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ASSIGNMENT AND ANALYSIS OF THE ABSORPTION AND EMISSION SPECTRA OF THE LOWEST $n\pi^*$ TRIPLET STATE IN 9,10-ANTHRAQUINONE

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Polarized Zeeman absorption experiments on 9,10-anthraquinone crystals show the lowest triplet state in this molecule to be a $g\ n\pi^*$ state. The gap between this state and the higher $u\ n\pi^*$ state is found to be 410 cm^{-1} . The phosphorescence spectrum of an isotopically mixed crystal of AQ- h_8 in AQ- d_8 is analyzed in detail and confirms the orbitally forbidden nature of the emitting state. The results are compared with those previously obtained for *p*-benzoquinone.

1. Introduction

In a series of recent papers [1–4] on the spectroscopy of *p*-benzoquinone (PBQ) crystals our interest was focused on the structure and dynamics of the lowest $n\pi^*$ (A_g) triplet state in this molecule. The reason for the spectroscopic anomalous behaviour of the lowest state in this molecule was finally pinned down to the occurrence of a double minimum potential (DMP) well in the lowest $n\pi^*$ triplet (and singlet) state in PBQ.

In the course of our experiments on PBQ we became interested in the question as to what extent can PBQ be considered in a spectroscopic sense a prototype for other aromatic diketones. In this paper we wish to present results of spectroscopic experiments on another centrosymmetric diketone, 9,10-anthraquinone (AQ). It will be shown that although the gap between the g and $u\ n\pi^*$ states in AQ is very similar to PBQ the effect of vibronic coupling between these states is not. However an attempt is made to correlate the spectra of these species.

2. Results

2.1. Absorption experiments

Fig. 1 shows the polarized absorption spectrum of

AQ- h_8 taken from the natural (*bc*) cleavage plane at 1.8 K. The lower part of the absorption spectrum, taken from a thicker crystal, is reproduced in the insert. The figure clearly shows that the spectrum is dominantly *c*-polarized with the exception of a line at 22262 cm^{-1} . The figure further shows that in the same spectral region sharp and broad absorption bands occur much like what would be expected in the case of closely-lying electronic states.

Table 1 shows that the results of fig. 1 can only be interpreted on the basis of medium-axis ($M = z(b_{1u})$; $L = y(b_{2u})$) polarized molecular transitions. The insert of fig. 1 also shows that next to a very weak line at 22150 cm^{-1} the absorption spectrum starts with a broad structure assigned by us as phonons that induce an orbitally forbidden transition. We therefore interpret the spectrum of fig. 1 as being caused by the overlap and interference between the lower B_{1g} and A_u (molecular symbols) $n\pi^*$ triplet states in AQ- h_8 . The center of the first broad band in the absorption spectrum at $22560 \pm 10\text{ cm}^{-1}$ is assigned as the origin of the $A_u\ n\pi^*$ triplet state while the lowest observed line in the spectrum at 22150 cm^{-1} is interpreted as the origin of the lowest $B_{1g}\ n\pi^*$ state.

The latter assignment however is somewhat problematic, as in the 77 K crystal structure of AQ the molecule is still at a center of inversion [5] and a g -type origin is therefore strictly forbidden. The alternative assignment of this line as the u -inversion level

Fig. 1. Polarized absorption spectra of a 1 mm thick 9,10-anthraquinone (AQ) single crystal at 1.8 K. The position marked with (0,0) was chosen as the origin of the $A_u n\pi^*$ triplet state. The sharp line at 23562 cm^{-1} in the b -polarized absorption spectrum is identified as the origin of the lowest $\beta n\pi^*$ singlet state in AQ. The insert shows the origin absorption spectrum of a 3 mm thick crystal of AQ.

Table 1

Direction cosines of molecular axes with respect to the crystallographic axis in 9,10-anthraquinone- h_8 at 77 K calculated from ref. [5]

	a	a^*	b	c^*	c
$L(y)$	0.520	0.667	0.448	0.731	0.599
$M(z)$	0.805	0.657	0.038	-0.591	-0.752
$N(x)$	0.292	-0.359	0.894	-0.339	-0.267

of the lowest B_{1g} state as in the case of PBQ [1] is neither warranted as no Stark effect is observed on any line in the absorption nor emission of an AQ crystal. We therefore ascribe the occurrence of the origin of the B_{1g} state in this crystal as either caused by a phase change of the AQ crystal below 77 K to a non-

centrosymmetric crystal structure or possibly to strain in the crystal. Emission experiments described in a later section of this paper will show that the AQ molecule apparently is very susceptible to environmental perturbations.

Dearman et al. [6] also concluded from polarized absorption experiments on AQ- h_8 performed at 77 K that the absorptions in this spectral region were polarized along the oxygen-oxygen (M) axis. Their conclusion however that the lowest triplet state in AQ is an $A_u n\pi^*$ state is at variance with the results and conclusions presented in this paper.

