[1]A. R. Adams and W. E. Spear, J. Phys. Chem. Solids 25, 1113 (1964); W. E. Spear and A. R. Adams, ibid. 27, 281 (1966); D. J. Gibbons and W. E. Spear, ibid. 27, 1917 (1966); P. K. Ghosh and W. E. Spear, J. Phys. C. 1, 1347 (1968); B. E. Cook and W. E. Spear, J. Phys. Chem Solids 30, 1125 (1969).

[2]S. A. Rice and J. Jortner, in Physics of Solids at High Pressures, edited by C. T. Tomizuka and R. M. Emrick (Academic, New York, 1965), p. 63.

[3]D. J. Gibbons (unpublished), report supplied by Professor W. E. Spear.

[4]J. E. Baer and M. Carmack, J. Am. Chem. Soc. 71, 1215 (1949).

[5]M. Wolfsberg and L. Helmholz, J. Chem. Phys. 20, 837 (1952).

[6]S. C. Abrahams, Acta Cryst. 8, 661 (1955); A. Caron and J. Donohue, ibid. 14, 548 (1961).

[7]G. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand, Princeton, N. J., 1966), Vol. III, p. 566.

[8]C. J. Ballhausen, Introduction to Ligand Field Theory (McGraw-Hill, New York, 1962), Chap. 7.

[9]R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. 17, 1248 (1949).

[10]R. E. Watson and A. J. Freeman, Phys. Rev. 123, 521 (1961).

[11]L. C. Cusachs, J. Chem. Phys. Suppl. 43, 157 (1965); L. C. Cusachs and J. W. Reynolds, ibid. 43, 160 (1965).

[12]C. J. Ballhausen and H. B. Gray, Molecular Orbital Theory (Benjamin, New York, 1964), p. 122.

[13]I. Chen, following paper, Phys. Rev. B 2, 1060 (1970).

Molecular-Orbital Studies of Charge-Carrier Transport in Orthorhombic Sulfur. II. Electronic States of the Crystal

Inan Chen

Research Laboratories, Xerox Corporation, Rochester, New York 14603
(Received 16 January 1970)

In order to interpret the difference of four orders of magnitude in the electron and the hole drift mobilities in orthorhombic sulfur, the intermolecular electronic-interaction energies for an excess electron and an excess hole are computed with the molecular orbitals obtained in the preceding paper. The excess-carrier energy bands are obtained by summing these energy integrals according to the symmetry characteristics of the crystal structure. Contrary to what Spear and co-workers have expected, the electronic contributions to the widths of an excess electron band and an excess hole band are found to be of the same order of magnitude and hence do not account for the large difference in the mobilities. The changes in the electronic charge distributions when an electron is added to or removed from a neutral molecule are used to estimate the relative values of molecular deformations and the polaron binding energies E_b. It is found that E_b associated with an excess electron is almost an order of magnitude larger than that associated with an excess hole. Holstein and Siebrand's theory is then used to show that this difference in electron-molecular vibration couplings is the major effect leading to the large difference in the electron and the hole mobilities. The same argument is used to explain the large difference in the charge-carrier mobilities of metal-free phthalocyanine and copper phthalocyanine. The excitation-transfer matrix elements are formulated in terms of molecular-orbital coefficients. The matrix elements for one of the excited states are found to be always almost zero due to the molecular symmetry. This is interpreted as the "localized excited state" which is responsible for the nonphotoconducting absorption observed in orthorhombic sulfur and vitreous selenium.

I. INTRODUCTION

In the preceding paper,[1] we have already mentioned the experimental works of Spear and co-workers[2] on the electric and optical properties of orthorhombic sulfur. The crystal of orthorhombic sulfur consists of S_8 molecules held together by van der Waals forces. It is therefore possible to study the electronic states of the crystal from those of an isolated S_8 molecule by treating the intermolecular interaction as a perturbation.[3]

With 16 molecules in a unit cell, the crystal structure of orthorhombic sulfur is considerably more complicated than those of well-studied organic molecular crystals such as naphthalene or anthracene. The crystal structure and the space group are analyzed in detail, and the symmetry-adapted—crystal wave functions are derived in Sec.

II. The energy-band structure of an excess charge carrier is formulated in the tight-binding approximation in Sec. III. The intermolecular energy integrals which determine the bandwidth are calculated in Sec. IV by expressing the molecular orbitals (MO) as linear combinations of atomic orbitals obtained in the preceding paper.[1] It is found that the bandwidths of electron bands are of the same order of magnitude as those of hole bands. This is in contradiction to the suggestion (by Spear and co-workers[2]) that the hole band, being of lone-pair-type orbitals, should have much larger intermolecular overlaps than the electron band which is made of σ-type orbitals. This suggestion was used in accounting for the difference in the electron and the hole mobilities in this crystal.

