

Vibronic spectra of radical cations of some hydroxyl substituted naphthalenes

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The fluorescence spectra of radical cations of some hydroxyl substituted naphthalenes have been investigated in boric acid glass. The emission spectra are found to have one intense band along with some weaker bands/shoulders. It is found that the shift of weaker bands/shoulders from the main band depends on the nature and position of the substituent. These frequency shifts from the main intense band are related to the vibrational frequencies of the cations in the ground state. Further, it is observed that the shift of the vibronic bands is much smaller when two -OH substituent groups are located at neighbouring sites. This has been interpreted as an evidence for the existence of intramolecular hydrogen bonding.

Hydroxyl substituted naphthalenes (HSNs) are important because of their presence in natural products and their extensive applications. The special interest in such systems arises due to their being good candidates for studying the behaviour of optical bands by varying the number and positions of substituent groups, hydrogen bonding within the system and associated solvent molecules. A number of workers¹⁻¹⁰ have studied the spectra of these substituted molecules, but little attention has been directed towards their radical cations. The first comprehensive study on ionic species of HSNs in boric acid glass was recently carried out by Sharma *et al.*^{11,12} and Bahervand *et al.*¹³.

Published infrared (IR) spectral data for radical cations are rare compared to those on molecules. This is probably due to experimental difficulties such as the availability of suitable matrix, transparent in the IR region. Therefore, the IR spectra of HSNs have not been reported. However, such information can be obtained from the analysis of vibronic structure of the fluorescence spectra. The present paper is an attempt to analyse the fluor-

escence spectra of radical cations of ten hydroxyl substituted naphthalenes.

Experimental

Boric acid crystals were obtained from Indian Drugs and Pharmaceutical and Sarabhi M. Chemical (Bombay). Naphthalene, 1- and 2-naphthols, and dihydroxynaphthalenes (DHNs) were obtained from Fluka AG (Switzerland) and Tokyo Kasei (Japan). All the chemicals used in the present investigation were of spectroscopic grade. The solute doped boric acids films were prepared by the method described elsewhere¹⁴. A high pressure mercury lamp of 250 W was used as a source of UV radiation. The experimental procedure followed was the same as described in the previous papers^{11,12}.

Results and discussion

To excite the fluorescence spectra of radical cations, we selected an absorption wavelength in the visible region for which the intensity of fluorescence emission was maximum. The emission spectra so obtained were found to consist of an intense band along with shoulders/weaker bands. The observed band maxima together with the visual estimates of the intensities and the differences between the successive band maxima $\Delta\tilde{\nu}$ (cm^{-1}) are given in Table 1. These differences give the vibrational frequencies of the cations in the ground state. These values are accurate to within $\pm 100 \text{ cm}^{-1}$. Tentative assignments of the vibrational frequencies^{15,16} are also given in Table 1. Some of the prominent vibrations of the cations, corresponding to the observed intense bands are discussed below:

271 and 425 cm^{-1} : In the case of 1,2-DHN and 2,3-DHN, due to proximity of -OH groups, there is a possibility of intramolecular hydrogen bonding. The weak bands at 271 and 425 cm^{-1} observed in the case of 1,2-DHN and 2,3-DHN respectively may be due to hydrogen bonding. The variation in frequencies could be on account of the change in the strength of hydrogen bonding which depends upon the nature and position of substituents¹⁵.

1040 to 1224 cm^{-1} : These bands fall in the region of C-H in plane bending modes and could be identified with fairly good intensity in a number

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Table 1—Absorption and fluorescence maxima (cm^{-1}) for the radical cations of hydroxyl substituted naphthalenes in boric acid glass

