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# Zero-field Energy Levels in Near-doubly-degenerate Triplet States

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**Synopsis.** The zero-field energy levels in near-doubly-degenerate triplet states are discussed on molecules which are distorted so as to lose their trigonal symmetry axes. As an example, the second excited triplet states of a deformed benzene molecule are calculated from the electron spin-spin interactions.

In a previous paper,[1] the zero-field splitting (ZFS) parameters of the lowest and second excited triplet states of molecules with a trigonal symmetry axis were calculated from the electron spin-spin interactions:

$$\begin{aligned}\mathscr{H}_{ss} &= \frac{\mu_0 g^2\beta^2}{4\pi}\left[\frac{(\boldsymbol{s}_1\cdot\boldsymbol{s}_2)}{r_{12}^3} - \frac{3(\boldsymbol{s}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{s}_2\cdot\boldsymbol{r}_{12})}{r_{12}^5}\right] \\ &= \frac{\mu_0 g^2\beta^2}{4\pi}\left[S_x^2\left(\frac{r_{12}^2-3x_{12}^2}{r_{12}^5}\right) + S_y^2\left(\frac{r_{12}^2-3y_{12}^2}{r_{12}^5}\right)\right. \\ &\quad + S_z^2\left(\frac{r_{12}^2-3z_{12}^2}{r_{12}^5}\right) - (S_yS_z + S_zS_y)\frac{3y_{12}z_{12}}{r_{12}^5} \\ &\quad - (S_zS_x + S_xS_z)\frac{3z_{12}x_{12}}{r_{12}^5} \\ &\quad \left. - (S_xS_y + S_yS_z)\frac{3x_{12}y_{12}}{r_{12}^5}\right] \end{aligned} \tag{1}$$

($\mu_0$: vacuum permeability; $\boldsymbol{S}=\boldsymbol{s}_1+\boldsymbol{s}_2$: total spin) When such molecules are slightly distorted so as to lose their trigonal symmetry axes, the separations of ZFS in such near-degenerate states are not so simple, because of the interaction between these states. Although the ZFS parameters in the degenerate states were given in the previous paper,[1] the change in the zero-field (ZF) energy levels in such conformations was not discussed in detail. Also, no similar discussion has yet been carried out for aromatic molecules,[2] possibly because of a lack of experimental evidence. In the present work, therefore, the influence of such molecular deformation upon the ZF energy levels in near-doubly-degenerate triplet states is studied semi-quantitatively. In the course of this study, the ZFS's were simply evaluated by assuming them to originate from the electron spin-spin interactions, $\mathscr{H}_{SS}$.

In discussing near-doubly-degenerate states, a set of the corresponding near-degenerate real orbital functions is expressed as $\Psi_X$ and $\Psi_Y$, which are orthogonal with each other and which are assumed to be symmetric with respect to the x and y axes respectively, and antisymmetric with respect to the y and x axes respectively [the x and y axes are perpendicular to the trigonal symmetry axis (z)]. It may be noted here that the ZF energy levels should not be calculated separately using each of these near-degenerate orbital parts because of the non-zero off-diagonal element of $\langle\Psi_X|-2x_{12}y_{12}/r_{12}^5|\Psi_Y\rangle$. Therefore, the basis set chosen consist of the following six functions:

$$\begin{gathered}|\Psi_X{}^3\Theta_X\rangle,\ |\Psi_X{}^3\Theta_Y\rangle,\ |\Psi_X{}^3\Theta_Z\rangle, \\ |\Psi_Y{}^3\Theta_X\rangle,\ |\Psi_Y{}^3\Theta_Y\rangle,\ \text{and}\ |\Psi_Y{}^3\Theta_Z\rangle.\end{gathered} \tag{2}$$

Here,

$$\begin{aligned}{}^3\Theta_X &= 2^{-1/2}[\beta(1)\beta(2) - \alpha(1)\alpha(2)] \\ {}^3\Theta_Y &= 2^{-1/2}i[\beta(1)\beta(2) + \alpha(1)\alpha(2)] \\ {}^3\Theta_Z &= 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)].\end{aligned} \tag{3}$$

