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Semi-Empirical Calculations on the ZFS Parameters of Phosphorescent Charge-Transfer Complexes

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A semi-empirical treatment of the calculation on the ZFS parameters of phosphorescent CT complexes is given, based on an extension of the method of Van der Waals and Ter Maten. The procedure is outlined and applied to two complexes, i.e. to DEA/*s*-triazine and DEA/benzonitrile. Numerical results are given and discussed in the light of the experimental data.

Introduction

During the last ten years the zero-field splitting (ZFS) parameters of the lowest $^3(\pi, \pi^*)$ states of many phosphorescent aromatic molecules have been determined from ESR experiments. Likewise several attempts to calculate the ZFS parameters theoretically have been reported in the literature [1, 2].

Optical measurements [3, 4] have shown that it is sometimes possible to observe phosphorescence of charge-transfer (CT) complexes. The triplet character of the emitting state of some of these complexes has been corroborated by ESR investigations [4, 5]. The optical and ESR experiments of the two CT complexes to be considered in this paper, i.e. N,N-diethylaniline (DEA)/s-triazine (I) and DEA/benzonitrile (II), have been reported elsewhere [3, 5]. In these complexes DEA is the electron donor and s-triazine and benzonitrile are the electron acceptors. Up to now little work has been done on the theoretical calculations of the ZFS parameters of such complexes.

We wish to report here the results of a semi-empirical calculation, which is an extension of the method of Van der Waals and Ter Maten [2]. The procedure will be demonstrated by the calculation of the ZFS parameters of the two CT complexes mentioned. The results of the calculations will be discussed in the light of the experimental data.

Method of Calculation

In calculations on CT complexes it is usual to assume that the aromatic donor and acceptor molecules are arranged in parallel planes (sandwich-like structure) [6]. The underlying geometrical model for the DEA/s-triazine (I) complex is shown in Fig. 1.

In order to calculate the ZFS parameters theoretically, we use as a basis the semi-empirical method introduced by Van der Waals and Ter Maten for homocyclic systems [2], extended by us to nitrogen containing molecules [7] (henceforth denoted by "extended WM method"). The calculation of the ZFS

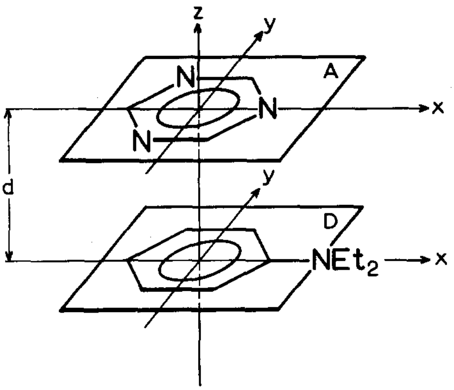

Fig. 1. Geometrical model of CT complex I

parameters D and E (for definitions of D and E see Ref. [7]) of aromatic systems in their lowest triplet states can be divided into two essential parts, i.e. the construction of the triplet wave function and the evaluation of the spin-spin integrals.

In our calculations the triplet wave function has been obtained from a MO description using the SCF method for closed shell systems with inclusion of the PPP approximations [8]. The parameters needed can be divided into two groups:

a) the intra-molecular parameters and
b) the inter-molecular parameters.

a) The parameters belonging to the first group have been reported in a previous paper [7]. Their values have been adopted from the isolated molecules in question. They have been kept fixed during the variation of the inter-molecular parameters. This implies that deformations of the electronic distributions in the components due to mutual interactions other than those arising from excitation to the triplet state, have been neglected.

b) The MO parameters needed for the description of the inter-molecular interactions in excited complexes have received less attention in the literature. Azumi, Armstrong and McGlynn [9] studied the energy of excimer luminescence and drew up a quantumchemical description of the inter-molecular interactions between two identical molecules. We wish to extend this formulation to unidentical molecules, assuming that the basic elements are not changed essentially by introduction of hetero-centers.

In our calculations the inter-molecular resonance integrals β_{pq} have been approximated according to Mulliken's formula [10]

$$\beta_{pq} = -\frac{(I_p + I_q) S_{pq}}{2(1 + S_{pq})} .$$

I_p and I_q are the ionization potentials of centers p and q, resp.; S_{pq} stands for the overlap integral between p and q. We have only taken into account overlap between the two $2p_z$ Slater-type atomic orbitals on corresponding atoms of different molecules, in conformity with Azumi's paper [9]. The overlap has been calculated by use of the analytical expression given by Parr and Crawford [11]

$$S_{pq} = 240^{-1} \exp(-\varrho/2)\,[240 + 120\varrho + 12\varrho^2 - 4\varrho^3 - \varrho^4]$$

in which $\varrho = Z_{pq} \cdot r_{pq}$ (r_{pq} is the internuclear distance in a.u.). In the case of non-identical centers p and q, the effective nuclear charge Z_{pq} has been approximated by $Z_{pq} = (Z_p \cdot Z_q)^{\frac{1}{2}}$, where Z_p and Z_q represent the effective nuclear charges of centers p and q. In our calculations a Z value of 2.83 has been chosen for carbon, close to that proposed by Murrell and Tanaka [12]. According to Slater's rules (see e.g. Ref. [13]), the Z values for N and N^+ then amount to 3.48 and 3.83.

