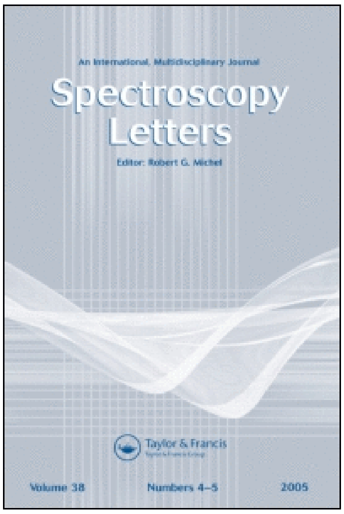

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Photoacoustic Spectroscopic Studies of Mono-Substituted Naphthalene Molecules

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PHOTOACOUSTIC SPECTROSCOPIC STUDIES OF MONO-SUBSTITUTED NAPHTHALENE MOLECULES

Key Words: Photoacoustic Spectroscopy, Polycyclic aromatic hydrocarbons, Naphthols, Singlet-Triplet Transitions, CNDO Calculations

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ABSTRACT

The present paper deals with the Photoacoustic (PA) studies of mono-substituted (hydroxy) naphthalene molecules, namely 1-naphthol and 2-naphthol in boric acid glass in the region 250-400 nm. The electronic transitions of these molecules observed experimentally, have been interpreted using the optimised geometries and CNDO/S-CI method. Assignments of observed electronic transitions are made on the basis of singlet-singlet and singlet-triplet transitions. The PA spectra of 1-naphthol and 2-naphthol are compared with its parent molecule i.e. naphthalene molecule, in terms of charge transfer character of -OH group and polarization of molecules. It is observed that the non-radiative transitions in mono-substituted naphthalene molecules shift towards the higher wavelength region when compared with naphthalene molecule, which may be attributed to increase in the charge density in the substituted ring.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) particularly Hydroxyl substituted naphthalene, are widely found in natural products and many of them are highly fluorescent. The importance of these derivatives is due to their use as food grade antioxidants in food stuffs [1], oils and oil additives [2], plastics [3], pharmaceuticals and in synthesis of some laser dyes [4]. The electronic interaction between simple aromatic structure and the substituent are often useful in understanding the absorption and emission spectra of substituted naphthalene. Although the electronic absorption, emission and fluorescence spectra of mono and dihydroxynaphthalene isomers have been studied by many workers [5-11], but so far no attempts have been made to study the non-radiative transitions of these molecules.

To know about non-radiative transitions of PAH molecules, we have carried out a systematic study of PAH molecules by Photoacoustic (PA) spectroscopy in our Laboratory [12-16]. The PA effect is the process of generation of acoustic waves in a sample resulting from the absorption of photons. Recently, PA spectroscopy has emerged as a new spectroscopic analytical and research tool for the investigations of optical and thermal properties of materials and surfaces, where the conventional spectroscopic technique fails [12-18]. The main advantage of PA spectroscopic technique is that even extremely low/high absorbing and/or reflecting and scattering samples can easily be investigated without any sample preparation problem. This technique can also be used to get information about non-radiative transitions and singlet-triplet electronic transitions.

The present paper deals with the PA studies of mono-substituted (hydroxy) naphthalene molecules. The study of electronic transitions of 1-naphthol and 2-naphthol are reported using PA and optical absorption spectra in boric acid glass in the region 250-400 nm. The PA spectra of 1-naphthol and 2-naphthol are compared with its parent molecule i.e. naphthalene molecule, in terms of charge transfer character of -OH group and polarization of molecules. On theoretical side, the ground state geometries are optimised using the MNDO molecular orbital method [19]. The electronic energy levels have been calculated using the optimised geometries and the CNDO/S-CI method [20-21].

