FT-IR and FT-Raman Studies on 3-Aminophthalhydrazide and N-Aminophthalimide[*]

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The FT-infrared (400-4000 cm^{-1}) and FT-Raman (100-3500 cm^{-1}) spectra of N-aminophthalimide and 3-aminophthalhydrazide were recorded. The observed frequencies were assigned to various modes of vibrations on the basis of normal coordinate analysis, assuming C_S point group symmetry. The potential energy distribution associated with normal modes is also reported. The assignments of fundamental vibrations agree well with the calculated frequencies.

Key Words: 3-aminophthalhydrazide, N-aminophthalimide, FTIR, FT-Raman and normal coordinate analysis.

Introduction

Infrared spectroscopy is a mature research tool which has enjoyed a renaissance in recent years due to the introduction of Fourier transform techniques[1]. The quantitative interpretation of IR spectra has been enhanced by the computer-assisted data analysis and storage that has come with this new technology. The IR spectrum characterises the vibrational modes of the molecules and has enfolded within it much information on chemical structure.

Raman spectroscopy can also provide exquisite structural insights into the molecule. Fourier transform Raman spectroscopy (FT-Raman) is a neonatal technology developed in the 1990s and it has brought a new impetus to Raman spectroscopy. It has allowed the study of materials that were previously "impossible" because of fluorescence[2−4] and provides ready access in the extensive data handling facilities that are available with a commercial Fourier transform infrared spectrometer. Thus, Raman spectroscopy is taking its place as an equal partner in vibrational spectroscopy. The combined use of FT-IR and FT-Raman spectroscopy extracts most of the obtainable information and these are the popular tools in the arsenal of the chemist and physicist.

The molecules 3-Aminophthalhydrazide (6-amino-2,3-dihydrophthalazine, $C_8H_7N_3O_2$) and N-Aminophthalimide (N,N-phthaloylhydrazine; $C_8H_6N_2O_2$) consist of one benzene ring and one heterocyclic ring

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fused together. These molecules exist in solid form at room temperature and have a melting point around 177°C and 162°C respectively. The optimised geometrical structures of 3-aminophthalhydrazide (3APH) and N-Aminophthalimide (NAPH) are shown in Figs. 1 and 2. 3-Aminophthalhydrazide is used for the sensitive chemiluminescent determination of serum haemoglobin and as a classical reagent for generating luminescence[5-7]. N-Aminophthalimide is useful for the preparation of phenolphthalein fluorescein dyes and plastics[8]. It is also used in the preparation of primary amines. It is a basic compound for many organic molecules.
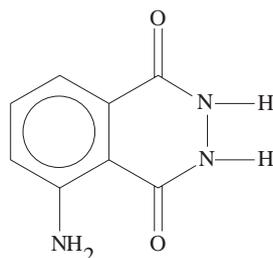
Figure 1. Structure of 3-Aminophthalhydrazide
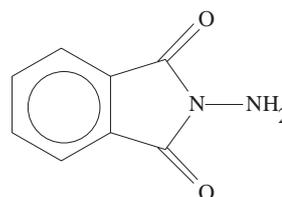
Figure 2. Structure of N-Aminophthalimide

Gulis et al.[9] investigated the intermolecular vibrational energy redistribution process in the molecules of phthalimide derivatives (3-aminophthalimide, 3-amino-N-methylphthalimide). To understand the intermolecular vibrational energy redistribution process in excited vibronic states and intermolecular interactions, an ideal model system was introduced.

Pryor et al.[10] studied the spectroscopy and excited state life times of 3- and 4-aminophthalimides, N-methyl-4-aminophthalimides and some complexes with polar molecules under supersonic jet conditions.

Due to their considerable importance, it is vital to investigate the molecules in detail. Various studies on phthalhydrazides and phthalimides have been widely investigated by several spectroscopists. However, very little work has been done on the analysis of the fundamental vibrations of 3APH and NAPH. In the present work, we present the utility of FT-IR and FT-Raman in the vibrational analysis of 3APH and NAPH; the spectra were analysed in terms of peak positions and intensities. With the help of the added data, the utilisation of group theory and normal coordinate analysis, an attempt was made to achieve a more satisfactory interpretation of the spectra of 3APH and NAPH molecules.

