

Polarised Raman and infrared spectra and vibrational analysis for α -naphthylamine

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Abstract. The Raman spectrum of polycrystalline α -naphthylamine was recorded in the region $100\text{--}4000\text{ cm}^{-1}$. Polarisation measurements were made in CS_2 and CHCl_3 solutions. The infrared spectrum was recorded in nujol mull in the region $200\text{--}4000\text{ cm}^{-1}$. The resolution was better than 2 cm^{-1} and the accuracy of the measurements was within $\pm 2\text{ cm}^{-1}$ for all the spectra. Vibrational assignments have been proposed for the observed frequencies. Out of the 54 normal modes of vibrations, 51 modes could be observed experimentally.

Keywords. Raman spectrum; infrared spectrum; vibrational spectrum; fundamental frequencies.

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1. Introduction

Amino aromatics form a very important class of organic compounds. α -Naphthylamine is a member of the double ring class which is obtained from naphthalene by replacing a hydrogen atom by an amino group from the α -position. On account of its cancerous properties, α -naphthylamine is of considerable biological importance. Therefore, the study of its vibrational spectrum is desirable which may be valuable in understanding the physiological properties of α -naphthylamine.

The IR spectrum of α -naphthylamine has been partly reported by Wang and Sanders (1959) and Nicole and Lagrange (1964). Recently, Singh (1970) recorded the IR spectrum of this molecule in nujol mull and proposed vibrational assignments for the observed frequencies. However, the Raman spectrum of α -naphthylamine has not been so far reported. In order to make more comprehensive vibrational assignments, we have recorded the polarised Raman and IR spectra of α -naphthylamine and have proposed vibrational assignments.

2. Experimental

α -Naphthylamine purity $> 99\%$. (Koch Light Laboratories, London) was recrystallized twice just before recording the Raman spectrum.

The Raman spectrum of the polycrystalline substance was recorded in the region

50–4000 cm^{-1} on a Jarrell-Ash 25–300 spectrometer using the 5145 Å line from an argon-ion laser. To measure the depolarisation ratios of the Raman lines, the spectra in CS_2 and CHCl_3 solutions were also recorded in the same region. The resolution was better than 1 cm^{-1} above 500 cm^{-1} and 2 cm^{-1} below 500 cm^{-1} , under the experimental conditions employed. The accuracy of the measurements was of the order of $\pm 2 \text{ cm}^{-1}$.

The IR spectrum of α -naphthylamine was recorded in nujol mull in the region 200–4000 cm^{-1} on a Perkin-Elmer 621 spectrometer using CsI optics. The spectrometer was calibrated with the spectrum of polystyrene thin film. The resolution was better than 2 cm^{-1} and the accuracy was within $\pm 2 \text{ cm}^{-1}$ under the experimental conditions employed.

3. Results and discussion

α -Naphthylamine is assumed to belong to the C_s point group. The NH_2 group is taken to be co-planar with the naphthalene skeleton and therefore, the 54 normal modes of vibrations of α -naphthylamine (total number of atoms = 20) are distributed between the two species a' and a'' of the C_s point group as: 37 a' + 17 a'' . Out of these 54 modes, 48 (33 a' + 15 a'') modes correspond to the naphthalene ring and 6 (4 a' + 2 a'') modes correspond to the NH_2 group which are given below:

a' species	a'' species
Symmetric NH_2 stretch- ν_s (NH_2)	NH_2 wagging- γ (NH_2)
Anti-symmetric NH_2 stretch- ν_{as} (NH_2)	NH_2 torsion- τ (NH_2)
NH_2 deformation- δ (NH_2)	
NH_2 rocking- ρ (NH_2)	

