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Local Stark Mixing in the Phosphorescent Processes of p-Benzoquinone

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Abstract

The phosphorescence spectra of p-benzoquinone are very sensitive to environments and electric fields since the molecule have small energy gaps between the first and second excited triplet states. The variable vibronic pattern from solvent to solvent is a manifestation of perturbation between the two triplet $n\pi^*$ states. The calculation of the local field strength of dipolar environments indicates that the effective electric fields coming from the environmental dipolar perturbations in polar solvents or binary-mixed nonpolar solvents are $\sim 10^6$ V/cm in order of magnitude in external bulk scales. It is also demonstrated that these rather intense fields lead the drastic increments of the phosphorescence origin band due to the local Stark mixing between ${}^3B_{1g}(n, \pi^*)$ and ${}^3A_u(n, \pi^*)$. Coupling matrix element obtained due to the solvent Stark fields is 212 cm^{-1} .

Introduction

It is advantageous to study interstate coupling in p-benzoquinone (PBQ) since this molecule belongs to a high symmetrical point group and has two closely-lying $n\pi^*$ triplet states between which the transition dipole moment is great in magnitude along the molecular C=O axis. Much spectroscopic interest in this type of molecules arises from this closeness in energy among the ${}^3(n, \pi^*)$ states. The manifestations of interstate mixing may be predominant in the electronic spectra. The small energy difference and the significant matrix elements of interstate interactions between T_1 (B_{1g}) and T_2 (A_u) may give a good example of *pseudo*-Jahn-Teller effects in molecular spectroscopy. The remarkable interstate coupling between T_1 and T_2 is responsible for photophysical and photochemical behaviors of PBQ.

The study on crystal field effects is extremely important, since the spectra of PBQ in the solid matrices are remarkably subjected to environmental effects as a matter of fact. The Stark spectroscopy provides us a useful information on the intramolecular interstate couplings of molecules with nearly degenerate electronic states. Several studies on the Stark effects have been reported for the lowest excited triplet state of PBQ in the crystal^{1,2,3}.

On the other hand, solvatochromism and electrochromism have been studied on the absorption and emission spectra of dye molecules in solutions. It is well known that environments sometimes affect significantly on the electronic charge distribution of the solute molecule. Environmental molecules with permanent dipole moments cause a bulk electric field at the site of the solute molecule and have

influences on the electronic spectra of the molecule. This type of effects may be called the "solvent Stark effects" originating in the characteristic role of environmental molecules as the source of electric field¹⁾. The local molecular field affects several spectral properties of the solute molecule such as band frequency, width and intensity.

An investigation on the properties of dielectrics was first carried out by Onsager⁵⁾. Most works in this field have been developed on his model. The results of the application of perturbation theory were reported by Longuet-Higgins and Pople⁶⁾, McRae⁴⁾, and Ooshika⁷⁾. Importance of quadratic terms has also been pointed out in explanation of band shifts observed in the absorption spectra of organic molecules by McRae⁴⁾. Investigating an effect of environmental molecules on the absorption intensity of solute molecules, on the other hand, Koyanagi demonstrated that a great intensity enhancement of the $S_1, S_2, \leftarrow S_0$ absorption transitions of PBQ in CS_2 compared with those in cyclohexane is attributed to strong dispersion forces of the former solvent⁸⁾.

Such solvent effects on the spectra of solute molecules may be investigated from two viewpoints: One is the polarization effect originating mainly in predominant solute-solvent interactions; and another the cage effect, *i.e.*, the effect of the substitutional "squeezed" or "cramped" sites of the solute to those of solvent. One of the present interests is to show to what extent the local fields due to polar solvent-molecules may act to bring the intensity enhancement of the forbidden transition of the solute molecule. We shall make a discussion about the nature of the "allowed type" band pattern in the emission spectra of PBQ observed in polar solvents, from a viewpoint of bulk polarization acting on the solute molecule. It will also be shown how much those external perturbations play an important role in the intensity-borrowing mechanisms of PBQ.

