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FTIR and FT-Raman Spectral Investigations on 4-Aminoquinaldine and 5-Aminoquinoline

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The FTIR spectra of 4-aminoquinaldine and 5-aminoquinoline were recorded in solid phase on a Bruker IFS 66V spectrometer in the region 4000–400 cm^{-1} . The FT-Raman spectra of these compounds were also recorded in the same instrument with a FRA 106 Raman module. The molecules under investigation are considered to have a C_S point group by assuming the $-\text{NH}_2$ and $-\text{CH}_3$ groups as point masses. All the vibrations are both IR and Raman active. The simple general valence force field (SGVFF) is adopted for both inplane and out of plane vibrations. All the frequencies are assigned in terms of fundamentals, overtones and combinations. The general agreements between the observed and calculated frequencies are satisfactory.

Key Words: FTIR, FT-Raman, normal coordinate analysis (NCA), potential energy distribution (PED), and simple general valence force field (SGVFF).

Introduction

4-Aminoquinaldine (AMQ) (4-amino-2-methylquinoline; $\text{C}_{10}\text{H}_{10}\text{N}_2$) and 5-aminoquinoline (AQ) ($\text{C}_9\text{H}_8\text{N}_2$) are derivatives of quinoline and resemble naphthalene. These 2 molecules are similar in geometrical structure. It consists of 1 benzene ring and 1 pyridine ring fused together. The geometrical structure of 4-aminoquinaldine and 5-aminoquinoline are shown in Figures. 1 and 2. Quinoline is present in coal tar and bone oil. It is a biologically and pharmaceutically important molecule. Quinoline dyes are present in photographic sensitizers¹. Quinoline yellow is used as textile dye for wool, nylon and silk as well as for dyeing paper. Printing ink contains quinoline yellow barium salt. It is also used as a colouring agent for food, drugs and in all cosmetics, except those that are used near the eyes. Quinoline yellow is soluble in spirit and hence it is widely used in lacquers, polystyrene, polycarbonates, polyamides and acrylic resins. Quinoline derivatives show promising antiphlogistic activity in rats², are bacterial inhibitors³ and are precursors to a number of antimalarial and cancer drugs⁴. Derivatives of aminoquinoline are used as inhibitors of the human immunodeficiency virus (HIV)⁵. Quinoline and isoquinoline are also active against staphylococcus, epidermis,

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neisseria and gonorrhoea⁶. The 4-Aminoquinoline nucleus of chloroquine is a drug linked to purines, adenine and guanine by a trimethylene group. Quinaldine is commonly used as an anaesthetic while handling fish. Quinoline derivatives are also used as a local anaesthetic⁷.

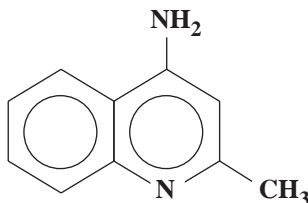


Figure 1. Structure of 4-aminoquinoline.

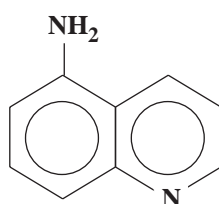


Figure 2. Structure of 5-aminoquinoline.

Kulkarni Jatkar⁸ recorded the Raman spectra of α - and β -picolines, quinoline, quinaldine and isoquinoline and also carried out preliminary studies. Picard et al.⁹ recorded the vapour phase ultraviolet absorption spectra of quinoline and quinaldine. Samuel et al.¹⁰ studied the ultraviolet absorption spectra of 7 monochloroquinolines and the 2-, 3-, 4-, 6-, 7- and 8- mono methylquinoline in 95% ethanol and 10% ethanol. The changes in intensity and the shifts in wavelength of the maxima of the monochloroquinolines were correlated with the molecular dimensions. The shifts in the wavelengths for the methylquinolines could not be associated with the dimensions of methylquinolines. Possible reasons, based on electron densities at the nitrogen atom, as influenced by the various substituents are given for the order of basis strength.

The infrared and Raman spectra of quinoline were discussed in detail by Chiorboli and Bertoluzza¹¹. Shashidhar et al.¹² recorded the absorption spectra of 2-, 4-, 6- and 7-methylquinolines in vapour phase in the near ultraviolet region on a medium quartz spectrograph.

Shashidhar et al.¹³ recorded and analysed the near ultraviolet absorption spectra of 4 methyl substituted quinolines, namely 2-, 4-, 6- and 7-methylquinolines in the vapour state. The spectra of these molecules were recorded in the region 3200-2800 Å. Shashidhar et al. also analysed the Raman and IR data of these molecules. The most intense bands at the longest wavelength side was the (0,0) band and the suggested assignments for 2-, 4-, 6- and 7-methylquinolines were given respectively. No ground state vibrations are recorded in these molecules. The spectra were analysed in association with the Raman and IR data for all these molecules. These molecules belong to C_S point group symmetry.

