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n–π^* Electronic Spectra of 2-Methyl-1,4-naphthoquinone in the Vapour Phase

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The visible emission glow of 2-methyl 1,4-naphthoquinone has been excited by an uncondensed transformer discharge in the presence of flowing vapour of benzene. The vapour absorption spectrum of the molecule has also been investigated in the region 4900—3800 Å at different temperature.

The wide occurrence of quinones in nature and their essential role in photochemistry makes the understanding of their electronic structure a most important matter. In recent years many interesting papers have appeared, both experimental and theoretical, on spectroscopic investigations of quinones. We have undertaken studies of quinone, and the sensitized emission spectra involving n–π^* electronic transitions of *p*-benzoquinone,[1] 1,4-naphthoquinone[2] and 9,10-anthraquinone[3] molecules in the vapour phase have already been reported.

The near ultraviolet absorption spectrum of 2-methyl-1,4-naphthoquinone (2-MeNQ) in solution[4] and vapour[5] phases have been studied and the absorption maxima at 40804 and 30294 cm^{-1} reported. The phosphorescence spectrum of the molecule in methyl cyclohexane at 77°K has been studied by Kuboyama.[6] He reported a system consisting of seven peaks at 20115, 19737, 18970, 18513, 18062, 17386 and 16858 cm^{-1} and assigned it to n–π^* (triplet-singlet) transition. However, no work in the vapour phase of the molecule has been done so far in the visible region. This paper deals with the electronic emission and absorption spectra in the vapour phase.

Experimental

The emission spectrum of 2-MeNQ vapour was excited by an uncondensed transformer discharge in the presence of the flowing vapour of benzene employing π-type discharge tube. The bright yellowish glow was photographed by a Fuess Glass Spectrograph employing Kodak IF plates in six hours. The absorption spectrum was also photographed on the same spectrograph employing HP-3 plates with slit width of 40 μ. The absorption cell used was a quartz to Pyrex graded seal cell of length 120 cm enclosed in an electric furnace. A tungsten filament lamp was used as the source of continuum in the visible region. All the bands were measured on a Hilger L-76 comparator.

Results

The emission spectrum lies in the region 22078—14663 cm^{-1} and consists of 35 bands. The observed bands are broad, diffuse and intense. The important feature observed is the irregular intensity distribution of bands like that of other *p*-quinones.[1–3] The bands in the region 22215—20825 cm^{-1} are weak as compared to those in the region 20827—17236 cm^{-1} and intensity abruptly falls again on the longer wavelength side. The spectrogram is shown in Fig 1. The entire absorption spectrum in the visible region lies in the region 20257—26659 cm^{-1} and is divided into two groups, developing at different temperatures with the same cell length of 120 cm. At about 150°C one system of bands develops in the region 22215—27019 cm^{-1} and while increasing the temperature up to 190°C three broad and very diffuse bands develop in the region 20402—22215 cm^{-1}. The bands in the former region are also diffuse but distinct. The observed spectrum is shown in Fig. 2. The analyses of the bands observed in emission and absorption spectra are given in Tables 1 and 2 respectively. Table 3 includes the comparison of the ground and excited state frequencies with those of Raman and infrared.[7]

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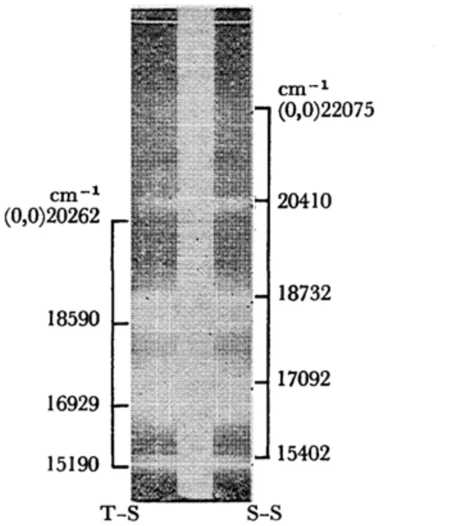

Fig. 1. Emission spectrum of 2-ethylnaphthoquinone.

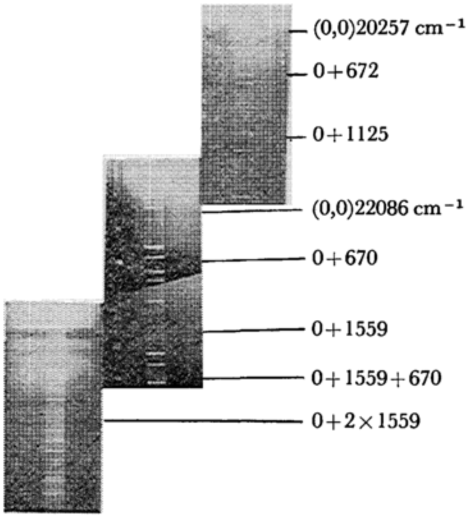

Fig. 2. Absorption spectrum of 2-methylnaphthoquinone.

