

better understanding of the autocorrelated motion in a liquid, there is a need to establish the model, if possible, from first principles. This is also true of other models mentioned in the previous section. Our only justification of the modified Langevin model lies in its close agreement with the experimental results. We emphasize that only one unknown parameter  $\lambda$  which has the dimensions of a length appears in the modified Langevin model. The significance of this parameter is not understood.

Although no significantly different conclusion from those of the present computations would result, future studies on liquid methane will include (11) in the computational program. There is further need for very accurate cold neutron experiments on liquid methane for scattering angles from  $90^\circ$  to as small a scattering angle as possible to further test the modified Langevin model. This need is accentuated by the experimental results of Whittemore<sup>24</sup> on liquid methane, which are in disagreement with the predictions of this model and

<sup>24</sup> W. L. Whittemore, Nucl. Sci. Eng. **18**, 182 (1964).

with the experimental data obtained at the Materials Testing Reactor.

In retrospect, it is perhaps plausible that the parameter  $\eta$  pertaining to the microscopic dynamics of the liquid is related to the viscous damping coefficient of the macroscopic system by an extrapolation as was done in Fig. 6. However, we had no *a priori* notions that such a relation might exist. In fact, it was the difficulty in regard to the principle of detailed balance mentioned in Sec. V which led the author to plot Fig. 6 from which this relation was found. Finally, we mention that although some evidence has been presented that the molecule is not rotating as freely as in gas, there is need for further experiments and analyses to make a firm decision.

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## Excited Electronic States of Crystalline Benzene

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In the present paper, the excited electronic states of crystalline benzene are examined with the use of exciton theory. Ion-pair exciton states are considered and it is shown that these may play a considerable role in determining the observed spectra. Their effect on the lowest triplet state is also considered. The results of the analysis are in agreement with the available experimental data and are also consistent with the analysis of the spectrum of crystalline naphthalene.

### I. INTRODUCTION

ONE of the major problems associated with the interpretation of the spectra of molecular crystals of aromatic molecules can be phrased in the following form: Is it possible to interpret the properties of the electronic states of a molecular crystal solely in terms of the excited states of the free molecule, or is it necessary to include in the description crystal states which do not exist for the free molecule, such as intermolecular ion-pair states? The Wannier exciton states observed in semiconductors<sup>1</sup> and in rare-gas solids<sup>2</sup> are good examples of the cases in which the band structure of the solid must be used to describe a set of excited electronic states that are obviously unrelated to the atomic or

molecular states of the crystal constituents. On the other hand, the lowest excited states of molecular crystals have been conventionally described within the framework of the tight-binding Frenkel exciton model.<sup>3</sup> In recent work from this laboratory,<sup>4,5</sup> the classical Frenkel exciton theory has been extended to include ion-pair states. The effect of configuration interaction between neutral and charge-transfer states was found to be of considerable importance in the case of weak electronic transitions, that is, for spin-forbidden transitions (triplet states)<sup>4</sup> and symmetry- and spin-allowed  $\alpha$  states<sup>5</sup> (the  ${}^1B_{3u}$  state of naphthalene). In the latter case the transition octopole

<sup>3</sup> See for example, D. P. Craig, in *Physics and Chemistry of Organic Solid State*, edited by M. Labes, M. Weissberger, and D. Fox (Academic Press Inc., New York, 1963).

<sup>4</sup> S. Choi, J. Jortner, S. Rice, and R. Silbey, *J. Chem. Phys.* **41**, 3294 (1964).

<sup>5</sup> R. Silbey, J. Jortner, S. Rice, and M. Vala, *J. Chem. Phys.* **42**, 2948 (1965).

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<sup>1</sup> See, for example, E. F. Gross, *Soviet Phys.—Usp.* **5**, 195 (1962) [*Usp. Fiz. Nauk* **76**, 433 (1962)].

<sup>2</sup> G. Baldini, *Phys. Rev.* **128**, 1562 (1962).

moments used by Craig *et al.*,<sup>6</sup> to account for the Davydov splitting within the framework of the Frenkel scheme, are one order of magnitude larger and of different sign than those estimated using the conventional  $\pi$ -electron wavefunctions.<sup>7</sup> We have demonstrated that an internally consistent interpretation of the spectral splittings and the polarization ratios of the Davydov components in the  $\alpha$  state of the naphthalene crystal can be provided in terms of configuration interaction between neutral and ion-pair states. Since the location of the ion-pair state in the naphthalene crystal is unknown, it is impossible at present to ascertain whether the Davydov splitting in the  $\alpha$  band arises from configuration interaction with this state, or is due to the effect of higher multipole moments which cannot be estimated using the currently available molecular wavefunctions.

In the present paper, we extend our previous analysis to the study of the crystal spectrum of benzene, and in particular to the properties of the first singlet state ( ${}^1B_{2u}$ ) and the first triplet ( ${}^3B_{1u}$ ) state of benzene. Transitions to the lowest two excited singlet states ( ${}^1B_{2u}$  and  ${}^1B_{1u}$ ) are symmetry forbidden in the free molecule, and consequently the observed intensity of the transition in the vapor phase is vibronically induced. The next higher singlet state ( ${}^1E_{1u}$ ) is a doubly degenerate state with an oscillator strength of 0.70 in the gas phase.<sup>8</sup> In the crystal, transitions to all of these states are observed<sup>9</sup> and the  $E_{1u}$  state is split because of crystal-field interactions. The 0-0 band of the  $\alpha$  state is also observed in the crystal, implying that the transition to this state is allowed in the crystal (this is possible since the site symmetry of the crystal is  $C_2$  and hence transitions to all the  $u$  states of the molecule are allowed in the crystal). The  $a_g$  vibrational progression built on the 0-0 band shows a total Davydov splitting of the order of  $150\text{ cm}^{-1}$ <sup>9</sup> (when the contributions of all the vibronic components are summed), while the progression built on the  $e_{2g}$  vibration is hardly split at all. This latter result is consistent with both ordinary exciton theory and with the formulation including charge-transfer states. The small observed splitting is due to vibrational exciton splitting of the  $e_{2g}$  vibration and not electronic exciton splitting.