Experimental Technique

The solid samples of 3-Aminophthalhydrazide and N-aminophthalimide were obtained form Fluka, Switzerland, with a stated purity of 99%, and were used as such without further purification to record the spectra. The FT-IR spectra of 3APH and NAPH were recorded in the region 4000-400 cm^{-1} by a Bruker IFS 66V spectrometer, with a scanning speed of 30 cm^{-1} min^{-1} with the spectral width 2.0 cm^{-1}. The FT-Raman spectra were also recorded with the same instrument with a FRA 106 Raman module equipped with Nd-YAG laser source operating 1.06 μm line with 200 mW in the wave number range 3500-50 cm^{-1}. The frequencies of all sharp bands are accurate to ± 2 cm^{-1}. The recorded FT-IR and FT-Raman spectra of 3APH and NAPH are shown in Figures 3-6.
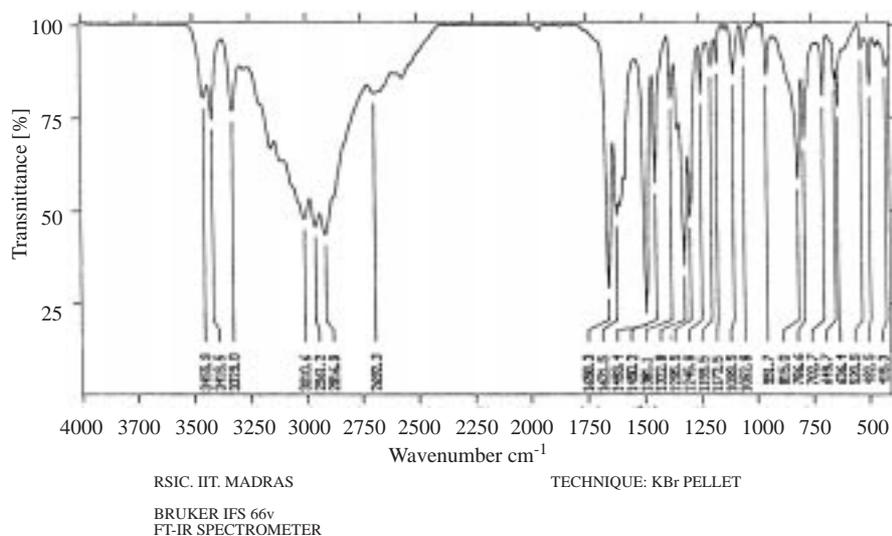
Figure 3. FTIR spectrum of 3-Aminophthalhydrazide
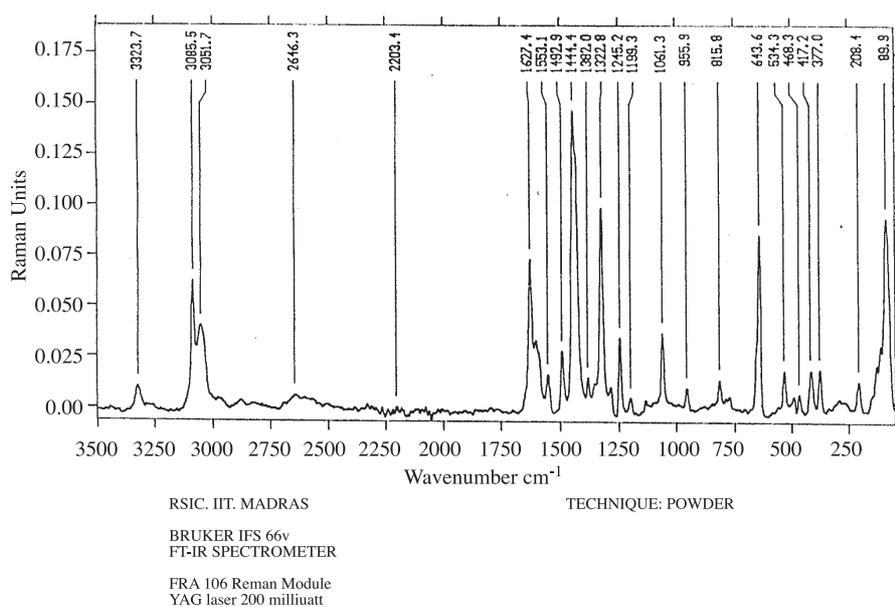
Figure 4. FTR spectrum of 3-Aminophthalhydrazide