Analysis and Discussion

The molecular symmetry C_{2v} of 1,4-naphthoquinone is reduced to C_s when a CH_3 group lying in the plane of the molecule replaces a hydrogen atom in its 2-position. Assuming C_s symmetry for the molecule both in the ground as well as in the excited state, the analyses of emission and absorption spectra have been given below.

In emission spectrum, the medium strong band at 22075 cm^{-1} on the shorter wavelength side of the spectrum has been taken as the (0−0) band of the system, corresponding to that of NQ[2] at 21945 cm^{-1}. This band in the absorption spectrum is identified at 22086 cm^{-1}. On the lower frequency side to this there are three more bands

Table 1. Analysis of the emission bands of 2-methyl-1,4-naphthoquinone

Wave number cm^{-1}	Intensity	Separation from 0-0 band	Assignment
22075	4	0	0−0
22005	2	70	0−70
21931	1	144	0−144 or 0−2×70
21860	1	215	0−144−70
21701	2	374	0−374
21616	2	459	0−459
21472	1	603	0−459−144
21382	4	692	0−692
20792	4	1282	0−1282
20718	2	1357	0−1357 or 0−1282−70
20410	7	1665	0−1665
20262	3	1813	0−1665−144
19947	2	2128	0−1665−459
19804	1	2270	0−1665−459−144
19197	1	2878	0−1665−692−459−70
19038	2	3038	0−1665−1357
18732	10	3343	0−2×1665
18590	10	3485	0−2×1665−144
18276	1	3799	0−2×1665−459
17913	2	4162	0−2×1665−459−372
17605	1	4470	0−2×1665−692−459
17477	1	4598	0−2×1665−1282
17092	8	4983	0−3×1665
16929	5	5146	0−3×1665−144
16610	6	5465	0−3×1665−459
16344	1	5731	0−3×1665−2×374
16017	1	6058	0−3×1665−2×459−144 or 0−3×1665−692−372
15908	1	6267	0−3×1665−1282
15619	3	6456	0−3×1665−2×692−70
15402	4	6674	0−4×1665
15190	5	6966	0−4×1665−144−70
15031	1	7044	0−4×1665−374

Table 2. Analysis of the absorption spectrum of 2-methyl-1,4-naphthoquinone

Wave-number	Intensity	Separation from 0-0 band	Assignment
Cell length 120 cm, Temp. 190°C			
20257	10	0	0−0
20929	2	672	0+672
21382	5	1125	0+1125
Cell length 120 cm, Temp. 150°C			
22086	8	0	0−0
22145	6	59	0+59
22449	4	363	0+363
22756	5	670	0+670
23120	3	1034	0+670+363
23344	5	1258	0+1258
23645	5	1559	0+1559
24006	2	1920	0+1258+670
24384	1	2298	0+1258+670
25107	2	3121	0+2×1559

TABLE 3. CORRELATION OF GROUND AND EXCITED STATE FREQUENCIES FOR 2-METHYLNAPHTHOQUINONE

Ground state frequencies			Excited state frequency	Mode of vibration
Raman[7]	Infrared[7]	Emission	Absorption	
215(2)		215(1)	195(5)	a'' C=O bending o. p.
380(3)		374(1.5)	363(8)	a' C=O bending i. p.
464(7)	460(5)	459(2)		a' skeletal deformation
698(4)	693(8)	692(4)	670(8)	a' ring breathing
890(1)	885(5)		843(1)	a' C-CH_3 stretching
1360(2)	1358(5)	1357(2)		a' C-H bending (symmetric in CH_3 group)
1662(10)	1670(10)	1665(7)	1559(3)	a' C=O stretching

i. p.=in-plane; o. p.=out-of-plane.