Compared to PBQ the spectrum of AQ in the gap between the two states, contains much more structure. Next to the phonon structure near the origin, we also observe several vibronic transitions. The three most in-

tense ones are found at 22262, 22319 and 22358 cm^{-1} in AQ- h_8 . In AQ- d_8 these lines shift 38, 35 and 30 cm^{-1} respectively to the blue. This shows that these modes apparently are skeletal modes that contain very little C-H stretch or bend character. In fact the overall change in absorption spectrum going from AQ- h_8 to AQ- d_8 is very minor, except for an average 35 cm^{-1} blue-shift and a change of the finer details in the region of the origin of the A_u $n\pi^*$ state.

A second difference with the absorption spectrum of PBQ is found in the width of the origin of the second (A_u) state. While in PBQ- h_4 this overall width is only 20 cm^{-1} [1] in AQ- h_8 this width is about 400 cm^{-1} . We interpret this width as a manifestation of the vibronic coupling that exists between the A_u $n\pi^*$ triplet states and modes of the correct symmetry built on the lower B_{1g} state at this energy. The difference with PBQ is explained rather as an increase in the density of states in AQ than as an increase in the vibronic coupling in this molecule.

We further note that the splitting between the g and u $n\pi^*$ triplet states is increased from 340 cm^{-1} in PBQ- h_4 to 410 cm^{-1} in AQ- h_8 . A large disparity between the spectra of PBQ and AQ however is found in the fact that in PBQ the absorption spectrum starts with a b_{1u} vibronic level that must be interpreted as a u-inversion level while such an absorption is absent in the AQ triplet absorption spectrum. In the next section we will return to this problem.

2.2. Zeeman experiments

Zeeman experiments performed on all the lines of the spectrum reported in fig. 1 show that all these absorptions are due to singlet-triplet transitions. In fact the Zeeman effect on all the lines is identical except for the one at 22319 cm^{-1} . We therefore take the lines at 22319 and 22358 cm^{-1} as examples to demonstrate the Zeeman effect on the absorption spectrum of AQ- h_8 and fig. 2 contains the results of these experiments. For a magnetic field parallel to the crystal b axis fig. 2 shows that in both polarizations ($\epsilon \parallel b$ and $\epsilon \perp b$), the $m_S = 0$ Zeeman component of the 22358 cm^{-1} absorption is absent. Using table 1 we immediately conclude that the z -spin sublevel is the spin active one, inducing primarily (95%) z -polarized electric dipole intensity into this level. The vibronic symmetry of this level is thus $B_{1g} \times B_{1u} = A_u$, and

the line at 22358 cm^{-1} is therefore assigned as a b_{1u} mode of 208 cm^{-1} built upon the origin of the lowest $^3B_{1g}(n\pi^*)$ state. Complete polarization experiments on this mode further show that the transition moment to this level is not completely parallel to the z axis, but also contains a component parallel y (4%) and x (1%).

The line observed at 22262 cm^{-1} shows exactly the same Zeeman effect but this transition is primarily polarized parallel to the b axis. We conclude that this line is a b_{3u} mode that induces primarily $x(N)$ intensity in the B_{1g} $n\pi^*$ triplet state. Fig. 2 further shows that the line at 22319 cm^{-1} behaves differently in a magnetic field. Analysis of the results shows that the b -polarized intensity is coming from a molecular B_{3u} singlet state that is induced by the y -spin substate. The perpendicular b (molecular z) polarized intensity can also be best explained as being induced by the y -spin substate with a minor (10%) interfering contribution of the x -spin sublevel. We therefore assign the absorption at 22319 cm^{-1} as a b_{2u} mode of 169 cm^{-1} . The further assignment of these lines to specific modes however seems impossible at this time. The Zeeman effect measurements presented here thus only serve to show that the lowest triplet state spectrum can be interpreted as vibronically induced by modes of b_{2u} , b_{3u} and primarily b_{1u} symmetry as expected for a B_{1g} $n\pi^*$ triplet state [3].

We finally note that the formal analogy between the lowest triplet state spectra in PBQ- h_4 and AQ- h_8 is restored by correlating the b_{1u} mode at 22358 cm^{-1} in the AQ- h_8 spectrum with the u-inversion level at 18620 cm^{-1} in PBQ- h_4 .

2.3. Emission experiments

Fig. 3 shows the unpolarized phosphorescence spectra (established by Zeeman experiments) of an isotopically mixed crystal of AQ- h_8 (1 mol %) in AQ- d_8 at 4.2 and 1.8 K. Careful examination of the 4.2 K spectrum and comparison with the infrared data of AQ- h_8 and AQ- d_8 obtained by Pecile and Lunelli [7] shows that this spectrum must be due to emission of an AQ- d_8 X-trap at a non-centrosymmetric site. The latter statement is deduced from the appearance of an origin at 22129 cm^{-1} in emission. The vibrational analysis of the phosphorescence based on the infrared work of Pecile and Lunelli [7] is included in the figure

Fig. 2. Polarized Zeeman absorption spectra of the absorptions at 22320 and 22358 cm^{-1} in AQ at 1.8 K. In all spectra the magnetic field of 50 kG is directed along the crystal b axis. The wing lines in the c -polarized spectrum of the 22358 cm^{-1} transition are most likely due to ^{13}C satellites.

and it is gratifying to note that the spectrum contains a variety of b_{1u} , b_{2u} and b_{3u} modes just as expected for emission from a g -type $n\pi^*$ triplet state [3].

