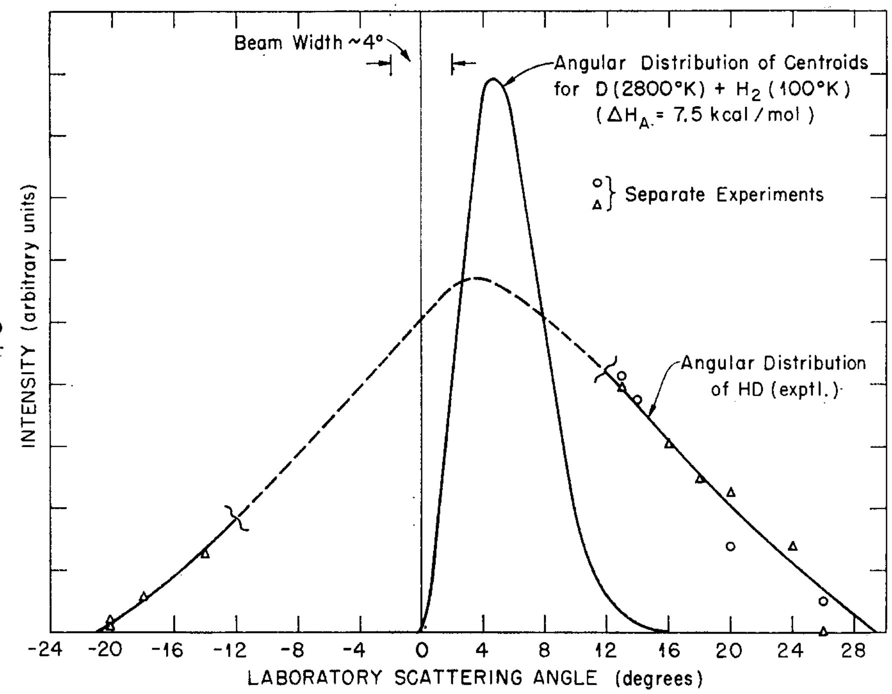

FIG. 2. Angular distribution of HD compared with that calculated for centroids.

Elastic scattering of a 1% HD impurity in the modulated beam obscured the region −12° to +12°, but did not contribute outside this range as shown by an experiment with He in place of H_2. The observed (Fig. 2) symmetrical broadening of only 10°–15° (half-width at half-maximum) over the centroid distribution is compatible with a linear complex of short life, or with high product excitation and any structure or lifetime. The speed of the product, 0.9 to 1.2×10^5 cm/sec (20°–30° phase lag behind unscattered atom beam), is incompatible with the latter alternative, since conversion of most of the heat of reaction ($\sim$1 kcal/mole) and relative energy to vibration or rotation would leave the HD with a forward speed of about 3.5×10^5 cm/sec. If the relative energy and heat of reaction are largely available for breakup of the complex, the calculated speed is 1.3×10^5, in good agreement with the observation. In summary, the results, although preliminary, are consistent with a linear complex of short life yielding largely unexcited products.

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* Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[1] For further details see S. Datz, G. E. Moore, and E. H. Taylor, "The Reflection of Modulated Helium and Deuterium Molecular Beams from Platinum Surfaces," in *Third International Symposium on Rarefied Gas Dynamics*, edited by J. A. Laurman (Academic Press Inc., New York, 1963) (to be published).

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Triplet Exciton Bands in Aromatic Crystals

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MOST of the work on the excited electronic states of aromatic molecular crystals has been concerned with the study of singlet exciton states.[1,2] The nature of triplet exciton states is of considerable current interest, as evidence is accumulating that triplet excitons are mobile, and energy transfer via triplet excitons has been conclusively demonstrated.[3,4] The purpose of this letter is to present a computation of the factor-group splittings for triplet exciton states in molecular crystals of naphthalene, anthracene, and several polyphenyls. We show that the factor-group splittings are not as small as previously assumed,[5] and are amenable to experimental observation.

All the compounds considered herein are characterized by a monoclinic unit cell containing two molecules[6] and belong to the symmetry group C_{2h}^5. The symmetry-adapted approximate wavefunctions of the tight-binding Hamiltonian are

$$\Psi_{\pm}^{f}(\mathbf{k})=[(2\sigma N)!]^{-\frac{1}{2}}\sum_{n}\exp(i\mathbf{k}\cdot\mathbf{r}_n)\Big[\mathcal{A}\phi_{n1}^{f}\prod_{mj\neq n1}\phi_{mj}^{0}$$

$$\pm\exp[i\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})/2]\mathcal{A}\phi_{n2}^{f}\prod_{mj\neq n2}\phi_{mj}^{0}\Big],\quad(1)$$

where the double index $ni(n=1\cdots N,\ i=1,\ 2)$ labels the unit cell and the appropriate molecule. The basic vectors of the direct lattice are labeled as **a**, **b**, and **c**, and σ is the number of electrons per molecule. The ground-state (ϕ^0) and excited-state (ϕ^f) functions are nonantisymmetrized Hartree products (or linear combinations of Hartree products) of molecular orbitals. For any triplet state, three ϕ^f functions can be constructed characterized by the spin angular momentum components $S_z=1$, 0 and -1. The antisymmetrization operator $\mathcal{A}=\sum_p(-1)^pP$ permutes all the crystal electrons. The values of the momentum vector **k** are limited within the first Brillouin zone.