EXPERIMENTAL

1-naphthol and 2-naphthol were obtained from M/S Fluka AG (Switzerland) and boric acid crystals of AR grade was obtained from M/S Glaxo Laboratories Ltd. (India). The boric acid glass doped with these two naphthols was prepared by the method described elsewhere [22]. The experimental set-up of PA spectrophotometer used for these studies was developed at National Physical Laboratory, New Delhi [23]. The schematic representation of the experimental set-up is given elsewhere [13].

The optical absorption spectrum was recorded on JASCO UV-VIS-NIR spectrophotometer (Model V-570).

RESULTS AND DISCUSSION

1-Naphthol

The PA and optical absorption spectra of 1-naphthol in boric acid glassin the region 250 to 400 nm are compared in Fig. 1. Ground state geometries of neutral 1-naphthol molecule optimized using MNDO molecular orbital method [19] is given in Fig. 2. The electronic states are calculated using the optimized geometries and the CNDO/S-CI method [20-21]. The PA spectrum shows some additional bands towards the longer wavelength side alongwith a modified intensity and shape of the bands.

In the PA spectrum of 1-naphthol in boric acid glass, the origin of first electronic transition is observed at 318.0 nm showing a shift of 1.0 nm towards higher wavelength side as compared to its optical spectrum. This corresponds to the electronic transition of type ($^1A_{1g} \rightarrow {}^1B_{3u}$) of naphthalene molecule and may be assigned as ($A' \rightarrow A'$), with the transition moment along the long axis of the molecule.

The structure attached to this electronic transition may be attributed to well known vibrational modes of the ground state of naphthalene molecule [24-25] and vibrations due to -OH group [26] as shown in Table 1. The band attached with this electronic transition and observed at 305.7 nm may be due to the OH in plane deformation vibration of frequency 1256 cm^{-1}, while the band at 302.2 nm having a difference of 1640 cm^{-1} from the origin may arise from a combination of the C-H out

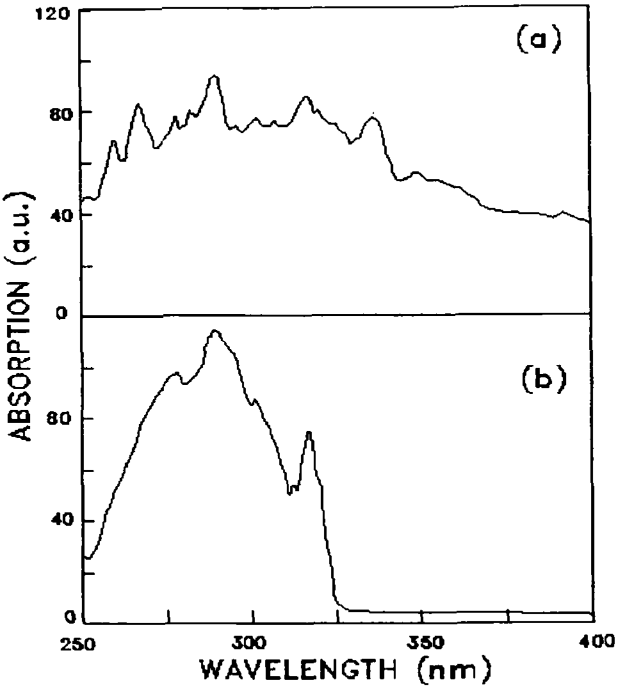

Fig. 1 (a) PA spectrum of 1-Naphthol in Boric acid glass.
(b) Optical absorption spectrum of 1-Naphthol in Boric acid glass.

of plane bending mode $\nu_8(a_g)$ and C-H in-plane bending mode $\nu_7(b_{1g})$. The other band at 299.4 nm is attributed to the second overtone of -OH in-plane deformation vibration of frequency 2510 cm^{-1}.

The second electronic transition in the PA spectrum is found at 290.0 nm which shows a shift of 2.0 nm towards higher wavelength side, when compared with its optical spectrum. The variation of 1.0 nm and 2.0 nm in the first and second transitions respectively are due to the time constants used in the Lock-in amplifiers to smoothen the spectra. This electronic transition may be due to the allowed (A'→A') transition with the transition moment along the short axis of the molecule and correspond to the electronic transition ($^1A_{1g} \rightarrow {}^1B_{2u}$) of naphthalene molecule.

