

Laser Raman and infrared spectra of 6-amino-m-cresol

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Received 5 September 1991, accepted 7 November 1991

Abstract : The Raman spectrum of 6-amino-m-cresol was recorded in the region 100-4000 cm^{-1} and its infrared spectrum as mull was also measured in the frequency range 250-4000 cm^{-1} . The spectra have been analysed assuming C_2 point group symmetry. Probable assignments to observed bands have been made with the help of intensities and normal coordinate analysis. The calculated normal frequencies are in good agreement with the experimental ones.

Keywords : Laser Raman and infrared spectrum, 6-amino-m-cresol, vibrational assignment

PACS Nos : 33.10. Gx, 33.20. -t, 33.20. Dz, 78.30. -j

Raman spectra of proteins give information not only on the structure of the main chain but also on the microenvironments of side chains (Harada and Takeuchi 1986). The important amino acid residues are tryptophan, tyrosine and phenylalanine which are used in the Raman spectroscopic studies of protein structure, because the side chain vibrations of these aromatic residues are strong in the Raman spectra of visible light excitation and further more, they can be selectively enhanced by ultraviolet excitation (Harada and Takeuchi (1986), Rava and Spiro (1984), Johnson *et al* (1984), Rava and Spiro (1985), Copeland and Spiro (1985), Johnson *et al* (1986) and Asher *et al* (1986)). From the knowledge of characteristic aromatic side chain, we can interpret the vibrational modes of the Raman spectra of proteins. Takeuchi and Harada (1986), have studied the vibrational modes of tryptophan side chain and tyrosine side chain.

The simplest model of the tyrosine side chain is p-cresol (4-methylphenol). The Raman spectra of this compound and its three deuterated derivatives in the liquid state and the I.R. spectra in the liquid solution, vapour and solid states have been reported partially by Jakobsen (1965). Davy-Dova *et al* (1965) calculated the normal frequencies of out-of-plane vibrations and assigned some of the infrared and Raman bands. Green *et al* (1971) proposed complete assignments of fundamental frequencies for non-deuterated p-cresol. As the vibrational data for 6-amino-m-cresol is not available in the literature, the present investigation has been undertaken to provide complete spectroscopic information. The

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vibrational analysis for 6-amino-m-cresol has also been carried out through laser Raman and infrared spectra.

The pure commercial sample obtained from M/s. Fluka A.G., Switzerland in solid form at room temperature was used as such. Raman spectra were recorded using a standard 90° configuration. The laser employed was a spectra physics Model 165 argon ion laser operating at 200-250 mW power on the 514.5 nm line. Scattered radiation was analysed with a Cary-82 triple monochromator fitted with a polarizer and an analyser. The frequencies obtained were correct to within $\pm 1 \text{ cm}^{-1}$. The infrared absorption spectrum of this compound was recorded in the region 250-4000 cm^{-1} on Perkin-Elmer IR spectrophotometer 521 in KBr pellet. The frequency for all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$.

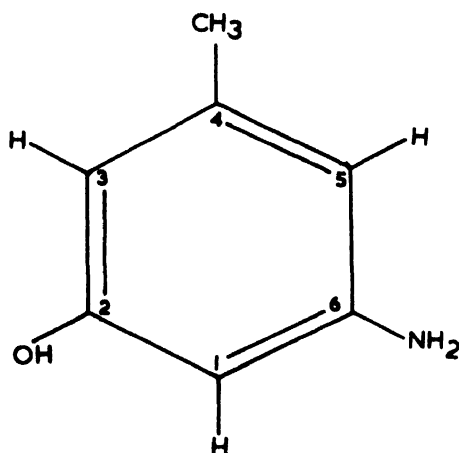


Figure 1. Structure of 6-amino-m-cresol.

The structural formula of the compound is shown in Figure 1. The normal coordinate calculations were performed using the programme due to Schachtschneider

Table 1. Initial and final sets of force constants of 6-amino-m-cresol (in units of mdyne \AA^{-1} and $\text{mdyne \AA}^{-1} \text{ rad}^{-2}$).

