Studies on 2-Aminopyridine Molecule by FTIR and Laser Raman Spectroscopy

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Laser Raman and FTIR spectra of 2-aminopyridine were recorded in the range of 4000–100 cm⁻¹ and 4000–500 cm⁻¹, respectively. Vibrational assignments have been made for many observed frequencies on the basis of C_S point group symmetry, group frequency consideration as well as comparison with accepted assignments for certain vibrational modes in other compounds with structural similarities and normal coordinate analysis. The potential energy distributions were also obtained. The results are briefly discussed.

INTRODUCTION

2-Aminopyridine is widely used in pharmacological and medicinal applications, such as anaesthetic agents and drugs for certain brain diseases. In addition to these applications, it is immensely used in analytical chemistry as a reagent. Inspite of these physiological applications and needs for its qualitative and quantitative characterisation in aqueous solutions, its vibrational assignments have not been thoroughly investigated. Sasaki[1] reported infrared and Raman spectra in the range 300–50 cm⁻¹ for charge transfer complex between aminopyridine and halogens. Earlier to this work Kydd[2] studied infrared vapour phase spectra of aminopyridines between 600 and 50 cm⁻¹ to study the amino inversion vibrations. Raman spectra has also been studied in aqueous solutions[3]. A literature survey shows that a complete study of infrared and Raman spectra of the compound have not been studied so far. Therefore the present investigation aims to give complete vibrational assignments of 2-aminopyridine through laser Raman and FTIR spectra.

EXPERIMENTAL

2-Aminopyridine molecule was obtained from M/s Sigma Chemical Company, USA in solid form and used as such without further purification (Fig. 1). The laser Raman spectra were recorded using the 488 nm line of Ar⁺ for excitation

(40 watts) in the region 4000–100 cm^{-1} on a Cary Model 82 grating spectrophotometer and signals were fed to a computer for storage, display, plotting and processing. The Fourier transform infrared spectrum in KBr disc was recorded using a Bruker IFS 85 spectrophotometer in the range 4000–500 cm^{-1}. The wavenumbers for all sharp bands are accurate to ± 1 cm^{-1}.
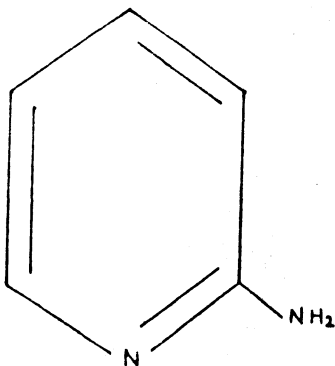

Fig. 1.   Structure of 2-Aminopyridine.

Normal Coordinate Analysis

Wilson's[4] F-G matrix method was used for the normal coordinate calculations. The molecule under investigation possesses C_S symmetry assuming NH_2 group as a single mass point. This leads to two types of vibrations and they are distributed as

$$\Gamma = 19a' \text{ (planar)} + 8a'' \text{ (non-planar)}$$

All the vibrations are active in both the infrared and Raman. Apart from these 27 vibrations there are 6 NH_2 group vibrations. The structural parameters employed in the present work are taken from Sutton's table[5]. The normal coordinate calculations were performed using the modified programme given by Mink et al[6]. Internal coordinates for the out-of-plane bending vibrations are defined as recommended by IUPAC. The general quadratic valence force field is adopted for both in-plane and out-of-plane bending vibrations.

The initial set of force constants were taken from similar pyridine deriva-tives[7–9]. This set of force constants was subsequently refined by keeping few interaction constants fixed throughout the refinement process so that only 21 of the 27 force constants were refined.

The final set of force constants are presented in Table-1 together with the initial values. The potential energy distribution (PED) obtained using the final set of force constants is given in Table-2 (contributions below 10% are not shown). Table 2 also contains observed and calculated frequencies along with their relative intensities.

TABLE-1

INITIAL AND FINAL SET OF FORCE CONSTANTS OF 2-AMINOPYRIDINE

(in units of mdyne $Å^{-1}$, mdyne rad^{-1} and mdyne $Å^{-1}$ rad^{-2})

Type of constants		Parameters	Coordinates involved	Initial values	Final values
Diagonal constants	Stretching	f_D	C=C	9.372	9.867
		f_d	C—C	5.130	2.691
		f_R	C—H	4.500	4.512
		f_r	C—N	5.130	4.508
		f_t	C=N	13.300	13.674
	Bend	f_α	CCC	0.540	0.567
		f_β	CCC	0.540	0.540
		f_v	HCC	0.310	0.271
		f_θ	HCN	0.350	0.212
		f_δ	CCN	0.315	0.308
		f_ϕ	CNC	0.262	0.217
Interaction constants	stretch-stretch	f_{Dd}	CC CC	0.101	0.101
		f_{RD}	HC CC	0.190	0.105
		f_{Rd}	HC CC	0.190	0.190
		f_{dt}	CC CN	0.298	0.142
		f_{Dr}	CC CN	0.9126	0.9126
		f_{rt}	CN NC	0.810	0.910
	stretch-bend	f_{Rv}	HC CCH	0.255	0.255
		f_{dv}	CC CCH	0.8127	0.409
		$f_{D\beta}$	CC CCC	0.360	0.215
		$f_{d\phi}$	CC CNC	0.425	0.302
		$f_{d\delta}$	CC NCC	0.3141	0.286
	bend-bend	$f_{\alpha\alpha}$	CCC CCC	0.112	0.112
		f_{vv}	HCC CCH	0.410	0.359
		$f_{\phi\alpha}$	CNC CCC	0.0913	0.189
		$f_{\alpha\delta}$	CCC CCN	0.091	0.091
		$f_{\beta v}$	HCC CCC	0.084	0.009