extending upto 20262 cm^{-1} and seems to belong to some other electronic transition. Since this latter system does not have any vibrational structure, an adequate analysis is not possible. However these bands will be discussed along with the phosphorescence bands. The medium strong band at 21701 cm^{-1} in the emission spectrum is associated with a frequency 374 cm^{-1} which corresponds to the Raman line 380 cm^{-1}. The excited state counterpart of this vibration is obsered in the absorption spectrum at 22449 cm^{-1} with a separation of 363 cm^{-1} from the (0-0) band. This frequency is suggested to be a C=O bending mode of vibration in the molecular plane. The strong band at 21383 cm^{-1} involves the ground state frequency 692 cm^{-1} in the emission and at 22756 cm^{-1} with a corresponding excited state frequency 670 cm^{-1} in the absorption spectrum. In the Raman spectrum this frequency is found to be 698 cm^{-1} and assigned to ring breathing mode of vibration. Another moderately intense band at 20793 cm^{-1} with a difference of 1282 cm^{-1} from the (0-0) band in the emission spectrum may be correlated to Raman frequency 1306 cm^{-1}. The excited state frequency is observed to be 1258 cm^{-1} associated with a strong band at 23344 cm^{-1} in the absorption spectrum. In the emission spectrum the strong band at 20410 cm^{-1} is due to excitation of a totally symmetric C=O stretching mode of vibration with value 1665 cm^{-1}. This frequency forms the progression in the spectrum and appears up to four quanta as well as in combinations with other frequencies.

The bands with two and three quanta of C=O stretching mode of vibrations are more intense than those of one and four quanta, indicating the increase in the equilibrium internuclear distance for the excited electronic state. On this account, the (0-0) band is weak and intense bands result, corresponding to the transition to the higher vibrational sublevels of the ground state rather than the lower ones. The difference between the successive bands involving the higher quanta of this vibration decreases in magnitude and gives the evidence of the anharmonicity in C=O vibration. The excited state counterpart of this vibration is found to be associated with a band at 23645 cm^{-1} having a separation of 1559 cm^{-1} from the (0−0) band in the absorption spectrum. Most of the other bands observed in the emission and absorption spectra are explained as combinations, overtones and quanta of this vibration. In regard to the nature of electronic transition involved, the system may be assumed to be due to n-π^* ($^1A'$-$^1A'$) transition agreeing with n-π^* (singlet-singlet) transition of NQ.[3] This is further confirmed by a blue shift of 130 cm^{-1} in the (0−0) band on 2-methyl substitution in NQ.

Comparison with Phosphorescence Bands. It has been observed that some of the bands in the present work agree well with those reported from phosphorescence in rigid glass solution and it is therefore worthwhile to compare them. Assuming the first intense band of the phosphorescence spectrum at 20115 cm^{-1} as the origin of the system, the band at 20262 cm^{-1} in the vapour emission spectrum may be taken to correspond to it, in the light of which a vibrational analysis has been suggested for these bands and shown in Table 4.

The totally symmetric vibrations 378 cm^{-1} (C=O bending), 1145 cm^{-1} (C-H bending) and 1672 cm^{-1} (C=O stretching) are found to be superposed on this (0−0) band of the new electronic system. The assignment of this new system was considered preferable for interpreting the unusual intensity distribution associated with the bands at 20262, 18590 and 16929 cm^{-1} analysed as $0-n\times 1665-144$, where $n=1, 2, 3$ respectively in the S-S system. In the case this system can be identified with the one observed in phosphorescence, it is due to (S-T) transition. The C=O stretching mode of vibration in both S-T vapour emission and phosphorescence spectra are prominent and appears strongly in combination and overtones.

The life time of the phosphorescence glow has been reported to be 0.001 sec which is favourable for a triplet-singlet emission under the present experimental conditions. Thus as presumed in

TABLE 4. COMPARISON OF PHOSPHORESCENCE BANDS WITH THE PRESENT EMISSION AND ABSORPTION BANDS OF 2-METHYL-1,4-NAPHTHOQUINONE

Phosphorescence band (rigid glass solution) Kuboyama6)	Absorption band (vapour) present work	Emission band (vapour) present work	Assignment
	21382(5)		0+1125
	20929(2)		0+672 (ring breathing)
20115 vs	20257(10)	20262(3)	0−0
19738		19947(2)	$0-\nu_1$ (378 cm^{-1})
18970		19038(2)	$0-\nu_2$ (1145 cm^{-1})
18513 vs		18590(10)	$0-\nu_3$ (1672 cm^{-1})
18061		18276(1)	$0-\nu_3-\nu_1$
17386		17477(1)	$0-\nu_3-\nu_2$
16859 s		16929(5)	$0-2\times\nu_3$
		15190(4)	$0-3\times\nu_3$

vs=very strong, s=strong

Table 4, some of the bands of 2-MeNQ may be assigned to an n–π^* ($^3A'$–$^1A'$) transition in agreement with that of NQ.3) However, such assignment should await further confirmation.

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