Types of constant		Parameter	Coordinates involved	Initial	Final
Diagonal constant	Stretching	f_D	C-H	4.50	4.548
		f_i	C-C	2.85	2.729
	bending	f_α	HCC	0.31	0.411
		f_β	CCC	0.54	0.385
		f_γ	CHC	0.29	0.312
Interaction constants	Stretch-	f_{Dd}	CH CC	0.19	0.198

Table 1. (Contd.)

Types of constant		Parameter	Coordinates involved	Initial	Final
constants	Stretch	(adj) f_{dd}	CC CC	0.06	0.156
		(opp) f_{dd}	C=C CC	0.65	0.821
		f_{DD}	CH CH		
	bend-bend	$f_{\alpha\alpha}$	HÔC HÔC	0.04	0.042
		$f_{\beta\beta}$	CÔC CÔC	0.12	0.184
		$f_{\alpha\gamma}$	HÔC CÔC	0.21	0.215
		$f_{\alpha\beta}$	HÔC CÔC	0.08	0.124
	Stretch-bend	$f_{D\alpha}$	CH HÔC	0.25	0.261
		$f_{D\gamma}$	CH CÔC	0.30	0.379
		$f_{D\beta}$	CH CÔC	0.45	0.456
		$f_{\alpha\alpha}$	CC CÔH	0.26	0.272
		$f_{\beta\beta}$	CC CÔC	0.36	0.374

Table 2. Vibrational assignments of 6-amino-m-cresol.

Type	IR frequency and intensity cm^{-1}	Laser Raman frequency and intensity cm^{-1}	Calculated frequency cm^{-1}	Assignment/ (PED)
	3465	—	3462	N-H asym. stretch
	3398 VS	3410 VS	3396	N-H sym. stretch
		3315 W		O-H stretch
	3120 S	2998 M	3118	CH ₃ asym. stretch
A'	3021 W		3019	C-H stretch (90)
A'	2993 W		2988	C-H stretch (89)
	2988 M	2981 S	2981	C-H ₃ asym. stretch
A'	2952 W		2943	C-H stretch (85)
	2851 S	2850 S	2841	CH ₃ sym. stretch
	1641		1622	O-H in-plane bending
A'	1621	1630	1624	C-C stretch (81)
	1610		1602	N-H torsion
A'	1605 VS	1607 S	1603	C-C stretch (80)
A'	1600	1600	1596	C-C stretch (82)
	1541 W		1519	N-H scissoring
A'	1534 S	1534 S	1526	C-C stretch (79)
	1460 M		1449	CH ₃ asym. deformation
	—	1457 M	1447	CH ₃ asym. deformation
A'	1442 M		1431	C-C stretch (78)
A'	—	1428 S	1422	C-C stretch (82)
A'	1403 S		1393	C-H in-plane bending
	1375 M		1361	CH ₃ sym. deformation
A	1350 M	1341 VS	1329	C-NH ₂ stretch (60)
A'	1297	1288 VS	1275	C-OH stretch (60)
A'	1261	1270 S	1254	C-H in-plane bending (71)
A'	1240 S	1238	1229	C-CH ₃ stretch (68)
	1240		1231	O-H in-plane bending
A'	1160 S	1165 VS	1152	C-H in-plane bending (76)

Table 2. (Contd.)