Robert et al.¹⁴ measured spin-lattice relaxation times, T_1 , of quinoline, quinaldine, isoquinoline, lepidine, 6-methylquinoline and 7-methylquinoline and of 2 quinoline related compounds having 2 nitrogen atoms in 1 fused 6 membered skeleton (quinazoline, quinoxaline) in a pure liquid form as a function of temperature using a ¹³C NMR spectrometer. They plotted the natural log of T_1 as a function of inverse temperature and found that for isoquinoline, 7-methylquinoline, quinazoline and quinoxaline there was 1 activation energy while there were 2 activation energies for quinoline, quinaldine and lepidine. For all

these compounds the higher temperature relaxation corresponds to an energy barrier less than $20.5 \text{ kJ mole}^{-1}$ and for low temperature processes an energy barrier close to 30 kJ mole^{-1} . They have also plotted the saturated specific heat, C_S , as a function of absolute temperature for quinoline and isoquinoline. These 2 graphs were similar and suggested the existence of dynamical transition in the liquid state at a given temperature similar to super-cooled liquids.

The temperature dependence of vertically (incident) and horizontally (scattered) depolarised spectra of benzene and quinoline has been investigated by Eloutassi et al.¹⁵ They also studied the anomalous effects in the temperature dependence of the depolarised Rayleigh spectra of benzene and quinoline. Hong-Cheu et al.¹⁶ reported the synthesis of heterocyclic liquid crystalline molecules through fusing aromatic rings containing 3,7-disubstituted quinoline with one of the widest smectic C phases. Their naphthalene analogues are compared. The nitrogen atom in a quinoline system introduces attractive forces to aid the formation of the tilted smectic C phase, and the flexible chain length also influences the tilted smectic C phase effectively.

In the present investigation, the FTIR and FT-Raman spectra of 4-aminoquinoline (AMQ) and 5-aminoquinoline (AQ) are recorded and analysed to obtain complete, reliable and accurate vibrational assignments through normal coordinate analysis.

Experimental

The compounds 4-aminoquinoline (AMQ) and 5-aminoquinoline (AQ) were obtained in solid form Aldrich chemicals, USA, with stated purity (AMQ 98% and AQ 97%) and used as such without further purification to record FTIR and FTR spectra. The FTIR spectra of these compounds were recorded in solid phase in the region between 4000 and 400 cm^{-1} using a Bruker IFS 66V spectrometer, with a scanning speed of $30 \text{ cm}^{-1} \text{ min}^{-1}$ and a spectral width 2.0 cm^{-1} . The frequencies for all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$. The FT-Raman spectra were also recorded in the same instrument with a FRA 106 Raman module equipped with Nd:YAG laser source operating at $1.064 \mu\text{m}$ line with 200 mW power and a spectral resolution of $\pm 2 \text{ cm}^{-1}$. The FTIR and FT-Raman spectra of AMQ are shown in Figures. 3 and 4 while for AQ are given in Figures. 5 and 6.

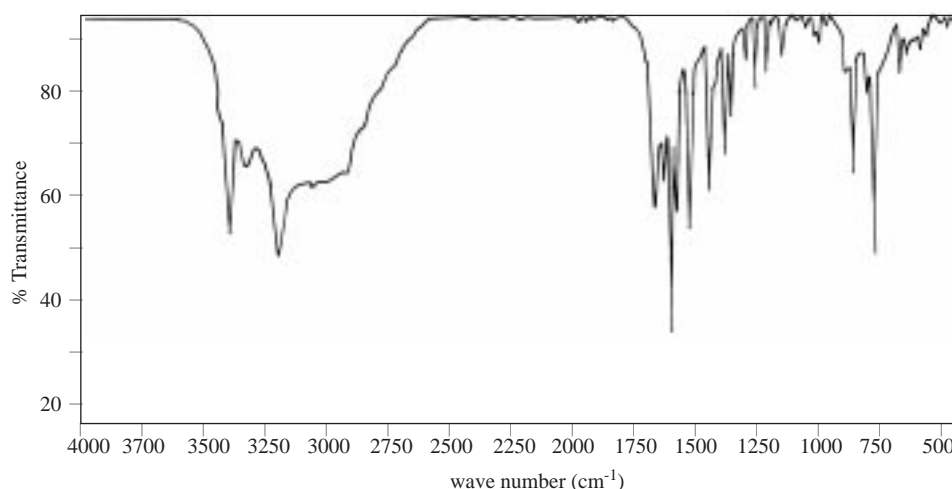


Figure 3. FTIR spectrum of 4-aminoquinoline.

