

## Infrared and Raman spectra and thermodynamic functions of 4-methoxypyridine N-oxide\*

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**Abstract.** The infrared spectrum of 4-methoxypyridine N-oxide in the region  $4000-30\text{ cm}^{-1}$  in the solid and liquid states and the polarized laser Raman spectrum of the molecule in the liquid state have been investigated. A vibrational assignment of the observed frequencies based on the state of polarization of the Raman lines and comparison with the related molecules is presented. Ideal gas state thermodynamic functions of the molecule are calculated in the temperature range  $273.15-1500^\circ\text{ K}$ .

**Keywords.** Infrared spectrum; Raman spectrum; thermodynamic functions; 4-methoxypyridine N-oxide.

### 1. Introduction

As a part of the earlier investigations on the vibrational assignments for some substituted pyridine molecules (Medhi *et al* 1965; Medhi 1965, 1972, 1977), the infrared and Raman spectra of 4-methoxy pyridine N-oxide have been studied in the present work. The infrared spectrum of this molecule in a limited frequency range was reported by Hideyo Shindo (1958), Costa and Blasina (1955) and Ghersetti *et al* (1973), and only a few frequencies were assigned. There is, however, no earlier study on the Raman spectrum of 4-methoxypyridine N-oxide.

The present paper gives a detailed account of the infrared and Raman spectra of the molecule of 4-methoxypyridine N-oxide, and a vibrational assignment of the observed frequencies, based on the polarization of the Raman lines and comparison with the assignments proposed for other related molecules (Green 1962; Green *et al* 1963; Long and George 1963; Allan *et al* 1971; Berezin and Elkin 1973a) is presented. The ideal gas state thermodynamic properties of the molecule are also calculated on the basis of this vibrational assignment.

### 2. Experimental

The sample of 4-methoxypyridine N-oxide was supplied by Aldrich Chemical Company, U.S.A. It was purified by repeated sublimation in vacuum.

The Raman spectrum of the sample in the liquid state at a temperature just above the melting point was recorded on a Cary 82 laser Raman spectrophotometer equipped with an argon ion laser. The 514.5 nm line (200 mw) was used to excite the spectrum. The polarization of the Raman lines was measured by the same method as described previously (Medhi 1977). A Carl-Zeiss Specord IR 75 spectrophotometer was employed to measure the mid infrared spectrum in the range 4000-400  $\text{cm}^{-1}$  either in hexachlorobutadiene (HCB) or in nujol mull as well as in thin liquid film prepared from the melt of the substance. The far infrared spectrum from 500 to 30  $\text{cm}^{-1}$  was obtained in nujol mull using a Perkin-Elmer Model 180 spectrophotometer. Because of the high boiling point of the substance, the vapour-phase infrared spectrum could not be obtained.

### 3. Results and discussion

Table 1 gives the details of the infrared and Raman spectra of 4-methoxypyridine N-oxide together with the probable assignments for the observed frequencies. The fundamental frequencies are summarized in table 2. The calculated values of the thermodynamic functions are listed in table 3.

Table 1. Observed infrared and Raman frequencies and assignments for 4-methoxypyridine N-oxide.