Theoretical Consideration

1. Effects of External Electric Field on Electronic Transitions of Molecules

In general, the perturbation theory is helpful for investigation on the effect of those field interactions on the wave functions. The perturbation term describing the interaction with the electric field is given by

$$H_s = -e \vec{d} \cdot \vec{F}, \quad (1)$$

where \vec{F} is the electric field and \vec{d} the dipole strength operator. Confining ourselves to non-degenerated states of a molecule, we obtain the state function Ψ_n as follows:

$$\Psi_n(F) = \Psi_n(0) - F \sum \frac{\mu_{ni}}{[E_i(0) - E_n(0)]} \Psi_i(0)$$

$$\begin{aligned}
& -F \sum_{l \neq \lambda} \sum_{\lambda \neq n} \frac{\mu_{\lambda n} (\mu_{\lambda l} - \mu_{\lambda l}^*)}{[E_l(0) - E_\lambda(0)][E_n(0) - E_l(0)]} F \Psi_l(0) \\
& - \frac{1}{2} - F \sum_{l \neq n} \frac{\mu_{nl} \mu_{ln}^*}{[E_l(0) - E_n(0)]} F \Psi_l(0), \quad (2)
\end{aligned}$$

where

$$\mu_{ij} = \langle \Psi_i | \vec{e} d | \Psi_j \rangle. \quad (3)$$

It is clear from eq. (2) that state-to-state mixings are, more or less, promoted by external electric fields. Now, let us suppose that the transition $\Psi_n(0) - \Psi_o(0)$ is electronically forbidden on an assumption of the dipole transition but the transition $\Psi_l(0) - \Psi_o(0)$ is allowed. Perturbation due to the electric fields may mix the state $\Psi_l(0)$ with the state $\Psi_n(0)$ to some extent and the transition $\Psi_n(0) - \Psi_o(0)$ may become slightly allowed by borrowing the intensity from the transition $\Psi_l(0) - \Psi_o(0)$. If the molecule has no permanent dipole just as PBQ, the second order terms of F may play an important role in the intensity-borrowing mechanism.

Using the perturbed wave function eq. (2) and truncating the power series to the first order of F , one obtains as transition dipole moment

$$\begin{aligned}
M_{mn} &= \mu_{mn} + \left\{ \sum_{l \neq m} \frac{\mu_{m*} \mu_{*n}}{[E_m(0) - E_l(0)]} + \sum_{l \neq n} \frac{\mu_{ml} \mu_{ln}}{[E_l(0) - E_n(0)]} \right\} F \\
&+ F \frac{\mu_{ml} \mu_{ll} \mu_{ln}}{[E_l(0) - E_m(0)][E_l(0) - E_n(0)]} F = M_{mn}(0) + \alpha_{mn} F + F \beta_{mn} F, \quad (4)
\end{aligned}$$

where α_{mn} is the transition polarizability and β_{mn} the hyper-polarizability. Since the transition dipole moment is expanded in terms of power series of F , one may expect an intensity enhancement with an increase in the electric fields because of an effective Stark mixing represented by the second and third terms of eq. (4). When the transition from the m -th to n -th state is forbidden under the dipole transition approximation, the field perturbation makes a remarkable gain in the transition intensity.

Most electronic transitions are governed by the selection rule regarding to the transition dipole moment. The rigorous rule holding in a free molecule, however, becomes to be loosened for the molecule in solid matrices; the "forbidden" bands sometimes appear in the emission and absorption spectra in condensed media. Under the employment of electric field the molecular wave functions are also modified so as to make those band appear.

