

Density of States of the First Vibronic Exciton Band in Anthracene

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were careful to select nontwinned and relatively strain-free samples by optical observation with crossed Polaroids and a microscope, and also through attention to spot quality in Laue and Buerger precession photographs. The resultant crystals are weakly hygroscopic, and so must be protected during handling and measurements. We performed this by storing the crystals under dried "Fluorolube" oil, and painting the sample crystals lightly on all surfaces with GE cement when they were to be measured. The concentration of Ce^{3+} in these samples was relatively high—in the range of a few percent—and in fact a number of satellite "ion pair" lines were observed. Above about $40^\circ K$, the Ce^{3+} became unobservable due to rapid relaxation to the lattice. As the temperature was lowered, the two main single ion resonance lines which were observed grew normally in intensity, and their behavior as a function of applied magnetic field was each fitted by an axially symmetric effective-spin equals one-half Hamiltonian. At approximately $20^\circ K$ (the exact transition temperature could not be accurately determined due to our experimental arrangement which allowed significant thermal gradients between the sample and the Ge resistance thermometer) both lines split when viewed with the magnetic field applied off the c axis, with the upper line splitting into two components and the lower into six components. The splitting grows as the temperature is lowered, achieving its maximum value within approximately $0.5^\circ K$ of the apparent "critical temperature"; this behavior would seem to indicate

some sort of second order phase change associated with a lattice distortion. Below this region the features of the spectrum remain essentially unaltered down to the lowest temperatures attainable in our apparatus.

In the region above the transition temperature, the g values obtained by fitting the spectrum are:

$$\text{"upper line"} \quad g_{\parallel} = 3.950 \pm 0.003, \quad g_{\perp} = 0.31 \pm 0.11,$$

$$\text{"lower line"} \quad g_{\parallel} = 3.665 \pm 0.007, \quad g_{\perp} = 0.38 \pm 0.16.$$

It is evident from these values that the ground state for the Ce^{3+} is principally composed of $J_z = \pm \frac{5}{2}$ for both sites (a pure $J_z = \pm \frac{5}{2}$ state would give $g_{\parallel} = 4.286$, $g_{\perp} = 0$), but one cannot readily determine from this information which site gives rise to which resonance—both sets of values are very close to those seen for Ce^{3+} in C_{3h} sites in other hosts.

Work on the detailed interpretation of the spectrum below $20^\circ K$ and the pair spectrum is continuing.

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Density of States of the First Vibronic Exciton Band in Anthracene*

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The structure of exciton bands and the density of states of these bands have recently become the subject of some interest. This is due to the measurement of reflection spectra from different faces of single crystals,¹ the observation of hot bands,² and the interest in the calculation of impurity spectra.³ In the present note, we report calculations of the density of states of the first vibronic singlet state of anthracene. We believe this to be the first such calculation for an exciton state with dipolar coupling. While this work was in its final stages, a report appeared⁴ on the calculation of the exciton band structure in certain directions for this transition.

Our calculations agree with those points calculated by Philpott.

We used the first vibronic states of the first electronic state (3800 Å in the free molecule) and the second electronic state (2500 Å). We assumed the same gas phase energies, transition moments, and Franck-Condon factors as did Philpott.^{4,5} We performed the calculations in two steps. First, the lattice sums of dipole interactions were calculated using Ewald's method⁶ for approximately 600 points in one quarter of the first Brillouin zone (these formed an equally spaced net) for both the equivalent and the inequiva-

lent molecules (there are two inequivalent sites in the crystal). From the symmetry of the space group, the calculations for \mathbf{k} can be shown to be the same as for $-\mathbf{k}$, $C\mathbf{k}$, and $\sigma\mathbf{k}$.⁷ Since the calculations were performed for general \mathbf{k} , no symmetry elements existed which allow the one-site functions to be combined in a simple fashion. Once the matrix elements of the Hamiltonian were calculated, we proceeded in two ways: (1) we diagonalized the 12×12 Hamiltonian matrix which resulted, (2) we assumed the excitons were bosons,⁸ and, using the Bogolubov–Tyablikov transformation,^{5,8} calculated the energies of the new boson modes (this allows for multiple excitations in a simple manner). The results from these two procedures agreed very well (within a few cm^{-1} for the lowest state), and we report only those based on procedure (2) in order to facilitate comparison with the calculation of Philpott.⁴ From the calculation, we have the 12 exciton energies for approximately 2400 points in the first Brillouin zone.