Infrared ( $\text{cm}^{-1}$ )		Raman ( $\text{cm}^{-1}$ )	Assignment
HCB or nujol mull	Melt	Melt	
3112 (s)	3108 (s)	3092 (3) p	$\nu_1 (a')$
3065 (mw)	3060 (mw)		$\nu_2 (a')$
3041 (s)			$\nu_3 (a')$
3026 (ms)	3025 (s)	3022 (1) p	$\nu_4 (a')$
2997 (mw)			$\nu_{29} (a')$ , $-\text{CH}_3$ asymmetric stretching
2951 (mw)	2943 (mw)	2948 (1) p	$\nu_5 (a')$ , $-\text{CH}_3$ asymmetric stretching
2932 (w)			$2 \times \nu_{11} (A')$
2897 (mw)	2895 (mw)	2901 (0)	$\nu_{11} + \nu_{12} (A')$
2847 (ms)	2840 (s)	2845 (2) p	$\nu_8 (a')$ , $-\text{CH}_3$ symmetric stretching
2812 (w)			$\nu_9 + \nu_{13} (A')$
2785 (ms)	2769 (ms)		$\nu_{11} + \nu_{13} (A')$
2581 (w)	2571 (w)		$\nu_8 + \nu_{20} (A')$
	2509 (w)		$\nu_9 + \nu_{20} (A')$
2235 b (ms)			$\nu_{16} + \nu_{19} (A')$
2045 (mw)	2038 (ms)		$\nu_{14} + \nu_{74} (A')$
2011 (w)			$\nu_{17} + \nu_{23} (A')$
1941 (w)	1927 (w)		$\nu_{17} + \nu_{24} (A')$
1903 (mw)			$\nu_{12} + \nu_{26} (A')$
1889 (sh)			$\nu_{19} + \nu_{23} (A')$
	1877 (mw)		$\nu_{20} + \nu_{22} (A')$
	1755 (w)		$\nu_{18} + \nu_{25} (A')$
			$\nu_{23} + \nu_{24} (A')$

Table 1 (Contd.)

Infrared (cm <sup>-1</sup> )		Raman (cm <sup>-1</sup> )		Assignment
HCB or nujol mull	Melt	Melt		
1623 (s)	1625 (s)	1624 (3) p	$\nu_7 (a')$	
1566 (sh)	1567 (sh)		$\nu_{18} + \nu_{26} (A')$	
1563 (ms)	1557 (ms)	1559 (1) p	$\nu_8 (a')$	
1520 (sh)	1520 (sh)		$\nu_{22} + \nu_{25} (A')$	
1509 (sh)	1510 (sh)		$2 \times \nu_{24} (A')$	
1496 (vs)	1490 (vs)	1490 (0) p	$\nu_9 (a')$	
1471* (s)	1466† (ms)		$\nu_{10} (a')$ and $\nu_{30} (a'')$ , -CH <sub>3</sub> asymmetric deformations	
1462* (vs)	1455† (ms)	1458 (0) p = 0.73	$\nu_{11} (a')$ , -CH <sub>3</sub> symmetric deformation	
1439 (s)	1441 (s)	1442 (sh)	$\nu_{12} (a')$	
		1415 (0) p	$\nu_{17} + \nu_{28} (A')$	
1319 (ms)	1310 (sh)	1310 (sh) p = 0.63	$\nu_{13} (a')$	
1298 (vs)	1289 (vs)	1290 (2) p	$\nu_{14} (a')$	
1291 (vs)			$\nu_{15} (a')$	
1233 (ms)			$\nu_{16} (a')$ , -N-O stretching	
1205 (vs)	1227 (vs)		$\nu_{25} + \nu_{40} (A')$	
1188 (sh)		1184 (sh) p	$\nu_{17} (a')$	
1180 (s)	1172 (s)	1175 (4) p	$\nu_{25} + \nu_{26} (A')$	
	1124 (w)		$\nu_{18} (a')$	
1111 (w)	1099 (s)	1102 (0) p	$\nu_{31} (a')$ , -CH <sub>3</sub> out-of-plane rocking	
		1058 (0) dp	$\nu_{19} (a')$	
1033 (s)			$\nu_{20} (a')$ and $\nu_{21} (a')$ , -O-CH <sub>3</sub> stretching	
1014 (vs)	1022 (vs)	1027 (1) p	$\nu_{32} (a')$	
962 (w)	955 (w)		$\nu_{33} (a')$	
900 (w)	897 (w)		$\nu_{22} (a')$ , -N-O in-plane deformation	
856 (sh)	855 (sh)	858 (10) p	$\nu_{34} (a')$	
850 (vs)			$\nu_{23} (a')$ , -CH <sub>3</sub> in-plane rocking	
836 (sh)	840 (vs)	842 (sh) p	$\nu_{25} (a')$	
811* (ms)	~ 810 (sh)		$\nu_{24} (a')$	
756 (vs)	758 (vs)	758 (0) p	$\nu_{36} (a'')$	
690 (mw)	704 (w)	708 (0) dp	$\nu_{25} (a')$	
657 (mw)	657 (mw)	661 (1) p = 0.74	?	
586 b (s)			$\nu_{27} (a'')$ , -N-O out-of-plane deformation	
542 (w)	540† (w)	541 (0) dp	$\nu_{28} (a'')$	
522 (s)	526 (ms)	530 (0) dp	$\nu_{26} (a')$ , $\angle$ COC deformation	
462 (ms)	463 (ms)	465 (0) p	$\nu_{29} (a'')$	
420 (sh)			$\nu_{27} (a')$	
405 (ms)		406 (1) p	$\nu_{40} (a'')$ , $\angle$ COC deformation	
376 (mw)		370 (0) dp	$\nu_{28} (a'')$	
252 (mw)		244 (0) p	$\nu_{41} (a'')$	
198 b (ms)			{ lattice modes	
148 (mw)				
85 (mw)				
47 (w)				

