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# RENDICONTI

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## Intensity distribution in sequences of the p-benzoquinone visible spectrum

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## SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

**Chimica fisica.** — *Intensity distribution in sequences of the *p*-benzoquinone visible spectrum.* Nota di LUCIANA MALPEZZI e GIORGIO ORLANDI, presentata (\*) dal Socio G. SEMERANO.

RIASSUNTO. — In questa Nota viene discussa la distribuzione delle intensità nelle sequenze della banda A e della banda *b* dello spettro del *p*-benzochinone. L'analisi presentata suggerisce che l'intensità di queste bande derivi da entrambi i meccanismi Herzberg-Teller e Born-Oppenheimer di accoppiamento vibronico.

### INTRODUCTION

The principal transition in the visible absorption spectrum of *p*-benzoquinone corresponds to excitation from the ground state to an excited state of symmetry  $B_{1g}$  (Mulliken's notation) and of the type  $n\pi$  [1]. This transition is dipole forbidden and is made allowed through a vibronic coupling mechanism involving  $a_u$  and  $b_{3u}$  vibrational modes. One of the most effective among them is the  $b_{3u}$  out of plane C = O vibration, designated  $\nu_{30}$ , which is also the main sequence forming vibration. This vibration is peculiar in that its frequency is very low and varies markedly between the ground and the excited state, namely from  $108.5 \text{ cm}^{-1}$  in the ground state and  $143 \text{ cm}^{-1}$  in the  $B_{1g} n\pi$  excited state.

The sequences in the band group A and in its hot counterpart *b* that are induced by the  $\nu_{30}$  mode, show an anomalous behaviour of the intensity of their members. They do not follow the expected Boltzmann distribution, but show a maximum at the second or third member of the sequence [1, 2]. An explanation for this has been put forward [2] in terms of the vibrational integral appearing in the Herzberg-Teller vibronic mechanism [3]. Such an integral for small distortion is of the form:

$$(1) \quad |\langle v+1 | Q | v \rangle|^2 \simeq (\hbar/\mu\omega) (v+1)$$

where  $Q$  is the inducing mode coordinate. Therefore it is an increasing function of  $v$ , the vibrational quantum number of the initial state. However the Boltzmann distribution also enters the intensity expression. If the ground state frequency of the inducing mode is sufficiently low, as it is for  $\nu_{30}$ , the result is that the vibrational integral is able to impose its trend in the first members of the sequence while the Boltzmann exponential prevails in the subsequent integrals so that an intensity maximum will be found somewhere along the

(\*) Nella seduta del 19 giugno 1973.



electronic integrals. When one of the two electronic states is the ground state and the other the lowest excited state, then in absorption  $K_{mn}^{\text{HT}}$  and  $K_{mn}^{\text{BO}}$  have opposite sign. For harmonic oscillators we have:

$$(3) \quad \begin{aligned} \langle \chi_k^{(m)}(v) | Q_k | \chi_k^{(n)}(w) \rangle &= (\hbar/2 \mu \omega)^{1/2} [w^{1/2} \langle \chi_k^{(m)}(v) | \chi_k^{(n)}(w-1) \rangle + \\ &\quad + (w+1)^{1/2} \langle \chi_k^{(m)}(v) | \chi_k^{(n)}(w+1) \rangle] \\ \langle \chi_k^{(m)}(v) | \partial/\partial Q_k | \chi_k^{(n)}(w) \rangle &= (\mu \omega/2 \hbar)^{1/2} [w^{1/2} \langle \chi_k^{(m)}(v) | \chi_k^{(n)}(w-1) \rangle - \\ &\quad - (w+1)^{1/2} \langle \chi_k^{(m)}(v) | \chi_k^{(n)}(w+1) \rangle] \end{aligned}$$

where  $\mu$  and  $\omega$  are the reduced mass and frequency of the mode  $Q_k$ . If the matrix of the overlap integrals appearing in the *rhs* of Eq (3) is close to the unit matrix, we have for "cold band" transitions  $v \rightarrow v+1$

$$(4) \quad \begin{aligned} K_{mn, v(v+1)}^{\text{HT}} &\simeq K_{mn}^{\text{HT}} [ (v+1) \hbar/2 \mu \omega ]^{1/2} = L_{mn}^{\text{HT}} (v+1)^{1/2} \\ K_{mn, v(v+1)}^{\text{BO}} &\simeq - K_{mn}^{\text{BO}} [ (v+1) \mu \omega/2 \hbar ]^{1/2} = -L_{mn}^{\text{BO}} (v+1)^{1/2}, \end{aligned}$$

while for "hot band" transitions  $v+1 \rightarrow v$  we have

$$(5) \quad \begin{aligned} K_{mn, v(v+1)}^{\text{HT}} &\simeq K_{mn}^{\text{HT}} [ (v+1) \hbar/2 \mu \omega ]^{1/2} = L_{mn}^{\text{HT}} (v+1)^{1/2} \\ K_{mn, v(v+1)}^{\text{BO}} &\simeq K_{mn}^{\text{BO}} [ (v+1) \mu \omega/2 \hbar ]^{1/2} = L_{mn}^{\text{BO}} (v+1)^{1/2}. \end{aligned}$$

We see from (4) and (5) that the signs associated with BO and HT contributions in cold bands are different from those appearing in hot bands. In absorption HT and BO transition moments add for cold bands, but subtract for hot bands. This general behaviour is followed even if the overlap matrix is not diagonal. Also, the interference of the two mechanisms will change the intensity trend relative to that of the HT mechanism alone, and will alter the intensity ratio between hot and cold bands.

We have applied these ideas to the A and *b* sequences of *p*-benzoquinone. We have evaluated the  $\langle Q \rangle$  and  $\langle \partial/\partial Q \rangle$  vibrational integrals pertaining to hot and cold bands assuming that the  $\nu_{30}$  oscillator is harmonic. Then the transition moments of the first few terms of both sequences can be evaluated considering various cases arising from different ratios  $L^{\text{HT}}/L^{\text{BO}}$ . The best agreement with the experimental data in terms of intensity distribution along the sequences is found for  $L^{\text{HT}}/L^{\text{BO}} \simeq 3/7$ . In fig. 1 the relative intensity of the first few members of both sequences is listed for the value 30/70 for the ratio  $L^{\text{HT}}/L^{\text{BO}}$ , together with the pure HT limiting case and with the experimental data.

## DISCUSSION

As one can see from fig. 1, inclusion of both inducing mechanisms leads to a better agreement with experiment than consideration of only the HT mechanism. Taking the uncertainty of the experimental results into account,

we can say that the intensity distribution in band *b* has been improved, while that in band A seems relatively insensitive to the interference between the BO and HT mechanisms. This result seems a reasonable indication that bands A, *b* are another example supporting our prediction [4] that in general the BO mechanism contributes substantially to the intensity borrowing.

Finally we wish to point out that in our argument we neglected the relative rotation of normal modes in the excited state with respect to the ground state. However this seems a reasonable assumption in view of the small frequency of the inducing mode and of the negligible deuterium effect on the frequency itself. Both these facts suggest a very small coupling with other modes between both electronic states and therefore seem to justify our assumption.

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