The first theoretical discussion of the crystal spectrum of benzene was carried out by Davydov<sup>10</sup> who was concerned with the classification and the polarization of the transitions to the crystal states. Davydov used the (incorrect) assumption that the four molecules in the unit cell can be divided into two separate pairs of parallel molecules. Fox and Schnepf<sup>11</sup> calculated the transition octopole moments from simple molecular-

orbitals wavefunctions (including overlap) and used these results to calculate the Davydov splittings in the first two excited electronic states. The calculated Davydov splitting (which should be divided between the vibronic components using the appropriate Franck-Condon factors) is about one order of magnitude smaller than the observed splitting. In recent calculations Thirunamachandran<sup>12</sup> has shown that a value of  $60\text{ \AA}^3$  for the transition octopole moment, treated as an adjustable parameter, leads to reasonable agreement between the predicted (multipole) splitting of the experimental Davydov splitting in the  ${}^1B_{2u}$  state. This octopole moment is rather large when compared with the value of  $23\text{ \AA}^3$  calculated from LCAO wavefunctions including overlap.<sup>11</sup>

There has been some confusion concerning the assignment of the polarizations of the transitions to the several crystal states, because Fox and Schnepf and Craig and Walsh<sup>13</sup> used very different definitions of the molecular axes in their respective group-theoretical analyses. For this reason, we have repeated the relevant group-theoretical treatment in the Appendix to this paper. Briefly stated, our analysis and those of Fox and Schnepf and Craig and Walsh lead to identical results when differences in definitions of the molecular axes are recognized.

The first triplet state of benzene has been studied by an elegant isotopic substitution method<sup>14</sup> and from these data, an estimate of the Davydov splitting in the triplet state has been obtained. The experimental situation regarding the assignment of the crystal states in the first singlet state of crystalline benzene is far from satisfactory, since the directions of polarization of the Davydov components have not yet been established unambiguously.<sup>15</sup> The higher singlet exciton states ( ${}^1B_{2u}$  and  ${}^1E_{1u}$ ) of crystalline benzene are so broad that there is little hope that the Davydov components will be resolved.

In the present work we present the results of a theoretical study of the Davydov splittings of the  ${}^1B_{2u}$ ,  ${}^1B_{1u}$ ,  ${}^1E_{1u}$ , and  ${}^3B_{2u}$  states of crystalline benzene. It can be demonstrated that the charge-transfer exciton states may play an important role in determining the Davydov splitting in the lowest excited singlet and triplet states of crystalline benzene.

## II. CRYSTAL STRUCTURE<sup>16</sup>

Benzene crystallizes in the space group  $D_{2h}^{16}$  of the orthorhombic crystal system. There are four translationally inequivalent molecules per unit cell located at  $(0, 0, 0)$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ , and  $(\frac{1}{2}, 0, \frac{1}{2})$  in the crystal axis system. These molecules are referred to as I, II, III, IV. The molecules II, III, IV are generated from I

<sup>6</sup> D. P. Craig and S. Walmsley, *Mol. Phys.* **4**, 113 (1961).

<sup>7</sup> We estimate that  $O_3=3.3\text{ \AA}^3$ ,  $O_1=2.7\text{ \AA}^3$ , whereas Craig *et al.* (Ref. 6) have  $O_3=12\text{ \AA}^3$ ,  $O_1=-9\text{ \AA}^3$ . The important difference is the sign.

<sup>8</sup> H. B. Klevens and J. R. Platt, *J. Chem. Phys.* **17**, 470 (1949).

<sup>9</sup> H. C. Wolf, *Solid State Phys.* **9**, 1 (1959).

<sup>10</sup> A. Davydov, *Theory of Molecular Excitons* (McGraw-Hill Book Company, Inc., New York, 1961).

<sup>11</sup> D. Fox and O. Schnepf, *J. Chem. Phys.* **23**, 767 (1955).

<sup>12</sup> T. Thirunamachandran, thesis, University of London, 1962.

<sup>13</sup> D. Craig and J. Walsh, *J. Chem. Soc.* **1958**, 1613.

<sup>14</sup> G. Nieman and G. W. Robinson, *J. Chem. Phys.* **39**, 1298 (1963).

<sup>15</sup> Compare Ref. 9 with V. L. Bronde, *Soviet Phys.—Usp.* **4**, 584 (1961) [*Usp. Fiz. Nauk* **74**, 577 (1961)].

<sup>16</sup> E. Cox, *Rev. Mod. Phys.* **30**, 159 (1958).

by screw-axis transformations parallel to the  $a$ ,  $b$ , and  $c$  axes, respectively. At 270°K, the lattice constants are

$$a = 7.640 \text{ \AA}, \quad b = 9.660 \text{ \AA}, \quad c = 7.034 \text{ \AA},$$

and the direction cosines of the three molecular axes of Molecule I are

$$L = \begin{pmatrix} -0.276 \\ 0.964 \\ -0.030 \end{pmatrix}, \quad M = \begin{pmatrix} 0.654 \\ 0.168 \\ -0.754 \end{pmatrix},$$

$$N = \begin{pmatrix} 0.709 \\ -0.224 \\ 0.668 \end{pmatrix},$$

where  $L$  is the axis in the molecular plane which passes through atoms,  $M$  is the in-plane axis which passes through bonds, and  $N$  is the axis perpendicular to the plane.

### III. GENERAL FORMALISM

As demonstrated in the Appendix, we find for the states of the free molecule that are  $u$  with respect to the operation of inversion, that the crystal states (exciton states) are given by the following linear combinations for  $\mathbf{k}=\mathbf{0}$  (or  $\mathbf{k}$  parallel to any crystal axis):

$$\Psi_i^f = (4N)^{-1/2} \sum_{n=1}^N \left\{ \Phi_{1-}^{\pm} \Phi_{2+}^{\pm} \Phi_{3-}^{\pm} \Phi_{4+}^{\pm} \right\}, \quad (1)$$

where  $i$  refers to the factor-group irreducible representation ( $i=1, 2, 3, 4$  refer to  $A_u, B_{1u}, B_{2u}, B_{3u}$ ).  $\Phi_i^f$  is a one-site exciton function of Site  $i$  and State  $f$ . In the above expression, the site functions II, III, and IV have been generated from the first site function by a screw axis transformation and not by a glide plane transformation.