\* Frequency observed in solid film prepared from the melt.

† Frequency observed in methylene chloride.

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

Table 2. The fundamental frequencies for 4-methoxypyridine N-oxide.

Symmetry species	Mode No. (Wilson 1934)	Fund.	Wavenumber (cm <sup>-1</sup> )	
<i>a'</i>	20b	$\nu_1$	3092	
	2	$\nu_2$	3060	
	20a	$\nu_3$	3041	
	7b	$\nu_4$	3022	
		$\nu_5$	2948	
		$\nu_6$	2845	
	8a	$\nu_7$	1624	
	8b	$\nu_8$	1559	
	19a	$\nu_9$	1490	
		$\nu_{10}$	1466	
		$\nu_{11}$	1458	
	19b	$\nu_{12}$	1441	
	14	$\nu_{13}$	1310	
	13	$\nu_{14}$	1290	
	3	$\nu_{15}$	1233	
		$\nu_{16}$	1227	
	9a	$\nu_{17}$	1175	
	15	$\nu_{18}$	1102	
	18a	$\nu_{19}$	1033	
	1	$\nu_{20}$	1027	
		$\nu_{21}$	(1027)	
		$\nu_{22}$	858	
		$\nu_{23}$	840	
	12	$\nu_{24}$	758	
	6b	$\nu_{25}$	661	
		$\nu_{26}$	465	
	6a	$\nu_{27}$	406	
	18b	$\nu_{28}$	244	
	<i>a''</i>		$\nu_{29}$	2997
			$\nu_{30}$	(1466)
		$\nu_{31}$	1058	
17a		$\nu_{22}$	955	
5		$\nu_{23}$	897	
10a		$\nu_{34}$	850	
10b		$\nu_{35}$	811	
4		$\nu_{36}$	708	
		$\nu_{37}$	541	
11		$\nu_{38}$	530	
16a		$\nu_{39}$	420	
		$\nu_{40}$	370	
	$\nu_{41}$	?		
16b	$\nu_{42}$	198		

( ) Frequency assigned more than once.

? Frequency not assigned.