The inter-molecular two-center Coulomb integrals of the type $\langle p_D p_D | q_A q_A \rangle$ (see Fig. 2) have been calculated by use of Parr's expression [14]

$$\langle p_D p_D \,|\, q_A q_A \rangle = r_{pq}^{-1} \left[1 + \frac{q}{2r_{pq}^2} (3\cos^2\gamma_{pq} - 1) + \frac{3q^2}{16 r_{pq}^4} (3 - 30\cos^2\gamma_{pq} + 35\cos^4\gamma_{pq}) \right]$$

where $q = 24/Z_{pq}^2$ and $Z_{pq} = (Z_p \cdot Z_q)^{\frac{1}{2}}$; furthermore $\cos\gamma_{pq} = d/r_{pq}$, in which d is the interplanar distance.

The Z_p values for C, N and N^+ centers used in these expressions have been published previously [7]. In our calculations of the ZFS parameters we have accounted for electronic repulsions between all centers in donor and acceptor molecules.

The spin-spin interaction integrals to be used in the extended WM method can also be divided into two groups. Concerning the intra-molecular interactions we refer to Ref. [7].

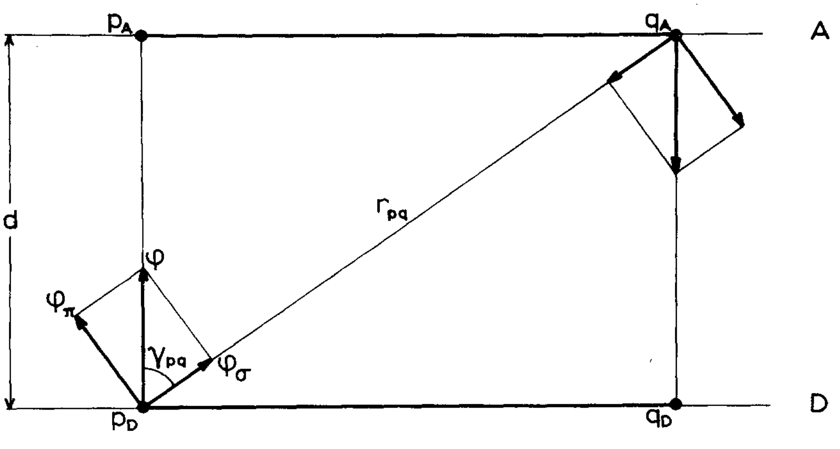

Fig. 2. Mutual positions of interacting centers and of atomic orbitals φ decomposed into π- and σ-parts

In order to obtain a proper treatment of the inter-molecular ZFS contributions D_{pq} and E_{pq}, the atomic orbitals φ of the respective centers have to be decomposed into π- and σ-parts (see Fig. 2).

This procedure leads to the following expression

$$D_{pq} = D_{pq}(\pi, \pi) \sin^4 \gamma_{pq} + \{D_{pq}(\pi, \sigma) + D_{pq}(\sigma, \pi)\} \sin^2 \gamma_{pq} \cos^2 \gamma_{pq} + D_{pq}(\sigma, \sigma) \cos^4 \gamma_{pq}$$

and an analogous formula for E_{pq}.

Semi-empirical (π, π) contributions to the ZFS values have already been reported [7]. The contributions resulting from (π, σ), (σ, π) and (σ, σ) interactions were not known. For that reason we have calculated these quantities theoretically by numerical integration of Coulomb repulsion integrals evaluated over basic charge distributions [15].

The four terms occurring in D_{pq} all give negative contributions to the ZFS parameters. Calculations by Van der Waals and Ter Maten [2] have shown that the $D_{pq}(\pi, \sigma)$ and $D_{pq}(\sigma, \pi)$ contributions are negative. The inter-molecular $D_{pq}(\pi, \pi)$ values have been reported [15] to be positive. In our calculations on CT complexes, however, one of the x axes of Roothaan's coordinate system [16] has been inverted. Consequently, the expression of the D_{op} as given in Ref. [15], changes its sign and the $D_{pq}(\pi, \pi)$ values become negative. For inter-molecular $D_{pq}(\sigma, \sigma)$ contributions the term $\langle r_{12}^2 - 3z_{12}^2 \rangle$, occurring in the expression of D_{op}, yields negative values, since $z_{12} = r_{12}$. As a consequence, all $D_{pq}(\sigma, \sigma)$ contributions are negative as well.

The $E_{pq}(\pi, \pi)$ values do not change sign by inversion of one of Roothaan's x axes and also the E_{pq} values for σ-bonds are not affected. According to Van der Waals and Ter Maten [2] the $E_{pq}(\pi, \sigma)$ and $E_{pq}(\sigma, \pi)$ values are positive.

