

The near UV vapour absorption spectra of 1-hydroxynaphthalene and 2-hydroxynaphthalene

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Abstract. Vibrational analyses, of the electronic bands of 1-hydroxynaphthalene and 2-hydroxynaphthalene corresponding to the 312 nm electronic transition in naphthalene, have been carried out from the vapour phase absorption spectra recorded under high resolution. It is found that the prominent vibronic bands owe their large intensities to a different vibronic interaction than that in naphthalene.

Keywords. UV vapour absorption spectra; hydroxynaphthalene; vibrational analyses.

1. Introduction

The effect of substituents on the excited electronic states of naphthalene can only be deduced from absorption spectra. Since the electronic wavefunctions of molecules are free from any external perturbations in the vapour phase these spectra are the least complicated to interpret. The greater number of allowed vibrations in the substituted naphthalenes, however, makes their spectra much more complex in appearance than the spectrum of naphthalene because of their lower symmetry. The perturbational role of molecular vibrations on the one hand and inductive substituents on the other is complementary in the electronic spectroscopy of alternant hydrocarbons but the recent studies on two-photon spectra of benzenes show that the complementarity of vibronic and inductive perturbations for a given electronic transition gets reversed as compared to that in one-photon spectra [Goodman and Rava 1982]. It has been possible to see these changes in perturbation effects due to the availability of vast amount of data on the one-photon absorption spectra of substituted benzenes. In substituted naphthalenes, however, there is paucity of data from the high resolution vapour phase absorption spectroscopy. In the present paper we summarize the results of our vibrational analyses of electronic bands of 1-hydroxynaphthalene (1-HN) and 2-hydroxynaphthalene (2-HN) corresponding to the 312 nm system of the parent naphthalene molecule.

2. Experimental

The absorption bands were developed in a pyrex cell fitted with quartz windows at temperatures 60°C for 1-HN and 100°C for 2-HN and were recorded on a 3.4 m Jarrell-

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Ash grating spectrograph using photographic plates. The plates were measured on a Russian comparator, the uncertainty of measurements being 0.1 cm^{-1} for sharp bands and 0.5 cm^{-1} for weak and diffuse bands.

3. Discussion

The O_0^0 bands of 1-HN and 2-HN have been assigned in the light of hot electronic bands and the vibrational frequencies determined from the infrared spectra (Hollas and Thakur 1973, 1974). In the present work about 200 bands in the spectra of both 1-HN and 2-HN were analysed. The prominent sequence bands in the neighbourhood of the O_0^0 band are shown in figures 1 and 2, for 1-HN and 2-HN respectively, where A, B, C etc., stand for sequence bands in the order of decreasing intensities.

The 312 nm electronic spectrum of the parent molecule consists of two parts—the Franck-Condon part of the intensity as represented by the O_0^0 band and the others involving totally symmetric vibrations which are small in comparison to the vibronic part of the intensity which is associated with the b_{3g} vibrations. The vibronic intensity arises from Herzberg-Teller type intensity stealing from the second excited state $^1B_{1u}$ of naphthalene (Craig *et al* 1961).

In the case of 1-HN and 2-HN both the first and the second excited states have A' symmetry of the C_s point group and any differences in the intensities of vibronic bands should reflect the effect of substituent site. The strong vibronic bands at $0-317 \text{ cm}^{-1}$ in 2-HN and at $0-274 \text{ cm}^{-1}$ in 1-HN have the same rotational contours as the corresponding O_0^0 bands and this implies that there are no changes in the orientation of the transition moments. It has been shown earlier that the electronic transition moments of 1-substituted naphthalenes are polarized largely along the long in-plane axis whereas those of 2-substituted naphthalenes are polarized largely along the short in-plane axis (Hollas and Thakur 1973, 1974). The weak vibronic bands at $0-531 \text{ cm}^{-1}$ in 1-HN and at $0-522 \text{ cm}^{-1}$ in 2-HN may be correlated to the ring distortion vibration of b_{3g} symmetry (506 cm^{-1}) in naphthalene which gives rise to the most active vibronic band in naphthalene. This observation shows that the bands at $0-274 \text{ cm}^{-1}$ in 1-HN and $0-317 \text{ cm}^{-1}$ in 2-HN may involve a intensity borrowing from an electronic state other than the second excited singlet state. One of the possibilities is the involvement of charge-transfer states corresponding to the promotion of an electron from a molecular orbital localized on the substituent to that localized on the ring. This idea gets support from the fact that the vibrational structures observed in the spectra of 1-fluoronaphthalene and 2-fluoronaphthalene (Singh 1981) are different from those of corresponding naphthols.

The vibrational intervals in the ground and the first excited states as determined from the present work are summarized in table 3 and the prominent vibronic bands are given in tables 1 and 2 for 1-HN and 2-HN respectively. It is seen that the rotational contours of the vibronic bands involving out-of-plane vibrations (symmetry a'') are not well-developed. The present analysis supersedes the earlier analyses from the low resolution work (Singh and Singh 1965, 1966).