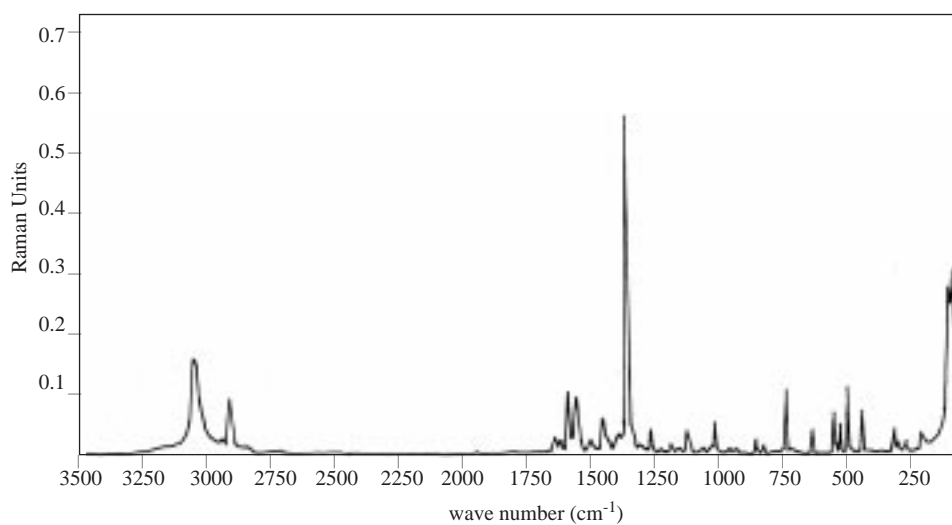


Figure 4. FT-Raman spectrum of 4-aminoquinoline.

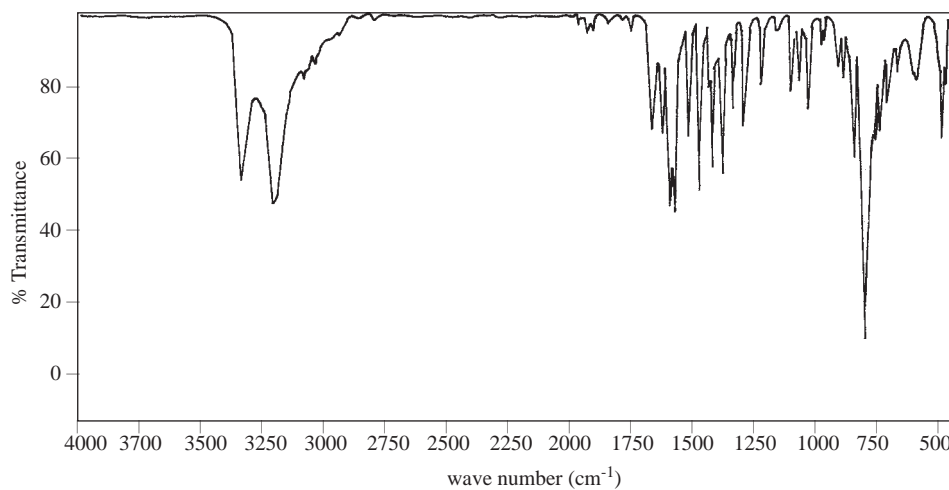


Figure 5. FTIR spectrum of 5-aminoquinoline.

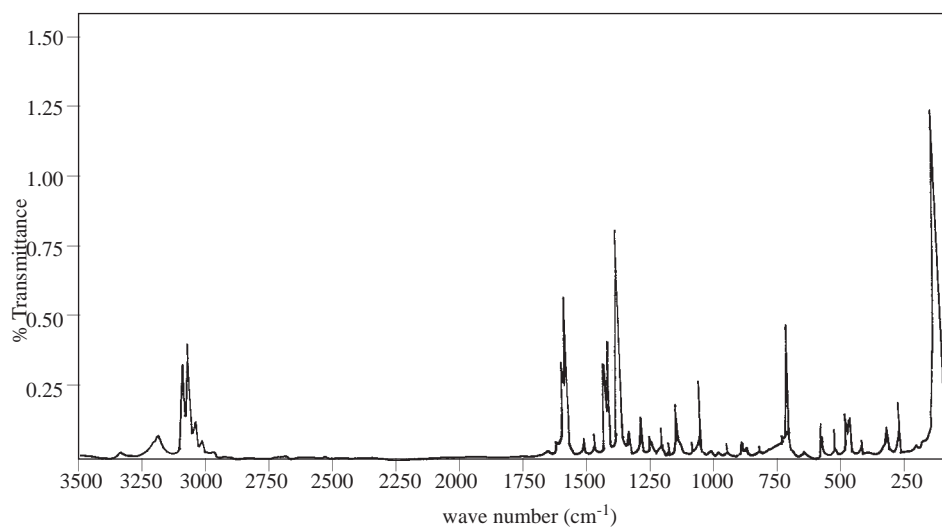


Figure 6. FT-Raman spectrum of 5-aminoquinoline.

