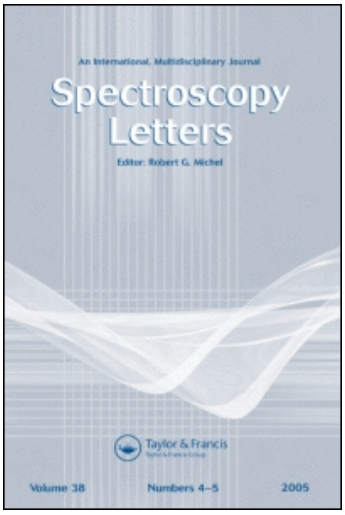

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PHOTOACOUSTIC SPECTROSCOPIC STUDIES OF POLYCYCLIC AROMATIC HYDROCARBONS: NAPHTHALENE CATION

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PHOTOACOUSTIC SPECTROSCOPIC STUDIES OF POLYCYCLIC AROMATIC HYDROCARBONS: NAPHTHALENE CATION

Key Words: Photoacoustic spectroscopy, Wasilewski molecular orbital calculations, Electronic spectra of naphthalene cation.

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ABSTRACT

The photoacoustic (PA) spectrum of naphthalene cation in boric acid glass, in the region 250-400 nm is reported for the first time and compared with its optical absorption spectrum. The energy levels for the ions are calculated using open shell Wasilewski method with limited configuration interaction and used to interpret the observed PA spectrum.

INTRODUCTION

Due to its importance in interstellar astrophysics[1] and in carcinogenic activity[2], Naphthalene cation has been studied in glassy organic solids[3], in solution[4], in argon and krypton matrices[5] and in boric acid glass[6]. These studies have been limited to optical spectroscopy so far giving information about radiative transitions only.

Photoacoustic spectroscopy[7-10] (PAS) has been used to characterize different materials because it gives information about non-radiative transitions also. Recently, we used this technique to study the PA spectrum of naphthalene molecule in UV region[11-12]. Several new electronic transitions related to non-radiative process were identified[12]. The present communication deals with the PA spectrum of naphthalene cation in boric acid glass, in the region 250-400 nm and its comparison with the optical spectrum. The PA spectrum of naphthalene cation studied for the first time, is interpreted on the basis of open shell Wasilewski method[13] with limited configuration interaction.

EXPERIMENTAL PROCEDURE

Naphthalene was obtained from M/S Fluka AG (Switzerland) and Boric acid crystals of AR grade were obtained from M/S Glaxo Laboratory Ltd. (India). The boric acid glass doped with naphthalene, were prepared by the method described else where[14]. A high pressure mercury lamp of 250 Watt was used as a source of UV radiation, for exposing the samples as described earlier[15].

The experimental set-up and the operating parameters to record the PA spectrum were same as described previously[12]. The optical absorption spectrum was recorded on a Perkin-Elmer UV-VIS Spectrophotometer (Model 552).

CALCULATIONS

The energy levels for naphthalene cation are calculated using open shell type Wasilewski method with limited configuration interactions. For computations, each ring of the naphthalene is assumed to have hexagonal structure with C-C bond length of 1.40 Å. Other parameters used are:

$$I_C = 11.16 \text{ eV}$$

$$A_C = 0.03 \text{ eV}$$

$$\beta_{CC} = -2.27 \text{ eV}$$

where I_C and A_C are the ionization potential and electron affinity of carbon atom respectively. β_{CC} represents the resonance integral corresponding to carbon

atom. A configuration interaction scheme is adopted where the computer programme automatically selects as many lower energy configurations, with a certain energy cut off, that do not exceed the maximum permissible limits of configurations (taken as 62 in the present case). The calculated energy levels have been given in Table I.

RESULTS AND DISCUSSION

The photoacoustic and optical spectra of naphthalene cation in boric acid glass are shown in Fig. 1. When compared, the PA spectrum not only shows additional absorption bands but the shape and intensity of the observed optical bands are also modified.

