

## On the vibrational structure involving C=O stretch in the vapour phase phosphorescence of *p*-benzoquinone- $h_4$ and - $d_4$

V N PANDEY† and S N THAKUR\*

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

†On leave from Pt. Jawaharlal Nehru College, Banda 210 001, India.

MS received 12 August 1982; revised 9 February 1983

**Abstract.** The high resolution spectrum of vapour phase phosphorescence from *p*-benzoquinone exhibits a mixing of normal modes involving symmetric C=O stretching and C=C stretching vibrations. The vibrational bands due to these mixed vibrations have been assigned on the basis of relative intensities of these bands in the vapour phase and also, using solid neon host.

**Keywords.** Vibrational structure; C=O and C=C stretching vibrations; *p*-benzoquinone; vapour phase phosphorescence; triplet-singlet transition.

### 1. Introduction

The two non-bonding orbitals of para-benzoquinone (PBQ) are in accidental degeneracy and its visible spectrum results from an electron promotion to the lowest  $\pi^*$  orbital (Hollas 1964). The splitting between the two singlet states ( $^1B_{1g}$  and  $^1A_u$ ) resulting from this electron promotion has been determined by studying the spectrum in a supersonic jet (Horst and Kommandeur 1979). It has also been found that the splitting between the two triplet states ( $^3B_{1g}$  and  $^3A_u$ ) is less than  $0.5\text{ cm}^{-1}$  (Kommandeur private communication). Another interesting aspect in this molecule is the occurrence of vibrational perturbation in the ground electronic state in the energy range  $1650$  to  $1690\text{ cm}^{-1}$  (Goodman and Brus 1978). In the present paper we report the results on our high resolution studies of the vapour phase phosphorescence spectra ( $^3A_u \rightarrow ^1A_g$ ) of para-benzoquinone- $h_4$  and - $d_4$ .

### 2. Experimental

The vapour phase phosphorescence was excited by a Schüller-type transformer discharge and by using a tesla coil of 4 MHz frequency. The spectra were recorded on a  $f/8.4$  one meter Spex grating spectrograph in the first order using Kodak Spectrum Analysis No 1 plates.

### 3. Results and discussion

The vibrational analysis of the spectrum is straightforward except in the region of the vibronic band involving one quantum of C=O stretching vibration in the ground state

\* To whom all correspondence should be addressed.

of  $\text{PBQ-}h_4$  (figure 1). This region is dominated by intense emission bands at 16993, 17006.9 and 17017.4  $\text{cm}^{-1}$ . The origin band of the vapour phosphorescence in  $\text{PBQ-}d_4$  lies at 18682.8  $\text{cm}^{-1}$  showing a blue shift of about 1  $\text{cm}^{-1}$  with respect to the corresponding origin band of  $\text{PBQ-}h_4$ . In this case however there is only one strong band at 17021.6  $\text{cm}^{-1}$  in the region corresponding to one quantum of C=O stretching vibration in the ground state (figure 2).

Goodman and Brus (1978) observed the phosphorescence spectrum of  $\text{PBQ}$  in solid neon host and found the  ${}^3\text{B}_{1g} \rightarrow {}^1\text{A}_g$  emission also which is forbidden in the free molecule. The vibrational structure of  ${}^3\text{Au} \rightarrow {}^1\text{A}_g$  system is very different from the former and the strongest band of this system involves a ground state vibrational frequency of 1676  $\text{cm}^{-1}$  in  $\text{PBQ-}h_4$  and of 1668  $\text{cm}^{-1}$  in  $\text{PBQ-}d_4$ . The interval of 1676  $\text{cm}^{-1}$  is in good agreement with that of 1675  $\text{cm}^{-1}$  associated with the band at 17006.9  $\text{cm}^{-1}$  in  $\text{PBQ-}h_4$  in our work. In the case of  $\text{PBQ-}d_4$  however there are two weak bands involving ground state vibrational intervals of 1667.5 and 1670.3  $\text{cm}^{-1}$  whose average separation (1669  $\text{cm}^{-1}$ ) is in good agreement with the vibrational interval of 1668  $\text{cm}^{-1}$  reported by Goodman and Brus (1978).

It has been suggested that the symmetric C=O stretch ( $\nu_3$ ) and the C=C stretch ( $\nu_2$ ) are both strongly mixed-vibrations (Goodman and Brus 1978). It is therefore likely that in the solid state neon host  $\nu_3$  becomes more prominent in the case of  $\text{PBQ-}h_4$  whereas  $\nu_2$  is more prominent in the case of  $\text{PBQ-}d_4$ . In our vapour phase phosphorescence we assume that it is the C=O stretching vibration ( $\nu_3$ ) which corresponds to the most intense band in both the molecules (17006.9  $\text{cm}^{-1}$  in  $\text{PBQ-}h_4$  and 17021.6  $\text{cm}^{-1}$  in  $\text{PBQ-}d_4$ ). This has been done in view of the fact that  $n \rightarrow \pi^*$  electron promotion is largely localized in the C=O bond region and the effects of external perturbations are minimal in the vapour phase. This leads to the assignment of the band at 16993.0  $\text{cm}^{-1}$  in  $\text{PBQ-}h_4$  as due to C=C stretching vibration ( $\nu_2$ ) which has an interval of 1689  $\text{cm}^{-1}$ . The corresponding interval in  $\text{PBQ-}d_4$  may be taken as 1669  $\text{cm}^{-1}$  (average value). It is to be noted that the bands involving C=C stretching vibration in both  $\text{PBQ-}h_4$  and  $\text{PBQ-}d_4$  are weak in comparison to the respective bands involving symmetric C=O stretching vibration.

