



Zeeman Effect Studies of the Triplet States of Benzene

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If the principal limitation on the coherence lifetime of the triplet exciton is trapping rather than phonon scattering, then the effective trapping rate constant is taken to be proportional to the product of the group velocity of the excitons perturbed by the microwave field $V_g(\omega)$ and the density of trapping sites D_T . Since $V_g(\omega) = \rho(\omega)^{-1}$, Eq. (2) becomes

$$\Delta N^t(\omega) \sim D_T \{ \exp[-E(\omega)/kT] \} (K_i^{-1} + K_j^{-1}). \quad (3)$$

The essential feature of Eq. (3) is that the change in trap spin alignment as a function of microwave frequency depends only upon the Boltzmann distribution of the population within the exciton spin manifolds. This dependence is illustrated by the trap-monitored exciton-electron spin transition in Fig. 1 and will be referred to as the concentrated trap limit.

In another limit,⁷ the dilute trap limit, when exciton-phonon scattering is faster than trapping, the effective trapping rate constant $K \sim \bar{V}_g D_T$, where \bar{V}_g is the average group velocity taken over the distribution within the exciton spin manifold. In this limit, $\Delta N^t(\omega)$ depends upon the Boltzmann population distribution and the density of states $\rho(\omega)$. Consequently, the trap-monitored exciton-electron spin transitions exhibit

a central band minimum associated with the minimum in $\rho(\omega)$ at $k = \pm\pi/2$.⁴

Experiments within the above limits should be extremely valuable for investigation of the dynamics of exciton migration inasmuch as intrinsic phosphorescence from exciton states of molecular crystals has been observed in only a few cases.

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* Alfred P. Sloan Fellow.

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Zeeman Effect Studies of the Triplet States of Benzene*

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In this Communication we present the results of high field Zeeman effect studies of the ${}^3B_{1u} \leftarrow {}^1A_{1g}$ transition of solid perdeuterobenzene, and preliminary results on magnetic field effects on the 2700 Å triplet state of benzene. We present data on the polarization of these transitions. The results are relevant to the vibronic coupling problem in benzene¹⁻³; to experiments on the distortion from D_{6h} symmetry of phosphorescing benzene⁴⁻⁶; and to recent absorption spectral analysis of vibronic states of ${}^3B_{1u}$ benzene.⁷

The spectroscopic measurements were made in the manner of Burland, Castro, and Robinson⁷ but with oriented crystals of benzene- d_6 in a Bitter solenoid that maintained a magnetic field of 105 kG.

Benzene crystals are orthorhombic, $Pbca$, with four molecules per unit cell.⁸ One of the three possible carbon-carbon 1,4 directions is nearly parallel to the b axis; the corresponding bond-bisecting axis (y) and principal inertial axis (z) project substantially only onto a and c .

The prominent absorption bands at 30 422, 30 070, and 30 087 cm^{-1} (the latter two we subsequently refer to as the 30 078 cm^{-1} doublet) display 3 times stronger absorption for light polarized along the a axis than for light polarized along the b axis. These transitions are therefore out-of-plane (z) polarized. Vibronically induced transitions do not usually manifest the crystal field induced intensity.^{9,10}

Figure 1 shows the spectrum of the 30 078 cm^{-1} doublet at zero field, and the spectrum obtained with $H = 105$ kG directed along the b axis. The $m_s = 0$ spin substate of the lower energy component, and the $m_s = \pm 1$ substates of the higher energy component are the radiatively active states. If the vibronic symmetry of an upper level were E_{1u} (such as from $e_{2g} \otimes B_{1u}$), then only the $m_s = \pm 1$ states would be radiatively active for fields along the b axis. We observed a severely broadened spectrum for fields along the a axis, implying a more complex Zeeman pattern, but resulting in a much poorer signal-to-noise ratio.

The above results prove that the two components of the $30\,078\text{ cm}^{-1}$ doublet have different vibronic symmetry. In D_{6h} and in all its subgroups containing a three-fold axis (only centrosymmetric subgroups included), it is impossible to find two vibronic states from the same nondegenerate electronic level that have the same (z) polarization yet different Zeeman effects. Therefore the unique symmetry group for ${}^3B_{1u}$ benzene- d_6 appropriate to the dominant features of the vibronic wavefunctions and spin-vibronic coupling selection rules is D_{2h} .