Normal coordinate analysis

Certain of the fundamentals of the molecules of this complexity cannot be predicted without a more detailed normal coordinate analysis. With the hope of providing some more effective information on the fundamental vibrations of these molecules, a normal coordinate analysis was carried out on 3APH and NAPH. The normal coordinate analysis program of Fuhrer et al. [11] was used after suitable modifications to calculate the vibrational frequencies and potential energy distribution (PED) in the framework of Wilsons FG-matrix method[12−14]. From the structural point of view, 3APH and NAPH molecules belong to C_S symmetry by assuming the NH_2 group in both molecules to be a point mass and lie in the plane of the molecule. The

simple general valence force field (SGVFF) method was adopted for both inplane and out of plane vibrational modes. The SGVFF method has been shown to be effective in normal coordinate analysis[15,16] and also the valence force constants can be transferred between the related molecules, which is very useful in the normal coordinate analysis. Hence, in the present work, the SGVFF method was employed to express the potential energy. The force constants were refined by the damped least square technique. The PED calculated using the final set of force constants are presented in Tables 1 and 2. A salient feature of the normal coordinate analysis and force field calculations was that it could reproduce the frequencies associated with the skeletal as well as the amino group within a reasonable limit (± 10 cm^{-1}) with an acceptable PED.

RSIC. IIT. MADRAS   TECHNIQUE: KBR PELLET

BRUKER IFS 66v
FT-IR SPECTROMETER
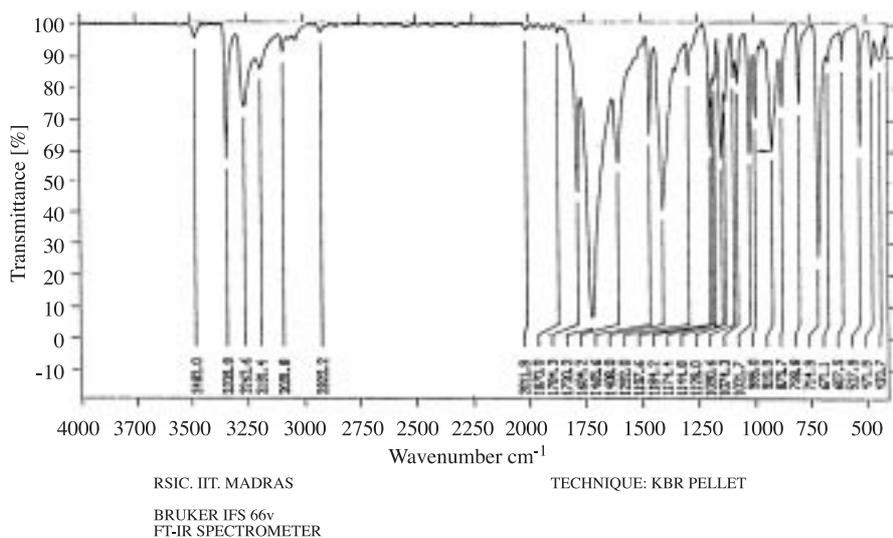
Figure 5. FTIR spectrum of N-Aminophthalimide

RSIC. IIT. MADRAS   TECHNIQUE: POWDER

BRUKER IFS 66v
FT-IR SPECTROMETER

FRA 106 Raman Module
YAG laser 200 milluatt
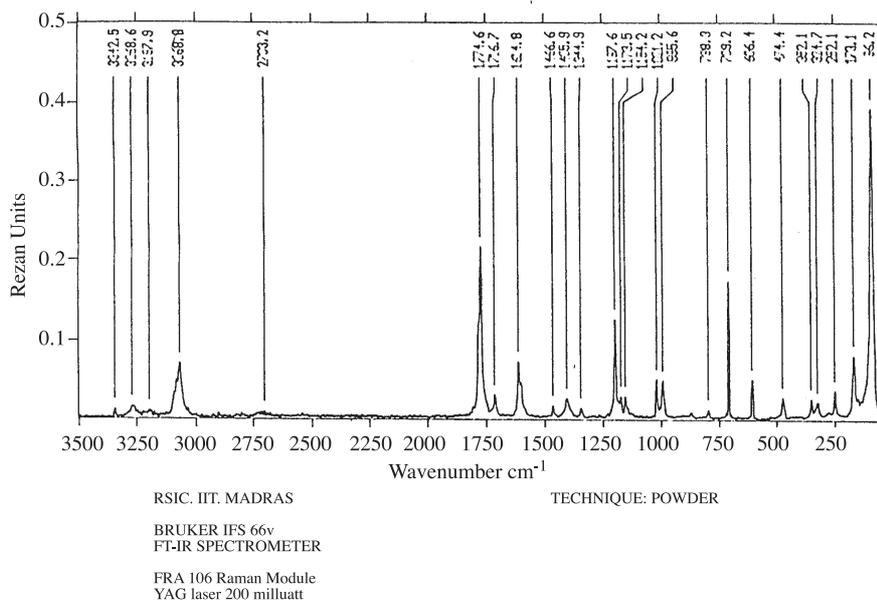
Figure 6. FTR spectrum of N-Aminophthalimide