In order to calculate the density of states for the lowest vibronic state, we fitted the calculated points to a series of Legendre functions with coefficients adjusted so that the series had the same moments as our calculated points. That is, the calculated density is a sum of delta functions,

$$\rho^c(E) = \sum_i \delta(E - E_i) \quad (1)$$

which we approximate as a series of Legendre functions of a variable x [$= (E - \bar{E}) / \frac{1}{2}(E_{\text{max}} - E_{\text{min}})$], which goes from -1 at the bottom of the band to $+1$ at the top. The moments of $\rho^c(x)$ with respect to the first 20 Legendre functions were calculated from Eq. (1), and the coefficients of the series of Legendre functions adjusted so that the series had the same moments. In Fig. 1, we plot $\rho(E)$ for the lowest vibronic state calculated in this way using the first 10 Legendre functions. The calculated density was insensitive to within 10% to the choice of the number of functions up to about 20. As the number of functions increased, how-

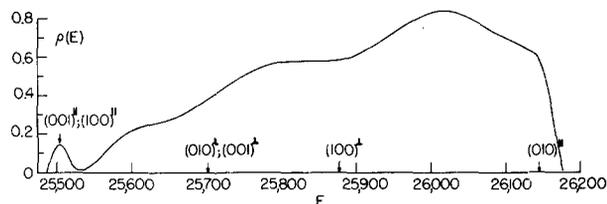


FIG. 1. The normalized density of states $\rho(E)$, plotted against energy, E , in cm^{-1} above the ground state. The energies of the small \mathbf{k} levels are shown with the direction of \mathbf{k} and the polarization (\parallel : parallel to \mathbf{b} ; \perp : perpendicular to \mathbf{b}). The degeneracies are accidental (see Ref. 4).

ever, $\rho(E)$ became more oscillatory. We arbitrarily took the 10-function result since it follows the simple histogram of the points rather well and is relatively smooth. The positions of the small k energies are indicated by arrows for various directions of \mathbf{k} .

We hope to use this calculation to perform impurity state calculations in anthracene. The density of states reported herein can in principle be found by using the technique of hot band spectroscopy. To our knowledge, such experiments have not yet been performed on anthracene crystals.

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⁴ M. Philpott, *J. Chem. Phys.* **54**, 111 (1971).

⁵ M. Philpott, *J. Chem. Phys.* **50**, 5117 (1969). The gas phase energies are $26\,000 + n\,1400\text{ cm}^{-1}$ for the 3800-Å band and $39\,000\text{ cm}^{-1}$ for the 2500-Å band. The Franck–Condon factors for $n=0$ to $n=4$ are 0.324, 0.316, 0.218, 0.092, and 0.050.

⁶ See, e.g., M. H. Cohen and F. Keffer, *Phys. Rev.* **99**, 1128 (1955); B. Nijboer and F. de Wette, *Physica* **23**, 309 (1957).

⁷ The factor group is C_{2h} , and contains the elements C (a rotation of π about the b axis) and σ (a reflection in the plane perpendicular to b).

⁸ S. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum, New York, 1967).

Dissociation–Excitation Reactions of Argon Metastables with Carbon Dioxide

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Collisions of the second kind between metastable rare gas atoms produced in a discharge and ground state molecules added to the afterglow are known to produce electronic molecular excitation.^{1–3} Reactions of this

type may also produce dissociation and excitation of a product molecule.^{4,5} Excitation of an atomic product might also be expected, but we know of no such reactions for afterglow studies.⁶ The study discussed here