Results

In the calculations of the ZFS parameters of the two CT complexes mentioned above the principal parameter is the interplanar distance, for this quantity determines implicitly the magnitude of all inter-molecular parameters and thus the resulting ZFS values. In the semi-empirical calculations on complex I two different symmetrical configurations have been considered. In the first situation, shown in Fig. 1, the "best" result with respect to the D value has been obtained at an inter-molecular distance of 2.90 Å, providing a theoretical D value of 0.042 cm^{-1} and an E value of 0.011 cm^{-1}. The latter quantity is decreased to 0.005 cm^{-1} if the acceptor molecule is shifted over a quarter of an aromatic CC bond (0.348 Å) in the direction of the diethylamino group. From calculations on the electron densities it follows that the percentage CT amounts to 58.3.

The other symmetrical configuration is realized by rotating the acceptor molecule over sixty degrees around the common z axis. Then the "best" inter-molecular distance appears also to be 2.90 Å. The resulting D and E values are 0.039 and 0.010 cm^{-1}, resp., and the percentage CT is 59.6. By shifting the s-triazine molecule over a quarter of a CC bond length, the E value is hardly decreased, whereas the D parameter is increased to 0.043 cm^{-1}. The results of the calculations on the two configurations have been summarized in Table 1.

Concerning the lowest triplet energy T_1, the first configuration is closer to the experimental value of 2.62 eV [3] than the second one. It is known from the literature that the lowest triplet energies, calculated in the (extended) WM method, are consistently too low by approximately 0.4 eV [17]. In view of this result the first configuration is to be preferred. Moreover, calculations show that this configuration has also a lower value of the total energy of the system.

For complex II also two symmetrical configurations have to be considered, one by placing the substituents of donor and acceptor molecules in the same direction and the other by putting them in opposite directions. From calculations on these two configurations (of which the two aromatic planes have the same x and y coordinates), it appears that agreement between the experimental and theoretical D values can be obtained in both cases. The resulting interplanar distances and the energies of the lowest triplet states (T_1) are different, however, as can be seen from Table 2.

From optical measurements by Beens and Weller [3] it is known that the maximum intensity of the CT phosphorescence of the DEA/benzonitrile complex occurs at 2.68 eV. Taking account of the effect of extensive CI [17], combination of the optically obtained data with those of Table 2, suggests that the second configuration is the more probable one. This configuration is also favoured with respect to the total energy of the complex.

In Table 3 the experimental and "best" theoretical results have been collected.

Table 1. *"Best" calculated values for two configurations of* CT *complex* I (DEA/*s-triazine*)

Configuration	r (Å)	T_1 (eV)	D (cm^{-1})	E (cm^{-1})	% CT
N above C–N$^+$	2.90	2.15	+0.042	+0.005	58.3
C above C–N$^+$	2.90	1.81	+0.039	+0.010	59.6

Table 2. *"Best" calculated values for two configurations of* CT *complex* II (DEA/*benzonitrile*)

Substituents	r (Å)	T_1 (eV)	D (cm^{-1})	E (cm^{-1})	% CT
parallel	3.45	2.80	+0.048	−0.007	66.2
opposite	3.15	2.33	+0.047	−0.008	65.6

Table 3. *Experimental and theoretical data of* CT *complexes* I (DEA/*s-triazine*) *and* II (DEA/*benzonitrile*)

Complex	experimental			theoretical				
	D (cm^{-1})	E (cm^{-1})	CT$^a_{max}$ (eV)	D (cm^{-1})	E (cm^{-1})	T_1 (eV)	r (Å)	% CT
I	0.039	0.002	2.62	+0.042	+0.005	2.15	2.90	58.3
II	0.047	0.008	2.68	+0.047	−0.008	2.33	3.15	65.6

[a] From Ref. [3].

Discussion

Reviewing the data given in Table 3, it may be concluded that the semi-empirical calculations on the ZFS parameters of the two CT complexes under consideration give satisfactory results. The CT character is demonstrated clearly by the relatively low *D* and *E* values found both experimentally and theoretically. The theoretical *D* values can be fitted on the experimental ones without causing unacceptable values for other physical quantities. Within the limitations of the method, the calculated lowest triplet energies, as an example, agree rather well with the experimental ones. Moreover, the interplanar distances are reasonable in comparison with values reported in the literature: From PPP calculations of the total energy Markov and Skancke [18] estimated the inter-molecular distance of the ground state cis-butadiene/ethylene complex at 3.10–3.30 Å; Hayashi and Nagakura [4] utilized 3.45 Å in their calculations on the ZFS parameters of methylbenzenes/tetracyanobenzene CT complexes, using a point charge model, whereas Beens [19] arrived at 3.0 Å based on calculations of physical properties like the total energy, the dipole moment and the transition probability of the emitting state of CT complexes.

The correspondence between the experimental and theoretical *E* values is also rather good. The small deviation between the theoretical and experimental *E* values of complex I may be attributed to the features of the WM method, which have been discussed in detail by Van der Waals [2].

In spite of the approximations introduced in the course of the calculations, it seems justifiable to apply the extended WM method as a basis for semi-empirical calculations of the ZFS parameters of phosphorescent CT complexes having $^3(\pi, \pi^*)$ character. Any possible improvement of the results should be found rather in refinements of the MO description than in a better evaluation of the two-center ZFS integrals.

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