Normal coordinate analysis

The compounds under investigation possess C_S point group symmetry by assuming $-NH_2$ and $-CH_3$ groups as point masses and lie in the plane of the molecule. C_S symmetry leads to 2 types of vibrations, namely a' (inplane) and a'' (out of plane), that are distributed into $\Gamma_{vib} = 43a' + 17a''$ in the case of AMQ and the 51 fundamental vibrations of AQ are distributed as $\Gamma_{vib} = 37a' + 14a''$. All the vibrations are active in both IR and Raman. The normal coordinate analysis program of Fuhrer et al.¹⁷ was used after suitable modification to calculate vibrational frequencies and potential energy distribution (PED). This program follows the Wilson's FG matrix method¹⁸⁻²⁰ of vibrational analysis in which the normal coordinates are defined with respect to a set of molecular coordinates. The structural parameters necessary for the compound are taken from the Sutton table²¹ and similar molecules. The simplified general valence force field (SGVFF) was adopted for both inplane and out of plane vibrations and the force constants were refined by the damped least square technique. The potential energy distributions are calculated using the final set of force constants. The SGVFF is shown to be very effective in normal coordinate analysis because the valence force constants can be transferred between the structurally related molecules, which is very useful in the NCA of large polyatomic molecules. A salient feature of NCA and force field calculations has been that it could reproduce the frequencies associated with the skeletal rings as well as the $-NH_2$ and $-CH_3$ groups within a reasonable limit ($\pm 10\text{ cm}^{-1}$) with an acceptable potential energy distribution. The common initial and final set of force constants used for both the molecules are given in Table 1.

Results and Discussion

All the wave numbers are assigned in terms of fundamentals, overtones and combination bands. The observed wave numbers of AMQ and AQ along with their relative intensities and probable assignments, calculated wave numbers and potential energy distribution are presented in Tables 2 and 3. The wave numbers were assigned on the basis of earlier assignments on naphthalene and normal coordinate analysis by assuming C_S symmetry for these molecules.

Carbon vibrations

In benzene, bands between 1400 and 1650 cm^{-1} have been assigned to C-C stretching modes. It has 2 double degenerate modes, 1596 cm^{-1} (e_{2g}) and 1485 cm^{-1} (e_{1u}), and 2 non-degenerate modes, 1310 cm^{-1} (b_{2u}) and 995 cm^{-1} (a_{1g}). In AMQ the observed stretching bands appeared at 1344 , 1371 , 1415 , 1438 and 1470 cm^{-1} and in AQ the bands seen at 1326 , 1366 , 1412 , 1425 and 1465 cm^{-1} have been assigned to C-C stretching vibrations. The bands occurring at 1570 , 1593 , 1617 and 1659 cm^{-1} in AMQ and 1586 , 1658 , 1740 and 1770 cm^{-1} in AQ correspond to C=C stretching modes. The band observed at 1617 cm^{-1} in AMQ is doubly assigned to C=C stretching and NH_2 deformation modes.

The inplane carbon bending vibrations are obtained from the non-degenerate 1010 cm^{-1} (b_{1u}) and 606 cm^{-1} (e_{2g}) modes of benzene. The degenerate e_{2g} modes are observed at 509 , 538 , 563 and 619 cm^{-1} in AMQ and 577 and 462 cm^{-1} in AQ. Carbon out of plane bending vibrations are defined with reference to the non-degenerate 707 cm^{-1} (b_{2g}) and degenerate 404 cm^{-1} (e_{2u}) modes of benzene. In the present work, the carbon out of plane bending vibrations under C_S symmetry are assigned to the bands at 449 , 648 and 759 cm^{-1} and 478 , 488 , 527 , 570 and 700 cm^{-1} in AMQ and AQ respectively. The bands observed at 648

and 759 cm^{-1} in AMQ are also doubly assigned to NH_2 wagging and CH_3 wagging respectively. The results are in good agreement with literature values.^{22,23}

Table 1. The common initial and final set of force constants used for 4-aminoquinoline and 5-aminoquinoline (units: stretching; mdyne.A^{-1} , bending; mdyne.A.rad^{-2} and stretching-bending; mdyne.rad^{-1}).

Types of force constants	Parameter	Coordinates involved	Initial	Final	
Diagonal constants	Stretching	f_D	C-H	4.500	4.489
		f_E	C-H	4.510	4.524
		f_d	C-C	2.850	2.816
		f_e	C-C	5.047	5.086
		f_p	C-N	5.224	5.281
		f_q	N-H	5.846	5.647
		f_R	N=C	10.510	9.921
Diagonal constants	Bending	f_α	HCC	0.310	0.216
		f_β	CCC	0.543	0.358
		f_γ	CNC	0.262	0.274
		f_δ	NCC	0.315	0.308
		f_θ	CCN	0.315	0.198
		f_ψ	CCN	0.262	0.212
		f_ξ	HNH	0.364	0.216
Interaction constants	Stretching-Stretching	f_{Dd}	CH CC	0.190	0.211
		f_{Ee}	CH CC	0.190	0.168
		f_{dd}	CC CC	0.062	0.054
		f_{de}	CC CC	0.062	0.052
		f_{dR}	CC N=C	0.800	0.587
		f_{ds}	CC CN	0.913	0.894
		f_{sR}	CN N=C	0.658	0.598
		f_{dp}	CC CN	0.903	0.873
Interaction constants	Stretching-Bending	$f_{D\alpha}$	CH HCC	0.255	0.264
		$f_{d\alpha}$	CC HCC	0.813	0.798
		$f_{d\beta}$	CC CCC	0.360	0.362
		$f_{s\gamma}$	CN CNC	0.102	0.099
		$f_{R\delta}$	N=C NCC	0.092	0.092
		$f_{e\theta}$	CC CCN	0.486	0.474
		$f_{e\psi}$	CC HCH	0.124	0.124
		$f_{p\psi}$	CN CCN	0.121	0.119
Interaction constants	Bending-Bending	$f_{p\xi}$	CN HNH	0.044	0.044
		$f_{\alpha\alpha}$	HCC HCC	0.041	0.041
		$f_{\alpha\beta}$	HCC CCC	0.084	0.062
		$f_{\beta\beta}$	CCC CCC	0.089	0.089
		$f_{\gamma\delta}$	CNC NCC	0.107	0.091
		$f_{\gamma\theta}$	CNC CCN	0.063	0.058
		$f_{\beta\psi}$	CCC CCN	0.091	0.090