It is also interesting to note that the normal modes of vibrations appearing strongly in the hot bands do not give rise to similarly intense cold bands. This may result from the different amounts of mixing between two or more vibrational modes in the two electronic states which can change the form of a particular mode of vibration in going

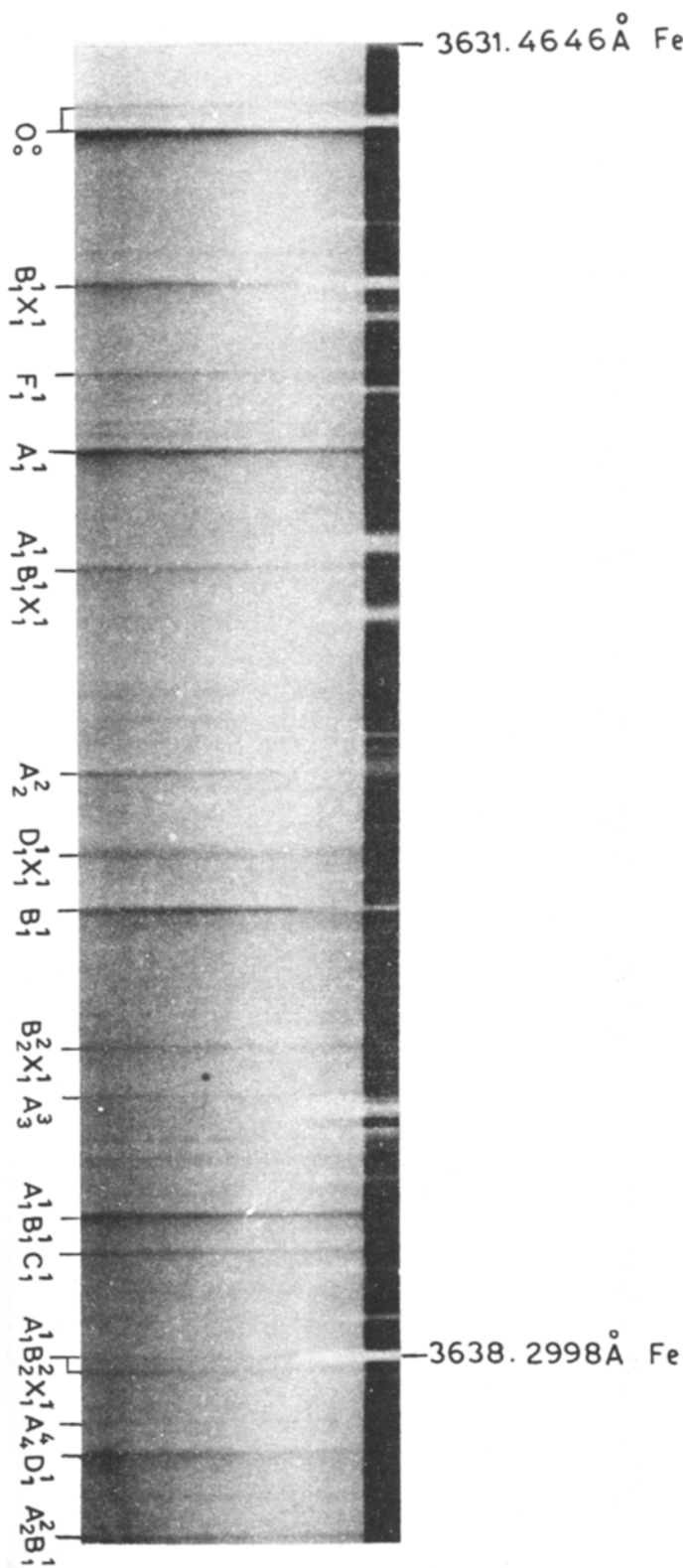


Figure 1. The O_0^0 band region of 1-hydroxynaphthalene.