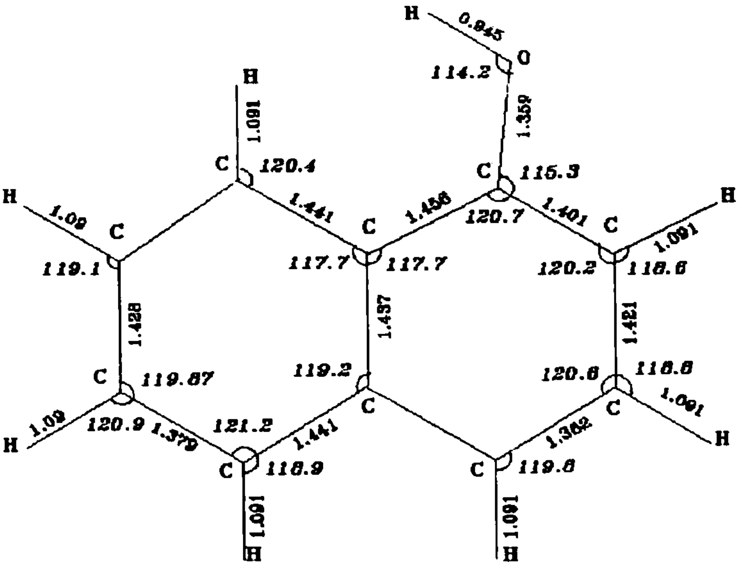

Fig. 2 Schematic representation of 1-Naphthol molecule showing optimized bond lengths (Å) and bond angles (deg).

The band observed at 281.9 nm shows a difference of 986 cm^{-1} from the origin of the second transition at 290.0 nm. It may correspond to the C-H in-plane bending mode $\nu_7(b_{1g})$. The other band observed at 276.8 nm, which is at a difference of 1640 cm^{-1} from the origin, may be attributed to the combination of $\nu_8(a_g)$ and $\nu_7(b_{1g})$. The third band is observed at 267.5 nm, which is 2890 cm^{-1} away from the origin. It can be considered as a combination of $\nu_8(a_g)$, $\nu_7(b_{1g})$ and -OH in-plane deformation vibration. The fourth band at 258.0 nm has a difference of 4266 cm^{-1} from the origin of the second transition, and may be attributed to the combination of $\nu_8(a_g)$, $\nu_7(b_{1g})$, $\nu_4(b_{1g})$ (C-C stretching) and -OH in-plane deformation vibration.

The CNDO/S-CI molecular orbital calculations and the structure of the observed bands suggest an additional non-radiative electronic transitions in PA spectrum at 336.0 nm. A close agreement has been found between the results obtained by experiment and by CNDO/S-CI molecular orbital calculations as shown in Table 1.

Table 1: Assignments of the observed bands in PA and optical spectra of 1-naphthol in boric acid glass.

Transition No.	Calculated Transition Energy (nm)	Observed maxima Optical (nm)	Observed maxima PAS (nm)	Observed maxima PAS (cm^{-1})	Shift from electronic origin (cm^{-1})	Assignments
I	**331.5**	-	**336.0**	**29762**	**0**	**Non-Radiative**
	(S--T)					
II	**316.2**	**317.0**	**318.0**	**31446**	**0**	**Radiative**
	(0.0496)*		305.7	32702	1256	0+1256
			302.2	33086	1640	0+730+910
			294.4	33956	2510	0+2x1256
III	**281.4**	**288.0**	**290.0**	**34482**	**0**	**Radiative**
	(0.21198)*		281.9	35468	986	0+986
			276.8	36122	1640	0+730+910
			267.5	37372	2890	0+729+907+1254
			258.0	38748	4266	0+730+910+1256+1370

* The number in parenthesis indicate oscillator strength

2-Naphthol

The PA and conventional spectra of 2-naphthol in boric acid glass are shown in Fig. 3. The PA spectrum shows some additional bands towards the longer wavelength side alongwith a modified intensity and shape of the bands. Ground state geometry of neutral 2-naphthol molecule optimized using MNDO molecular orbital method [19] is shown in Fig. 4. The electronic states are calculated using the optimized geometries and the CNDO/S-CI method [20-21].