Table 1. Observed and calculated wavenumber and PED distribution for 3 - Aminophthalhydrazide

Species	Observed wavenumber/Int.		Cal. wave-number	Assignments	% PED
	FTIR	FTR			
		90s		Lattice vibration	
a″		113m	102	CNN out of plane bending	$46\gamma_{CNN} + 34\gamma_{NH}$
a″		132m	122	CCN out of plane bending	$48\gamma_{CCN} + 30\gamma_{NH}$
a″		146m	127	CCN out of plane bending	$46\gamma_{CCN} + 28\gamma_{C=O}$
a″		208vw	201	CCN out of plane bending	$46\gamma_{CCN} + 31\gamma_{C=O}$
a′ a″		292vw	288	CNN inplane bending / C - NH$_2$ out of plane bending	$41\beta_{CNN} + 26\beta_{C=O} + 6\beta_{NH}$
a′ a′		377w	361	CCN inplane bending / C - NH$_2$ in plane bending	$45\beta_{CCN} + 28\beta_{C=O} + 11\beta_{NH}$
a″ a′	419w	417w	410	C = O out of plane bending/ CCN inplane bending	$49\gamma_{C=O} + 20\gamma_{C-H} + 12\gamma_{NH}$
a″		468vw	461	CCC out of plane bending	$58\gamma_{CCC} + 19\gamma_{C-H} + 19\gamma_{C=O}$
a″	493w	492vw	498	CCC out of plane bending	$54\gamma_{CCC} + 14\gamma_{C-H} + 18\gamma_{C=O}$
a″	531vw	534w	528	CCC out of plane bending	$51\gamma_{CCC} + 16\gamma_{C-H} + 24\gamma_{CNH_2}$
a′ a″		563s	560	C = O inplane bending / CCC out of plane bending	$61\beta_{C=O} + 24\beta_{CN}$
a″	636w	644vw	638	N - H out of plane bending	$68\gamma_{NH} + 19\gamma_{CN}$
a′ a″	650w		642	CCC inplane bending / N - H out of plane bending	$62\beta_{CCC} + 21\beta_{CN}$
a′	703w		695	CCC inplane bending	$58\beta_{CCC} + 11\beta_{CN} + 24\beta_{C-H}$
a″		772vw	778	NH$_2$ wagging	$56\omega_{NH_2} + 22\gamma_{N-H}$
a″ a″	787m	788vw	781	C - H out of plane bending / NH$_2$ twisting	$60\gamma_{CH} + 11\gamma_{C=O} + 21\gamma_{CCC}$
a″ a′	815m	816vw	811	C - H out of plane bending / ring breathing	$64\gamma_{CH} + 28\gamma_{CCC}$
a″	917vw		909	C - H out of plane bending	$71\gamma_{CH} + 21\gamma_{CCC} + 11\gamma_{C-NH_2}$
a′	952w	956m	951	Trigonal bending	$88\beta_{CCC} + 10\beta_{CC}$
a′	1053vw	1061vw	1058	NH$_2$ rocking	$61\rho_{NH_2} + 18\beta_{C=O} + 22\beta_{CC}$
a′	1100vw		1104	C - H inplane bending	$59\beta_{CH} + 21\nu_{CC} + 14\beta_{CC}$
a′	1136w	1133vw	1136	C - H inplane bending	$62\beta_{CH} + 28\beta_{CC}$
a′	1173vw		1161	C - H inplane bending	$60\beta_{CH} + 22\beta_{CC}$
a′	1200w	1199m	1189	C - N stretching	$81\nu_{N-N} + 16\nu_{NH}$
a′ a′	1246w	1245vw	1238	C - N stretching / C - C stretching	$74\nu_{C-N} + 17\nu_{N-H}$ $71\nu_{CC} + 21\nu_{C-N}$
a′		1285vw	1278	C - NH$_2$ stretching	$61\nu_{C-NH_2} + 26\nu_{CC}$
a′	1296s		1282	C - C stretching	$71\nu_{CC} + 19\beta_{CC}$
a′	1323vs	1323s	1320	N - N stretching	$74\nu_{N-N} + 21\beta_{NH}$
a′	1350m	1354w	1351	C - C stretching	$70\nu_{CC} + 18\beta_{CH}$
a′	1381w	1382vw	1378	C - C stretching	$74\nu_{CC} + 21\beta_{CC}$
a′		1435vs	1431	C - C stretching	$80\nu_{CC} + 11\beta_{CC}$
a′	1450s	1444vs	1444	N - H inplane bending	$78\beta_{NH} + 18\nu_{CN}$
a′	1493vs	1493w	1489	N - H inplane bending	$71\beta_{NH} + 20\nu_{CN}$
a′		1553vw	1551	C = C stretching	$74\nu_{CC} + 14\beta_{CC} + 10\nu_{C-H}$
a′	1593s		1584	C = C stretching	$61\nu_{CC} + 16\nu_{CH} + 12\beta_{CC}$
a′		1605w	1601	C = C stretching	$68\nu_{CC} + 21\beta_{CH}$
a′	1615s		1605	NH$_2$ deformation	$71\rho_{C-NH_2} + 12\nu_{CC} + 10\nu_{CH}$
a′	1622s	1627m	1629	C = O stretching	$84\nu_{C=O} + 14\nu_{CH}$