The energy of the  $i$ th-factor-group component of the  $f$ th electronic state relative to the ground state of the crystal is given in first order by

$$E_i^f - E_0 = e^f + D^f + J_i^f(\mathbf{k}). \quad (2)$$

As usual,  $e^f$  is the excitation energy of the free molecule from the ground state of the  $f$ th excited state,  $D^f$  is the "environmental shift," and  $J_i^f$  is a sum of intermolecular excitation exchange integrals, which are usually taken to be sums of dipole-dipole interactions, where the dipole moment is the transition dipole moment. The  $J_i^f$  depend on  $i$  through the signs in Eq. (1). We include higher  $\pi$  states in the discussion, and so the interaction of exciton states with each other (configuration interaction) must be included. The off-diagonal elements are given by

$$H_i^j = J_i^j(\mathbf{k}). \quad (3)$$

In the above we have neglected small matrix elements that do not depend on  $\mathbf{k}$ . The molecular wavefunctions

used in these calculations are those of Geoppert-Mayer and Sklar<sup>17</sup> (Use of extensive CI wavefunctions such as those of Parr, Craig, and Ross<sup>18</sup> made little difference in the reported results for the lowest pi states):

$$\Psi_0 = \alpha \{ 1\bar{1}2\bar{2}3\bar{3} \},$$

$$\Psi_{1B_{1u}} = \frac{1}{2} \alpha \{ 1\bar{1}2\bar{4}3\bar{3} - 1\bar{1}243\bar{3} - 1\bar{1}2\bar{2}3\bar{5} + 1\bar{1}2\bar{2}3\bar{5} \},$$

$$\Psi_{1B_{2u}} = \frac{1}{2} \alpha \{ 1\bar{1}2\bar{2}3\bar{4} - 1\bar{1}2\bar{2}34 + 1\bar{1}2\bar{5}3\bar{3} - 1\bar{1}253\bar{3} \},$$

$$\Psi_{1B_{1u}}(\beta) = \frac{1}{2} \alpha \{ 1\bar{1}2\bar{4}3\bar{3} - 1\bar{1}243\bar{3} + 1\bar{1}2\bar{2}3\bar{5} - 1\bar{1}2\bar{2}3\bar{5} \},$$

$$\Psi_{1B_{1u}}(\beta') = \frac{1}{2} \alpha \{ 1\bar{1}2\bar{2}3\bar{4} - 1\bar{1}2\bar{2}34 - 1\bar{1}2\bar{5}3\bar{3} + 1\bar{1}253\bar{3} \}, \quad (4)$$

where the numbers refer to LCAO molecular orbitals including atomic overlap, and the bar means spin of  $\frac{1}{2}$  in the usual sense.

For mixing of ion-pair states into neutral exciton states, we must find factor-group-symmetrized ion-pair states. We include only ion-pair states which involve a molecule and one of its translationally inequivalent neighbors (previous work<sup>4,5</sup> has shown that those involving translationally equivalent molecules have the same mixing coefficient into the neutral states for all factor-group components, and thus may be neglected). Since the lowest unfilled and highest filled molecular orbitals of benzene are degenerate, there are four possible ion-pair states formed by removing an electron from a molecule and putting it on the adjacent molecule in one of the lowest unfilled orbitals. Since there are three inequivalent neighbors for the molecule at the origin, there are a total of 24 ion-pair states (counting the  $+-$  and the  $-+$  states). Using these states, one may find the symmetrized states of the crystal.

The matrix elements of the Hamiltonian between these states and the neutral states given above are then found to be

$$\mathcal{H}_i^j(I, II) = 2^{-1} \left\{ [B^j(I, II) + B^j(II, I)] \right. \\ \left. \pm [C^j(I, II) + C^j(II, I)] \right\},$$

$$\mathcal{H}_i^j(I, III) = 2^{-1} \left\{ [B^j(I, III) + B^j(III, I)] \right. \\ \left. \pm [C^j(I, III) + C^j(III, I)] \right\},$$

$$\mathcal{H}_i^j(I, IV) = 2^{-1} \left\{ [B^j(I, IV) + B^j(IV, I)] \right. \\ \left. \pm [C^j(I, IV) + C^j(IV, I)] \right\}. \quad (5)$$

<sup>17</sup> M. Geoppert-Mayer and A. Sklar, J. Chem. Phys. **6**, 645 (1938).

<sup>18</sup> R. Parr, D. Craig, and I. Ross, J. Chem. Phys. **18**, 1561 (1950).

There are three more such matrix elements where the  $C$  and  $B$  elements are reversed in the above (these are for those ion-pair states where the ion charges are reversed). As usual,  $i$  refers to the factor-group component, and the positive and negative signs are for these states in the order  $A_u$ ,  $B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$ . The matrix elements  $B$  and  $C$  are defined by formulas of the form:

$$B^f(m, n) = \langle m^f | H | m, n \rangle - \langle m^f | H | m^f \rangle \langle m^f | m, n \rangle, \quad (6)$$

$$C^f(m, n) = \langle m^f | H | n, m \rangle - \langle m^f | H | m^f \rangle \langle m^f | n, m \rangle, \quad (7)$$

where the  $|m, n\rangle$  refers to a positive ion at Site  $m$  and a negative ion at Site  $n$ .

