FACTOR GROUP SPLITTING IN THE LOWEST TRIPLET STATE
OF \textit{p}-BENZOQUINONE-\textit{d}_4 CRYSTALS

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Polarized Stark-modulated Zeeman absorption experiments on \textit{p}-benzoquinone-\textit{d}_4 single crystals at 2 K show the factor group splitting in the origin of the lowest $B_{1g}$ ($n\pi^*$) triplet state at 18649 cm$^{-1}$ to be 0.62±0.06 cm$^{-1}$. The ordering of the crystal states is such that the orbital plus state lies at higher energy. The absence of a measurable factor group splitting in the $^3A_u$ ($n\pi^*$) state at 12.1 cm$^{-1}$ from the origin is taken as a further confirmation of the vibronic nature of this state. The ZFS parameter $D$ of this level is found to be $-10.3$ GHz.

For an understanding of the dynamics of energy migration in organics, be it coherent or incoherent, a knowledge of the intermolecular exchange forces, both translational equivalent (t.e.) and translational inequivalent (t.i.) is indispensable \cite{1}. We became recently intrigued by the energy migration processes in \textit{p}-benzoquinone-\textit{d}_4 (PBQ-\textit{d}_4) crystals \cite{2} and started therefore a study of the intermolecular exchange forces in this crystal. In this note we present the results of a Stark-Zeeman experiment which measures the ordering and splitting of the factor group states in the Laporte spin forbidden origin of the lowest $n\pi^*$ triplet state in PBQ-\textit{d}_4 crystals. The results of this experiment also confirm the suggested \cite{3,4} double minimum potential energy surface of the lowest electronically excited state in PBQ. In a previous paper \cite{4} we reported, using Stark modulation spectroscopy, the position of the origin of the lowest $B_{1g}$ ($n\pi^*$) triplet state in pure PBQ-\textit{d}_4 crystals. The origin intensity in this experiment was electric field induced through coupling with a $^3A_u$ ($n\pi^*$) state at 12.1 cm$^{-1}$ from the origin\textsuperscript{a}.

Even under the highest optical resolution ($\approx 1$ cm$^{-1}$) used in that experiment neither of these levels showed a splitting, from which one must conclude that the factor group splitting of these states is within the optical linewidth. In these circumstances polarized Zeeman absorption experiments may be helpful as was first demonstrated by Clarke and Hochstrasser \cite{5} in a study of the factor group splitting in the lowest triplet state of phenazine.

This experiment is based upon the notion that in a monoclinic crystal (\textit{b}-symmetry axis) with 2 molecules per unit cell, the electric dipole intensity in the triplet factor group components is induced through spin–orbit coupling with uniquely polarized singlet factor group states \cite{6}. In fact for the case of one molecular active spin substate the oscillator strength for absorption into the crystal field spin states is, for light polarized parallel to the \textit{b} axis, proportional to,

\begin{equation}
I_{\text{\textit{b}}}^B(T_\uparrow \uparrow) = \langle 1 \psi_+^S | H_{\text{so}} | 3 \psi_3^T \text{ } T_\downarrow \text{ } \mu_{\text{S (+)}} \cdot \hat{\sigma}_1 \rangle^2, \tag{1}
\end{equation}

and for light polarized perpendicular to the \textit{b} axis:

\begin{equation}
I_{\text{\textit{b}}}^C(T_\uparrow \uparrow) = \langle 1 \psi_+^S | H_{\text{so}} | 3 \psi_3^T \text{ } T_\downarrow \text{ } \mu_{\text{S (-)}} \cdot \hat{\sigma}_1 \rangle^2, \tag{2}
\end{equation}

where $H_{\text{so}} = h_{\text{so}}(\alpha) + h_{\text{so}}(\beta)$ is the crystal spin–orbit coupling operator, $^1\psi_3^T$ the mixing singlet and $^3\psi_3^T$ the triplet factor group states, $T_\uparrow$ the crystal spin sub-

\textsuperscript{a} In a previous paper \cite{4} we erroneously reported the inversion splitting in pure PBQ-\textit{d}_4 crystals to be 13.4 cm$^{-1}$. 