Out of the 48 normal modes of the $\text{C}_{10}\text{H}_7\text{X}$ molecule (X is a substituent) 24 modes correspond to the C–H/C–X modes (8 stretching, 8 in-plane bending and 8 out-of-plane bending modes) and the remaining 24 modes correspond to the naphthalene skeleton modes. Since for the $\text{C}_{10}\text{H}_7\text{X}$ molecule, there are 15 non-planar modes 8 of which belong to the C–H/C–X modes, the remaining 7 modes correspond to the CCCC torsional modes. Thus, there are 24 – 7 = 17 planar modes for naphthalene skeleton which contain C–C stretching and C–C–C angle bending modes. For naphthalene, Lal (1971) suggested that out of these 17 normal modes, 9 correspond to the C–C stretching modes and 8 to the C–C–C angle bending modes whereas Ram *et al* (1983) correlated 10 modes to the C–C stretching and 7 to the C–C–C angle bending modes. Since redundancies are not involved in the bond stretching and there are 11 C–C bonds, there must be 11 C–C stretching modes and consequently, 17 – 11 = 6 C–C–C angle bending modes. However, because of strong coupling between the C–C stretching and C–C–C angle bending modes, it is very difficult to differentiate between C–C stretching and C–C–C angle bending modes. The assignments for these modes can be made on the basis of magnitudes of the frequencies.

The frequencies observed in the Raman and IR spectra of α -naphthylamine along with their relative intensities, depolarisation ratios of the Raman lines and proposed vibrational assignments are given in table 1.

Table 1. Raman and IR frequencies* and proposed vibrational assignments for naphthylamine.

Solid	Raman		IR		Proposed vibrational assignments
	CS ₂ sol.	CHCl ₃ sol.	nujol mull	Species	
165 (vw)				<i>a''</i>	C-C-C-C-torsion
185 (vw)	185 (vw, dp)	185 (vw, dp)		<i>a''</i>	C-C-C-C torsion
266 (m)	262 (w, dp?)			<i>a''</i>	C-NH ₂ o.p. wag
276 (sh)			278 (vw)	<i>a''</i>	C-C-C-C torsion
305 (m)	292 (w, p)	292 (w, p)		<i>a'</i>	C-C-C angle bend
315 (sh)				<i>a''</i>	NH ₂ torsion
			358 (sh)	<i>a''</i>	C-C-C-C torsion
	395 (vw, dp?)		385 (sh)	<i>a''</i>	C-C-C-C torsion
418 (vw)	416 (vw?)	415 (vw, dp)	420 (w)	<i>a''</i>	C-C-C-C torsion
{ 458 (ms)	454 (ms, p)	454 (m, p)	444 (vw)	{ <i>a'</i>	{ C-NH ₂ i.p. bend
515 (m)	513 (ms, p)	512 (m, p)	510 (w)	<i>a'</i>	C-C-C angle bend
575 (m)	575 (m, p)	573 (m, p)	565 (m)	<i>a'</i>	C-C-C angle bend
628 (vw)				<i>a'</i>	C-C-C angle bend
655 (vw)			650 (ms, d)	<i>a''</i>	NH ₂ wag
			685 (ms)	<i>a''</i>	C-C-C-C torsion
711 (s)	712 (s, p)	710 (s, p)	710 (ms)	<i>a'</i>	C-C stretch (ring breathing)
733 (sh)					
			755 (vs)	<i>a'</i>	C-C-C angle bend
			775 (vs)	<i>a''</i>	C-H o.p. wag
790 (vw)				<i>a'</i>	C-C-C angle bend
			840 (m)	<i>a''</i>	C-H o.p. wag
860 (sh)	856 (sh, dp)		855 (w)	<i>a''</i>	C-H o.p. wag
878 (w)	876 (w, dp?)	878 (w, dp?)	875 (w)	<i>a''</i>	C-H o.p. wag
~ 950 (vw)	~ 945 (vw, -)	~ 950 (vw, -)	940 (w)	<i>a''</i>	C-H o.p. wag
			965 (w)	<i>a''</i>	C-H o.p. wag
1010 (sh)			1000 (m)	<i>a''</i>	C-H o.p. wag
1030 (m)	1030 (ms, p)	1030 (m, p)		<i>a'</i>	C-C stretch (ring breathing)
1090 (m)	1088 (m, p)	1088 (m, p)	1080 (w)	<i>a'</i>	NH ₂ rock
1125 (w)	1120 (w, p)	1122 (w, p)	1125 (vw)	<i>a'</i>	C-H i.p. bend
1142 (m)	1141 (w, p)	1142 (w, p)	1150 (w)	<i>a'</i>	C-H i.p. bend
1168 (w)	1166 (w, p)	1164 (w, p)		<i>a'</i>	C-H i.p. bend
1178 (w)	1178 (sh, -)	1176 (w, -)		<i>a'</i>	C-H i.p. bend
1218 (w)	1218 (w, p)			<i>a'</i>	C-H i.p. bend
1252 (w)	1250 w, p)	1250 (w, p)	1245 (w)	<i>a'</i>	C = C stretch
1291 (w)	1289 (m, p)	1289 (vw, p)	1285 (ms)	<i>a'</i>	C-NH ₂ stretch
1359 (sh)	1358 (sh, p)	1356 (sh, p)	1360 (vs)	<i>a'</i>	C-H i.p. bend
1377 (vs)	1377 (vs, p)	1376 (vs, p)		<i>a'</i>	C = C stretch
1392 (sh)		1390 (sh, -)	1385 (s)	<i>a'</i>	C = C stretch
1455 (ms)	1452 (ms, p)	1453 (ms, p)	1450 (s)	<i>a'</i>	C-H i.p. bend
1514 (vw)	1514 (w, p)	1514 (vw, p)	1505 (ms)	<i>a'</i>	C = C stretch
1545 (vw)	1542 (vw, -)	1543 (vw, p)		<i>a'</i>	C = C stretch
			1565 (vs)	<i>a'</i>	C = C stretch
1576 (s)	1576 (ms, p)	1576 (ms, p)	1575 (sh)	<i>a'</i>	C = C stretch
1590 (sh)	1590 (sh, -)	1590 (sh, p)		<i>a'</i>	C = C stretch
			1615 (s)	<i>a'</i>	NH ₂ scissor
1625 (w)	1622 (w, p)	1622 (w, p)	1625 (sh)	<i>a'</i>	C = C stretch