2. Environmental Field Effects on Electronic Transition of Molecules

Environmental field effects on the electronic states of molecules may be generally treated with second order perturbation theory^{4,7)}. Let us consider a system in which a solute (PBQ) molecule is surrounded by n identical solvent molecules. Putting the perturbation term of Hamiltonian as H_{1i} , we obtain the next equation for the interaction matrix elements:

$$\begin{aligned}
\langle H_{st} \rangle = & \sum \langle \Psi_i^{(m)} \Psi_j | H_{st} | \Psi_i^{(m)} \Psi_j \rangle + \sum_{i' = i} \sum_{m=1}^n \frac{\langle \Psi_i^{(m)} \Psi_j | H_{st} | \Psi_i^{(m)} \Psi_j \rangle}{E_i - E_{i'}} \\
& + \sum_{j' = j} \sum_{m=1}^n \frac{\langle \Psi_i^{(m)} \Psi_j | H_{st} | \Psi_i^{(m)} \Psi_{j'} \rangle}{E_j - E_{j'}} \\
& + \sum_{i' = i} \sum_{j' = j} \sum_{m=1}^n \frac{\langle \Psi_i^{(m)} \Psi_j | H_{st} | \Psi_i^{(m)} \Psi_{j'} \rangle}{(E_i - E_{i'})(E_j - E_{j'})}. \quad (5)
\end{aligned}$$

Here Ψ_j and $\Psi_i^{(m)}$ denote the zeroth wave functions of the solute molecule in the electronic state j and those of the m -th solvent in the electronic state i , respectively, and E 's are the zeroth energies in each state. In many cases the perturbation term may be taken as the sum of dipole-dipole interactions although the higher terms that it become to play not a little a contribution to the perturbation, especially when the solutes with large permanent dipole are employed⁹⁾. The dipole approximation will be employed throughout this work. The first term of eq. (5) represents a sum of interactions between the permanent dipole of the solvent molecule in the electronic state i and that of the solute molecule in the electronic state j . The second term, on the other hand, corresponds to the interaction of the permanent dipoles of the solvent molecule. The first and second term may be, however, neglected when the system consists of dipolar solvent non-polar solute in each electronic states. The third and fourth terms are induction and dispersion effects, respectively, and often affect remarkably an electronically forbidden transition of the solute molecule as has been shown in the 2600 Å band system of benzene⁸⁾. An anisotropic effect of solvent orientation appears on the spectrum of the solute molecule through the third term rather than through the fourth one. It is interesting to know to what extent solvent Stark field affects the solute spectra. We devote thus our attention to the analysis of the third term. Here let us describe the fields of polar solvent molecules in terms of the effective electric field F_m^{eff} . This is sufficient to bring about our present purpose. The solute molecule interacts with the electric field that is produced at the site of the solute molecule by the permanent dipoles of the surrounding solvent molecules:

$$H_{st} = F \cdot \mu_s, \quad (6)$$

where μ_s is the transition dipole of the solute molecule. Substituting a relation eq. (6) into the third term of eq. (5), we obtain as the square of mixing matrix element between the states j and κ of the solute molecule

$$\left\{ \sum_{m=1}^n | \langle \Psi_i^{(m)} \Psi_j | H_{st} | \Psi_i^{(m)} \Psi_{j'} \rangle | \right\}^2 = (F_m^{eff} \mu_{j\kappa})^2, \quad (7)$$

where

$$F_m^{eff} = \sum_{m=1}^n \langle \phi_i^{(m)} | F_m | \phi_i^{(m)} \rangle, \quad (8)$$

and

$$\mu_{j\kappa} = \langle \Psi_j | e r | \Psi_\kappa \rangle. \quad (9)$$

If we are able to estimate effective field F_m^{eff} from statistical and geometrical considerations for the system, we may have a simpler form than eq. (7).

$$\left\{ \sum_{m=1}^n | \langle \Psi_i^{(m)} \Psi_j | H_s | \Psi_i^{(m)} \Psi_j \rangle | \right\}^2 = (F_m^{eff})^2 \mu_j^2. \quad (10)$$

Calculations

1. Solvent Stark Field

The solvent Stark field in the systems of PBQ in condensed media is evaluated similarly to the treatment given by Nicol¹⁰. To start with let us assume that one PBQ molecule and n identical solvent molecules are bound each other with short range intermolecular interactions to form a sphere, at the dielectric constant ϵ . We suppose further that a net resultant polarization, M_s , for an orientation of solvent molecules in sphere appears with a uniform density of dipole, μ_s , in the solvent region and an induction field, F_s , is produced at the core site of PBQ molecule by M_s . If the sphere has a radius of R , the density of dipole moment, μ_s , is given by

$$\mu_s = [(4\pi/3)R^3]^{-1} M_s. \quad (11)$$

Polarization distribution of a spherical cavity, whose radius, a , is assumed to be very close to that of the PBQ molecule, is characterized by elastical bound-charges.