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states $i = a^\pm$, $b$ or $c^\pm$ in a monoclinic crystal, $\mu_S(\pm)$ the singlet factor group transition moment polarized parallel (for $+$) and perpendicular (for $-$) to the $b$ axis, and $\hat{b}$ and $\hat{b}$, unit vectors in the direction of polarization of the exciting light. These expressions show that for an orbitally allowed triplet level the $|T_b^+\rangle$, $|T_a^-\rangle$ and $|T_c^-\rangle$ factor group states are polarized parallel to the crystal $b$ axis. The other factor group states $|T_b^-\rangle$, $|T_a^+\rangle$ and $|T_c^+\rangle$ are polarized perpendicular to the crystal $b$ axis. In a high magnetic field ($g\beta H \gg$ ZFS parameters!) parallel to the crystal $b$ axis $|T_b^+\rangle$ and $|T_b^-\rangle$ remain eigenstates of the total hamiltonian (ignoring small level crossings effects [7]), while in this limit the other eigenstates of the system become:

$$2^{-1/2}(|T_a^\pm\rangle \pm i|T_c^\pm\rangle).$$

In the presence of a factor group splitting the polarized Zeeman spectra for $H||b$ thus show a characteristic asymmetric pattern for $\epsilon||b$ that reverses on rotating the plane of polarization to $\epsilon\perp b$. The situation is depicted schematically in fig. 1. Careful measurement of the difference in peak position of $|T_b^+\rangle$ and $|T_b^-\rangle$ for $\epsilon||b$ and $\epsilon\perp b$ respectively and $H||b$ thus yields directly the factor group splitting $2V_{ab}$. So far we have ignored the effects of the molecular zero field splitting (ZFS) on the Zeeman spectra. In the limit where the t.i. exchange interaction $V_{ab}$ is much larger than the crystal ZFS parameters $P_i$, thus $V_{ab} \gg P_i (i = a^\pm, b, c^\pm)$, the asymmetry in the Zeeman pattern is still dominated by the factor group splitting. In the situation where $P_i \gg V_{ab}$, the asymmetry in the Zeeman spectrum is determined only by the ZFS parameters and an anisotropic Zeeman study in this case yields both $2V_{ab}$ and the ZFS parameters [7,8]. Finally in the limit $P_i \gg 2V_{ab}$ the asymmetry in the Zeeman pattern is determined by the ZFS parameters only and a rotation of the plane of polarization will not reverse the asymmetry in the Zeeman spectrum.

It is interesting however to note that as long as the relation $g\beta H \gg P_i$ holds for all values of $2V_{ab}$, for a magnetic field parallel to the $b$ axis the eigenfunctions of the total hamiltonian can always be represented, to high accuracy, by the following crystal field spin states:

$$|T_b^\pm\rangle$$

and $2^{-1/2}(|T_a^\pm\rangle \pm i|T_c^\pm\rangle)$. (3)

This shows that in a high magnetic field for $H||b$ (symmetry axis) the factor group states are always uniquely polarized.

We will now turn to the case of PBQ-$d_4$, which crystallizes in the monoclinic space group $P_{2_1}$ [9]...
Fig. 3. Polarized Zeeman absorption (A) and Stark-modulated Zeeman absorption (B) spectra of the triplet state origin of crystalline p-benzoquinone-$d_4$ with optical resolution of 1 cm$^{-1}$ at 2 K. The spectra were calibrated using known iron arc emission line positions. The figure clearly shows the effect of rotating the plane of polarization of the incident light from parallel (upper) to perpendicular (lower) to the $b$ axis. Compare also figs. 1 and 2. The magnetic field (46 kG) is parallel to the $b$ axis and the electric field (48 kV/cm) perpendicular to it ($\| p(102)$ axis).