Table 1. (Contd.)

Solid	Raman		IR		Proposed vibrational assignments
	CS ₂ sol.	CHCl ₃ sol.	nujol mull	Species	
3015 (w)	3018 (vw, p)		3020 (s)	<i>a'</i>	C-H stretch
			3035 (sh)	<i>a'</i>	C-H stretch
3056 (s)	3060 (s, p)	3060 (s, p)	3090 (s)	<i>a'</i>	C-H stretch
			3225 (s)		C-H stretch
			3285 (ms)		
3342 (w)	3385 (w, p)	3370 (wb, p)	3360 (m)	<i>a'</i>	NH ₂ symmetric stretch
3420 (vw)				<i>a'</i>	NH ₂ antisymmetric stretch

* The frequencies in cm^{-1} are given outside the brackets under columns 1, 2, 3 and 4 and relative intensities and depolarisation of the Raman lines are given within the brackets.

vw = very-weak, w = weak, m = medium, ms = medium-strong, s = strong, vs = very-strong, sh = shoulder, p = polarised, dp = depolarised, b = broad, i.p. = in-plane, o.p. = out-of-plane, d = diffused.

4. Vibrational assignments

The vibrational assignments have been proposed on the basis of magnitudes and relative intensities of the frequencies observed in the Raman and IR spectra and depolarisation ratios of the Raman lines. Assistance has also been taken from the vibrational assignments proposed for the α -substituted naphthalenes (Ram *et al* 1983; Singh 1970; Singh *et al* 1978).

The normal modes of vibrations of α -naphthylamine are discussed in §§ 4.1 and 4.2.

4.1 Naphthalene modes

4.1a C-H modes: Out of the 7 C-H stretching modes expected to be observed for α -naphthylamine only five could be observed experimentally. On account of their characteristic frequencies the C-H modes are easily assigned. The C-H in-plane and out-of-plane bending modes for naphthalene appear in the region 1050–1450 and 700–1000 cm^{-1} respectively. These modes are not affected too much by substitutions. The assignments for all the C-H modes are presented in table 1.