Compound	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\delta\bar{\nu}$ (cm^{-1})	Assigned mode of vibration
1,2-DHN	23256	22321 (s)		
		21368 (m)	953	C-H o.p. bending
		21097 (sh)	1224	C-H i.p. bending
			271	hydrogen bonding
1,3-DHN	25840	24390 (w)		
		21834 (m)		
		20408 (s)	1426	C=C stretching
1,4-DHN	26455	22124 (sh)		
		21053 (s)	1071	CH i.p. bending
1,5-DHN	26667	25253 (s)		
		24213 (sh)	1040	C-H i.p. bending
		23474 (m)	1779	C=O stretching
1,7-DHN	25974	24631 (s)		
		23042 (sh)	1589	C=C stretching
2,3-DHN	25126	23474 (sh)	1716	C=O stretching
		22124 (s)	1350	C=C stretching
		20833 (sh)	1291	C-O stretching
		20408 (sh)	425	hydrogen bonding
2,7-DHN	26385	23810 (sh)		
		22222 (sh)	1588	C=C stretching
		21097 (s)	1125	C-H i.p. bending
		19724 (m)	1373	C=C stretching

w = weak, m = medium, s = strong, sh = shoulder
i.p. = in plane, o.p. = out of plane

of -OH substituted naphthalene cations; for example, at 1040 cm^{-1} in 1,5-DHN; at 1071 cm^{-1} in 1,4-DHN; at 1125 cm^{-1} in 2,7-DHN and at 1224 cm^{-1} in 1,2-DHN. The 953 cm^{-1} band observed in case of 1,2-DHN cation could be assigned to the out-of-plane C-H bending.

1291 cm^{-1} : This band corresponds to C-O stretching and could be easily identified in 2,3-DHN cation.

1350 to 1589 cm^{-1} : The bands in this range are due to C=C stretching vibration. In the case of cations of 1,3-DHN; 1,7-DHN; and 2,3-DHN, these bands occur at $\sim 1400 \text{ cm}^{-1}$ and at 1588 cm^{-1} in the case of 2,7-DHN. The difference may be due to the change in the position of hydroxyl group which modifies the substituted system.

1716 and 1779 cm^{-1} : These bands fall in the region of C=O stretching. However, there are no C=O bonds in the molecules investigated. The radical cations were produced by irradiating the

compounds by UV radiation. It appears that during the process of irradiation some hydroxyl groups get dissociated¹⁷. This is illustrated in Fig. 1 for 2-naphthol. It can be seen that along with the radical cations, there is a possibility of having ions (structure I, Fig. 1) and the anionic mesomeric quinonoids (structures II and III, Fig. 1). Similar dissociation products can occur for other HSNs also. The observed bands at 1716 cm^{-1} in the case of 2,3-DHN; and at 1779 cm^{-1} in the case of 1,5-DHN can, therefore, be assigned to C=O

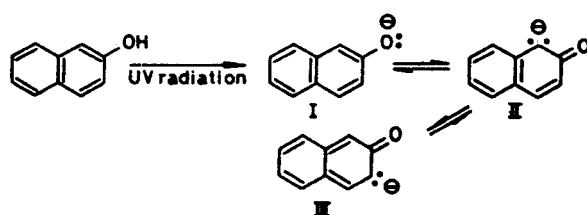


Fig. 1—Effect of UV radiation on 2-naphthol

stretching mode of vibrations of the anionic mesomeric forms. This assignment is supported by the recent observation made by Ahmad *et al.*¹⁶ who have reported a strong C=O band at 1705 cm^{-1} for 3,5-dinitrobenzoic acid in KBr.

Assignment of OH-dissociated bands

Hercules *et al.* and Williams^{18,19} have reported that on UV irradiation, some hydroxyl groups get dissociated (Fig. 1) and give rise to a weaker band with large shift from the main band of the cation. They have reported a weak band at 429 nm for the dissociated 2-naphthol which agrees well with the emission band observed by us at 426 nm in 2-naphthol. This indicates that on UV irradiation, the radical cations and the dissociated species co-exist and give to their individual characteristic emission bands. According to Hercules *et al.* and Williams^{18,19}, this shift is greater in the emission spectrum than in absorption. Similar emission bands are observed at 421 nm in 1-naphthol and at 426 nm in 1,6-DHN.

The present investigation thus shows that:

(i) Some of the prominent vibrational frequencies of radical cations can be obtained from the analysis of the vibronic structure of the emission spectra.

(ii) UV irradiation of the doped boric acid glass films gives rise to radical cations and in the process dissociation of some of the hydroxyl groups also takes place.

(iii) Whenever two substituent -OH groups occur at neighbouring sites, intramolecular hydrogen bonding takes place.

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