The band at 17017.4  $\text{cm}^{-1}$  in  $\text{PBQ-}h_4$  has a vibrational interval of 1665  $\text{cm}^{-1}$  and has been assumed to involve one quantum of antisymmetric C=O stretching vibration. This is in good agreement with the assignments of Dunn and Francis (1974) and of Anno and Sado (1958). In the case of  $\text{PBQ-}d_4$  (figure 2) we get three closely-spaced weak bands with an average ground state interval of 1646  $\text{cm}^{-1}$  and this has been assigned as due to antisymmetric C=O stretching vibration in the light of an observed band at 1648  $\text{cm}^{-1}$  in the vapour phase infrared spectrum of this molecule (Goodman and Brus 1978).

#### 4. Conclusion

We have been able to assign three prominent bands in the vapour phosphorescence spectrum of  $\text{PBQ-}h_4$  and one prominent and two weak bands in the corresponding spectrum of  $\text{PBQ-}d_4$  on the basis of our high resolution work.

#### Acknowledgements

The authors are thankful to Dr J M Hollas of Reading University of providing experimental facilities to SNT and to the UGC (New Delhi) for a Teacher Fellowship to VNP.

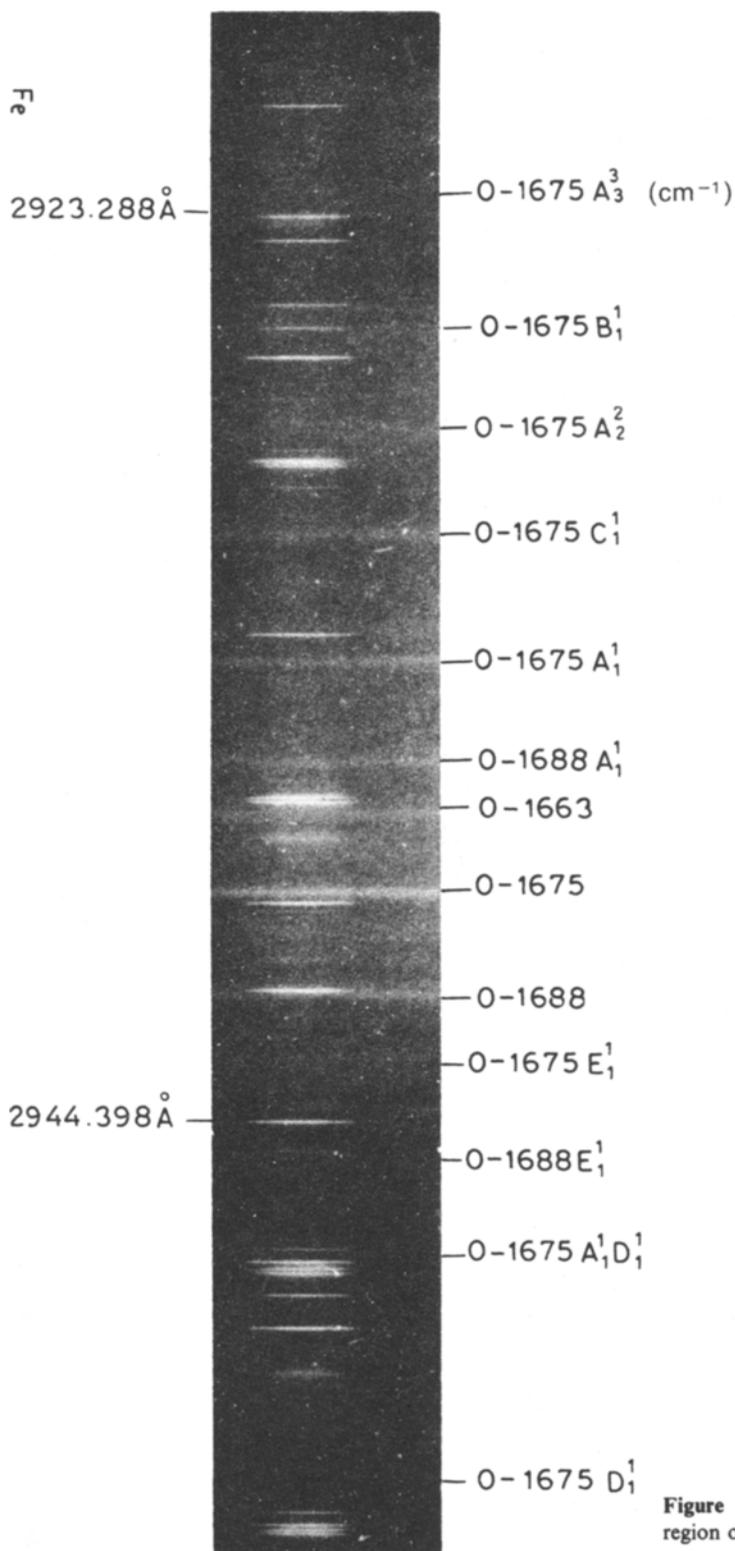


Figure 1. The C=O stretching region of  $\text{PBQ-}h_4$ .

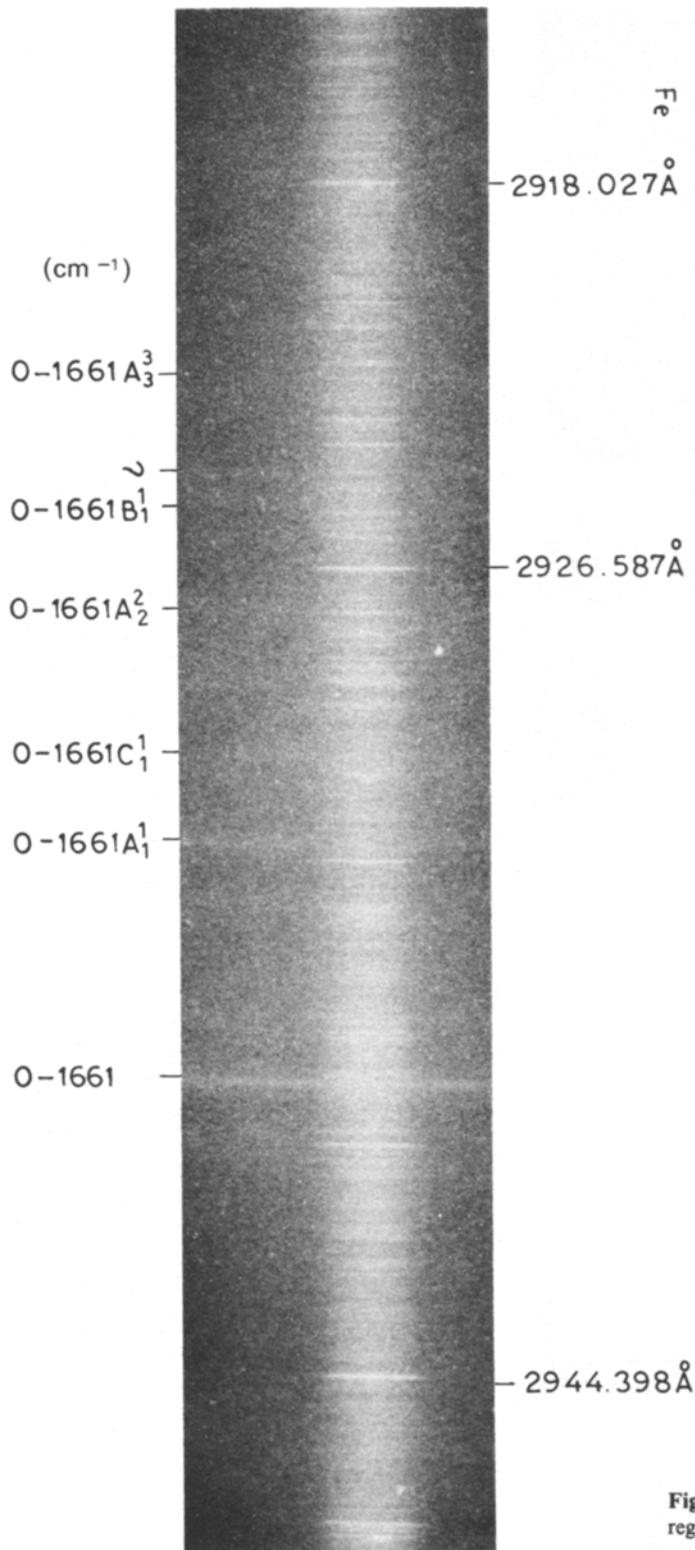


Figure 2. The C=O stretching region of PBQ-d<sub>4</sub>.

**References**

- Anno T and Sado A 1958 *Bull. Chem. Soc. Jpn.* **31** 734  
Dunn T M and Francis A H 1974 *J. Mol. Spectrosc.* **50** 14  
Goodman J and Brus L E 1978 *J. Chem. Phys.* **69** 1604  
Hollas J M 1964 *Spectrochim. Acta* **20** 1563  
Horst G T and Kommandeur J 1979 *Chem. Phys.* **44** 287