Ring breathing

In benzene the C–C–C ring breathing (a_{1g}) and C–C–C trigonal bending (b_{1u}) exhibit their characteristic frequency at 995 and 1010 cm^{-1} respectively. In the present study the corresponding C–C ring breathing and trigonal bending have been assigned to the bands at 783 and 1032 cm^{-1} in AMQ and 827 and 1013 cm^{-1} in AQ respectively. These assignments agree well with Mohan *et al.*²⁴

C–H Vibrations

The AQ molecule gives rise to 6 C–H stretching modes, whereas AMQ provides 7 C–H stretching modes, 5 from the ring and 2 from the methyl group. The aromatic structure shows the presence of C–H stretching vibrations around 3000 cm^{-1} . These stretching frequencies arise from the modes of (a_{1g}) 3062 cm^{-1} , (e_{2g}) 3047 cm^{-1} , (b_{1u}) 3060 cm^{-1} and (e_{1u}) 3080 cm^{-1} . In AQ these modes are observed at 2916, 2971, 3008, 3033, 3067 and 3080 cm^{-1} and in AMQ these are identified at 3060, 3037, 2783, 2722 and 2650 cm^{-1} . In general, the methyl group has shown 2 characteristic C–H stretching vibrations at around 2962 and 2872 cm^{-1} . In AMQ these bands are observed at 2917 cm^{-1} for asymmetric stretching and 2873 cm^{-1} for symmetric stretching, which are in good agreement with literature values.²⁵

In benzene-like molecules C–H inplane bending vibrations are observed in the region 1000–1300 cm^{-1} and are usually weak. The C–H out of plane bending modes of usually medium intensity arise in the region 600–900 cm^{-1} .²⁵ In the present case the bands observed at 1082, 1133, 1150, 1172, 1207 and 1250 cm^{-1} in AQ and 1129, 1166, 1194, 1241 and 1280 cm^{-1} in AMQ are assigned to the C–H inplane bending vibrations, while 1241 and 1280 cm^{-1} in AMQ are doubly assigned. The C–H out of plane bending modes for AMQ and AQ are also assigned within the said region and are presented in Tables 2 and 3.

C=N, C–N Vibrations

The assignment of C=N and C–N stretching frequencies is a difficult task, since there are problems in identifying these frequencies from other vibrations. In AQ the medium bands at 1507 and 1281 cm^{-1} are assigned to C=N and C–N stretching modes respectively. These assignments are in good agreement with earlier works.^{22,26} In AMQ these modes are observed in IR at 1518 and 1280 cm^{-1} respectively.

CNC, NCC Bending modes

The CNC inplane bending vibration is attributed to the band observed at 325 cm^{-1} in AMQ. The results of normal coordinate analysis are used to assign the CNC and CCN inplane bending vibration in AQ at 337 and 430 cm^{-1} respectively. In AMQ the CCN inplane bending mode is observed in IR at 404 cm^{-1} . The CNC and CCN out of plane bending modes of these molecules are presented in Tables 2 and 3.