The **k**-dependent portion of the triplet band energy is

$$E_{\pm}(\mathbf{k})=\sum_{mj\neq ni}(\pm1)^j(J_{mj}+K_{mj})\cos(\mathbf{k}\cdot\mathbf{r}_{mj}), \quad (2)$$

with

$$J_{mj}=\langle\phi_{ni}{}^f\prod_{lr\neq ni}{}'\phi_{lr}{}^0\mid V_{mj,ni}\mid\phi_{mj}{}^f\prod_{lr\neq mj}{}'\phi_{lr}{}^0\rangle,$$

$$K_{mj}=\langle(\mathcal{A}-1)\phi_{ni}{}^f\prod_{lr\neq ni}{}'\phi_{lr}{}^0\mid V_{mj,ni}\mid\phi_{mj}{}^f\prod_{lr\neq mj}{}'\phi_{lr}{}^0\rangle. \quad (3)$$

The Coulomb integral J_{mj} for the triplet exciton may be approximated by the Coulomb interaction term for the first singlet exciton state multiplied by the oscillator strength ratio for the $G\rightarrow T$ and $T\rightarrow S$ transitions.[7] The Coulomb integral for singlet excitons is 10–10^4 cm^{-1}, while the oscillator strength ratio is 10^{-6}–10^{-10},[8,9] hence $J_{mj}\leq0.01$ cm^{-1} and is negligible in all cases.

The exchange term is reduced to the expression

$$K_{mj}=-\langle u_0{}^{ni}(1)u_0{}^{mj}(1)\mid r_{12}{}^{-1}\mid u_f{}^{ni}(2)u_f{}^{mj}(2)\rangle, \quad (4)$$

where $u_\mu{}^{ni}$ is the molecular orbital located on the ith molecule in the nth cell, the subscripts 0 and f referring to the highest filled and the lowest empty MO's, respectively. The MO's located on different molecules are chosen to be orthogonal.

The molecular orbitals were represented as a linear combination of carbon orbitals. Both Hückel coefficients without overlap and SCF coefficients for the triplet state[10] were used. In the present calculation the behavior of the wavefunctions at large distances is of utmost importance. We used the best available $2p$ carbon atom SCF atomic orbitals represented in the form of a linear combination of four Slater-type functions,[11] characterized by proper asympotic behavior. Two further approximations were involved in obtaining numerical results from Eq. (4): (a) The nonorthogonality correction terms introduced by applying the Schmidt orthogonalization method to MO's located on different molecules were found to contribute less than 10% to K_{mj} and were thus neglected. (b) The contribution of three- and four-center exchange integrals was neglected. It is very difficult to estimate the magnitude of these terms; previous experience[12] indicates that the contribution of the many-center terms will not exceed 50%.

The two-center exchange integrals between two carbon SCF $2p$ orbitals located on neighboring molecules were expressed in terms of the six atomic integrals[13] $\sigma\sigma\sigma\sigma$, $\pi\pi\sigma\sigma$, $\pi\sigma\pi\sigma$, $\pi\sigma\sigma\pi$, $++++$, and $+--+$. These exchange integrals were computed on an IBM 7094 computer using an integral program supplied by the Laboratory of Molecular Structure of the University of Chicago. The intermolecular exchange integrals for the first triplet band were computed using the known crystal structures of the aromatic compounds,[6] considering the interactions with 13 differently oriented nearest-neighbor molecules. The largest values for K_{mj} were found for interaction with molecules located at $\boldsymbol{\beta}=\frac{1}{2}(\mathbf{a}+\mathbf{b})$ and at **b**, i.e., for crystalline naphthalene $K(\boldsymbol{\beta})=-5.62\times10^{-4}$ eV and $K(\mathbf{b})=9.46\times10^{-4}$ eV, while for crystalline anthracene $K(\boldsymbol{\beta})=-5.37\times10^{-4}$ eV and $K(\mathbf{b})=9.10\times10^{-4}$ eV. The following values for the factor-group splitting for the first triplet exciton band were calculated: naphthalene, 36.1 cm^{-1}; anthracene, 34.5 cm^{-1}; biphenyl, 1.89 cm^{-1}; and terphenyl, 2.85 cm^{-1}.

The present semiquantitative treatment leads to the following conclusions: (a) The factor-group splittings for triplet excitons in some aromatic crystals are of sufficient size to be observed experimentally. An obvious system for experimental study is crystalline iodonaphthalene at sufficiently low temperatures where the ground-state→triplet transition can be observed in the absorption spectra.[9] (b) The size of the exchange integral is of the order of 5–10 cm^{-1}. This value is in good agreement with a very recent measurement.[14,15] The triplet exciton motion must be described in terms of a localized exciton,[1] whose motion is followed by the lattice distortion.