Table 1. Continued

a′	1658vs		1657	C = O stretching	$79\nu_{C=O} + 11\nu_{CC}$
		2080vw		788 + 1285	
		2203vw		956 + 1245	
		2333vw		956 + 1382	
	2570w			952 + 1615	
	2917s			1323 + 1593	
	2961s			1350 + 1615	
a′	3011s		3002	C - H stretching	$83\nu_{CH}$
a′	3041s		3040	C - H stretching	$81\nu_{CH}$
		3052m		1435 + 1627	
a′	3072s	3086	3076	C - H stretching	$78\nu_{CH} + 12\nu_{CC}$
	3122m			2x1350 + 419	
	3162m			2x2882 - 2x1296	
a′	3283w		3285	N - H stretching	$88\nu_{NH}$
a′	3329w	3324w	3330	N - H stretching	$87\nu_{NH}$
a′	3420m		3423	NH2 symmetric stretching	$94\nu_{NH_2}$
a′	3456w		3455	NH2 asymmetric stretching	$89\nu_{NH_2}$

vs - very strong, s - strong, m - medium,w - weak, vw - very weak, ν - stretching, β - inplane bending, δ-deformation, γ - out of plane bending, ω - wagging, τ - twisting, ρ-rocking

Results and Discussion

The observed spectra of 3APH and NAPH are analysed on the basis of C_S symmetry by assuming the amino group to be a point mass in both the molecules. The distribution of the 54 fundamental modes of 3APH among the irreducible representations for this C_S symmetry is given by $\Gamma_{vib} = 37$ a′ (inplane) + 17 a″ (out of plane) vibrations. In NAPH the 48 fundamental vibrational modes are distributed as $\Gamma_{vib} = 33$ a′ (inplane) + 15 a″ (out of plane) vibrations. All vibrations are active in both IR and Raman. The observed and calculated frequencies of 3APH and NAPH in the infrared and Raman along with their relative intensities and proposed assignments are summarised in Tables 1 and 2 respectively. Assignments were made on the basis of relative intensities, magnitude of frequencies and mainly on the normal coordinate calculations, as well as literature data of molecules of similar structure. The purity of the normal modes is further confirmed by calculating the PED to each fundamental vibration of 3APH and NAPH molecules.

Carbon vibrations

Benzene has two doubly degenerate modes, e_{2g} (1596 cm^{-1}) and e_{1u} (1485 cm^{-1}), and two non-degenerate modes, b_{2u} (1310 cm^{-1}) and a_{1g} (995 cm^{-1}), due to skeletal C-C stretching. In general, the bands around 1650 to 1350 cm^{-1} in benzene are assigned to skeletal C-C stretching modes. The actual positions are determined not so much by the nature but by the position of the substitution around the ring[17]. The band observed at 1593 cm^{-1} in FT-IR and 1605 and 1553 cm^{-1} in FT-Raman are assigned to C=C stretching vibrations of 3APH while the bands at 1604, 1520, 1498 cm^{-1} in FT-IR and 1602 cm^{-1} in FT-Raman are assigned to C=C stretching vibrations of NAPH.

