasonably assigned to the a″ species. The infrared spectrum shows weak absorptions at 972 and 934 cm^{-1}. As in the case of other substituted pyridines, they are attributed to the C–H out-of-plane deformations. The assignments of these frequencies to the a″ species are in agreement with the previous assignments.[1]

Thermodynamic Functions

Ideal gas state thermodynamic functions of 2,3-dichloropyridine molecule have been calculated using the standard expressions[14] and the following wavenumbers of the fundamentals observed in the infrared and Raman spectra (where available, the vapor-phase frequencies are used):

3068, 3068, 3054, 1563, 1556, 1438, 1401, 1298, 1215, 1165, 1127, 1064, 1031, 971, 934, 792, 772, 763, 730, 650, 506, 474, 428, 353, 255, 204, and 142. Thermodynamic contributions from over-all rotation and vibration are calculated on the basis of the above data and those given in Table 1 by assuming a rigid-rotator harmonic-oscillator approximation.

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