with two molecules in the unit cell. The molecules are all nearly parallel in the 201 cleavage plane. Polarized Zeeman experiments on the $^3A_u$($n\pi^*$) level in the origin region of the lowest $B_{1g}$($n\pi^*$) triplet state of PBQ-$d_4$ further show that only the $z$-spin subspace ($L = z$) is active, coupling to a molecular $B_{1u}$ ($z$-polarized) state. The results obtained from the previous discussion thus can be immediately applied to the polarized Zeeman spectra of the Stark induced origin, if the additional selection rules imposed by the electric field on the system are included. It is therefore necessary to realize that the molecular $B_{1g}$ and $A_u$ triplet states in the crystal thus correlate with the $A_g(\uparrow)$, $B_g(\downarrow)$ and $A_u(\uparrow)$, $B_u(\downarrow)$ factor group states respectively (in C$_2h$). The electric field ($E$) thus only couples those factor group states that are polarized along its spatial orientation, e.g., with $E\| b$, the following transitions will be observed: $A_g(\uparrow) \leftrightarrow A_u(\uparrow)$ and $B_g(\downarrow) \leftrightarrow B_u(\downarrow)$. With $E\perp b$ the transitions $A_g(\uparrow) \leftrightarrow B_u(\downarrow)$ and $B_g(\downarrow) \leftrightarrow A_u(\uparrow)$ are induced as shown in fig. 2.

With these things in mind we will now consider the Stark-modulated Zeeman absorption spectra shown in fig. 3 for $H\| b$ and $E\perp b$($\| p(102)$ axis). Fig. 3 shows the absorption and Stark modulated absorption spectra in a magnetic field parallel to the crystal $b$ axis. Careful examination of the polarized Zeeman absorption spectra of fig. 3 in the molecular $^3A_u$($n\pi^*$) state region shows that the asymmetric Zeeman pattern is polarization independent. The asymmetry in the Zeeman pattern of this state must thus be due to a ZFS effect and assuming $E/D \ll 1$, which is an excellent assumption for the ZFS parameters of the molecular $^3B_{1g}$($n\pi^*$) state [2], we calculate from the Zeeman spectrum $D(3A_u)$ ($n\pi^*$)) = $-10\pm 3$ GHz. In the Stark induced Zeeman pattern in the origin region of the $B_{1g}$($n\pi^*$) triplet state we observe a clear asymmetry that reverses on rotating the plane of polarization of the excitation. The contribution of the zero field splitting to this asymmetric pattern can be best calculated from the measured ZFS parameter of PBQ-$d_4$ in this state [2] (determined through interpolation in a PBQ-$d_4$ host crystal) and is found to be $0.05$ cm$^{-1}$. Including this shift the factor group splitting is found to be $2V_{\alpha\beta} = 0.62\pm 0.06$ cm$^{-1}$. Recalling that for $H\| b$ and $E\perp b$ only the $A_u(\uparrow)$ factor group component of the upper state is observed and that an electric field perpendicular to $b$ couples this state to the $B_g(\downarrow)$ component of the lower state, fig. 3 clearly shows the orbital plus ($B_g$) factor group state to lie at higher energy.

This conclusion is fully confirmed by Stark–Zeeman experiments for $H\perp b$ ($\parallel p(102)$ axis) and $E\parallel b$, where the Stark induced Zeeman factor group pattern of the origin obeys the same polarization selection rules as those of an orbitally allowed state.

It is interesting to note that these Stark–Zeeman experiments on PBQ-$d_4$ confirm the suggested correlation [2] between the lowest electronic states of $p$-benzoquinone and toluquinone. Trommsdorff has recently measured the factor group splitting in the allowed origin of the lowest triplet state of toluquinone [8].
and found $2V_{\alpha\beta} = 0.3\,\text{cm}^{-1}$ with the same orbital level ordering. Further the absence of a factor group splitting ($2V_{\alpha\beta} < 0.05\,\text{cm}^{-1}$) in the $3\Lambda_u(n\pi^*)$ state (at 12.1 cm$^{-1}$ from the origin in PBC$_d$4) nicely confirms the assignment of this state $[3,4]$ as a vibronic level of the $B_{1g}(n\pi^*)$ triplet state. Finally the tremendous increase in ZFS parameter $|D|$ from 3.0±1 GHz in the zero point level to 10.0±3.0 GHz in the $A_u$ vibronic level explains (at least partly) the previously reported [10] hypersensitivity of the ZFS parameter $D$ of the zero point level to asymmetric isotopic substitution.

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References