In this paper we are concerned with the structure of those crystal states derived from the  $\alpha$  and  $p$  states of benzene. The eight ion-pair states corresponding to a given molecular pair are

$$\begin{aligned} & | \mathbf{R}_n(3)\mathbf{R}_m(5) \rangle, \quad | \mathbf{R}_n(3), \mathbf{R}_m(4) \rangle, \\ & | \mathbf{R}_m(2), \mathbf{R}_n(5) \rangle, \quad | \mathbf{R}_n(2), \mathbf{R}_m(4) \rangle \\ & | \mathbf{R}_m(3)\mathbf{R}_n(5) \rangle, | \mathbf{R}_m(3)\mathbf{R}_n(4) \rangle, \\ & | \mathbf{R}_m(2)\mathbf{R}_n(5) \rangle, \quad | \mathbf{R}_m(2)\mathbf{R}_n(4) \rangle, \end{aligned} \quad (8)$$

where  $\mathbf{R}_n(i)$  refers to an ionic state of the molecule, and the numbers in parentheses designate the orbital from which an electron has been removed and the orbital into which the electron has been placed. Consider, for example, the evaluation of  $B_p(n, m)$ . Using Eq. (6),

$$\begin{aligned} B_{ij}^p(n, m) &= \langle \phi_n^p | H | \mathbf{R}_n^i \mathbf{R}_m^j \rangle \\ &\quad - \langle \phi_n^p | H | \phi_n^p \rangle \langle \phi_n^p | \mathbf{R}_n^i \mathbf{R}_m^j \rangle \\ &= 2^{-3} \{ \langle \phi_n^{3-4} + \phi_n^{2-5} | H | \mathbf{R}_n^i \mathbf{R}_m^j \rangle \\ &\quad - \frac{1}{2} \langle \phi_n^{3-4} + \phi_n^{2-5} | \mathbf{R}_n^i \mathbf{R}_m^j \rangle \\ &\quad \times \langle \phi_n^{3-4} + \phi_n^{2-5} | H | \phi_n^{3-4} + \phi_n^{2-5} \rangle \}. \end{aligned} \quad (9)$$

Further algebraic manipulation of the expanded form of Eq. (9) leads to

$$B_{ij}^p(n, m) = 2^{-3} \{ B_{ij}^{3-4}(n, m) + B_{ij}^{2-5}(n, m) + RR \}, \quad (10)$$

where  $i$  and  $j$  again represent the two orbitals involved

$$B_{2-4}^{3-5} = \langle \phi_m^{3-5} \phi_n^0 | H | \mathbf{R}_{m+}^3 \mathbf{R}_{n-}^4 \rangle - \langle \phi_m^{3-5} \phi_n^0 | \mathbf{R}_{m+}^3 \mathbf{R}_{n-}^4 \rangle \langle \phi_m^{3-5} | H | \phi_m^{3-5} \rangle, \quad (16)$$

$$B_{2-5}^{3-5} = \langle \phi_m^{3-5} \phi_n^0 | H | \mathbf{R}_{m+}^2 \mathbf{R}_{n-}^5 \rangle - \langle \phi_m^{3-5} \phi_n^0 | \mathbf{R}_{m+}^2 \mathbf{R}_{n-}^5 \rangle \langle \phi_m^{3-5} | H | \phi_m^{3-5} \rangle, \quad (17)$$

$$C_{3-4}^{3-5} = \langle \phi_m^{3-5} \phi_n^0 | H | \mathbf{R}_{n+}^3 \mathbf{R}_{m-}^4 \rangle - \langle \phi_m^{3-5} \phi_n^0 | \mathbf{R}_{n+}^3 \mathbf{R}_{m-}^4 \rangle \langle \phi_m^{3-5} | H | \phi_m^{3-5} \rangle, \quad (18)$$

$$C_{2-5}^{3-5} = \langle \phi_m^{3-5} \phi_n^0 | H | \mathbf{R}_{m+}^2 \mathbf{R}_{n-}^5 \rangle - \langle \phi_m^{3-5} \phi_n^0 | \mathbf{R}_{m+}^2 \mathbf{R}_{n-}^5 \rangle \langle \phi_m^{3-5} | H | \phi_m^{3-5} \rangle. \quad (19)$$

 TABLE I. Dipole terms for excluded volume ( $\text{cm}^{-1}$ ).

	$J_{11}$	$J_{12}$	$J_{13}$	$J_{14}$
$\beta\beta$	37.4	-840.0	-822.4	-8.8
$\beta\beta'$	-3.6	213.6	0.0	-862.4
$\beta'\beta'$	-52.0	1398.2	-1752.0	-2736.0

in the electron transfer. The remainder term in the  $p$  matrix element,

$$\begin{aligned} RR &= \frac{1}{2} \langle \phi_n^{3-4} | \mathbf{R}_n^i \mathbf{R}_m^j \rangle \{ \langle \phi_n^{3-4} | H | \phi_n^{3-4} \rangle \\ &\quad - \langle \phi_n^{2-5} | H | \phi_n^{2-5} \rangle - 2 \langle \phi_n^{2-5} | H | \phi_n^{3-4} \rangle \} \\ &\quad + \frac{1}{2} \langle \phi_n^{2-5} | \mathbf{R}_n^i \mathbf{R}_m^j \rangle \{ \langle \phi_n^{2-5} | H | \phi_n^{2-5} \rangle \\ &\quad - \langle \phi_n^{3-4} | H | \phi_n^{3-4} \rangle - 2 \langle \phi_n^{2-5} | G | \phi_n^{3-4} \rangle \} \end{aligned} \quad (11)$$

can be reduced to

$$RR = - \langle \phi_n^{2-5} | H | \phi_n^{3-4} \rangle \{ \langle \phi_n^{3-4} | \mathbf{R}_n^i \mathbf{R}_m^j \rangle + \langle \phi_n^{2-5} | \mathbf{R}_n^i \mathbf{R}_m^j \rangle \}, \quad (12)$$

since

$$\langle \phi_n^{3-4} | H | \phi_n^{3-4} \rangle = \langle \phi_n^{2-5} | H | \phi_n^{2-5} \rangle, \quad (13)$$

including only two-center integrals and neglecting *three-center* terms involving the Goepfert-Mayer-Sklar<sup>17</sup> (GMS) potential of the atomic cores. The leading term in Eq. (12) may be expanded as follows:

$$\begin{aligned} & \langle \phi_n^{2-5} | H | \phi_n^{3-4} \rangle \\ &= 2 \langle u_n^5(1) u_n^2(1) | r_{12}^{-1} | u_n^3(2) u_n^4(2) \rangle \\ &\quad - \langle u_n^5(1) u_n^4(1) | r_{12}^{-1} | u_n^3(2) u_n^2(2) \rangle. \end{aligned} \quad (14)$$