The well known energy transitions occurring in 2-naphthol are found to consist of two electronic transitions in the range 250-400 nm [5-11]. The observed optical spectrum of 2-naphthol in boric acid glass has origins of the above mentioned first and second electronic transitions at 313.6 nm and at 275.3 nm respectively. These are

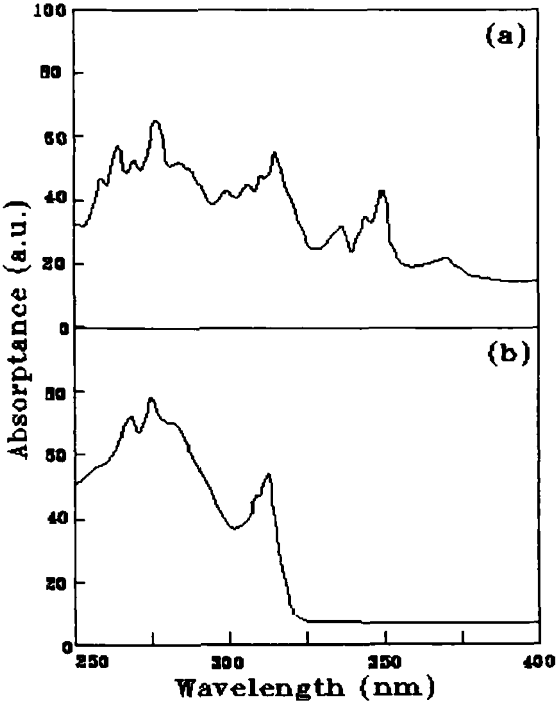

Fig. 3 (a) PA spectrum of 2-Naphthol in Boric acid glass,
(b) Optical absorption spectrum of 2-Naphthol in Boric acid glass.

radiative transitions between the singlet-singlet levels. Both these transitions are also observed in the PA spectrum with their origins at 315.3 nm and 276.6 nm respectively.

The band at a difference of 444 cm^{-1} attached with the origin of the first transition is due to $\nu_8(b_{1g})$, (out of plane bending). The other band, at a difference of 907 cm^{-1} from the origin, may be due to $\nu_7(b_{1g})$ skeletal motion (out of plane bending). The third band at 299.8 nm, which is at a distance of 1637 cm^{-1} from the origin, is attributed to the combination of $\nu_7(b_{1g})$ and $\nu_8(a_g)$ [24-25].

The origin of second radiative transition observed at 276.6 nm in the PA spectrum of 2-naphthol in boric acid glass, has three vibrational bands. The first band at 269.6

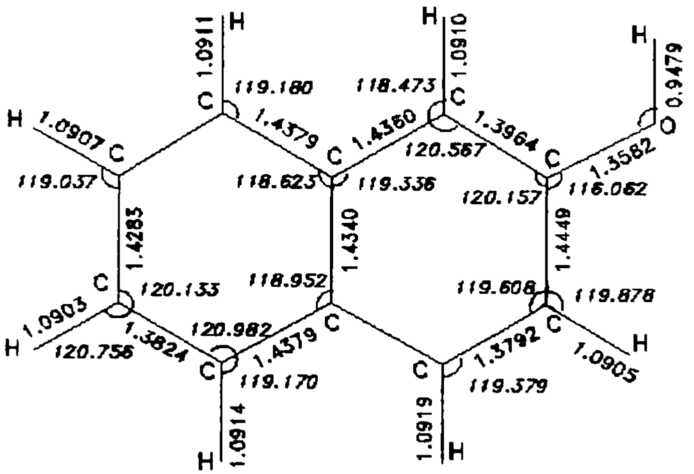

Fig. 4 Schematic representation of 2-Naphthol molecule showing optimized bond lengths (Å) and bond angles (deg).