The general agreements between the calculated and observed frequencies for both in-plane and out-of-plane vibrations are good.

RESULTS AND DISCUSSION

The observed frequencies of 2–aminopyridine along with their relative intensities and probable assignments are presented in Table-2. The observed frequen-

cies are explained on the basis of C_S point group symmetry. Assignments have been made on the basis of relative intensities and normal coordinate analysis. In addition to the above, the assignments of the spectra have also been made by analogy with substituted pyridine and benzene derivatives[8, 9].

TABLE-2

OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION FOR 2-AMINOPYRIDINE

Species	Observed frequency and Intesity		Calculated Frequency	Assignments/(PED, %)
	FTIR	Laser Raman		
	3928 w			$(2 \times 1440 + 1040)$
	3900 w			$(2 \times 1278 + 1330)$
	3801 w			$(2 \times 1330 + 1138)$
	3706 w			$(2 \times 1330 + 1040)$
	3683 w			$(2 \times 1330 + 1020)$
	3631 w			$(3010 + 621)$
	3561 m			N—H asymm. stretching in NH_2 group
	3444 s			N—H sym. stretching in NH_2 group
	3314 w			$(2 \times 1020 + 1278)$
	3230 w			$(2 \times 1020 + 1175)$
a′	3167 m	3180 m	3172	C—H stretching (97)
a′	3150 w		3144	C—H stretching (89)
a′	3062 m	3073 w	3064	C—H stretching (91)
a′	3010 w		3021	C—H stretching (85)
	2866 w			(2×1440)
	2755 w			$(1489 + 1278)$
	2225 w			$(1175 + 1040)$
	1954 w			$(2 \times 1559 - 1175)$
	1829 w			$(2 \times 1559 - 1278)$
a′	1628 s	1635 m	1632	C=C stretching (86)
	1599 w	1594 w		NH_2 scissoring
a′	1559 s		1555	C=C stretching (92)
a′	1489 s	1489 ms	1479	C=N stretching (84)
a′	1440 vs		1433	C—C stretching (88)
a′		1374 m	1370	C—C stretching (84)
a′	1330 m	1320 m	1308	C—NH_2 stretching (89)
a′	1278 s		1279	C—N Stretching (98)
a′	1175 w	1163 w	1164	C—H in-plane bending (99)
a′	1138 vs		1133	C—H in-plane bending (82)
a′		1076 w	1068	C—H in-plane bending (72)
a′	1040 vs		1026	C—H in-plane bending (68)

Species	Observed frequency and Intesity		Calculated Frequency	Assignments/(PED, %)
	FTIR	Laser Raman		
a′	1020 w	1018 m	1005	CCC in-plane bending (64)
a″	987 vs		974	C—H out-of-plane bending (81)
a″	950 w		952	C—H out-of-plane bending (86)
a″		881 vs	870	C—H out-of-plane bending (75)
a″	864 w		855	C—H out-of-plane bending (68)
	810 w	807 s		NH_2 wagging
	767 vs			NH_2 twisting
a″	738 vs		730	CCC out-of-plane bending (89)
a″	655 s	661 w	640	CCC out-of-plane bending (79)
a′	623 s		619	CCC in-plane bending (55)
a′	540 s	547 m	532	CCC in-plane bending (66)
a′		440 w	428	C—NH_2 in-plane bending (61)
a″		398 w	390	CCC out-of-plane bending (71)
a″		236 w	226	C—NH_2 out-of-plane bending (54)
		200 w		NH_2 torsion
		109 vs		Lattice vibration

vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Ring vibrations: The ring stretching vibrations are very much prominent in the spectrum of pyridine and its derivatives and are highly characteristic of the aromatic ring itself. The benzene doubly degenerate vibrations e_{2g} (1596 cm^{-1}) and e_{1u} (1485 cm^{-1}) consist of lateral dilation and contraction of the ring, produced mainly by stretching and compressing of the bonds. On removal of the degeneracy, the components of this vibration will appear separately, since it involves both stretching and bending of the carbon bonds. Under reduced symmetry the bands at 1628 and 1559 cm^{-1} are assigned to C=C stretching modes and bands at 1440 and 1374 cm^{-1} to C—C stretching modes in the present work.