The matrix elements which determine the mixing of the ion-pair states with the neutral exciton states arising from the  $\alpha$  state of benzene are slightly different in form. For example, for the  $\alpha$  state we must evaluate

$$\begin{aligned} & \langle \phi_n^{3-5} | H | \phi_n^{3-5} \rangle - \langle \phi_n^{2-4} | H | \phi_n^{2-4} \rangle \\ &= 2 \sum_{i=1}^3 \langle u_n^i(1) | J_m^5 - J_m^3 | u_n^i(1) \rangle, \end{aligned} \quad (15)$$

where  $J_m^k$  is the Coulomb potential operator of the  $k$ th molecular orbital of the  $m$ th molecule. Thus we must evaluate the following matrix elements:

On reduction, these elements are found to have the form

$$\begin{aligned}
 B_{3-4}^{3-5} &= \langle u_n^4 | V_n^{\text{GMS}} - \sum_i^3 K_n^i + 2K_m^3 - J_m^3 | u_m^5 \rangle - \langle u_m^4 | u_n^5 \rangle \langle u_m^5 | 2K_m^3 - J_m^3 | u_m^5 \rangle \\
 &+ \sum_{i=1}^3 \{ - \langle u_n^i | u_m^4 \rangle \langle u_m^i | 2K_m^3 - J_m^3 | u_m^5 \rangle + \langle u_n^i | u_m^5 \rangle \langle u_n^i | J_m^3 | u_n^4 \rangle \\
 &+ \langle u_n^i | u_m^1 \rangle \langle u_m^1 u_m^5 | u_n^4 u_n^i \rangle + \langle u_m^2 | u_n^i \rangle \langle u_m^2 u_m^5 | u_n^4 u_n^i \rangle \}, \\
 C_{3-4}^{3-5} &= 2 \langle u_m^3 u_m^5 | u_m^4 u_n^3 \rangle - \langle u_m^4 u_m^5 | u_m^3 u_n^3 \rangle \\
 &- 2 \sum_i^3 \{ \langle u_m^i | u_n^3 \rangle \langle u_m^4 u_m^i | u_m^3 u_m^5 \rangle + \langle u_m^4 | u_n^i \rangle \langle u_m^3 u_m^5 | u_n^3 u_n^i \rangle \\
 &- \frac{1}{2} \langle u_n^3 | u_m^i \rangle \langle u_m^4 u_m^5 | u_m^3 u_m^i \rangle - \frac{1}{2} \langle u_m^3 | u_n^i \rangle \langle u_m^4 u_m^5 | u_n^3 u_n^i \rangle \}, \quad (20) \\
 B_{2-5}^{3-5} &= 2 \langle u_m^3 u_m^5 | u_m^2 u_n^5 \rangle - \langle u_n^5 u_m^5 | u_m^2 u_m^3 \rangle \\
 &+ \sum_{i=1}^3 \{ \langle u_m^5 | u_n^i \rangle \langle u_m^2 u_m^3 | u_n^3 u_n^i \rangle + \langle u_n^5 | u_m^i \rangle \langle u_m^2 u_m^3 | u_m^5 u_m^i \rangle \\
 &- 2 \langle u_m^i | u_n^5 \rangle \langle u_m^3 u_m^5 | u_m^2 u_m^i \rangle - 2 \langle u_m^2 | u_n^i \rangle \langle u_m^5 u_m^3 | u_n^5 u_n^2 \rangle \}, \\
 C_{2-5}^{3-5} &= - \langle u_m^3 | V_m^{\text{GMS}} - \sum_i^3 K_m^i - 2K_m^5 + J_m^5 | u_n^2 \rangle + \sum_{1,2,5} \langle u_n^2 | u_m^i \rangle \langle u_m^3 u_m^i | u_n^2 u_n^2 \rangle \\
 &- \sum_i^3 \{ \langle u_n^1 | u_m^3 \rangle \langle u_m^3 u_m^5 | u_n^2 u_n^i \rangle - \langle u_n^i | u_m^3 \rangle \langle u_n^2 | J_m^5 - J_m^3 | u_n^i \rangle \} \\
 &+ \sum_{i=1}^2 \langle u_n^2 | u_m^i \rangle \langle u_m^3 | J_m^5 - K_m^5 | u_m^i \rangle. \quad (21)
 \end{aligned}$$

In Eqs. (20)–(22),  $u_m^k$  is the  $k$ th molecular orbital of the  $m$ th molecule,  $V_m^{\text{GMS}}$  is the Goepert-Mayer-Sklar potential of Molecule  $m$  and  $K_m^k$  is the exchange operator of the  $k$ th molecular orbital on Molecule  $m$ .

#### IV. NUMERICAL CALCULATIONS

The dipole-dipole sums corresponding to the neutral states were carried out exactly for a crystal volume of  $\sim 100 \times 100 \times 100$  Å. The results for the  $E_{1u}$  states are given in Table I.

The long-range dipole-dipole interactions for the neutral states were calculated in the continuum approximation previously used, and the results are given in Table II for the case of  $k \parallel b^{-1}$ .

The results using the wavefunctions of Eq. (4) and assuming the interaction between molecules to be the repulsion of the electrons (only two-center Coulomb integrals were calculated) are given in Table III, for the same volume of crystal as used in calculating Table I.

The transition dipole moments for the  $\beta$  and  $\beta'$  states were calculated on the basis of an oscillator strength of 0.35 for each state, since the total oscillator strength for the  $E_{1u}$  state is 0.7 and simple molecular orbital theory predicts equal transition dipole moments in both states. Therefore, we find a transition dipole length of 0.76 Å for each state.

The secular matrix including ion-pair states was of

order  $28 \times 28$ . However, because of the symmetry of the matrix elements in Eq. (5) and those not explicitly displayed but referred to beneath those equations, we may reduce this matrix to order  $16 \times 16$  immediately. This reduction is possible because of the neglect of three molecule terms in the matrix element for the mixing of the ion-pair states and the neutral states, and the near-neighbor approximation, and is *not* due to crystal symmetry. The matrix elements between the neutral and ion-pair states are given in Table IV.

