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Linear Dependence of ODMR Transition Frequency on $T_1 \rightarrow S_0$ Transition Energy. *p*-Dichlorobenzene in Various Matrices

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Synopsis. The linear dependence of ODMR transition frequency on the $T_1 \rightarrow S_0$ transition energy of *p*-dichlorobenzene in various matrices was interpreted with the spin-orbit couplings of the lowest triplet state with the triplet and singlet manifold, by assuming that the matrix dependent shifts in the triplet and singlet state energy are correlated with each other.

Lemaistre and Zewail have explained the origin of the difference in the linewidth between ODMR (optically detected magnetic resonance) and optical transitions, by considering selective spin-orbit coupling (SOC) between singlet and triplet states.[1–3] Their theory has also provided an explanation for the linear dependence of the ODMR transition frequency on the optical transition energy in a system where the ODMR and optical transitions show inhomogeneous broadening.[4] On the other hand, Egmond *et al.* have explained the linear relation of these two transitions by the interaction between triplet states.[5]

Recently we have found a linear correlation between the ODMR transition and the $T_1 \rightarrow S_0$ transition energy of *p*-dichlorobenzene (*p*-DCB) in various matrices,[6] but the origin for the correlation has not yet been clarified. In this note, we apply their methods to the systems of *p*-DCB in various matrices, and show that the SOC with a higher triplet and a singlet state can provide a possible explanation for the correlation between the ODMR transition frequency and the $T_1 \rightarrow S_0$ transition energy rather than the vibronic coupling between triplet states.

At first we apply Zewail's method to a compound which has different electronic energies in various matrices. We assume that the contribution of the solvent to the spin-orbit matrix element is very small, and only the difference of the electronic energies between a perturbing state and the T_1 state has an influence on the ODMR transition energy. We neglect the inhomogeneous broadening in a matrix. The full widths at half maxima (fwhm) of the 0,0 bands of the phosphorescence spectra of *p*-DCB in the matrices are 3—4 cm^{-1} except for fwhm of 20 cm^{-1} in benzene. Therefore, the inhomogeneous broadening effect in the $T_1 \rightarrow S_0$ and ODMR transitions discussed by them is rather small in the case of *p*-DCB and may be neglected compared to the variation of the transition energies with matrix. We thus consider, instead of inhomogeneous broadening, the matrix dependence of the electronic and ODMR transition energies in terms of their method. The electronic energy shifts of the singlet and triplet excited states in various matrices may be written as

$$E^{r} = E_0^{r} + \delta_M^{r}, \tag{1}$$

where r denotes the singlet (S) or the triplel (T) state, E_0^r is the electronic energy of the molecule in a certain standard matrix (M_0) and δ_M^r denotes the energy shift of the molecule in a matrix (M) from E_0^r. We assume that only one magnetic sublevel (say T_y) of its lowest triplet state effectively couples with a particular singlet state through SOC (mechanism 1). According to their method,[2] the total energy for each sublevel is given by

$$E_z^T = E_0^T + Z + \delta_M^T, \tag{2-a}$$

$$E_y^T = E_0^T + Y + \delta_M^T - |\tau^y|^2/[(E_0^S + \delta_M^S) - (E_T^0 + \delta_M^T + Y)], \tag{2-b}$$

$$E_x^T = E_0^T + X + \delta_M^T, \tag{2-c}$$

where X, Y, and Z denote the zero-order energies of the sublevels of the triplet state in zero-magnetic field and τ^y is the SOC matrix element between the perturbing singlet state and the T_y sublevel. The sublevel order of *p*-DCB is $T_y > T_z > T_x$ in energy. The shift of the ODMR transition frequency between the spin-orbitally active magnetic sublevel (T_y) and the inactive sublevel (T_x) is

$$\Delta\hbar\omega_{yx} = -|\tau^y|^2/(\Delta_{ST} - Y + \delta_M^S - \delta_M^T), \tag{3}$$