The in-plane carbon bending vibrations are derived from non-degenerate b_{1u} (1010 cm^{-1}) and degenerate e_{2g} (606 cm^{-1}) modes of benzene. The non-degenerate b_{1u} (1010 cm^{-1}) frequency under C_S symmetry has been observed at 1020 cm^{-1} in the present work. The degenerate e_{2g} (606 cm^{-1}) vibration splits into two non-totally symmetric components and the bands are observed at 623 and 540 cm^{-1} in 2-aminopyridine molecule.

The carbon out-of-plane bending vibrations are defined with reference to the non-degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2g} (404 cm^{-1}) modes of benzene. The non-degenerate b_{2g} (703 cm^{-1}) frequency under C_S symmetry is observed at 738 and 665 cm^{-1} The degenerate e_{2g} (404 cm^{-1}) frequency is observed at 398 cm^{-1} in the present work. The above results are in good agreement with the literature values[2].

Two more ring stretching vibrations at 1489 and 1278 cm^{-1} are assigned to

C=N and C—N stretching vibrations respectively. These results agree very well with the literature values[10, 11].

C—H Vibrations: The 2-aminopyridine gives rise to four C—H stretchings, four C—H in-plane bending and four C—H out-of-plane bending vibrations. The aromatic structure shows the presence of the C—H stretching vibrations in the region 3100–3000 cm^{-1}, C—H in-plane bending vibrations in the region 1100–1000 cm^{-1} and C—H out-of-plane bending vibrations in the region 980–800 cm^{-1}, which permits ready identifications for this structure. These bands not affected by the nature of the substituents in benzene derivatives. The C—H stretching frequencies arise from the modes a_{1g} (3062 cm^{-1}), e_{2g} (3047 cm^{-1}), b_{1u} (3060 cm^{-1}) and e_{1u} (3080 cm^{-1}). The bands are observed at 3167, 3150, 3062 and 3010 cm^{-1} in 2-aminopyridine have been assigned to C—H stretching vibrations. These assignments are in good agreement with the literature values[12].

Studies of the benzene spectra show that there appear two degenerate e_{2g} (1178 cm^{-1}) and e_{1u} (1037 cm^{-1}) and two non-degenerate b_{2u} (1152 cm^{-1}) and a_{2g} (1340 cm^{-1}) frequencies involving C—H in-plane bending vibrations. In the present work these modes yield four planar bending vibrations involving the hydrogen atom. The frequencies 1175, 1138, 1076 and 1040 cm^{-1} in 2-amino-pyridine are assigned to C—H in-plane bending vibrations.

The C—H out-of-plane bending results from b_{2g} (985 cm^{-1}), e_{2u} (970 cm^{-1}), e_{1g} (850 cm^{-1}) and a_{2u} (671 cm^{-1}) modes of benzene and they are expected to occur in the region 1000–600 cm^{-1}. Hence, the bands at 987, 950, 881 and 864 cm^{-1} are assigned to C—H out-of-plane bending vibrations.

C—NH$_2$ Vibrations: Carmona *et al.*[3] assigned C—NH$_2$ stretching vibrations in the region 1340–1250 cm^{-1} in all the primary aromatic amines. The intensity of the bands appears to be rather variable and probably it is associated with some substitutions, or other structural features. Here in the present work, the band observed at 1330 cm^{-1} is assigned to C—NH$_2$ stretching vibration.

The C—NH$_2$ in-plane and out-of-plane bending vibrations are assigned at 440 and 236 cm^{-1} in the laser Raman spectrum respectively. The above results agree quite well with the results of Padhya *et al.*[13]

Amino group vibrations: The molecule under consideration possesses only one NH$_2$ group and hence one expects one symmetric and one asymmetric N—H stretching vibrations in the amino group. In all the primary aromatic amines the NH stretching frequencies occur[14] in the region 3500–3000 cm^{-1}. Hence, the bands at 3561 and 3444 cm^{-1} are assigned to N—H asymmetric and symmetric stretching vibrations, respectively. These observation agree well with the earlier work[15].

The characteristic frequency of the NH$_2$ scissoring vibration is usually located[16] in the region 1650–1600 cm^{-1}. On this basis, the NH$_2$ scissoring mode is assigned at 1599 cm^{-1} in the present work. The wagging NH$_2$ mode is assigned to the band at 810 cm^{-1}, the twisting mode is assigned to 767 cm^{-1} and the NH$_2$ torsion mode is identified at 200 cm^{-1} in the present work. The above results agree well with the reported work[17].

The general agreement between the calculated and observed frequencies for both in-plane and out-of-plane bending vibrations are reasonable.

Potential Energy Distribution

To check whether the chosen set of vibrational frequencies contribute maximum to the potential energy associated with the normal coordiantes of the molecule, the potential energy distribution (PED) has been calculated using the relation:

$$PED = F_{ii} L_{ia}^2 / \lambda_a$$

PED is the contribution of ith symmetry coordinate to the potential energy of the vibration whose frequency is v_a. F_{ii} = the force constant, $L_{ia} = L$ matrix elements and $\lambda_a = 4\pi^2 c^2 v^2 a$.

Thus complete vibrational assignments and analysis of 2–aminopyridine molecule are available for the first time in the present work.

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