The only remaining elements arise from the mixing of the ion-pair states with the  $E_{1u}$  states, the mixing of the ion-pair states with one another, and the diagonal elements of the ion-pair states. We neglect the first elements mentioned since the  $E_{1u}$  state is so far away from the ion-pair state in energy that retention of these elements will lead to small effects compared to the effects arising from the dipole sums. We neglect the mixing of ion-pair states with one another, since careful examination shows these terms to be small. The diagonal matrix elements of the ion-pair states are then taken to be the energies of these states. We estimate the energy, as before, by the classical formula

$$E = \text{I.P.} - \text{E.A.} + C + P, \quad (22)$$

where I.P. is the ionization potential of ground-state benzene, E.A. is the electron affinity of benzene,  $C$  the Coulomb energy in the crystal, and  $P$  the polarization

TABLE II. Long-range dipole terms (cm<sup>-1</sup>).

	$J_{11}$	$J_{12}$	$J_{13}$	$J_{14}$
$\beta\beta$	-512.3	45.8	573.9	-107.4
$\beta\beta'$	264.4	-66.4	90.9	-249.6
$\beta'\beta'$	970.6	-1032.2	1033.3	-971.7

 TABLE III. Results using LCAO-MO wavefunctions for excluded volume (cm<sup>-1</sup>).

	$J_{11}$	$J_{12}$	$J_{13}$	$J_{14}$
$p\bar{p}$	7.8	-216.0	424.0	-119.2
$p\beta$	-13.4	121.6	-125.6	4.4
$p\beta'$	1.2	-113.6	188.6	689.7
$\beta\beta$	430.6	-1564.0	-1669.6	-19.2
$\beta\beta'$	11.4	296.4	103.6	-1382.4
$\beta'\beta'$	-260.6	2158.0	-1431.6	-2589.2

TABLE IV. Matrix elements of ion-pair neutral exciton mixing.

	Ion-pair states <sup>a</sup>			
	3, 4	2, 4	2, 5	3, 5
	$B_{1u}$			
( $^1\alpha$ 1, 2) <sup>b</sup>	0.023	-0.129	-0.144	-4.966
( $^1\alpha$ 1, 3)	1.035	-0.936	-1.040	4.517
( $^1\alpha$ 1, 4)	-0.782	-16.838	1.843	-0.472
( $^1p$ 1, 2)	4.340	0.040	0.580	-0.112
( $^1p$ 1, 3)	-3.615	0.927	1.090	0.990
( $^1p$ 1, 4)	-0.151	1.354	-18.208	-0.807
( $^3p$ 1, 2)	0.339	-0.044	-0.997	0.032
( $^3p$ 1, 3)	-0.974	0.062	-0.447	1.368
( $^3p$ 1, 4)	-0.200	-1.383	0.775	-2.191
	$B_{2u}$			
( $^1\alpha$ 1, 2)	-0.097	-0.619	-0.024	4.566
( $^1\alpha$ 1, 3)	1.295	-0.320	0.024	-5.201
( $^1\alpha$ 1, 4)	-0.782	-16.838	1.843	-0.472
( $^1p$ 1, 2)	-1.000	+0.196	-0.191	-0.298
( $^1p$ 1, 3)	2.259	-0.863	0.640	-0.702
( $^1p$ 1, 4)	-0.151	1.354	-18.208	-0.807
( $^3p$ 1, 2)	2.189	-0.268	0.415	0.038
( $^3p$ 1, 3)	-1.264	-0.008	-0.240	-0.528
( $^3p$ 1, 4)	-0.200	-1.383	0.775	-2.191
	$B_{3u}$			
( $^1\alpha$ 1, 2)	-0.097	-0.619	-0.024	4.566
( $^1\alpha$ 1, 3)	1.035	-0.936	-1.040	4.517
( $^1\alpha$ 1, 4)	0.952	14.976	-2.397	-1.326
( $^1p$ 1, 2)	-1.000	0.196	-0.191	-0.298
( $^1p$ 1, 3)	-3.615	0.927	1.090	0.990
( $^1p$ 1, 4)	1.241	-0.824	8.108	1.303
( $^1p$ 1, 2)	2.189	-0.268	0.415	0.038
( $^1p$ 1, 3)	-0.974	0.062	-0.447	1.368
( $^1p$ 1, 4)	0.870	0.619	10.625	-1.791

<sup>a</sup> All energies measured in  $\sqrt{2}\times 10^{-2}$  eV.

<sup>b</sup> Matrix elements between neutral state listed at left with ion-pair state formed from two molecules listed at right and orbitals listed in column headings.

energy of the crystal with two ions. We find

$$E = (9.2 + 1.1 - C - 2.0) \pm 1.0,$$

$$E(\text{I, II}) = 5.9 \pm 1.0 \text{ eV},$$

$$E(\text{I, III}) = 5.8 \pm 1.0 \text{ eV},$$

$$E(\text{I, IV}) = 5.5 \pm 1.0 \text{ eV}. \quad (23)$$

The uncertainty in the figures cited arise from uncertainties in ( $P$ -E.A.). No experimental data for either the electron affinity or the polarization energy are available; however, Hoyland and Goodman<sup>19</sup> calculate E.A. to be -1.1 eV, and we find  $P \sim -2.0$  eV.

The results of diagonalizing the secular matrix are given in Table V for various choices of the energy of the lowest ion-pair state.

### Triplet States

The lowest  $\pi$  triplet state of benzene is known to be the  $^3B_{2u}$  state. The neutral exciton formalism leads to the result (for the small spin-orbit coupling characteristic of aromatic hydrocarbons) that the intermolecular energy exchange integrals are reduced to electron-exchange integrals. We have calculated these integrals in the same spirit as described earlier, using the  $2p\pi$  orbital of the  $^3P(1s^2 2s^2 2p^2)$  state of atomic carbon and including only two center terms. The results are displayed in Table VI for the interactions with the nearest-neighbor molecules. These terms are much too small to account for the experimentally determined quasis resonant shifts.<sup>14</sup>

We have also calculated the matrix elements of the mixing of the ion-pair states with the triplet state and the results are displayed in Table IV. The matrix elements for the mixing of the triplet state with the triplet ion-pair state are slightly different in form from those given above.