Table 2. Observed and calculated wave numbers and potential energy distribution (PED) for 4-aminoquinaldine.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
		91s		Lattice mode	
a''		105m	111	CNC out of plane bending	$36\eta_{CNC} + 26\eta_{CCC} + 20\eta_{CH}$
a''		220vw	231	CCN out of plane bending/ C-NH ₂ out of plane bending	$44\eta_{CCN} + 41\eta_{C-NH_2}$
a''		280vw	296	C-CH ₃ out of plane bending	$48\eta_{C-CH_3} + 20\eta_{CCC}$
a'		325vw	328	C-CH ₃ inplane bending/ CNC inplane bending	$47\beta_{C-CH_3} + 41\beta_{CNC}$
a''			378*	CCC out of plane bending	
a'	404vw		410	C-NH ₂ inplane bending/ CCN inplane bending	$39\beta_{C-NH_2} + 42\beta_{CCN} + 14\beta_{CH}$
a'	449w	450w	458	NCC inplane bending/ CCC out of plane bending	$51\beta_{NCC} + 19\beta_{CH_3} + 24\beta_{CH}$ $49\eta_{CCC} + 19\eta_{CNC} + 21\eta_{CH}$
a'		509w	511	CCC inplane bending	$56\beta_{CCC} + 21\beta_{CCN}$
a'	538vw	539vw	544	CCC inplane bending	$48\beta_{CCC} + 18\beta_{CNC}$
a'	563w	564w	569	CCC inplane bending	$50\beta_{CCC} + 11\beta_{NH_2}$
a'	619w		627	CCC inplane bending	$59\beta_{CCC} + 20\beta_{CH_3}$
a''	648w	649vw	658	NH ₂ wagging/ CCC out of plane bending	$51\omega_{NH_2} + 31\eta_{CCC} + 14\tau_{NH_2}$
a''	759vs	752w	759	CH ₃ wagging/ CCC out of plane bending	$48\omega_{CH_3} + 24\eta_{CCC} + 18\tau_{CH_3}$
a'	783m		788	CCC Ring breathing	$86\beta_{CCC}$
a''			810*	CCC out of plane bending	
a''	845s	845vw	849	C-H out of plane bending	$54\eta_{CH} + 30\eta_{CH_3}$
a''	864w	872vw	871	C-H out of plane bending	$62\eta_{CH} + 21\eta_{NH_2}$
a''	949vw	959vw	955	C-H out of plane bending	$48\eta_{CH} + 16\eta_{NH_2} + 24\eta_{CH_3}$
a'	979w	983vw	985	C-NH ₂ stretching/ C-H out of plane bending	$70\nu_{C-NH_2} + 18\nu_{CH}$ $44\eta_{CH} + 28\eta_{CH_3} + 12\eta_{CNH_2}$
a''	1000vw		1002	C-H out of plane bending	$69\eta_{CH} + 14\eta_{CNH_2}$
a'	1032vw	1032w	1030	CCC Trigonal bending	$81\beta_{CCC}$
a'		1051vw		CH ₃ rocking	$64\rho_{CH_3} + 29\delta_{CH_3}$
a'	1067vw	1076vw	1081	NH ₂ rocking	$39\rho_{NH_2} + 22\rho_{CH_3} + 12\beta_{CH}$
a'	1129w	1137w	1135	C-H inplane bending	$62\beta_{CH} + 28\beta_{NH_2}$
a'	1166vw	1170vw	1170	C-H inplane bending	$66\beta_{CH} + 19\beta_{CH_3}$
a'	1194m	1199vw	1191	C-H inplane bending	$44\beta_{CH} + 18\beta_{NH_2} + 22\beta_{CH_3}$
a'	1241m	1243vw	1240	C-CH ₃ stretching/ C-H inplane bending	$56\nu_{CCH_3} + 24\beta_{CH} + 11\beta_{C-NH_2}$
a'	1280w	1279w	1285	C-N stretching/ C-H inplane bending	$81\nu_{C-N} + 16\beta_{CH}$ $64\beta_{CH} + 21\beta_{C-NH_2}$
a'	1344m		1345	C-C stretching	$88\nu_{C-C}$
a'	1371s	1366vs	1361	C-C stretching/ CH ₃ symmetric deformation	$74\nu_{C-C} + 11\nu_{CN}$
a'	1415w	1408vw	1415	C-C stretching	$69\nu_{C-C} + 21\nu_{C-N}$
a'	1438s		1445	C-C stretching	$79\nu_{C-C} + 12\nu_{CH}$
a'	1470vw	1464w	1468	C-C stretching/ CH ₃ asymmetric deformation	$81\nu_{C-C} + 10\nu_{CN}$ $41\delta_{CH_3} + 28\delta_{NH_2} + 18\beta_{CH}$
a'	1518s	1517vw	1527	C=N stretching/ CH ₃ asymmetric deformation	$79\nu_{C=N} + 12\nu_{CCH_3}$ $54\delta_{CH_3} + 38\delta_{NH_2}$
a'	1570s	1565m	1569	C=C stretching	$84\nu_{C=C}$

Table 2. Continue.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
a'	1593vs	1593m	1598	C=C stretching	88 $\nu_{C=C}$
a'	1617s	1619vw	1628	C=C stretching/ NH ₂ deformation	74 $\nu_{C=C}$ + 11 ν_{CN} 67 δ_{NH_2} + 28 δ_{CH_3}
a'	1659s	1649vw	1652	C=C stretching	89 $\nu_{C=C}$
	1815vw			864 + 949	
	1842vw			3203 – 1371	
	1900vw			2 x 949	
	1928vw			3399 – 1470	
	1962vw			2 x 979	
	2188vw			2122 – 538	
	2382vw			2917 – 538	
	2630w			1194 – 1438	
a'	2650w		2654	C–H stretching	90 ν_{C-H}
a'	2722w	2724vw	2726	C–H stretching	94 ν_{C-H}
a'	2783m		2781	C–H stretching	89 ν_{C-H}
a'	2873m		2876	C–H stretching	91 ν_{C-H}
a'	2917m	2920m	2929	C–H stretching	90 ν_{C-H}
a'		3037w	3042	C–H stretching	96 ν_{CH}
a'	3060m	3062m	3066	C–H stretching	99 ν_{C-H}
a'	3203s		3205	N–H symmetric stretching	94 ν_{N-H}
	3334m			619 + 2722	
a'	3399s		3389	N–H asymmetric stretching	94 ν_{N-H}