Employing a pair-correlation function, we have expressed the induction field, F_s , as follows

$$\begin{aligned} F_s &= (1/2) \int_0^\pi \mu_s \cos^2 \theta \, d\theta \int_0^R g(r)^{-1} dr \\ &= (12/R^3) \mu_s \ln(R/r). \end{aligned} \quad (12)$$

As is well known, the field induced at the cavity site polarizes environmental solvent molecules in turn. This induction field just corresponds to the reaction field, F_r , in the treatment on liquid dielectrics given by Onsager⁵.

The total field, F_m , which the central PBQ molecule experiences is thus given by

$$F_m = F_s + F_r. \quad (13)$$

By using the theoretical treatment given by Fröhlich¹¹, we have finally obtained the mean-squared polarization-field as follow,

$$\langle F_m^2 \rangle = \frac{48 [1n(R/a)] kT}{R^3} \left[\frac{(\epsilon - 1)(2\epsilon + 1)}{\epsilon} \right]. \quad (14)$$

The most effective electric field perturbation for the interstate coupling between ${}^3B_{1g}(n, \pi^*)$ and ${}^3A_u(n, \pi^*)$ states is the electric field change along the C=O axis of PBQ molecule. This will be true for environmental dipolar perturbations. Therefore, a preliminary model calculation shows that the effective solvent Stark field of a polar solvent molecule with 10^{-1} D over a PBQ molecule distant by 8 Å from it amounts to $\sim 10^6$ V/cm in external bulk scales.

2. Coupling Matrix Element between ${}^3B_{1g}(n, \pi^*)$ and ${}^3A_u(n, \pi^*)$ due to Electric Fields

The off-diagonal matrix element for electric-field perturbation on two nearly degenerate states contain the transition moment between two states and the strength of electric field. For the case of PBQ, a set of LCAO-MO's wave functions obtained by the Pariser-Parr-Pople method is employed¹²⁾. The relevant wave functions are given in Table 1.

Table 1. Molecular n- and π -orbitals for p-benzoquinone obtained by Pariser-Parr-Pople method (after Anno et al., reference 12).

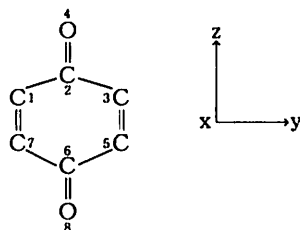
(1)

MO	Symmetry	Atomic orbital coefficients
π_1	b_{1u}	$0.475(2p_x^4 - 2p_x^8) - 0.380(2p_x^2 - 2p_x^6) - 0.254(2p_x^1 - 2p_x^3 - 2p_x^5 - 2p_x^7)$
π_2	b_{2g}	$0.601(2p_x^4 - 2p_x^8) - 0.349(2p_x^2 - 2p_x^6) - 0.088(2p_x^1 - 2p_x^3 - 2p_x^5 - 2p_x^7)$
π_3	b_{3u}	$0.471(2p_x^4 + 2p_x^8) - 0.100(2p_x^2 - 2p_x^6) - 0.366(2p_x^1 - 2p_x^3 - 2p_x^5 - 2p_x^7)$
π_4	b_{1g}	$0.500(-2p_x^1 + 2p_x^3 + 2p_x^5 - 2p_x^7)$
π_5^*	b_{2g}	$0.353(2p_x^4 - 2p_x^8) - 0.464(2p_x^2 - 2p_x^6) - 0.282(2p_x^1 - 2p_x^3 - 2p_x^5 - 2p_x^7)$
π_6^*	b_u^3	$0.227(2p_x^4 - 2p_x^8) - 0.587(2p_x^2 - 2p_x^6) - 0.226(2p_x^1 - 2p_x^3 - 2p_x^5 - 2p_x^7)$
π_7^*	a_u	$0.500(-2p_x^1 + 2p_x^3 - 2p_x^5 + 2p_x^7)$
π_8^*	b_g^2	$0.114(2p_x^4 - 2p_x^8) - 0.402(2p_x^2 - 2p_x^6) - 0.403(2p_x^1 - 2p_x^3 - 2p_x^5 - 2p_x^7)$
n_+	b_{2u}	$2^{-1/2}(2p_y^4 - 2p_y^8)$
n_-	b_g^3	$2^{-1/2}(2p_y^4 - 2p_y^8)$