Perturbation theory was used to calculate the position of the various Davydov components and the results are given in Table VII for several choices of the energy of the lowest triplet ion-pair state. Since the difference between the triplet and singlet ion-pair states should be small (the exchange integral is extremely small), we have used the same approximate energies as quoted above for the ion-pair states.

### V. DISCUSSION

The known experimental splittings of the benzene crystal spectrum pertain only to the  $^1B_{2u}(\alpha)$  state. However, individual experimentalists have reported different polarization assignments for the various Davydov components, although all investigators agree on the magnitude of the splitting between  $a$  and  $c$  axis polarizations.<sup>15</sup> The various experimental values

<sup>19</sup> J. Hoyland and L. Goodman, J. Chem. Phys. **36**, 12, 21 (1962).

TABLE V. Energy levels of benzene for  $k \parallel b^{-1}$ .

$E$ (ion pair) (eV)	State	$\parallel a$ ( $\text{cm}^{-1}$ )	$\parallel b$ ( $\text{cm}^{-1}$ )	$\parallel c$ ( $\text{cm}^{-1}$ )	$E(a-c)$ ( $\text{cm}^{-1}$ )
4.42	$\alpha$	1754	1736	1667	77
	$\beta$	-216	1068	-349	133
4.50	$\alpha$	1305	1366	1273	32
	$\beta$	-196	1082	-344	148
4.60	$\alpha$	1057	1028	926	131
	$\beta$	-161	1107	-344	183
4.75	$\alpha$	-2000	-2003	-1799	-201
	$\beta$	-105	1145	-321	216
4.90	$\alpha$	-1497	-1500	-1308	-189
	$\beta$	-33	1192	-301	268
5.00	$\alpha$	-1224	-1227	-1051	-173
	$\beta$	35	1235	-281	316
5.08	$\alpha$	-1080	-1084	-920	-160
	$\beta$	90	1268	-265	355
...	$\beta$	-900	-616	2900	
	$\beta'$	6840	3750	-3900	

<sup>a</sup> All energies measured from the 0-0 line of the respective transitions.

are given in Table VIII. The latest data are those of Bronde; unfortunately in two separate papers he has reversed his position concerning the polarization assignments.

Notice that the experimental splittings and polarization assignments can be fit with a value of ion-pair state energy that is quite close to the energy of the  ${}^1B_{2u}$  state (see Table V). There is not sufficient experimental evidence (or theoretical work) to say anything further about the agreement between theory and experiment.

Nieman and Robinson<sup>14</sup> have estimated the Davydov splitting in the triplet state by finding experimentally, from their isotopic studies, a sum of squares of nearest-neighbor interactions. This estimate is quite close to ours ( $\sim 100 \text{ cm}^{-1}$  for the first vibrational band),<sup>20</sup> however, the comparison that should be made is between our quasisonant shifts and their measured shifts.

In our approximation, the shifts would arise from the

TABLE VI. Electron-exchange contributions to intermolecular energy exchange integrals for triplet ( ${}^3B_{1u}$ ).

Molecule	Position	Integral ( $-K$ )
2	$(\frac{1}{2}, \frac{1}{2}, 0)$	$0.03 \text{ cm}^{-1}$
3	$(0, \frac{1}{2}, \frac{1}{2})$	$0.87 \text{ cm}^{-1}$
4	$(\frac{1}{2}, 0, \frac{1}{2})$	$-0.07 \text{ cm}^{-1}$
5	$(0, 0, 1)$	$-0.05 \text{ cm}^{-1}$

<sup>20</sup> I. Ross in a private communication has informed us that using his and Body's recently developed formalism for isotopic impurities and the data of Ref. 14, they find a total splitting in the first triplet of  $200 \text{ cm}^{-1}$ .

TABLE VII. Energy levels of benzene triplet (strong coupling).

$E$ (ion pair)	$\parallel a$	$\parallel b$	$\parallel c$
4.7 eV	$-32 \text{ cm}^{-1}$	$-20 \text{ cm}^{-1}$	$-200 \text{ cm}^{-1}$
5.7 eV	$-16 \text{ cm}^{-1}$	$-10 \text{ cm}^{-1}$	$-100 \text{ cm}^{-1}$

ion-pair state interaction with the triplet (since the exchange integrals are so small). The difference in energy between the ion-pair state consisting of one  $\text{C}_6\text{H}_6$  molecule and one  $\text{C}_6\text{H}_n\text{D}_{6-n}$  molecule and the triplet state of  $\text{C}_6\text{H}_6$  must be calculated for  $n=0, 2, 3$ . Then the quasisonant shifts are given by

$$\delta = \sum \beta^2 / \Delta E,$$

where  $\sum \beta^2$  is the sum of ion-pair-triplet interactions (assumed independent of extent of deuteration) and  $\Delta E$  is the energy difference mentioned in the last sentence. Hence, the difference in shifts for  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{D}_6$  and for  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{H}_3\text{D}_3$  is given by

$$\Delta\delta = \sum \beta^2 [(1/\Delta E_{D_6}) - (1/\Delta E_{D_3})].$$

Now the first ionization potential of perdeuterobenzene is  $30 \text{ cm}^{-1}$  higher than that of perprotobenzene.<sup>21</sup> This is the only experimental fact available with which to calculate  $\Delta\delta$ . Let us assume that the difference in the ionization potentials of trideuterobenzene and perprotobenzene is  $15 \text{ cm}^{-1}$  and this is the only difference in the energy of the ion-pair states. The calculated difference in the shift between  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{D}_6$  and  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{H}_3\text{D}_3$  for the ion-pair state 2 eV above the triplet (and assuming that the matrix elements are identical for all the isotopically substituted compounds) is  $0.2 \text{ cm}^{-1}$  in the strong coupling limit, while the experimental difference is  $3.5 \text{ cm}^{-1}$ . The difference in shifts between  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{D}_6$  and  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{H}_4\text{D}_2$  is calculated to be  $0.2 \text{ cm}^{-1}$  (experimental is  $7 \text{ cm}^{-1}$ ). It is clear that the agreement is not very good, even though the triplet splitting is predicted to be large.

TABLE VIII. Experimental splittings in  ${}^1B_{2u}$  state.