Table 3. Thermodynamic functions of 4-methoxypyridine N-oxide\*

Temperature (° K)	$C_p^\circ$ Cal/degree/ mole	$\frac{(H^\circ - E_0^\circ)}{T}$ Cal/degree/ mole	$S^\circ$ Cal/degree/ mole	$-\frac{(F^\circ - E_0^\circ)}{T}$ Cal/degree/ mole
273·15	26·93	15·45	81·58	66·13
298·15	29·43	16·52	84·04	67·53
300	29·61	16·60	84·22	67·63
400	39·06	21·06	94·06	73·01
500	47·03	25·48	103·67	78·19
600	53·46	29·63	112·83	83·20
700	58·65	33·42	121·47	88·06
800	62·89	36·84	129·59	92·75
900	66·40	39·94	137·20	97·27
1000	69·35	42·74	144·36	101·62
1100	71·83	45·27	151·09	105·82
1200	73·93	47·58	157·43	109·86
1300	75·73	49·67	163·42	113·75
1400	77·27	51·59	169·09	117·50
1500	78·60	53·35	174·47	121·12

\* Ideal gas state at standard pressure of 1 atom.

The molecule of 4-methoxypyridine N-oxide is assumed to have the  $C_s$  symmetry with  $28a'$  and  $14a''$  normal modes of vibrations predicted from group theoretical considerations. All the forty-two normal vibrations are active both in the infrared and Raman spectra. The Raman lines of  $a'$  species should be polarized, and those belonging to the  $a''$  species depolarized.

### 3.1. Pyridyl vibrations

3.1a *Class a'*: There appear four frequencies in the C-H stretching region. These are readily assigned to such valence oscillations. The polarized Raman lines observed at 1624, 1559 and 1490  $\text{cm}^{-1}$  and the strong infrared band at 1439  $\text{cm}^{-1}$  may be attributed to the modes primarily derived from the stretching of the ring. The infrared spectrum shows very strong absorption at 1291  $\text{cm}^{-1}$ ; its Raman counterpart located at 1290  $\text{cm}^{-1}$  is polarized. This may be confidently assigned to the mode characterised as C-O stretching in agreement with the assignments made in the case of other molecules (Katritzky and Coats 1959; Briggs *et al* 1957; Sax *et al* 1960; Spinner and White 1962; Katritzky 1959). Two other substituent-sensitive modes belonging to the  $a'$  class may be identified with the polarized Raman lines at 758 and 244  $\text{cm}^{-1}$ . Infrared bands of medium strength are observed at 657 and 405  $\text{cm}^{-1}$ . The corresponding Raman line at 661  $\text{cm}^{-1}$  appears to be depolarized and that at 406  $\text{cm}^{-1}$  is polarized. These may be reasonably assigned to the planar ring angle deformation modes (Green *et al* 1963; Berezin and Elkin 1973a). The remaining modes belonging to the  $a'$  class may be

identified with the polarized Raman lines at 1310, 1175, 1102, 1027, 758  $\text{cm}^{-1}$  and the moderately intense infrared band at 1233  $\text{cm}^{-1}$ .

3.1b *Class a''*: The Raman lines observed at 708 and 530  $\text{cm}^{-1}$  are depolarized and are assigned as *a''* fundamentals arising principally from the out-of-plane bending motions of the ring carbon atoms and the ring hydrogen atoms respectively. The remaining *a''* modes are identified with the observed infrared frequencies at 962, 900, 850, 811, 420 and 198  $\text{cm}^{-1}$  in agreement with the assignments proposed for related molecules (Medhi 1977 ; Green *et al* 1963 ; Long and George 1963).

### 3.2. N-O vibrations

The infrared spectrum shows very strong absorption at 1205  $\text{cm}^{-1}$ , this may be attributed to the mode that involves the stretching of the N-O bond in agreement with the previous assignment (Costa and Blasina 1955). The in-plane N-O deformation mode is unambiguously assigned to the intensely strong polarized Raman line at 858  $\text{cm}^{-1}$ , whilst the out-of-plane bending mode may be responsible for the depolarized Raman shift observed at 541  $\text{cm}^{-1}$  (Berezin and Elkin 1973 b ; Katritzky and Coats 1959 ; Wiley and Slaymaker 1957 ; Colthup *et al* 1975).