The optical absorption spectrum of naphthalene cation has been studied in different matrices[1-4,16-18] and is found to consist of three electronic transitions in the region 250-400 nm. The corresponding transitions in PA spectrum are observed at 380.0 nm, 303.0 nm and 280.5 nm. These are the radiative transitions corresponding to singlet-singlet transitions nominated as R1, R2 and R3 respectively. The positions of absorption maxima together with their assignments on the basis of the MO calculations using Wasilewski method are given in Table II. The other bands attached to these electronic transitions are attributed to well known vibrational modes of the ground state of naphthalene[19,20].

The band observed at 34168 cm^{-1} shows a difference of 1165 cm^{-1} from the origin of R2 at 33003 cm^{-1} and should be due to the combination of out of plane skeleton bending mode $\nu_8(b_{1g})$ and C-H out of plane bending mode $\nu_8(a_g)$of naphthalene.

The 36420 cm^{-1} band attached to R3 transition, shows a difference of 770 cm^{-1} from the origin at 35650 cm^{-1} and may be attributed to vibrational mode $\nu_8(a_g)$. The next band at 36810 cm^{-1} may arise due to the combination of vibrational mode $\nu_8(b_{1g})$ and $\nu_8(a_g)$ of frequency 1160 cm^{-1}. The third band at 37726 cm^{-1} at a distance of 2076 cm^{-1} form the origin is attributed to the

TABLE I

Energy levels of Naphthalene Cation calculated by Open shell Wasilewski method with limited configuration interaction.

Energy Level	Energy (eV)	Energy (cm^{-1})
1.	0.0000	00000
2.	0.9259	7468
3.	1.6192	13060
4.	2.2697	18306
5.	2.7634	22288
6.	3.4228	27607
7.	4.0791	32900
8.	4.5178	36439
9.	5.0104	40412
10.	5.2164	42074
11.	5.4785	44188
12.	5.7443	46331
13.	5.8477	47165
14.	6.1155	49325
15.	6.4185	51769
16.	6.6851	53920
17.	6.8157	54973
18.	6.9818	56313
19.	7.0229	56644
20.	7.5763	61108
21.	7.6094	61375
22.	7.8029	62936
23.	7.9351	64002
24.	8.0816	65184
25.	8.0994	65327
26.	8.1500	65735
27.	8.3565	67401
28.	8.5771	69180
29.	8.7269	70388
30.	8.7341	70446
31.	9.0536	73023
32.	9.2838	74880
33.	9.3755	75620
34.	9.5918	77364

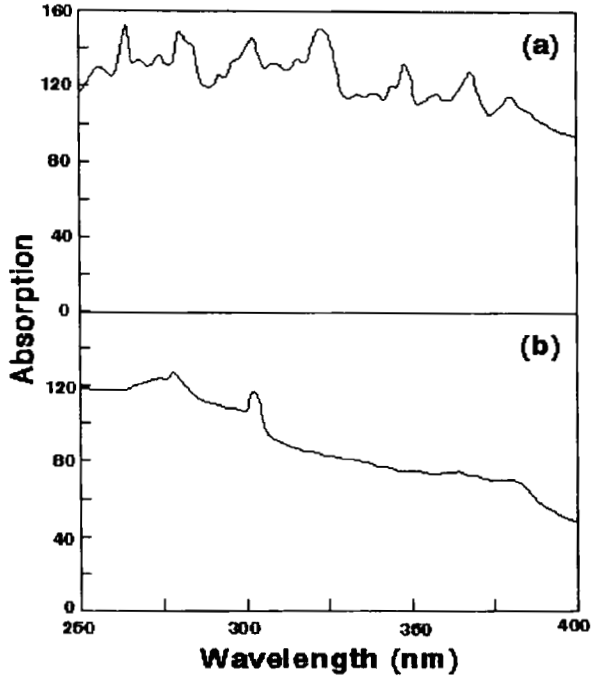

Fig. 1 (a) Photoacoustic spectrum of naphthalene cation in boric acid glass,

(b) Optical absorption spectrum of naphthalene cation in boric acid glass.

combination of $\nu_8(b_{1g})$, $\nu_8(a_g)$ and $\nu_7(b_{1g})$ vibrational modes of ground state of naphthalene. The next band at 38898 cm^{-1} attached to R3 transition, shows a difference of 3248 cm^{-1} from the origin. It may be attributed to the combination of second overtone of $\nu_8(a_g)$ and $\nu_7(b_{1g})$ vibrational modes.