4.1b C-NH₂ modes: For benzene derivatives containing a NH₂ group, C-NH₂ stretching frequency appears near 1300 cm^{-1} (Kartrizky and Zones 1959). For aniline, Evans (1960) assigned the frequency 1278 cm^{-1} to the C-NH₂ stretching mode whereas Shanker *et al* (to be published) have assigned the frequency 1310 cm^{-1} to this mode for 2-chloro 6-methyl aniline. The C-NH₂ stretching frequency is expected not to be affected much in going from aniline to naphthylamine. In the present case, the frequency 1288 cm^{-1} observed with weak and medium-strong intensities in the Raman and IR spectra respectively is assigned to the C-NH₂ stretching mode. In the Raman spectrum of solid α -naphthylamine the two frequencies 458 and 480 cm^{-1} are observed with medium-strong and medium intensities respectively. The corresponding IR frequencies are observed at 444 and 475 cm^{-1} with very weak intensities. The appearance of the two frequencies 458 and 480 cm^{-1} is explained in terms of Fermi resonance of the frequency 469 cm^{-1} (the average of the frequencies 458 and

480 cm^{-1}) with the combination frequency $185 + 277 = 462 \text{ cm}^{-1}$. The frequency 469 cm^{-1} is assigned to the C-NH₂ in-plane bending modes. Similarly, the frequency 266 cm^{-1} is assigned to the C-NH₂ out-of-plane bending modes.

4.1c C-C stretching modes: As discussed earlier, 11 C-C stretching frequencies are expected to be observed in this case. Out of these 9 correspond to the C=C stretching modes and 2 correspond to the ring breathing modes. The two ring breathing modes result from in-phase and out-of-phase mixing of the two single ring breathing modes.

Since single ring breathing frequency is observed at 992 cm^{-1} for benzene, one of the two ring breathing modes should occur at a magnitude higher than 992 cm^{-1} whereas the other ring breathing mode should occur at a magnitude lower than 992 cm^{-1} . Lippincott and O'Reilly (1955) assigned the frequencies 1025 and 876 cm^{-1} to the two ring breathing modes for naphthalene. Ram *et al* (1983) assigned the frequencies 1045 and 710 cm^{-1} to these two modes for α -naphthol. However, they have termed the higher frequency mode (1045 cm^{-1}) as simply C-C stretching mode and the lower frequency mode as the ring breathing mode. In the present case, the frequencies 1030 and 710 cm^{-1} are assigned to the two ring breathing modes. The C=C stretching modes are expected to give rise to their characteristic frequencies above 1250 cm^{-1} and the assignments for these modes are presented in table 1.

The C-C-C angle bending modes in substituted naphthalenes are mixed with C-X modes, provided X is substituted at a carbon atom directly involved in the C-C-C angle bending. But such mixing is insignificant if the substitution is made at atoms other than those directly involved in the C-C-C angle bending. Furthermore, the C-C-C angle bending frequencies occur at considerable lower magnitudes below 1000 cm^{-1} . Therefore, the interaction of C-C-C angle bending modes with C-X modes having frequencies above 1100 cm^{-1} is not expected. As discussed earlier, 6 C-C-C angle bending modes are expected in the present case. The frequencies 790, 755, 628, 570, 513 and 305 cm^{-1} are assigned to the C-C-C angle bending modes. These frequencies may be correlated with the frequencies 760 cm^{-1} (a_g), 752 cm^{-1} (b_{2u}), 618 cm^{-1} (b_{3u}), 585 cm^{-1} (b_{1g}), 511 cm^{-1} (a_g) and 361 cm^{-1} (b_{2u}) of naphthalenes assigned to the C-C-C angle bending modes by Lippincott and O'Reilly (1955). It appears that in going from naphthalene to naphthylamine the frequency 760 cm^{-1} (a_g) is shifted upward whereas the frequency 361 cm^{-1} (b_{2u}) is shifted downwards due to interaction of the C-C-C angle bending modes with the C-X modes. The remaining 4 C-C-C angle bending modes appear to be fairly insensitive to substitution.