Type	IR frequency and intensity cm^{-1}	Laser Raman frequency and intensity cm^{-1}	Calculated frequency cm^{-1}	Assignment/ (PED)
	1103	1109	1101	N-H twist
	1020 S		1012	O-H out-of-plane bending
A'	1010 MS	1015 MS	1011	C-C-C trigonal bending (85)
	950 M		941	O-H out-of-plane bending
A''		940 S	930	C-H out-of-plane bending (61)
A''	891 S	901 VS	890	C-H out-of-plane bending (68)
	850		839	C-H twist
A''	842 S		830	C-OH out-of-plane bending (64)
	810 S		801	C-H wagging
A''	810 S	811 S	796	C-C out-of-plane bending (57)
A''	733	730	721	C-H out-of-plane bending (60)
A''	—	675 M	661	C-C out-of-plane bending (55)
	620		602	N-H wagging
A'	598 S	601 S	589	C-C in-plane bending (67)
A'	580 S	581 S	562	C-OH in-plane bending (54)
A'	470 VS	475 VS	462	C-C in-plane bending (72)
A'	386 W	386 W	365	C-NH ₂ in-plane bending (57)
A'	357	349	341	C-CH ₃ in-plane bending (55)
A''	331 W	—	321	C-C out-of-plane bending (64)
A''	315 S	—	301	C-NH ₂ out-of-plane bending (59)
A''	290	285	267	C-CH out-of-plane bending (61)

(1969). Internal coordinates for the out-of-plane torsional vibration are defined as recommended by International Union of Pure and Applied Chemistry (IUPAC). The valence force field was adopted for both in-plane and out-of-plane vibrations. The initial force constants were taken from similar benzene derivatives. This set of force constants was subsequently refined by keeping few interaction constants fixed throughout refinement process. The final force constants were presented in Table 1.

The observed frequencies of the compound together with relative intensity, probable assignments and calculated frequencies are presented in Table 2. The observed spectra are explained on the basis of C_s point group as shown in Figure 2.

Assuming NH₂, CH₃ and OH groups as single mass point, the molecule under consideration would belong to C_s point group. This simplified model gives rise to 30 normal mode of vibrations along with 18 additional vibrations due to substituent groups NH₂, CH₃ and OH. All the vibrations are active in both Raman and infrared spectra. Out of 30 normal vibrations 21A' are planar vibration and 9A'' are non-planar vibrations.

The trisubstituted benzene which form the subject of the present investigation give rise to three C-H stretching, three out-of-plane bendings and three C-H in-plane bendings. The aromatic structure shows the presence of C-H stretching vibrations in the region 3000-

3100 cm^{-1} , which permits a ready identification for this structure. In this region, the bands are not appreciably affected by the nature of substituents. The frequencies 3021 , 2993 and 2952 cm^{-1} in 6-amino-m-cresol have been assigned to C-H stretching modes. The rest of the vibrations, viz., three C-H in-plane bendings and three C-H out-of-plane bendings of 6-amino-m-cresol molecule are given in Table 1. They are in good agreement with literature values (Silver and Wood 1964).

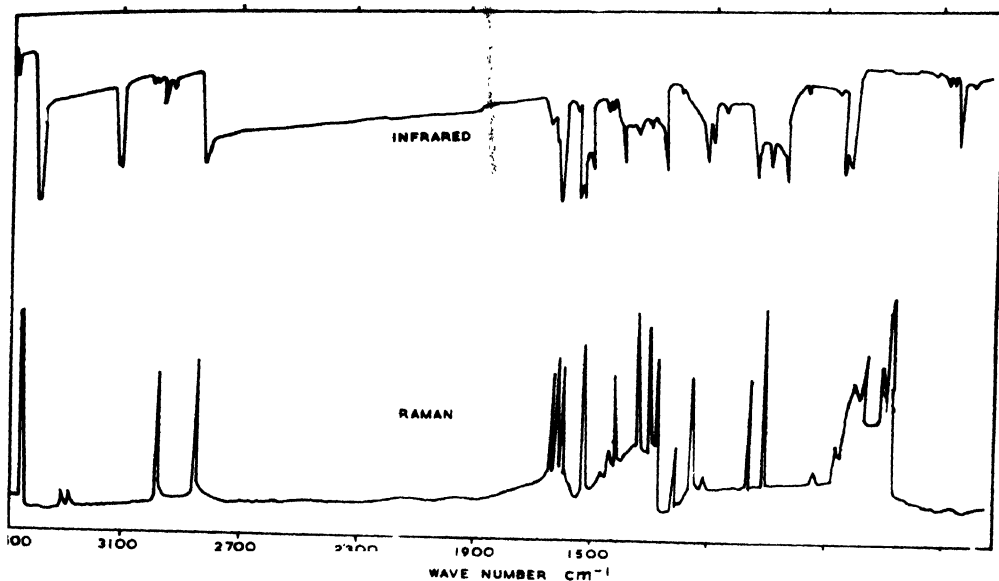


Figure 2. Infrared and Raman spectra of 6-amino-m-cresol.