The results from Wasilewski calculations and the structure of observed bands in PA spectrum suggest that three additional bands at 368.0 nm, 347.0 nm and 323.0 nm are due to electronic transitions. As in PA spectroscopy, one can observe the transitions between any of the excited states due to cascade process,

TABLE II

Assignments of the observed band maxima in PA and Optical spectra of naphthalene cation in boric acid glass.

Transition No.	Calculated frequency (cm^{-1})	Observed maxima Optical (nm)	PAS (nm)	PAS (cm^{-1})	Shift from Electronic Origin (cm^{-1})	Assignments
I	**26295 (33-14)***	**380.0**	**380.0**	**26315**	**0**	**R1**
II	**27107 (28-10)***	-	**368.0**	**27173**	**0**	**NR1**
			358.0	27932	759	$\nu_0+\nu_8(a_g)$
III	**28977 (8-2)***	-	**347.0**	**28818**	**0**	**NR2**
			340.8	29338	520	$\nu_0+\nu_9(a_g)$
			338.0	29578	760	$\nu_0+\nu_8(a_g)$
			332.2	30098	1280	$\nu_0+\nu_9(a_g)+\nu_8(a_g)$
IV	**31104 (23-7)***	-	**323.0**	**30959**	**0**	**NR3**
			315.1	31726	767	$\nu_0+\nu_8(a_g)$
			308.5	32409	1450	$\nu_0+\nu_4(a_g)$
V	**32905 (7-1)***	**305.0**	**303.0**	**33003**	**0**	**R2**
			292.6	34168	1165	$\nu_0+\nu_8(b_{1g})+\nu_8(a_g)$
VI	**35637 (36-13)***	**278.0**	**280.5**	**35650**	**0**	**R3**
			274.5	36420	770	$\nu_0+\nu_8(a_g)$
			271.6	36810	1160	$\nu_0+\nu_8(b_{1g})+\nu_8(a_g)$
			265.0	37726	2076	$\nu_0+\nu_8(b_{1g})$ $+\nu_8(a_g)+\nu_7(b_{1g})$
			257.0	38898	3248	$\nu_0+2\nu_8(a_g)$ $+2\nu_7(b_{1g})$

* Probable MO Energy Levels involved.

therefore, the above transitions are attributed to non-radiative transitions. These are designated as NR1, NR2 and NR3 respectively in Table II.

With NR1 transition, the band at 27932 cm^{-1} may be on account of vibrational mode $\nu_8(a_g)$ of frequency 759 cm^{-1}.

The 29338 cm^{-1} band attached to NR2 transition shows a difference of 520 cm^{-1} from its origin and may be attributed to the out of plane bending vibrational mode $\nu_9(a_g)$. The next band at 29578 cm^{-1} may arise due to vibrational mode $\nu_8(a_g)$ of frequency 760 cm^{-1}. The third band at 30098 cm^{-1}, having frequency of 1280 cm^{-1}, corresponds to the combination of vibrational modes $\nu_9(a_g)$ and $\nu_8(a_g)$.

The band observed at 31726 cm^{-1}, attached to NR3 transition, shows a difference of 767 cm^{-1} from its origin and may be on account of vibrational mode $\nu_8(a_g)$. The other band at 32409 cm^{-1} is at a distance of 1450 cm^{-1} from the origin and is attributed to the $\nu_4(a_g)$ vibration of C-C bond common to both benzene rings.

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