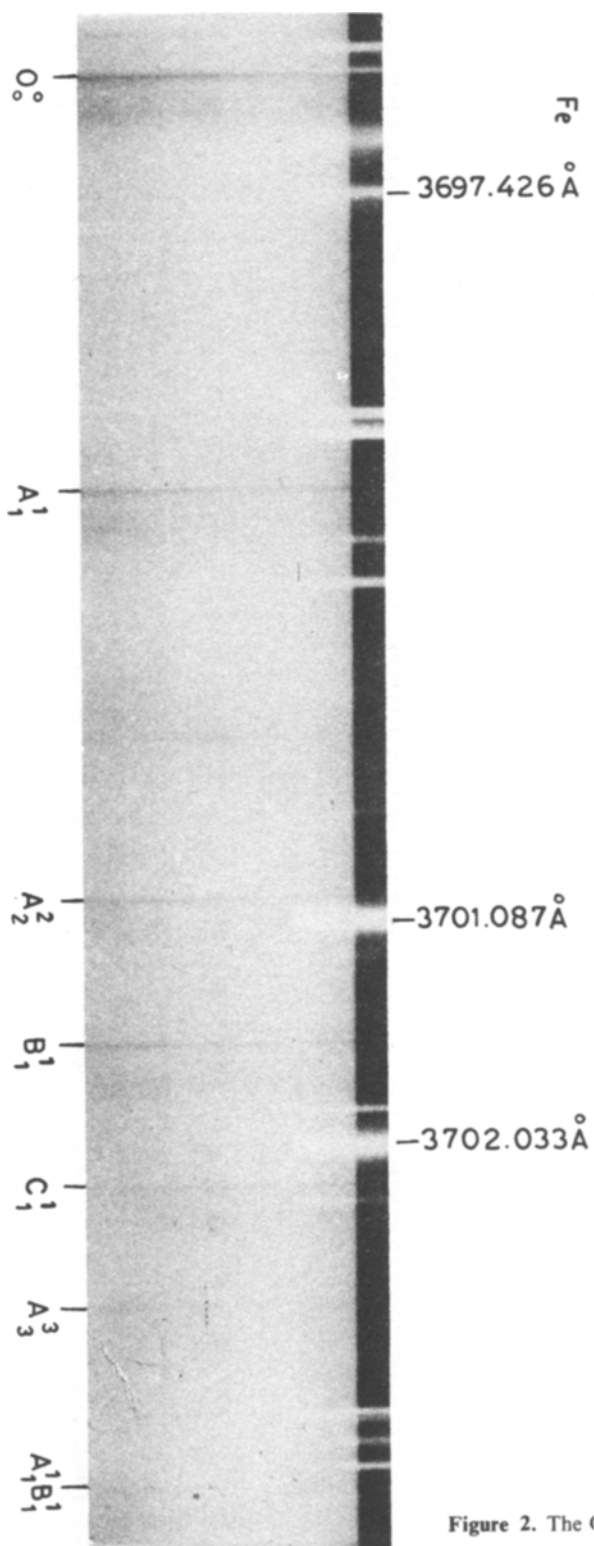


Figure 2. The O_0^0 band region of 2-hydroxynaphthalene.

Table 1. Prominent bands in the $S_1 \leftarrow S_0$ vapour absorption of 1-hydroxynaphthalene.

Wave number (cm^{-1})	Relative intensity	Separation from O_0^0 band (cm^{-1})	Assignments
30925	2	-531.0	0-531
31029	2.5	-427.1	0-427
31182	5	-274.4	0-274
31260	2	-196.7	0-197
31345	4	-111.6	E_1^1
31377	2	-79.7	G_1^1
31407	4	-49.1	C_1^1
31422	8	-34.2	
31422	8	-34.1	B_1^1
31422	8	-34.0	
31433	2	-23.8	H_1^1
31442	6	-14.0	A_1^1
31446	2	-10.6	F_1^1
31456.5	10	0.0	O_0^0
31457	1	+0.7	
31457	1	+0.9	Y_1^1
31458	1	+1.1	
31483	6	+26.9	X_1^1
31564	3	+107.4	0+107
31731	6	+274.4	0+274
31869	5	+412.4	0+412
31908	3	+452.0	0+452
32140	4	+683.2	0+683

Table 2. Prominent bands in the $S_1 \leftarrow S_0$ vapour absorption of 2-hydroxynaphthalene.

Wave number (cm^{-1})	Relative intensity	Separation from O_0^0 band (cm^{-1})	Assignments
30383	1.5	-522.1	0-522
30495	3	-410.9	0-411
30589	8	-316.8	0-317
30703	2	-202.1	0-202
30778	1	-127.1	
30779	1	-126.7	0-127
30815	1.5	-90.5	D_1^1
30859	2.5	-46.4	C_1^1
30865	3	-40.5	B_1^1
30888	2	-17.3	A_1^1
30905	10	0.0	O_0^0
30923	1.5	+17.9	X_1^1
30986	2	+80.7	0+81
31197	1	291.5	0+292
31301	1.5	+395.5	0+395
31309	1.5	+403.4	0+403
31625	2	+719.3	0+719

Table 3. Correlation of ground and excited state frequencies of 1-hydroxy and 2-hydroxy naphthalene.

Molecule	Ground state (cm ⁻¹)	Excited state (cm ⁻¹)	Sequence internal (cm ⁻¹)
1-hydroxynaphthalene	156 (a'')	107 (a'')	-49
	197 (a'')	163 (a'')	-34
	274 (a')	260 (a')	-14
	470 (a')	412 (a')	-58
	531 (a')	452 (a')	-79
	740 (IR) (a')	683 (a')	
	770 (Raman) (a')		
2-hydroxynaphthalene	127	81	-46
	202	162	-40
	317		
	411	395	-17
	522		
	740 (IR)	719	
	765 (Raman)		

from the ground to the excited electronic state. This effect makes the task of correlating ground and excited state vibrational frequencies very difficult. The observed sequence intervals have been used in making such correlations wherever possible and are shown in table 3 for the two molecules.

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