Band	$(\parallel a) - (\parallel c)$	Source
0-0	45	Wolf
	-41	Broude
0-1 925 $\text{cm}^{-1}$ $A_g$ vibration	45	Wolf
	-39	Broude
0-2 925 $\text{cm}^{-1}$ $A_g$ vibration	25	Wolf
	-20	Broude

<sup>21</sup> M. El-Sayed, M. Kasha, and Y. Tanaka, *J. Chem. Phys.* **34**, 334 (1961).

There are many possible sources of error in the present calculations. The most serious for the calculations involving the ion-pair states and the triplet states are the neglect of three- and four-center integrals; and the use of an atomic carbon orbital with a long "tail" for molecular calculations. The first-mentioned source of error will be most serious in the triplet calculations since three- and four-center atomic exchange integrals are *a priori* just as important as two-center integrals (there are 6480 three- and four-center terms for every pair of molecules). In the ion-pair state calculation, the four-center terms will be much smaller than the three- and two-center terms, but neglect of the three-center terms may be an extremely bad approximation. Until these integrals are evaluated, one cannot say *a priori* how bad an approximation is involved in the neglect of three-center terms. The use of an orbital with a long "tail" will, of course, overestimate the atomic exchange and hybrid integrals and recent work<sup>22</sup> has tried to estimate this effect. For example, use of the "atomic" orbital of the Hartree-Fock C<sub>2</sub> molecule<sup>22</sup> decreases the exchange integral by about 70% from the value calculated using the orbital employed in our analysis. Certainly, in going from C<sub>2</sub> to larger molecules, more charge density will be removed from the tail of the wavefunction and hence the integrals will decrease further.

So far we have said nothing about the assumptions made in calculating the dipole sums for the singlet states other than the  $\alpha$  state. The biggest source of error here, we feel, is the use of crystal structure data taken at 270°K. There is still some doubt as to the position of the benzene molecules in the crystal at 20°K where the experimental spectra are recorded.

The errors resulting from the factors cited are extremely difficult to estimate. However, within the error of the present analysis, we believe that the experimental data can be explained by the use of ion-pair exciton states.

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#### APPENDIX

Benzene crystallizes in the orthorhombic system with space group  $D_{2h}^{15}$ . Thus, the factor group is isomorphic

<sup>22</sup> R. Silbey, N. Kestner, J. Jortner, and S. Rice, *J. Chem. Phys.* **42**, 444 (1964).

to  $D_{2h}$ . The lattice may be considered as four interpenetrating simple orthorhombic lattices. The four types of molecules (one at each lattice point in each type of lattice) are translationally inequivalent. However, one may generate three sets of molecules from one set by the action of three different screw-axis transformations, each parallel to a different crystal axis. Thus, if we form one-site functions  $\Phi_i^f$ :

$$\Phi_i^f(K) = \sum_{n(\text{unit cells})} \exp(-i\mathbf{k}\cdot\mathbf{R}_{ni}) \phi_{ni}^f \prod_{m \neq ni}^f \phi_{mj}^0, \quad (\text{A1})$$

then

$$\{C_2^a | \frac{1}{2}(a+b)\} \Phi_1^f(\mathbf{k}) = \Phi_2^f(\mathbf{k}'), \quad (\text{A2})$$

$$\{C_2^b | \frac{1}{2}(b+c)\} \Phi_1^f(\mathbf{k}) = \Phi_3^f(\mathbf{k}''), \quad (\text{A3})$$

$$\{C_2^c | \frac{1}{2}(a+c)\} \Phi_1^f(\mathbf{k}) = \Phi_4^f(\mathbf{k}'''). \quad (\text{A4})$$

Now for molecular states that are antisymmetric with respect to inversion ( $u$  states), the one-site functions will be  $u$  (since the inversion occurs in both the site group and the molecular point group). Hence

$$\{i | 0\} \Phi_i^f(\mathbf{k}) = \Phi_i^f(-\mathbf{k}). \quad (\text{A5})$$

Therefore

$$\{\sigma^a | \frac{1}{2}(a+b)\} \Phi_1^f(\mathbf{k}) = \Phi_2^f(-\mathbf{k}') \quad (\text{A6})$$

since

$$\{\sigma^a | \frac{1}{2}(a+b)\} = \{i | 0\} \{C_2^a | \frac{1}{2}(a+b)\} \quad (\text{A7})$$

for the factor-group operations (which are, of course, sets of operations). Hence we can see by using the Wigner projection operator and the character table of the point group  $D_{2h}$ , that for  $\mathbf{k}=0$ , the symmetrical functions of the factor group (i.e., exciton functions) are

$$\begin{aligned} \Psi_{A_u}^f &= \frac{1}{2}(\Phi_1^f + \Phi_2^f + \Phi_3^f + \Phi_4^f), \\ \Psi_{B_{1u}}^f &= \frac{1}{2}(\Phi_1^f + \Phi_2^f - \Phi_3^f - \Phi_4^f), \\ \Psi_{B_{2u}}^f &= \frac{1}{2}(\Phi_1^f - \Phi_2^f + \Phi_3^f - \Phi_4^f), \\ \Psi_{B_{3u}}^f &= \frac{1}{2}(\Phi_1^f - \Phi_2^f - \Phi_3^f + \Phi_4^f), \end{aligned} \quad (\text{A8})$$

for all  $u$  states. Also, the transition to the state  $B_{1u}$  is polarized parallel to the  $a$  axis, to  $B_{2u}$  to the  $b$  axis, and to  $B_{3u}$  to the  $c$  axis (transitions to  $A_u$  are not allowed).

For  $\mathbf{k} \neq 0$ , but along any crystal axis direction, the factor group of the group of the  $\mathbf{k}$  vector is  $C_{4v}$ , and we define the same one-site functions.

We find (only for  $\mathbf{k} \parallel \mathbf{a}^{-1}$ ,  $\mathbf{b}^{-1}$ , or  $\mathbf{c}^{-1}$  axes) that the same linear combinations as in (A8) are valid for *all* states of the free molecule.

Another interesting point is that, if the nearest-neighbor approximation is made, then the functions (A8) are valid for any general  $\mathbf{k}$ . This was first pointed out by Fox and Schnepp.