*Predicted from NCA, vs: very strong, s: strong, m: medium, w: weak, vw: very weak, ν : stretching, β : inplane bending, δ : deformation: η : out of plane bending, τ : twisting, ρ : rocking and ω : wagging.

C–NH₂, C–CH₃ Group vibrations

The bands observed at 975 cm⁻¹ in AQ and 979 cm⁻¹ in AMQ are assigned to C–NH₂ stretching vibrations. The C–NH₂ inplane and out of plane bending vibrations in AQ are assigned at 421 and 200 cm⁻¹ respectively. Similarly, in the case of AMQ these vibrations are identified at 404 and 220 cm⁻¹ respectively. The NH₂ rocking mode is normally expected at 1050 cm⁻¹ and is observed in the present IR spectrum at 1067 cm⁻¹ in AMQ and at 1050 cm⁻¹ in the case of AQ. The NH₂ out of plane wagging mode is found in the region 550-700 cm⁻¹ and is seen in the IR spectrum at 648 and 653 cm⁻¹ in AMQ and AQ respectively. The assignments mentioned above are in good agreement with Shukla et al.²⁷ The assignment of NH₂ deformation vibrations in AMQ and AQ are presented in Tables 2 and 3.

Shukla et al.²⁷ assigned the C–CH₃ stretching modes at 1208 and 1223 cm⁻¹ in toluene and o-xylene respectively. In AMQ it is observed at 1241 cm⁻¹. The modes observed at 325 and 280 cm⁻¹ are assigned to planar inplane bending and nonplanar out of plane bending vibrations of C–CH₃, which agree favourably with Prabakaran et al.²⁸ The other characteristic modes of CH₃ group vibrations such as deformation, wagging, methyl asymmetric and symmetric stretching are presented in Table 2.

Table 3. Observed and calculated wave numbers and potential energy distribution (PED) for 5-aminoquinoline.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
		83w		lattice mode	
		105vs		lattice mode	
		167vw		980 – 818	
a''		200vw	191	C-NH ₂ out of plane bending	47 η_{C-NH_2} + 31 η_{CH}
a''		267w	260	CNC out of plane bending	49 η_{CNC} + 28 η_{CH}
a'		311vw	302	CCC inplane bending	34 β_{CCC} + 31 β_{CH}
a'		318vw	311	CCC inplane bending	44 β_{CCC} + 21 β_{CCN}
a'			337*	CNC inplane bending	
a'	421w	418vw	409	C-NH ₂ inplane bending	48 β_{C-NH_2} + 26 β_{CH}
a'			430*	CCN inplane bending	
a'	462m	462w	469	CCC inplane bending	51 β_{CCC} + 38 β_{CNC} + 11 β_{CH}
a''	478m	474w	472	CCC out of plane bending	64 η_{CCC} + 12 η_{CNC}
a''		488vw	480	CCC out of plane bending	52 η_{CCC} + 14 η_{CCN} + 22 η_{CH}
a''		527vw	520	CCC out of plane bending	68 η_{CCC} + 18 η_{CNC}
a''	570w	567vw	556	CCC out of plane bending	44 η_{CCC} + 18 η_{CCN} + 20 η_{CH}
a'	577w	578vw	564	CCC inplane bending	41 β_{CCC} + 24 β_{NH} + 16 β_{CH}
a''	653w	648vw	639	NH ₂ wagging	49 ω_{NH_2} + 38 η_{CH}
a''	700m	708m	710	CCC out of plane bending	54 η_{CCC} + 34 η_{CNC}
a''	729m	735vw	739	C-H out of plane bending	41 η_{CH} + 30 η_{NH_2}
a''	750m		741	C-H out of plane bending	58 η_{CH} + 11 η_{NH_2}
a''	793vs		784	C-H out of plane bending	54 η_{CH} + 21 η_{CCC}
a'	827m	818vw	820	CCC ring breathing	81 β_{CCC}
a''	875w	868vw	859	C-H out of plane bending	52 η_{CH} + 18 η_{CCC}
a''	893w	889vw	875	C-H out of plane bending	49 η_{CH} + 29 η_{C-NH_2}
a''	950vw	949vw	939	C-H out of plane bending	54 η_{CH} + 24 η_{CCC}
		960vw		1281 – 311	
a'	975vw	980vw	976	C-NH ₂ stretching	64 ν_{C-NH_2} + 21 ν_{CH}
a'	1013m	1008vw	1010	CCC trigonal bending	85 β_{CCC}
a'	1050m	1052w	1041	NH ₂ rocking	51 ρ_{NH_2} + 38 β_{CH}
a'	1082m	1082vw	1074	C-H inplane bending	60 β_{CH} + 18 β_{CNC}
a'	1133vw		1125	C-H inplane bending	51 β_{CH} + 24 β_{C-NH_2}
a'	1150vw	1149w	1141	C-H inplane bending	64 β_{CH} + 11 β_{CCC}
a'		1172vw	1165	C-H inplane bending	48 β_{CH} + 12 β_{CCC}
a'	1207m	1206vw	1214	C-H inplane bending	55 β_{CH} + 24 β_{CCC}
a'		1250vw	1256	C-H inplane bending	54 β_{CH} + 21 β_{NCC}
a'	1281m	1283vw	1280	C-N stretching	90 ν_{C-N}
a'	1326m	1330vw	1338	C-C stretching	70 ν_{C-C} + 12 ν_{C-N}
a'	1366s	1367s	1359	C-C stretching	78 ν_{C-C} + 11 ν_{C-H}
a'	1412s	1411m	1405	C-C stretching	82 ν_{C-C} + 11 β_{CCC}
a'	1425m	1422w	1420	C-C stretching	84 ν_{C-C}
a'	1465s	1467vw	1458	C-C stretching	88 ν_{C-C}
a'	1507m	1509vw	1513	C=N stretching	81 $\nu_{C=N}$
		1574s	1568	1150 + 421	
a'	1586s	1587w	1581	C=C stretching	85 $\nu_{C=C}$
a'	1613m	1613vw	1613	NH ₂ deformation	94 δ_{NH_2}
a'	1658m		1651	C=C stretching	88 $\nu_{C=C}$
a'	1740vw		1734	C=C stretching	84 $\nu_{C=C}$ + 11 β_{CCC}