### 3.3. OCH<sub>3</sub> vibrations

The two components of the out-of-phase CH<sub>3</sub> stretching mode may be assigned to the polarized Raman shift observed at 2948  $\text{cm}^{-1}$  and the moderately intense infrared band at 2997  $\text{cm}^{-1}$ , while the symmetric stretching mode is identified with the polarized Raman line at 2845  $\text{cm}^{-1}$  (Green 1962 ; Badger and Moritz 1959 ; Pozefsky and Coggeshall 1951 ; Wiberley *et al* 1960 ; Henbest *et al* 1957 ; Seth-Paul *et al* 1974). It is known that the symmetric CH<sub>3</sub> deformation mode, being somewhat sensitive to the electronegativity of the attached oxygen atom in the O-CH<sub>3</sub> group, shifts to higher frequency (Sheppard 1955 ; Bellamy and Williams 1956 ; Wilmschurst 1957). Thus the infrared band appearing with considerable intensity at 1462  $\text{cm}^{-1}$  is reasonably assigned to this mode. The CH<sub>3</sub> asymmetric deformations may be responsible for the observed frequency at 1471  $\text{cm}^{-1}$ . While the assignments of the CH<sub>3</sub> rocking modes are less certain, the torsional mode is not located in this case.

In methoxy compounds usually a strong band appears in the interval 1050-1010  $\text{cm}^{-1}$  which has been interpreted as O-CH<sub>3</sub> stretching fundamental (Katritzky and Coats 1959 ; Briggs *et al* 1957 ; Sax *et al* 1960 ; Spinner and White 1962). In agreement with this the strong infrared band observed at 1014  $\text{cm}^{-1}$  is assigned to such mode. The in-plane and out-of-plane O-CH<sub>3</sub> deformation may be represented by the polarized Raman line at 465  $\text{cm}^{-1}$  (Allan *et al* 1971) and the depolarized Raman shift observed at 370  $\text{cm}^{-1}$ , respectively.

In addition to these, the infrared spectrum shows strong but somewhat broad absorption at 586  $\text{cm}^{-1}$  in the solid state ; but the band completely disappears on melting the substance by raising the temperature, or when the compound is dissolved in methylene chloride. Therefore, it cannot be assigned as a fundamental or a combination band. This may, however, arise from some associated groups of molecules in the crystalline state,

### 3.4. Overtones and combination bands

Besides the above fundamental frequencies, the infrared and Raman spectra of 4-methoxy pyridine N-oxide show some weaker bands which are interpreted as overtones and combination bands.

## 4. Thermodynamic properties

Ideal gas state thermodynamic functions of 4-methoxy pyridine N-oxide were determined at several temperatures between 273.15 and 1500° K using the fundamental frequencies given in table 2 and the following structural parameters and relative atomic masses :

$$\text{C-C} = 1.397 \text{ \AA}, \text{C-H} = 1.084 \text{ \AA}, \text{N-O} = 1.37 \text{ \AA}, \angle \text{CCC} = \angle \text{CNC} = \angle \text{CCH} = \angle \text{CNO} = \angle \text{COC} = 120^\circ.$$

For  $\text{OCH}_3$  group  $\text{-C-H} = 1.0936 \text{ \AA}$ ,  $\text{C-O} = 1.426 \text{ \AA}$ , and all angles are tetrahedral.

$$\text{H} = 1.0079, \text{C} = 12.011, \text{O} = 16.0, \text{N} = 14.01 \text{ amu.}$$

The rotational constants and the reduced moment of inertia of the methyl group, as calculated from the structure defined above, were found to be  $A = 0.14860 \text{ cm}^{-1}$ ,  $B = 0.03347 \text{ cm}^{-1}$ ,  $C = 0.02746 \text{ cm}^{-1}$  and  $I_m = 5.2668 \times 10^{-40} \text{ gm cm}^2$ . The thermodynamic functions were calculated by assuming a rigid rotor, harmonic oscillator approximation and free internal rotation of the methyl group.

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