nm shows a difference of 910 cm^{-1} from its origin and is assigned to $\nu_7(b_{1g})$. The second band at 264.5 nm, having a difference of 1643 cm^{-1} from its origin is due to the combination of $\nu_7(b_{1g})$ and $\nu_8(a_g)$. The third band at 258.3 nm showing a difference of 2556 cm^{-1} from the origin is attributed to the combination of second overtone of $\nu_7(b_{1g})$ and $\nu_8(a_g)$.

The CNDO/S-CI calculations and the structure of observed bands suggest that the two additional bands with their origins at 370.2 nm and 349.8 nm, may be due to the electronic transitions. These bands are due to singlet-triplet (S-T) absorption (lowest energy triplet level). In Table 2, these transitions are denoted as non-radiative transitions.

We could not observe any vibrational band attached to the first non-radiative electronic transition with its origin at 370.2 nm. The first vibrational band observed at 344.4 nm, attached to the second non-radiative electronic transition having its origin at 349.8 nm, may be attributed to vibrational mode $\nu_8(b_{1g})$ of frequency 445

Table 2: Assignments of the observed bands in PA and optical spectra of 2-naphthol in boric acid glass.

Transition No.	Calculated Transition Energy (nm)	Observed maxima Optical (nm)	Observed maxima PAS (nm)	Observed maxima PAS (cm^{-1})	Shift from electronic origin (cm^{-1})	Assignments
I	**371.3** (S--T)	-	**370.2**	**27012**	**0**	**Non-Radiative**
II	**349.7**	-	**349.8**	**28588**	**0**	**Non-Radiative**
	(S-T)		344.4	29033	445	0+445
			336.2	29741	1153	0+445+708
III	**315.4**	**313.6**	**315.3**	**31716**	**0**	**Radiative**
	(0.020664)*		311.0	32160	444	0+444
			306.5	32623	907	0+907
			299.8	33353	1637	0+730+907
IV	**273.1**	**275.3**	**276.6**	**36153**	**0**	**Radiative**
	(0.133678)*		269.8	37063	910	0+910
			264.5	37796	1643	0+733+910
			258.3	38709	2556	0+2x910+736

* The number in parenthesis indicate oscillator strength

cm^{-1}. The second band at 336.2 nm shows a difference of 1153 cm^{-1} from the origin and may be due to the combination of vibrational modes $\nu_8(b_{1g})$ and $\nu_8(a_g)$ [24-25].

A close agreement has been found between the results obtained by experimental and by CNDO/S-CI molecular orbital calculations as shown in Table 2.

Effect of Hydroxyl Substituents on the PA spectrum of Naphthalene

In the PA spectra of 1-naphthol and 2-naphthol, the radiative transitions are found to be shifted towards the higher wavelength side as compared to naphthalene molecule. The characteristic spectral changes in the position of the transitions in naphthalene caused by substitution are explained in terms of charge transfer character of OH group and polarization of molecule [6, 27-28]. Due to electron donating property of hydroxyl group, the charge is transferred from it to the naphthalene nucleus. The presence of stronger mesomeric effect than the inductive effect of OH group is responsible for this charge transfer in the system. The changes of charge densities at different atomic centres and variation in dipole moment of the molecules are responsible for the shifting in the PA spectra of above mentioned molecules.

When compared with the PA spectrum of naphthalene molecule, the non-radiative transitions are found to be shifted towards the higher wavelength region in case of 1-naphthol and 2-naphthol. Also in contrast to 1-naphthol, the non-radiative transitions of 2-naphthol is shifted towards red. This is because, that in 2-naphthol, the charge density increases more in the substituted ring as compared to 1-naphthol. However, we could not observe the second non-radiative transition in 1-naphthol, which has been observed both in naphthalene and 2-naphthol.

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