Table 2. Observed and calculated wavenumber and potential energy distribution (PED) for N-Aminophthalimide

Species	Observed wavenumber/Int.		Cal. wave-number	Assignments	% PED
	FTIR	FTR			
		96vs		Lattice vibration	
a″		173w	161	CNC out of plane bending /	$44\gamma_{CNC} + 21\gamma_{N-NH_2}$
a″				CCN out of plane bending	
a″		252vw	241	CCN out of plane bending	$48\gamma_{CCN} + 29\gamma_{C=O}$
a′		325vw	318	CNC inplane bending /	$38\beta_{CNC}$
a″				N - NH$_2$ out of plane bend	$+ 21\beta_{C=O} + 20\beta_{CCN}$
a′		352w	345	N - NH$_2$ inplane bending	$31\beta_{N-NH_2}$
					$+ 21\beta_{C=O} + 11\beta_{CNC}$
a″	434w		424	C = O out of plane bending /	$48\gamma_{C=O} + 21\gamma_{NN}$
a′				CCN inplane bending	
a″	472w	474vw	465	CCC out of plane bending /	$50\gamma_{CCC} + 19\gamma_{CH}$
a″				C = O out of plane bending	
a″	528m		519	CCC out of plane bending	$51\gamma_{CCC} + 14\gamma_{CH}$
a″	608w	606w	602	CCC out of plane bending /	$54\gamma_{CCC} + 16\gamma_{CH}$
a′				C = O inplane bending	
a′	671w		662	CCC inplane bending	$57\beta_{CCC} + 12\beta_{CH}$
a′		709m	692	CCC in plane bending	$63\beta_{CCC} + 14\beta_{CH}$
a″	715vs		700	NH$_2$ wagging	$56\omega_{NH_2} + 31\tau_{NH_2}$
a″	799m	798vw	787	NH$_2$ twisting	$66\tau_{NH_2} + 28\omega_{NH_2}$
a′	876m	874vw	879	Ring breathing	$87\beta_{CCC}$
a″	908m		902	C - H out of plane bending	$72\gamma_{C-H} + 26\gamma_{CCC}$
a″	920m		911	CH out of plane bending	$68\gamma_{C-H} + 20\gamma_{CCC}$
a″	967w		954	CH out of plane bending	$65\gamma_{C-H} + 21\gamma_{CC}$
a″	995m	996w	991	C - H out of plane bending	$70\gamma_{CH} + 18\gamma_{CC}$
a′	1022m		1021	Trigonal bending	$88\beta_{CCC}$
a′	1074w		1066	NH$_2$ rocking	$62\rho_{NH_2} + 18\beta_{CN} + 10\beta_{C=O}$
a′	1091w		1082	C - H inplane bending	$66\beta_{CH} + 21\beta_{CC}$
a′	1129w		1121	C - H inplane bending	$68\beta_{CH} + 26\beta_{CC}$
a′	1145m	1154vw	1147	CH inplane bending	$74\beta_{CH} + 18\beta_{CC}$
a′	1174w	1173vw	1168	CH inplane bending	$64\beta_{CH} + 21\beta_{CC}$
a′	1184w		1172	C - N stretching	$67\nu_{CN} + 20\nu_{C=O}$
a′	1198m	1198m	1188	C - N stretching	$75\nu_{C-N} + 18\nu_{C=O}$
a′	1292w		1290	C - C stretching /	$89\nu_{CC}$
a′				N - NH$_2$ stretching	
a′	1350w	1345vw	1341	C - C stretching	$86\nu_{CC} + 10\nu_{C=O}$
a′	1408s	1406vw	1412	C - C stretching	$76\nu_{CC} + 16\nu_{CH}$
a′	1466m	1467vw	1461	C - C stretching	$80\nu_{CC} + 11\nu_{CN}$
a′	1498w		1491	C = C stretching /	$69\nu_{CC} + 21\nu_{CH}$
a′				C - C stretching	
a′	1520vw		1506	C = C stretching	$78\nu_{CC} + 11\nu_{CH}$
a′	1604s	1602vw	1602	C = C stretching	$71\nu_{CC} + 14\nu_{CH}$
a′		1615m	1614	NH$_2$ deformation	$72\delta_{NH_2} + 21\beta_{CN}$
a′	1720vs	1717vw	1711	C = O stretching	$81\nu_{C=O} + 14\nu_{CN}$
a′	1784s	1784m	1781	C = O stretching	$88\nu_{C=O} + 10\nu_{CC}$
	1850vw			1184 + 671	
	1870vw			967 + 908	
	1900vw			1292 + 608	