If the spin-free Hamiltonian is expressed as $\mathscr{H}_0$, the matrix of the Hamiltonian $\mathscr{H}=\mathscr{H}_0+\mathscr{H}_{SS}$ with the above six basis functions may be described as follows:

$$\begin{array}{l|c}
\langle\Psi_X{}^3\Theta_X| & \\
\langle\Psi_X{}^3\Theta_Y| & \\
\langle\Psi_X{}^3\Theta_Z| & \\
\langle\Psi_Y{}^3\Theta_X| & \\
\langle\Psi_Y{}^3\Theta_Y| & \\
\langle\Psi_Y{}^3\Theta_Z| &
\end{array}\!\!\!\begin{pmatrix}
W_X+\frac{1}{3}D_X-E_X & 0 & 0 & 0 & -F_{XY} & 0 \\
0 & W_X+\frac{1}{3}D_X+E_X & 0 & -F_{XY} & 0 & 0 \\
0 & 0 & W_X-\frac{2}{3}D_X & 0 & 0 & 0 \\
0 & -F_{XY} & 0 & W_Y+\frac{1}{3}D_Y-E_Y & 0 & 0 \\
-F_{XY} & 0 & 0 & 0 & W_Y+\frac{1}{3}D_Y+E_Y & 0 \\
0 & 0 & 0 & 0 & 0 & W_Y-\frac{2}{3}D_Y
\end{pmatrix} \tag{4}$$

where:

$$W_i = \langle\Psi_i|\mathscr{H}_0|\Psi_i\rangle \qquad (i = X, Y) \tag{5}$$

$$\begin{aligned}D_i &= \frac{3\mu_0 g^2\beta^2}{16\pi hc}\left\langle\Psi_i\left|\frac{r_{12}^2-3z_{12}^2}{r_{12}^5}\right|\Psi_i\right\rangle \\ E_i &= \frac{3\mu_0 g^2\beta^2}{16\pi hc}\left\langle\Psi_i\left|\frac{y_{12}^2-x_{12}^2}{r_{12}^5}\right|\Psi_i\right\rangle \qquad (i = X, Y)\end{aligned} \tag{6}$$

and

$$F_{XY} = \frac{3\mu_0 g^2\beta^2}{16\pi hc}\left\langle\Psi_X\left|\frac{-2x_{12}y_{12}}{r_{12}^5}\right|\Psi_Y\right\rangle.$$

When $\Psi_X$ and $\Psi_Y$ are perfectly degenerate, that is, $W_X=W_Y=W°$, the following relations are obtained:

$$D_X = D_Y = \mathrm{D}°$$

$$\text{and} \qquad E_X = -E_Y = F_{XY} = E° \tag{7}$$

As a result, the energies of the ZF levels obtained are two single and two doubly degenerate ones:

$$\begin{aligned}W &= \frac{1}{3}D° + 2E°, \frac{1}{3}D°, \frac{1}{3}D°, \\ &\quad \frac{1}{3}D° - 2E°, -\frac{2}{3}D°, \text{and} -\frac{2}{3}D°,\end{aligned} \tag{8}$$

relative to $W°$. Since the representation of the spin function ${}^3\Theta_i$ (i=X, Y, Z) is the same as that of the corresponding component of angular momentum (*e.g.*, $E_{1g}$ and $A_{2g}$ for the $D_{6h}$ symmetry), the above numbers of single and doubly degenerate levels can be deduced from a consideration of the group theory. For example, in the case of the ${}^3E_{1u}$ state of benzene with the $D_{6h}$ symmetry,

$$E_{1u} \times (A_{2g} + E_{1g}) = A_{1u} + A_{2u} + E_{1u} + E_{2u}. \tag{9}$$

The above conclusion should not be changed if the complex orbital parts of $2^{-1/2}[\Psi_X \pm i\Psi_Y]$ are used instead of the real functions of $\Psi_X$ and $\Psi_Y$.

When the molecule is distorted very slightly so as to lose a trigonal symmetry axis and the electronic energy

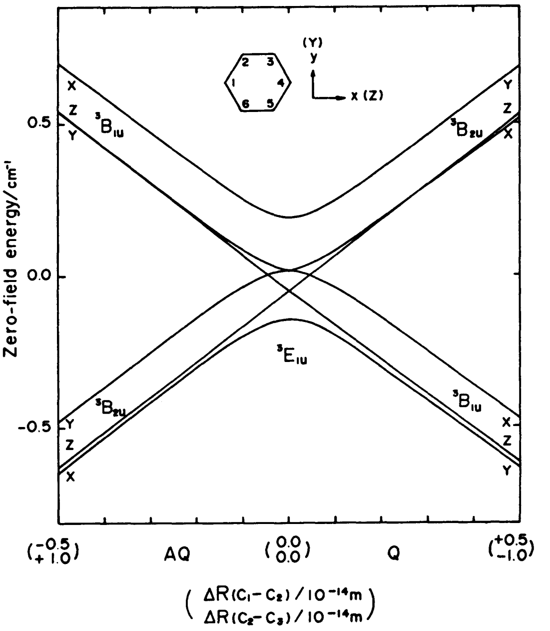

Fig. 1. Zero-field energy levels in the second excited triplet states of benzene with antiquinonoidal(AQ) and quinonoidal (Q) forms. The axis system for $D_{2h}$ symmetry is indicated in parentheses.

