

## Exciton Bands in Crystalline Benzene

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The structures of the two lowest exciton bands of crystalline benzene have been investigated. The separations are given between those band levels to which optical transitions are allowed from the crystal ground state.

BY assuming that the lower excited electronic states of crystals of aromatic molecules are exciton states, Davidov<sup>1</sup> has shown that the sharp absorptions in the ultraviolet can be explained on the basis of strictly obeyed translational selection rules. Recently, Broude, Medvedev, and Prikhoto'ko<sup>2</sup> have investigated the absorption spectrum of single crystals of benzene in polarized light and found two lines polarized at right angles to each other, separated by 25 cm<sup>-1</sup>, and corresponding, in the molecule, to the pure electronic transition from the ground state to the lowest excited singlet state. This lowest molecular state has been interpreted as belonging to the irreducible representation  $B_{2u}$  of the symmetry group  $D_{6h}$  of the molecule, although it may possibly belong to  $B_{1u}$  instead.<sup>3</sup> Davidov<sup>4</sup> concluded that the observations of Broude *et al.* confirm the former assignment. However, he made an approximation with regard to the crystal structure; in the light of more recent x-ray data,<sup>5</sup> his conclusions must be reexamined. Winston<sup>6</sup> concluded that three transitions, with mutually perpendicular polarizations, are allowed in each of the exciton bands corresponding to the  $B_{1u}$  and  $B_{2u}$  molecular states.

We have investigated the intensities of allowed transitions and the band structure in the benzene crystal. In first-order perturbation theory, the energy can be separated into two groups of terms: "band-

shift" terms, which are independent of the wave vector,  $\mathbf{K}$ , of the exciton wave function, and "band-splitting" terms, which depend on  $\mathbf{K}$ . The intermolecular interaction energy was expanded in a multipole-multipole series, and only the lowest-order nonvanishing terms were retained. For the band-splitting terms, it was found group-theoretically that the significant terms were matrix elements of octupole-octupole interactions between pairs of molecules and that the molecular matrix element of every octupole component could be expressed in terms of a single parameter, whose value depended on the choice of molecular wave functions. In this way, the structure of each band was determined to within a scale factor from crystal data alone; the scale factors were calculated by assuming the wave functions of Mayer and Sklar.<sup>7</sup> For the levels to which transitions are allowed by the translational selection rules (states with  $\mathbf{K}=0$ ), the energies, referred to the center of the band, and the polarizations of the transitions are given in Table I. One state in each band is forbidden by factor group selection rules. It may be shown that, to within the accuracy of the present calculations (about 10 percent), translationally allowed levels lie at the extrema of each band. The band widths are thus 720 cm<sup>-1</sup> and 58 cm<sup>-1</sup>. By comparing the results in the table with the observations of Broude *et al.*,<sup>2</sup> we conclude that the lowest excited state of molecular benzene does indeed belong to the representation  $B_{2u}$ . To obtain level separations of the order of 25 cm<sup>-1</sup> in the  $B_{1u}$  case would require much more radical modifications in the Mayer and Sklar wave functions than are reasonable.

The results of the intensity calculations and the details of the energy calculations will be given elsewhere. The incompleteness of experimental data prevents full comparison with the theoretical predictions. An absorption experiment, using polarized light, in which the crystal directions are known from an independent determination, seems desirable. Agreement between such an experiment and the predictions would lend support to the assumption of the existence of exciton states in crystals of aromatic molecules.

TABLE I. Energies and transition polarizations of  $\mathbf{K}=0$  exciton states corresponding to  $B_{1u}$  and  $B_{2u}$  molecular benzene states.

Polarization	$B_{1u}$ Energy (cm <sup>-1</sup> )	Polarization	$B_{2u}$ Energy (cm <sup>-1</sup> )
a	-360	a	-29
c	-180	c	-7
b	180	forbidden	7
forbidden	360	b	29

<sup>1</sup> A. S. Davidov, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 210 (1948).

<sup>2</sup> Broude, Medvedev, and Prikhoto'ko, J. Exptl. Theoret. Phys. (U.S.S.R.) **21**, 665 (1951).

<sup>3</sup> Spomer, Nordheim, Sklar, and Teller, J. Chem. Phys. **7**, 207 (1939); Parr, Craig, and Ross, J. Chem. Phys. **18**, 1561 (1950).

<sup>4</sup> A. S. Davidov, J. Exptl. Theoret. Phys. (U.S.S.R.) **21**, 673 (1951).

<sup>5</sup> E. G. Cox and J. A. S. Smith, Nature **173**, 75 (1954).

<sup>6</sup> H. Winston, J. Chem. Phys. **19**, 156 (1951).

<sup>7</sup> M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).