BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2048—2050 (1969)

Triplet-Singlet Emission Spectrum of Acenaphthenequinone Vapour

S. Nath Singh, M. G. Jayswal and R. S. Singh

Department of Spectroscopy, Banaras Hindu University, Varanasi-5, India

(Received September 11, 1968)

The phosphorescence spectrum of acenaphthenequinone has been reported by Kuboyama and Yabe[1] at 77°K in various solvents and in the crystalline state. These authors have identified it as due to n–π^* (Triplet-Singlet) transition from the position of bands, solvent effect and life-time considerations. Recently, we have reported infrared and Raman spectra[2] of the molecule and the observed bands were assigned to different modes of vibrations. In the present work, the emission spectrum of the molecule in the vapour phase has been reported and discussed.

Experimental

The Eastman L. R. grade sample of acenaphthene-

---

[1] A. Kuboyama and S. Yabe, This Bulletin, **40**, 2475 (1967).

[2] S. Nath Singh and R. S. Singh, *Current Sci.*, **36**, 624 (1967).

quinone was sublimed before use and yellow needles were obtained. The emission was excited by using an uncondensed transformer discharge in the presence of flowing vapour of benzene, employing the conventional π-type of discharge tube. The yellowish emission glow was photographed by Fuess glass spectrograph with $60\,\mu$ slit width in 10 hr using Kodak I-F plates. Two different plates were measured on Hilger L-76 comparator and the average values of the measurements have been reported.

Results and Discussion

The emission spectrum of acenaphthenequinone lies in the region 5700—6900 Å and consists of thirteen diffuse but intense bands (Fig. 1). The intensity distribution of bands is unusual similar to those observed in various *p*-quinones[3] where the bands in the middle of the spectrum are more intense compared to those on the either sides. The wave numbers, visually estimated intensities and analysis of bands are given in Table 1.

The moderately strong band at 17552 $\mathrm{cm^{-1}}$ has been taken as the (0,0) band of the system. From the gross structure of bands, it is evident that the system is due to an allowed transition, as most of the totally symmetric fundamental frequencies are found to be superposed on this (0,0) band. Assuming C_{2v} symmetry for the molecule both in the ground as well as in the excited state, the spectrum has been analysed in terms of three totally symmetric vibrations: 572 (ring deformation), 778 (ring breathing) and 1708 $\mathrm{cm^{-1}}$ (C=O stretching) for which the corresponding Raman frequencies[2] have been reported at 575, 790 and 1723 $\mathrm{cm^{-1}}$. The weak band at 17271 $\mathrm{cm^{-1}}$, which is 281 $\mathrm{cm^{-1}}$ apart from the (0,0) band, may in all probability be due to excitation of a nontotally symmetric skeletal deformation type of vibration, the corresponding Raman value of which is 276 $\mathrm{cm^{-1}}$. It is found that the ring breathing and C=O stretching mode of vibrations are predominent in the spectrum and most of the bands may be explained in terms of these two frequencies. The magnitude 1708 $\mathrm{cm^{-1}}$ for C=O stretching mode of vibration which has a higher value as compared to *p*-quinones[4] shows aliphatic character of the substituent group and molecule has been characterised not as a "true quinone.[5]"

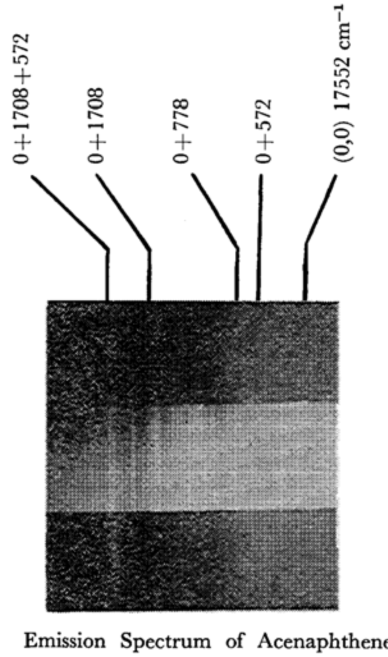

Fig. 1. Emission Spectrum of Acenaphthenequinone.

Table 1. Emission bands of acenaphthenequinone

Wave number ($\mathrm{cm^{-1}}$)	Intensity	Difference from (0,0) band	Assignment
17552	(5)	0	(0,0)
17271	(1)	281	0+281
16980	(6)	572	0+572
16774	(6)	778	0+778
16493	(2)	1059	0+778+281
16194	(4)	1358	0+778+572
16009	(4)	1543	0+2×778
15844	(10)	1708	0+1708
15574	(5)	1978	0+1708+281
15264	(10)	2288	0+1708+572
15082	(2)	2470	0+1708+778
14793	(1)	2759	0+1708+778+281
14481	(1)	3071	0+1708+778+572

In the phosphorescence study[1] an intense band has been reported at 5990 Å (16690 $\mathrm{cm^{-1}}$) in the crystalline state at 77°K and may be the electronic origin of the system. The (0,0) band identified at 5696 Å (17552 $\mathrm{cm^{-1}}$) in the present vapour emission spectrum is at a higher energy value by 862 $\mathrm{cm^{-1}}$ as compared to the electronic origin in the phosphorescence spectrum in the crystalline state. This value is in conformity with the common observation that the electronic origin of the same system lies at a higher energy in the vapour phase as compared to the crystalline state. The two spectra seem to correspond to each other and the present vapour emission may be assigned as due

---

3) M. G. Jayswal and R. S. Singh, *Spectrochim. Acta*, **21**, 1597 (1965); *J. Mol. Spectry.*, **17**, 6 (1965); S. N. Singh, Ph. D. Thesis, B.H.U. (1968).

4) S. N. Singh and R. S. Singh, *Spectrochim. Acta*, **24A**, 1591 (1968); H. Stamureich and T. T. Sans, *J. Chem. Phys.*, **42**, 920 (1965).

5) C. N. R. Rao, "Chemical Application of Infrared Spectroscopy," Academic Press, New York (1963), p. 229.

to n–π^* (Triplet-Singlet) electronic transition. The life-time of the phosphorescence emission at low temperature[1] has been reported of the order of 10^{-2} sec which is a favourable value for observing a triplet-singlet emission even in the vapour state and such type of observation has been made in several *p*-quinones.[3] Moreover, the presence of benzene vapours seems to be quite important which possibly transfer its energy to excite the quinone molecule.[6]

The authors are thankful to Professor N. L. Singh for his keen interest in the work. One of them S. N. S. is grateful to N. B. S. (PL-480), U. S. A. for financial assistance.

---

6) R. S. Singh, *Indian J. Pure & Appl. Phys.*, **6**, 91 (1968).