The dominance of the b_{1u} C=O stretching mode in the emission spectrum is also a striking feature of the PBQ phosphorescence spectrum. At 1.8 K additional lines appear in the emission spectrum and we attribute these lines to emission from an AQ- h_8 trap substitutionally incorporated in the AQ- d_8 host lattice. The origin in this case under our experimental conditions is not observed but can be obtained as follows. The origin of absorption of the B_{1g} $n\pi^*$ triplet state in pure AQ- h_8 was placed at 22150 cm^{-1} . In an isotopically mixed crystal of AQ- h_8 in AQ- d_8 (1 mol %) we observe a 6 cm^{-1} blue-shift of the 208 cm^{-1} b_{1u} mode at 22358 cm^{-1} in the pure AQ- h_8 crystal. Assuming a negligible (≤ 1 cm^{-1}) exciton bandwidth of the lowest B_{1g} $n\pi^*$ triplet state in AQ, the unobserved origin of emission of the AQ- h_8 trap in the AQ- d_8

host crystal is found at 22156 cm^{-1} . With this origin a completely satisfactory analysis of the phosphorescence spectrum of AQ- h_8 is obtained and is also included in fig. 3. The overall conclusion from the emission spectra is that they confirm the assignment of the lowest triplet state in AQ as a B_{1g} $n\pi^*$ triplet state.

3. Experimental

AQ- h_8 was bought as such from Merck and purified by recrystallization from alcohol, and finally zone refining. AQ- d_8 was synthesized through oxidation of anthracene- d_{10} [8] that was obtained from Merck. All spectroscopic experiments were performed on a 0.75 meter 1702 Spex equipped with a grating blazed at 1 μ . The Zeeman experiments were performed using a cryostat and magnet from BOC that was capable of producing fields up to 75 kG.

4. Summary and discussion

The results contained in this paper can be summarized as follows:

- (i) The lowest triplet state in AQ is a $B_{1g} n\pi^*$ state.
- (ii) The gap between the g and u $n\pi^*$ triplet state is 410 cm^{-1} .
- (iii) The absorption and emission spectrum of the lowest triplet state in AQ is induced by b_{1u} , b_{2u} and b_{3u} modes.
- (iv) The 208 cm^{-1} b_{1u} mode [9]^{*} in the AQ- h_8 spectrum should be correlated with the 17 cm^{-1} b_{1u} mode (u-inversion level) in the absorption spectrum of PBQ- h_4 .

These results show that PBQ indeed is a prototype for aromatic diketones, as far as the general features of the $n\pi^*$ triplet state spectra are concerned. However our results on AQ indicate that the DMP well in the lowest triplet state of this molecule, if there is any, is much less pronounced than in the case of PBQ. In the simple model that describes the situation of a DMP well in the lower of two vibronically interacting states [10] the prerequisite for the occurrence of such a DMP well is $2V_k^2/f_k \Delta\epsilon \gg 1$. Here V_k is the electronic coupling matrix element between the interacting states, f_k the zero-order force constant (assumed to be identical for both states) and $\Delta\epsilon$ the energy gap between the

combining states. Intensity measurements on the corresponding b_{1u} modes in the spectra of PBQ and AQ strongly suggest these modes to be induced by vibronic coupling between the B_{1g} and A_u triplet states from which we conclude that V_k for both molecules is very similar. $\Delta\epsilon$ is very similar too, so in this simple model the only difference can be the force constant f_k of the vibronic coupling mode. If the b_{1u} C=O stretching mode is indeed the vibronic coupling mode that induces the false spectral origins in the g $n\pi^*$ triplet state of both PBQ [11] and AQ one must conclude that the upper state force constant of this b_{1u} mode in PBQ is considerably lower than in AQ. This also implies that in the case of AQ the lowest $n\pi^*$ transition is less localized than in the case of PBQ. This conjecture is amenable to experimental verification by means of EPR and ENDOR measurements on the lowest triplet state of AQ.

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* In ref. [9] which came to our attention after submission of this paper, Sano et al. interpret the mode at 22358 cm^{-1} as the origin of the $A_u n\pi^*$ triplet state in AQ- h_8 . This assignment however seems incorrect in view of the following facts. (a) The integrated oscillator strength of this line decreases from 1.2×10^{-8} in AQ- h_8 to 8.3×10^{-9} in AQ- d_8 . (b) The integrated oscillator strength of the broad feature centered at 22560 cm^{-1} , and assigned by us as the origin of the $A_u n\pi^*$ triplet state in AQ- h_8 , is virtually independent of deuteration and found to be 2.9×10^{-7} . This number is in good agreement with the corresponding absorption strength found (2.8×10^{-7}) for the origin of the $A_u n\pi^*$ triplet state at 18947 cm^{-1} in PBQ- h_4 .