separation between these near-degenerate states, $\Delta W = |W_X - W_Y|$, becomes the same order as $|F_{XY}|$, the ZF energy levels except for $|\Psi_X{}^3\Theta_Z\rangle$ and $|\Psi_Y{}^3\Theta_Z\rangle$ are somewhat complicated because of the considerable contribution of $F_{XY}$, as can be seen in Fig. 1. However, when the molecule is further distorted with an energy separation of $\Delta W \gg |F_{XY}|$, the energies of these states with ZFS may be approximately expressed as:

$$\begin{aligned} W = {} & W_X - \frac{2}{3}D_X, \\ & W_X + \frac{1}{3}D_X \pm E_X + F_{XY}{}^2/(W_X - W_Y), \\ & W_Y - \frac{2}{3}D_Y, \text{ and} \\ & W_Y + \frac{1}{3}D_Y \pm E_Y - F_{XY}{}^2/(W_X - W_Y). \end{aligned} \tag{10}$$

As a result, the apparent $D$ values observable in these states are:

$$D_X{}^\dagger = D_X + F_{XY}{}^2/(W_X - W_Y)$$

and (11)

$$D_Y{}^\dagger = D_Y - F_{XY}{}^2/(W_X - W_Y),$$

while the $E$ values are not changed from $E_X$ and $E_Y$ respectively. As $D_X \approx D_Y$ in these near-degenerate states, the difference in the apparent $D$ values may possibly be useful as a factor in estimating the molecular distortion. In the above cases, the principal magnetic x and y axes are not perfectly parallel to any symmetry axis of the molecule, for example, the x and y axes of the distorted benzene molecule shown in Fig. 1. On the other hand, when the magnetic field is applied not parallel to the trigonal symmetry axis (z), the energy levels are more complicated because of the mixing of more than two basis functions (2).

As a typical example, Fig. 1 shows the ZF energy levels of distorted benzene in the second excited triplet states with the $D_{2h}$ symmetry. The coordinate system and the numbering of the constituent carbon atoms are taken as shown in Fig. 1. The conformation of the distorted molecule is assumed to be as follows: (i) All the bond angles are unchanged from those of the ground state with the $D_{6h}$ symmetry;³⁾ and (ii) the bond lengths are changed as follows:

$$\begin{aligned} & \Delta R(C_1\text{–}C_2) = \Delta R(C_3\text{–}C_4) = \Delta R(C_4\text{–}C_5) \\ & \quad = \Delta R(C_6\text{–}C_1) = -\Delta R(C_2\text{–}C_3)/2 = -\Delta R(C_5\text{–}C_6)/2. \end{aligned}$$

The calculations carried out for the electronic energy and for the ZFS parameters were quite the same as those of Treatment (C) in the previous paper.¹⁾ Further, the influence on the change of bond angels was examined on the assumptions that: (i) all the C–C bond lengths are unchanged from those of the ground state;³⁾ and (ii) the bond angles are changed as follows:

$$\begin{aligned} & \Delta\angle C_6C_1C_2 = \Delta\angle C_3C_4C_5 = -2\Delta\angle C_1C_2C_3 \\ & \quad = -2\Delta\angle C_2C_3C_4 = -2\Delta\angle C_4C_5C_6 = -2\Delta\angle C_5C_6C_1. \end{aligned}$$

In this case, the trend of the ZF energy levels due to the changes in the bond angles is very close to that due to the changes in the bond lengths within the ranges shown in Fig. 1 if one reads $\Delta\angle C_6C_1C_2 \approx \pm(2.7\times10^{-2})^\circ$ for $\Delta R(C_1\text{–}C_2) = \pm 0.1\times10^{-14}$ m, respectively.

In general, the excited molecules trapped in host glasses or crystals are more distorted than the distortion discussed here.⁴⁾ As a result, it may actually be impossible to observe transitions among ZF energy levels in degenerate triplet states, while there remains some possibility of detecting molecules with a very slight Jahn-Teller distortion in the gas phase. Although the experimental technique has not yet been improved for observing the magnetic resonance of the second excited triplet states of aromatic molecules, the present relation expected in near-degenerate triplet states may be of interest in discussing the molecular deformation due to environmental influence in orbitally degenerate phosphorescent triplet states of molecules such as aromatic ions, ESR experiments on which were made by de Groot *et al.*⁵⁾

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## References

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