The C-C-C-C torsional modes of naphthalene are slightly affected upon substitution and usually appear with weak IR and Raman intensities. The assignments for these modes for α -naphthylamine are presented in table 1. The C-C-C-C torsional modes for α -naphthylamine (except the frequency 419 cm^{-1}) have nearly the same magnitude as in the case of naphthalene (Lippincott and O'Reilly 1955). The frequency 419 cm^{-1} of α -naphthylamine may be correlated with the frequency 475 cm^{-1} of naphthalene. The reduction of the frequency 475 cm^{-1} by 56 cm^{-1} may be due to interaction of C-C-C-C torsional mode with the C-X non-planar modes.

4.2 NH₂ group vibrations

As discussed earlier, the NH₂ group gives rise to 4 normal modes under the species a' and 2 normal modes under the species a'' .

The modes ν_s (NH₂) and ν_{as} (NH₂) are easily assigned on account of their characteristic magnitudes. The mode ν_{as} (NH₂) has a slightly higher frequency compared to the ν_s (NH₂) mode. Moreover, the ν_s (NH₂) mode appears with greater IR intensity compared to the ν_{as} (NH₂) mode. In the present case, the frequencies 3342 and 3420 cm⁻¹ observed in the Raman spectrum of solid α -naphthalene with weak intensities are assigned to the modes ν_s (NH₂) and ν_{as} (NH₂) respectively. The frequency corresponding to the ν_s (NH₂) mode is observed at 3345 cm⁻¹ with medium intensity and that corresponding to the ν_{as} (NH₂) mode could not be observed in the IR spectrum. For these frequencies (3342 and 3420 cm⁻¹), the well-known relationship $\nu_{sym} = 345.5 + 0.876 \nu_{asym}$, developed by Bellamy and Williams (1956) holds good. In the Raman spectra of CS₂ and CHCl₃ solutions the frequencies 3385 and 3370 cm⁻¹ respectively correspond to the 3342 cm⁻¹ Raman frequency of the solid spectrum. It appears that in solid state N-H bonding reduces the NH₂ stretching frequencies.

The δ (NH₂) mode appears near 1600 cm⁻¹ with usually strong intensity in the IR spectra of aromatic amines. The frequency 1615 cm⁻¹ observed with strong IR intensity is assigned to this mode. The NH₂ rocking mode— ρ (NH₂) gives rise to its characteristic frequency in the region 1000–1100 cm⁻¹. The frequency 1075 cm⁻¹ observed with weak intensity in the IR spectrum of α -naphthylamine is assigned to the ρ (NH₂) mode.

The NH₂ wagging mode— γ (NH₂) appears near 750 cm⁻¹. For *p*-trifluoromethyl aniline Yadav (1983) assigned the frequency 745 cm⁻¹ to this mode whereas for 2-chloro 6-methyl aniline Shanker *et al* (to be published) assigned the frequency 738 cm⁻¹ to this mode. In the present case, the IR frequency 755 cm⁻¹ observed with very strong intensity is assigned to the γ (NH₂) mode. The NH₂ torsional mode is expected to have the lowest magnitude of all the internal modes of the NH₂ group and is expected to appear below 400 cm⁻¹. The frequency 358 cm⁻¹ is assigned to this mode.

5. Conclusion

In the present case, out of the 54 normal modes of vibrations of α -naphthylamine, 52 normal modes could be assigned, whereas only 39 modes could be assigned earlier by Singh (1970). The relationship ν_{sym} (NH₂) = 345.5 + 0.875 ν_{asym} holds good only when the two NH bonds are equivalent. As expected, the validity of the above relationship for the frequencies 3342 and 3420 cm⁻¹ suggests that the two NH bonds are equivalent. The NH₂ stretching frequency is shifted upward in going from solid to solution phase by 30–40 cm⁻¹. The lowering of NH₂ stretching frequency in solid phase compared to the solution phase may be the result of intermolecular N...H bonding.

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