Table 2. Continued

Species	Observed wavenumber/Int.		Cal. wave-number	Assignments	% PED
	1933vw			1408 + 528	
	1972vw			1498 + 472	
	2012vw			1408 + 608	
	2320vw			1520 + 799	
	2425vw			1292 + 1145	
a′	3033vw		3025	C - H stretching	$94\nu_{C-H}$
a′	3067vw	3069w	3061	C - H stretching	$92\nu_{C-H}$
a′		3085w	3071	C - H stretching	$89\ \nu_{C-H}$
a′	3092vw	3095w	3086	C - H stretching	$88\nu_{C-H}$
	3191w	3198vw		2 x 1602	
	3263m	3269vw		1784 + 1466	
a′	3340m	3343vw	3331	NH$_2$ symmetric stretching	$95\nu_{N-H}$
a′	3482w		3498	NH$_2$ asymmetric stretching	$87\nu_{N-H}$

vs - very strong, s - strong, m - medium, w - weak, vw - very weak, ν - stretching, δ-deformation, β - inplane bending, γ - out of plane bending, ω - wagging, τ - twisting, ρ-rocking

The ring breathing a$_{1g}$ (995 cm^{-1}) and CCC trigonal bending non-degenerate b$_{1u}$ (1010 cm^{-1}) vibrations of benzene give rise to combined modes under C$_S$ symmetry. In the present study, the characteristic medium absorptions bands at 876 and 815 cm^{-1} in FT-Raman correspond to the ring breathing mode of NAPH and 3APH respectively. Similarly, the bands observed at 1022 cm^{-1} in FT-IR and 956 cm^{-1} in FT-Raman are assigned to the CCC trigonal bending of NAPH and 3APH respectively. These values are in good agreement with the ring breathing mode at about 800 cm^{-1} and trigonal bending vibration at around 1000 cm^{-1} in substituted benzene[18,19].

The inplane carbon vibrations are related to non-degenerate b$_{1u}$ (1010 cm^{-1}) and degenerate e$_{2g}$ (606 cm^{-1}) modes of benzene. The e$_{2g}$ (606 cm^{-1}) degenerate frequency under C$_S$ symmetry is observed at 703 and 650 cm^{-1} in 3APH, and 709 and 671 cm^{-1} in NAPH. The carbon out of plane bending vibrations are related to non-degenerate b$_{2g}$ (703 cm^{-1}) and degenerate e$_{2u}$ (404 cm^{-1}) modes of benzene. The former is found to be constant in substituted benzene[20]. The e$_{2u}$ degenerate mode under C$_S$ symmetry is observed at 563 and 534 cm^{-1} in 3APH, while the bands in NAPH are seen at 519 and 465 cm^{-1}.

C-H vibrations

Normally the bands around 3100-3000 cm^{-1} are assigned to the C-H stretching vibrations in aromatic compounds. They are not appreciably affected by the nature of the substituents. In the present work, the bands observed at 3092, 3067 and 3033 cm^{-1} in FTIR, and 3095, 3085 and 3069 cm^{-1} in FT-Raman are assigned to the C-H stretching of NAPH. The bands seen at 3072, 3041 and 3011 cm^{-1} in FTIR, and 3086 and 3052 cm^{-1} in FT-Raman are attributed to the C-H stretching modes of 3APH. The C-H inplane and out of plane bending vibrations of these molecules are given in Tables 1 and 2.

Heterocyclic ring vibrations

C-N and N-N vibrations: The C-N stretching of 3APH is assigned to the band at 1246 cm^{-1} in FTIR and 1199 cm^{-1} in FT-Raman. The PED calculation shows that the C-N stretching is slightly coupled with the N-H stretching vibrations. The bands observed at 1198 and 1184 cm^{-1} in FT-IR are attributed to the C-N stretching of NAPH. The very strong band seen at 1323 cm^{-1} is assigned to the N-N stretching of 3APH.