The numerical calculation of exchange integrals mentioned herein was stimulated by discussion with Professor G. W. Robinson who pointed out the inadequacy of an earlier approximate calculation. We wish to thank Mr. A. C. Wahl and Dr. P. E. Cade for the basic exchange integral program, and Professor C. C. J. Roothaan for the facilities of the Computation Laboratory. This research was supported by the AFOSR, NSF, and USPHS; we have also benefited from the use of facilities provided by general grants from the U. S. Atomic Energy Commission and ARPA for materials research at the University of Chicago.

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Intramolecular Heavy-Atom Effect on the Polarization of Naphthalene Phosphorescence*

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THE phosphorescence radiative lifetime of halonaphthalenes (H.N.) is known to decrease as the atomic number of the halogen atom increases.[1] The observed effect has been attributed[1] to the great dependence of the spin–orbit Hamiltonian on the atomic number of the heaviest atom in the system. The exact mechanism by which the halogen enhances the spin–orbit perturbation is not yet known. For example, the halogen atom could enhance the coupling which is already present in the parent hydrocarbon or it might actually introduce new strong perturbing states of its own. Using polarization techniques it will be shown that the halogen does introduce new perturbing states which might result from the carbon–halogen electronic system.

The method of photoselection[2] is used for determining the polarization of the phosphorescence spectrum of naphthalene, α- and β-H.N. in 4:1 isopentane–butanol glass at 77°K. The emission is activated in the ^1L_a and ^1L_b bands (both of which are mainly polarized along the short axis in naphthalene) by a 1-kW Hg lamp (BH_6) and recorded using a 0.5-m Jarrell–Ash spectrometer. The experimental procedure is described elsewhere.[3]

The results are summarized in Fig. 1. The most interesting observations can be stated as follows: (1) For the naphthalene spectrum[4] and the 0,0 band of all the halo derivatives, the degree of polarization P is negative and independent of the wavelength of the in-plane excitation (i.e., the emission is greatly out of plane). (2) For the spectra of α-H.N., except for the 0,0 bands, P is positive (i.e., the emission is in plane) and increases as the atomic number of the halogen atom increases. (3) For α-methylnaphthalene spectrum P is similar to that of naphthalene. This might indicate that the effect of the halogen is not merely destructive of the D_{2h} symmetry of naphthalene. (4) In the nonpolarized spectrum, the intensity of the 0,0 band is comparable to the other bands (which are enhanced by in-plane mixing). This might indicate that the halogen also enhances the out-of-plane mixing which is the main mixing present in the parent hydrocarbon.[4] (5) While P is positive for α-H.N., it is found to be negative for β-H.N., but is sensitive to the wavelength of excitation (thus might still be in the plane). The great dependence of P on the position of the halogen as well as its atomic number in α-H.N. (Result 2) might suggest that the in-plane emission is due to mixing of in-plane states involving the halogen. (6) Contrary to α-H.N., P is found to be relatively insensitive to changes in the halogen in β-H.N. Results 2, 5, and 6 might be understood if the perturbing transition has its moment along the C–X

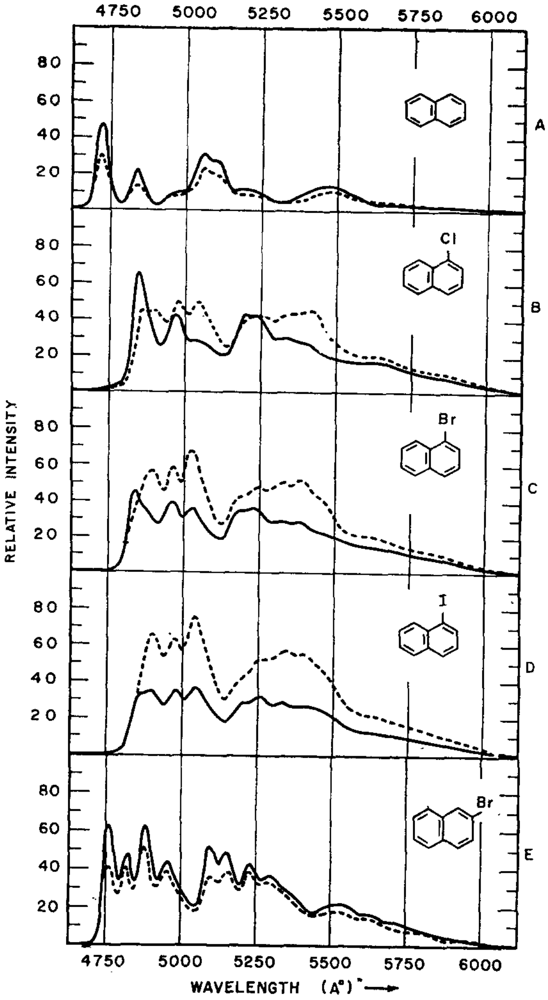

FIG. 1. The dependence of the polarization of the halonaphthalene's phosphorescence spectrum on the atomic number (compare *A*, *B*, *C*, and *D*) and the position (compare *C* and *E*) of the halogen atom.——, Emission perpendicular to ^1L_a excitation; ----, emission parallel to ^1L_a excitation.