where $\Delta_{ST} = E_0^S - E_0^T$ is the singlet and triplet energy separation of the molecule in the standard matrix (M_0). Since $\Delta_{ST} \gg Y$, $(\Delta_{ST} - Y) \sim \Delta_{ST}$. In the case of *p*-DCB, the magnitude of Δ_{ST} is larger at least by a factor of about 10^2 than δ_M^T. Although we have not measured δ_M^S, δ_M^S is expected to be comparable with δ_M^T. Therefore, we may expand the denominator in Eq. 3 as

$$\Delta\hbar\omega_{yx} = |\tau^y|^2(\delta_M^S - \delta_M^T)/(\Delta_{ST})^2, \tag{4}$$

where we have omitted the term $-|\tau^y|^2/\Delta_{ST}$ which does not depend on matrices. Assuming that the energy shifts of the singlet and triplet states are correlated as $\delta_M^S = \alpha\delta_M^T$, we obtain

$$\Delta\hbar\omega_{yx} = |\tau^y|^2(\alpha - 1)\delta_M^T/(\Delta_{ST})^2. \tag{5}$$

Equation 5 shows that the ODMR microwave transition frequency depends linearly on the energy shift of the 0,0 band in the phosphorescence spectrum except for the case of $\alpha = 1$. In the case of $\alpha > 1$, *i.e.*, the shift of the singlet energy being larger than that of triplet one, the slope of a plot of $\Delta\hbar\omega_{yx}$ *vs.* δ_M^T becomes positive.

Next we consider the SOC between triplet states (mechanism 2). We assume the two magnetic sublevels (say T_z and T_x) effectively couple with each other. The shifts of the ODMR microwave transitions are given by

$$\Delta\hbar\omega_{zx} = 2|\tau_{jl}^{xz}|^2\varepsilon(\alpha - 1)\delta_M^l/(\Delta_{jl})^3, \tag{6}$$

$$\Delta\hbar\omega_{yx} = -|\tau_{jl}^{xz}|^2(\alpha - 1)\delta_M^l/(\Delta_{jl})^2, \tag{7}$$

where $\varepsilon = (Z_j - X_j) + (Z_l - X_l)$ is the sum of the $T_z - T_x$ transition energies of the interacting triplet states, and $\alpha\delta_M^l = \delta_M^j$. Note the negative sign of Eq. 7, which is opposite to Eq. 5.

Finally, we consider an interaction with a higher triplet state, T_j. If V is the operator for the perturbation which does not include spin, for example, one for the vibronic coupling or one for the solvent field perturbation (mechanism 3),[5] the perturbation matrix elemenls are given by

$$\langle T_1\tau_r|V|T_j\tau_s\rangle = V_{1j}\delta_{rs}. \tag{8}$$

The shift of the energy of the T_{1x} state becomes

$$\Delta E_{1x} = -|V_{j1}|^2/(E_0^j+X_j-E_0^1-X_1), \tag{9}$$

where the super- or subscripts l and j denote the lowest and j-th triplet states, respectively. The shift of the ODMR microwave transition frequency between two sublevels (say, T_z and T_x) is

$$\Delta\hbar\omega_{zx} = -|V_{j1}|^2\varepsilon'/(\Delta_{j1})^2, \tag{10}$$

where $\Delta_{jl}=E_0^j-E_0^l$ is the energy separation of two triplet states, and $\varepsilon'=(Z_j-X_j)-(Z_l-X_l)$ is the energy difference between the T_z — T_x transitions in the lowest and j-th triplet states. We have used the relation $\Delta_{jl}\gg Z_l$, X_l, Z_j, and X_j. Using the equation for the shift of the phosphorescence S,

$$S = -|V_{j1}|^2/\Delta_{j1}, \tag{11}$$

we obtain

$$\Delta\hbar\omega_{zx} = \varepsilon' S/\Delta_{j1}. \tag{12}$$

It may be noted in this case that the perturbation which shifts the phosphorescence origin is the same as that on the ZFS parameters.

The ODMR transition energies are plotted against the $T_1\rightarrow S_0$ transition energies in various matrices[6,7] in Fig. 1. Only the $T_1\rightarrow S_0$ transition energy in p-xylene is deviated far apart from that in the other matrices. The ODMR transitions related to the T_y sublevel show the wavelength dependence, while the T_z-T_x transition does not. The slopes of the lines for the T_y-T_x and T_y-T_z transitions are found to be 2.7×10^{-5}, and 3.1×10^{-5}, respectively.