It is noted from the literature that a strong band around 1200 cm^{-1} appears due to valence oscillations in toluene and substituted toluenes. Hence, the strong band at 1240 cm^{-1} in 6-amino-m-cresol is assigned to C-CH₃ stretching mode. The bands at 357 and 290 cm^{-1} in 6-amino-m-cresol have been assigned to C-CH₃ in-plane bending and C-CH₃ out-of-plane bending respectively. This conclusion agrees well with the literature values (Sing *et al* 1966, Padhye and Vilodkar 1959).

The C-NH₂ stretching frequency appears at about 1300 cm^{-1} . The band at 1350 cm^{-1} in 6-amino-m-cresol is assigned to this mode. The bands at 386 and 315 cm^{-1} have been assigned to C-NH₂ in-plane bending and out-of-plane bending respectively.

According to Bellamy (1959), in primary aromatic amines the N-H stretching vibrations occur in the region 3300 - 3500 cm^{-1} . According to this, the bands at 3465 and 3398 cm^{-1} in 6-amino-m-cresol have been designated to represent the N-H stretching modes. The higher value in the above case is assumed to be asymmetric stretching while the remaining to the symmetric stretching. The NH₂ scissoring mode normally lies in the

region $1590\text{--}1650\text{ cm}^{-1}$ in primary aromatic amines (Bellamy 1959). This seems to fall at 1541 cm^{-1} in this case. NH_2 wagging mode is assigned to the band at 620 cm^{-1} by analogy with aniline (Evans 1960).

The CH_3 active asymmetric stretching modes have been assigned to the lines at 2998 and 2981 cm^{-1} in the Raman spectra of the solid and CH_3 symmetric stretch is assigned to the line at 2850 cm^{-1} . The three deformations of the methyl group are observed in the Raman spectrum of solid at 1460 and 1457 cm^{-1} for the antisymmetric deformation and 1375 cm^{-1} for the symmetric motion. These observation agree very well with Durig *et al* (1990).

The C-OH stretching frequency for this molecule appears at 1288 cm^{-1} in Raman spectrum. OH stretching vibration gives rise to a Raman band at 3315 cm^{-1} and O-H in-plane bending frequency have been found in 6-amino-m-cresol at 1641 and 1240 cm^{-1} . The O-H out-of-plane bending modes gives rise to frequency at 1020 cm^{-1} and 950 cm^{-1} . These observation are also in agreement with Pasquier *et al* (1990).

In order to obtain a more complete interpretation of the vibrational spectrum and to determine the degree of mixing of normal modes, a normal coordinate analysis of 6-amino-m-cresol was carried out. This analysis was made using the Wilson's GF matrix method (Wilson *et al* 1955), employing the programs developed by Schachtschneider (1969). The G matrix was calculated using the structural parameters C- $\text{CH}_3 = 1.541\text{ \AA}$, C-H = 1.073 \AA , C-C = 1.527 \AA , C-OH = 1.260 \AA and C- $\text{NH}_2 = 1.47\text{ \AA}$. Initial values for the force constants were also taken from benzene derivatives. From the modified valence force constants the observed frequencies were fitted to 23 cm^{-1} (8.0%) for the 6-amino-m-cresol.

In the present study, a complete vibrational assignment and the analysis of 6-amino-m-cresol are available using the frequencies obtained from infrared and laser Raman spectra on the basis of C_s symmetry.

Acknowledgment

One of the authors (NSG) thanks CSIR for the award of Senior Research Fellowship.

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