(2)

State	Excited configurations
$B_{1g}(n, \pi^*)$	$n_- \rightarrow \pi_5^*$
$A_u(n, \pi^*)$	$n_+ \rightarrow \pi_5^*$
$B_{1u}(\pi, \pi^*)$	$\pi_3 \rightarrow \pi_5^*$

(3)



The geometrical data of PBQ for the numerical calculation of the electric dipole moment is taken from the X-ray analysis by Trotter¹³⁾. The value of coupling matrix element between ${}^3B_{1g}(n, \pi^*)$ and ${}^3A_u(n, \pi^*)$ due to the environmental electric field is thus obtained. For the root-mean-squared polarization-field,

$$\langle F_m^2 \rangle^{1/2} \sim 10^6 \text{ V/cm},$$

$$\langle \Psi^3 B_{1g}(n, \pi^*) | H_s | \Psi^3 A_u(n, \pi^*) \rangle = -e F_m \langle (n, \pi^*) | Z | (n_+, \pi^*) \rangle = 212 \text{ cm}^{-1}.$$

The perturbed wave function of the phosphorescent state (T_1) is then given by

$$\Psi(T_1) = 0.84 \Psi_3 B_{1g}(n, \pi^*) + 0.55 \Psi_3 A_u(n, \pi^*).$$

The intensity enhanced by local Stark mixing, f' , is thus calculated to be,

$$f' = 2.64 \times 10^{-7}.$$

The ratio of enhanced intensity to the overall intensity,

$$f' / f_3 A_u \leftarrow s_0 = 0.42 .$$

This result suggests that 42% of the total intensity of ${}^3B_{1u} - {}^1A_g$ transition comes from the environmental dipolar field perturbation.

Concluding Remarks

The magnitude of the coupling matrix element between $T_1(B_{1u})$ and $T_2(A_u)$ due to the local Stark mixing is closeness in energy spacing among the ${}^3(n, \pi^*)$ states. The result obtained here suggests that the bulk polarization fields produced by polar solvent molecules at the site of PBQ play an important role as the driving force for intramolecular interstate coupling of PBQ. Therefore, it is expected that the phosphorescent state (T_1) of PBQ has a heavy $T_2(A_u)$ -character and shows the "allowed-type" band patterns with active a_g normal modes in the phosphorescence spectra in polar solvents. As a matter of fact, the phosphorescence spectral patterns in polar environments^{14,15)} rather resemble that of the ${}^3A_u - S_0$ phosphorescence emission in the vapor^{16,17)} except for moderate participation of several phonon modes and weak appearance of some u-modes.

The initial purpose of this work was to investigate the intensity change of the phosphorescence origin band and the "allowed-type" band system observed in polar solvents of PBQ from solvent to solvent and give a reasonable explanation for them in terms of the "solvent Stark effects".

The most important factor responsible for the success of this study has been the simplicity of the PBQ system, primarily a result of the high symmetry and the forbiddenness of the $T_1 - S_0$ transition. If the $T_1 - S_0$ transition were allowed more than the $T_2 - S_0$ one and if the $T_1 - T_2$ energy separation were of $\sim 10^3 \text{ cm}^{-1}$ or more, no remarkable perturbation effects would be detected.

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