Table 3. Continue.

Species	Observed wave number		Calcd. Wave number	Assignments	% PED
	FTIR	FTR			
a'	1770vw		1761	C=C stretching	90 $\nu_{C=C}$
	1827vw			3033 - 1207	
	1898vw			2 x 950	
	1917vw			3332 - 1412	
	1950vw			1050 + 893	
	2272vw			2 x 1133	
	2420vw			2 x 1207	
	2783vw			1574 + 1207	
a'	2916vw		2909	C-H stretching	86 ν_{C-H}
a'	2971vw	2972vw	2971	C-H stretching	91 ν_{C-H}
a'		3008vw	3012	C-H stretching	94 ν_{C-H}
a'	3033w	3033vw	3029	C-H stretching	97 ν_{C-H}
a'		3067w	3061	C-H stretching	82 ν_{C-H}
a'	3080w	3080w	3071	C-H stretching	88 ν_{C-H}
		3190vw		2 x 1587	
a'	3203s		3210	N-H symmetric stretching	91 ν_{NH2}
a'	3332m		3331	N-H asymmetric stretching	94 ν_{NH2}

*Predicted from normal coordinate analysis, vs: very strong, s: strong, m: medium, w: weak, vw: very weak, ν : stretching, β : inplane bending, δ : deformation, η : out of plane bending, τ : twisting, ω : wagging and ρ : rocking.

N-H Stretching

The molecules under consideration have only 1 NH₂ group and hence we expect 1 N-H asymmetric and N-H symmetric stretching vibrations. In the primary aromatic amines, the N-H stretching frequency occurs in the region 3300–3500 cm⁻¹. Hence the absorption bands observed at 3399 and 3203 cm⁻¹ in AMQ and at 3332 and 3203 cm⁻¹ in AQ are assigned to N-H asymmetric and symmetric stretching modes in the NH₂ group respectively. These observations agree very well with a large number of studies.^{29,30}

The rest of the observed frequencies may be accounted for as resulting from the allowed combinations of selected fundamentals, as indicated in Tables 2 and 3.

Potential energy distribution

To check whether the chosen set of assignments contribute the most to the potential energy associated with the normal coordinates of the molecules, the potential energy distribution (PED) has been calculated using the relation

$$PED = \frac{F_{ii}L_{ik}^2}{\lambda_k}$$

where PED is the contribution of the i^{th} symmetry coordinate to the potential energy of the vibrations, whose frequency is ν_k , F_{ii} is the force constant evaluated by the damped least square technique, L_{ik} is the normalised amplitude of the associated element (i,k) and λ_k is the eigen value corresponding to the

vibrational frequency k ($\lambda_k = 4\pi^2c^2\nu_k^2$). The PED contribution values corresponding to each of the observed frequencies are listed in Tables 2 and 3.

Conclusion

Complete vibrational spectral assignments and analyses are available in the present work for 4-aminoquinaldine and 5-aminoquinoline molecules. The close agreement between the observed and calculated frequencies confirms the validity and precision of the present assignments. The purity of the modes is ascertained by the potential energy distribution associated with each frequency of vibration.

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