Mechanism 3 can provide an explanation for the linear dependence of the T_y-T_x and T_y-T_z transitions, but is not to give the explanation for the T_z-T_x transition. Independence of the microwave transition from the $T_1\rightarrow S_0$ transition energy means $\varepsilon'=0$. This may not be acceptable, since we can not expect the same microwave transition energy in different electronic states.

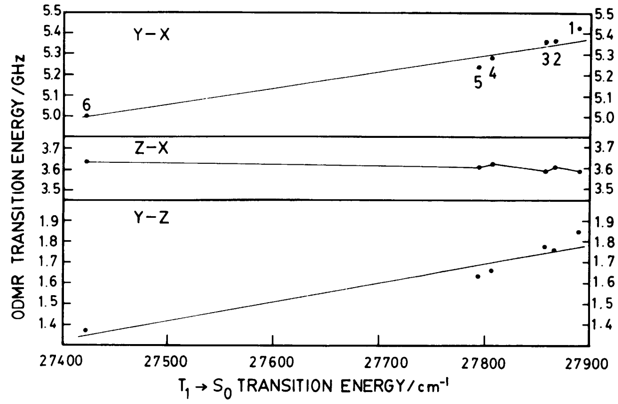

Fig. 1. The plots of the frequencies of the three sublevel transitions *versus* the $T_1\rightarrow S_0$ transition energy of p-dichlorobenzene in various matrices: 1; in p-dichlorobenzene-d_4, 2; trap 1 in the neat crystal, 3; in p-dibromobenzene, 4; trap 2 in the neat crystal, 5; in benzene, 6; in p-xylene.

We apply mechanism 1 to the system of p-DCB. The triplet state ($^3B_{1u}$) of p-DCB directly couples with the singlet state ($^1B_{3u}$) through the top sublevel, T_y by SOC. This mechanism expects the linear dependence of the T_y-T_x and T_y-T_z transition energies on the $T_1\rightarrow S_0$ transition energy, and independence of the T_z-T_x transition. This is just the case we have observed in p-DCB. If we assume $\alpha-1\sim1$ and $\tau^y=63\,\text{cm}^{-1}$ for p-DCB, the latter being the value for 1,2,4,5-tetrachlorobenzene,[8] we get $\Delta_{ST}\approx10^4\,\text{cm}^{-1}$. This value seems to be plausible.

The T_z and T_x sublevels of the lowest triplet state of p-DCB couple with the $^3B_{3u}$ by SOC, and mechanism 2 would also explain the experimental results. The shift of the T_x-T_z transition is smaller by a factor of $\varepsilon/\Delta_{jl}\approx10^{-5}-10^{-6}$ than that of the other two transitions, as shown in Eqs. 6 and 7. The slope is opposite to the case of mechanism 1.

The magnitude of τ, α, and Δ determines which mechanism, 1 or 2, is dominant. As both α and τ are expected to be comparable for the triplet and singlet B_{3u} states and may be used commonly, the shift of the microwave transition may be written as

$$\Delta\hbar\omega_{yx} = |\tau|^2(\alpha-1)\delta\left(\frac{1}{(\Delta_{ST})^2}-\frac{1}{(\Delta_{j1})^2}\right). \tag{13}$$

Since Δ_{jl} is smaller than Δ_{ST}, the second term in Eq. 13 surpasses the first term. The slopes of microwave transitions are found to be positive, and we expect $\alpha<1$ in p-DCB. We have neglected completely the spin-distribution change in the triplet state with varying matrices. Especially, the values in p-xylene are very far away from those in the other systems. Therefore, we might have to consider the spin-distribution change of p-DCB in p-xylene. However, the linear dependence of the ODMR microwave transition energy on the $T_1\rightarrow S_0$ transition energy is well explained by the mechanisms 1 and 2, namely by the SOC's with the triplet and singlet manifolds, with an assumption that the matrix dependent shifts in the triplet and singlet energy are correlated with each other.

Since Δ_{jl} is smaller than Δ_{ST}, the second term in Eq. 13

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