The absorption bands seen at 417 and 377 cm^{-1} are assigned to CCN in plane bending of 3APH. These vibrations are moderately coupled with the carbonyl in plane bending vibrations. The band observed at 434 cm^{-1} is assigned to CCN inplane bending of NAPH. The bands corresponding to CNN inplane and out of plane vibrations of NAPH are given in Table 2. Normal coordinate analysis is very helpful for predicting these frequencies. In NAPH, the CNC inplane and out of plane vibrations are found at 325 and 173 cm^{-1} respectively.

C=O Vibrations

The C=O stretching frequencies usually lie in the region between 2000 and 1500 cm^{-1}. Various other vibrations, such as C=C, C=N stretching and N-H bending vibrations, also occur in this region. However, C=O stretching is normally more intense than any other vibrations in this region. The position of C=O stretching depends upon conjugation, hydrogen bonding and the size of the ring to which it is attached. For cyclic imide, two carbonyl stretching bands are normally expected, one lying in the region 1790-1735 cm^{-1} and the other in the region 1750-1680 cm^{-1}. In NAPH, these are observed at 1784 and 1720 cm^{-1} in IR, and 1784 and 1717 cm^{-1} in Raman. The carbonyl stretching frequency of secondary amides appears in the region 1680-1620 cm^{-1}. In 3APH it appears at 1658 and 1622 cm^{-1} in FTIR, and 1627 cm^{-1} in FT-Raman. The lower value of carbonyl stretching may be due to a mechanical effect[21]. In small rings the ring is rigid. This is unlike open chain compounds and larger ring systems, which are quite flexible, since neighbouring carbons can undergo small compensating displacements during the C=O stretch. Compression of the C=O in small ring systems results in compression of adjacent bonds, more energy is required and hence the stretching frequency increases as the ring becomes more rigid. Thus in 3APH C=O stretching is observed at a lower wave number than in NAPH. In earlier works, C=O stretching frequency was reported at 1651, 1701, 1653, 1750, 1775, 1710 cm^{-1} and 1661, 1658, 1664, 1671 cm^{-1} in naphthrazin[22], indigoids[23], 3-hydroxypyridines[24], cyclopentane[21], cyclic ester[21], N-phenylmaleimide[25] and para disubstituted Benzophenones[26].

The inplane bending modes of C=O are observed at 563 cm^{-1} in 3APH and in the case of NAPH it is observed at 606 cm^{-1} in Raman. The out of plane bending vibrations of C=O are also observed at 472 and 434 cm^{-1} for NAPH, and 419 cm^{-1} for 3APH. The present assignments are in good agreement with the literature values[23,25,27].

N-H vibrations

The N-H stretching frequencies of secondary amide are observed in the region 3370-3170 cm^{-1}. The N-H stretching vibrations of 3APH are found at 3329 and 3283 cm^{-1}. The N-H inplane bending modes are seen at 1493 and 1450 cm^{-1} in the infrared, and 1493 and 1444 cm^{-1} in Raman. The N-H out of plane bending vibrations of 3APH are attributed to 650 and 636 cm^{-1}.

NH$_2$ Group vibrations

Aromatic primary amines display two medium intensity absorption bands: the one near 3500 cm^{-1} corresponds to the asymmetrical and the other, near 3400 cm^{-1}, to symmetrical N-H stretching modes. In 3APH, the bands found at 3456 and 3429 cm^{-1} correspond to the asymmetric and symmetric N-H stretches respectively. The bands appearing at 3482 and 3340 cm^{-1} are attributed to the asymmetric and symmetric stretching of NAPH. The N-H deformation mode is observed in the region 1650-1580 cm^{-1} . The strong and medium intensity band found at 1615 cm^{-1} is assigned to the N-H deformation mode of 3APH and NAPH.

The out of plane NH$_2$ wagging band appears from 850 to 700 cm^{-1}. The bands appearing at 772 and 715 cm^{-1} are assigned to the NH$_2$ wagging of 3APH and NAPH respectively. The wagging mode is moderately coupled with the twisting mode of the NH$_2$ group. The other bands corresponding to the NH$_2$ rocking and twisting are given in Tables 1 and 2. These above assignments agree well with the literature values[28−34].

Conclusion

In the present work a complete vibrational assignments for 3-aminophthalhydrazide and N-aminophthalimide along with the potential energy distributions are reported. For all the fundamentals, the close agreement between the observed and calculated frequencies is satisfactory, confirming the validity of the SGVFF for spectral assignments, even for complex molecules. The PED contributions to each of the observed frequencies show the reliability and accuracy of the spectral analysis.

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