The distinctive intensity distribution of the b -axis Zeeman pattern indicates that the b axis is not significantly far removed from a principal (in-plane) axis of a molecule: the $1,4$ axis (x) oriented nearly parallel (x makes an angle of 16° with b)⁸ to the b axis is thereby identified as being approximately aligned with a principal direction.¹¹ This axis is likely to be the same as the x fine-structure axis for the phosphorescent state of benzene in benzene- d_6 at 1.95°K reported by de Groot, Hesselmann, and van der Waals to make an angle of 16.6° to the b axis.¹²

Conventional spin-orbit coupling rules applied to the b -axis field data yield the vibronic symmetries (in D_{2h}) of the two components of the $30\,078\text{ cm}^{-1}$ doublet as $30\,087\text{ cm}^{-1}$, $B_{3u}(\hat{y})$ and $30\,070\text{ cm}^{-1}$, $B_{2u}(\hat{x})$. The calculated results pertaining to these assignments are sketched in Fig. 1 using the direction cosines for our choice of x and y , and the crystallographic data.⁸

The unique explanation for in-plane spin activity and out-of-plane polarization is that the state involves e_{2g} vibronic coupling. We therefore conclude that the $30\,078\text{ cm}^{-1}$ doublet arises because of the splitting of the vibronic level ${}^3E_{1u}$ (in D_{6h}) into ${}^3B_{2u}$ and ${}^3B_{3u}$ (in D_{2h}) vibronic levels of a statically distorted form of benzene.

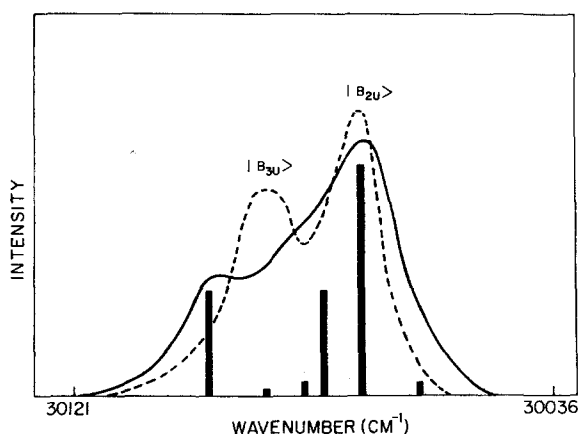


FIG. 1. Singlet-triplet absorption of solid benzene- d_6 recorded in the manner of Ref. 7 using phosphorescence excitation at 4.2°K . The dashed line refers to the $30\,078\text{ cm}^{-1}$ doublet ($0+231\text{ cm}^{-1}$), and the solid line is the same system in a 105 kG magnetic field directed along the b axis of the crystal. The solid vertical bars represent the expected pattern from two states, one (B_{2u}) having spin quantization in a plane perpendicular to the b axis and the other (B_{3u}) in a plane containing the b axis.

This splitting is caused by an asymmetric (in D_{6h}) crystal field perturbation.

Preliminary results on the level at $30\,422\text{ cm}^{-1}$ indicate that the vibronic symmetry is E_{1u} , and therefore that the vibration involved is e_{2g} . The assignments of Burland, Castro, and Robinson⁷ based on an electronic origin at $29\,847\text{ cm}^{-1}$ that associate this mode with ν_6' (575 cm^{-1}), and the $30\,078\text{ cm}^{-1}$ doublet with a transition involving ν_8' ($\sim 231\text{ cm}^{-1}$), are consistent with the present study which definitively characterizes both these active modes as e_{2g} . The proximity of ν_6' to ν_6'' (579 cm^{-1}) and the large reduction of ν_8'' (1558 cm^{-1}) on excitation confirm the predictions of vibronic theory.

The Colson and Bernstein system¹³ at 2700 \AA was also studied: the polarization measurements favor an in-plane transition moment, and the b -axis magnetic field line broadening (*thereby verifying the triplet nature of the upper state*) is larger than for the a -axis broadening, indicating that the upper state symmetry is ${}^3E_{1u}$ as suggested.¹³ We will present an analysis of the spin and orbital momentum properties of this state in a forthcoming paper.

Note added in proof: Recent work by V. L. Broude [Opt. Spectrosc. **30**, 46 (1971)] has shown that a molecular principal axis of the ${}^1B_{2u}$ state is nearly parallel to the b -crystallographic axis of benzene.

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