In Sec. V we show that an alternative factor, namely, the electron-molecular vibration coupling, could cause the observed large difference in the transport parameters. This argument is also used to account for the large difference in the mobilities of the organic semiconductors, metal-free phthalocyanine,[4] and copper phthalocyanine.[5] On the other hand, in another type of organic semiconductors (e. g., naphthalene), the same argument does predict the electron and the hole mobilities to be of the same order of magnitude, in agreement with the experimental results.[6]

Another interesting finding of Spear's experiments[2] is that there is a nonconducting optical-absorption band at 4 eV. A similar absorption was also observed in vitreous selenium.[7] In both cases, it was interpreted as due to "localized excitons."[2,7] In Sec. VI we study the excited states of the crystal and show that a localized excited state does exist in solids with puckered eight-atom rings as building blocks.

II. CRYSTAL STRUCTURE AND SPACE GROUP

The crystal structure of orthorhombic sulfur is a face-centered orthorhombic lattice with 16 molecules (S_8) in a structural unit cell.[8] The molecules are arranged such that the molecular planes are parallel to the c axis and make an angle of $\arctan(\pm b/a)$ with the a axis (Fig. 1).

The primitive cell, which is defined by the three primitive translations

$$\vec{t}_1 = \tfrac{1}{2}(a\hat{i} + b\hat{j}), \quad \vec{t}_2 = \tfrac{1}{2}(b\hat{j} + c\hat{k}),$$
$$\vec{t}_3 = \tfrac{1}{2}(c\hat{k} + a\hat{i}) \quad , \tag{1}$$

has one-fourth the volume of the structural unit cell abc and contains four molecules. The coordinates of a point (x, y, z) expressed in fractions of a, b, and c, respectively, and those expressed in terms of t_1, t_2, and t_3 (ξ, η, ζ, respectively), are related by
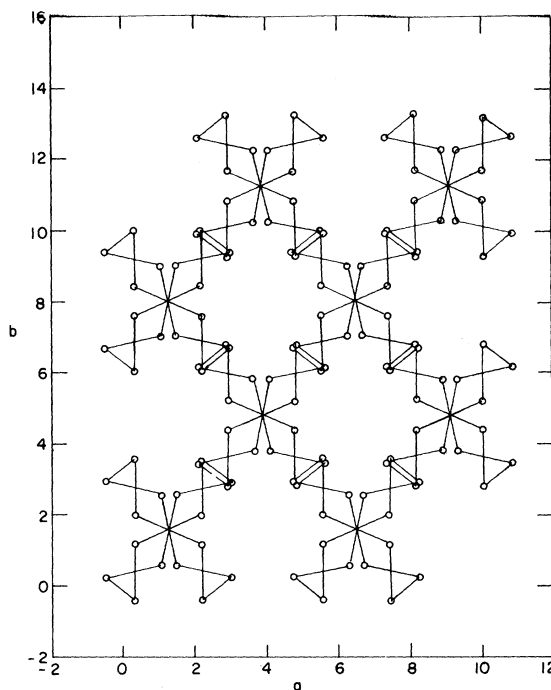

FIG. 1. Crystal structure of orthorhombic sulfur, showing atomic positions in a unit cell projected on the ab plane.

$$x a\hat{i} + y b\hat{j} + z c\hat{k} = \tfrac{1}{2}\xi(a\hat{i} + b\hat{j}) + \tfrac{1}{2}\eta(b\hat{j} + c\hat{k}) + \tfrac{1}{2}\zeta(c\hat{k} + a\hat{i}) \tag{2}$$

or

$$\xi = x + y - z, \quad \eta = -x + y + z, \quad \zeta = x - y + z. \tag{3}$$

The primitive vectors of the reciprocal space are given in terms of a, b, and c as

$$\vec{q}_1 = \hat{i}/a + \hat{j}/b - \hat{k}/c, \quad \vec{q}_2 = -\hat{i}/a + \hat{j}/b + \hat{k}/c,$$
$$\vec{q}_3 = \hat{i}/a - \hat{j}/b + \hat{k}/c. \tag{4}$$

Conversely, the reciprocal unit vectors in the a, b, and c directions are, in terms of $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$,

$$\vec{q}_a = \hat{i}/a = \tfrac{1}{2}(q_3 + q_1), \quad \vec{q}_b = \hat{j}/b = \tfrac{1}{2}(q_1 + q_2),$$
$$\vec{q}_c = \hat{k}/c = \tfrac{1}{2}(q_2 + q_3). \tag{5}$$

The space group is D_{2h}^{24}, and the factor group is isomorphic to the point group D_{2h} and contains the following eight operations:

$$E(x, y, z), \quad C_a(x, -y \pm \tfrac{1}{4}, -z \pm \tfrac{1}{4}),$$
$$C_b(-x \pm \tfrac{1}{4}, y, -z \pm \tfrac{1}{4}), \quad C_c(-x \pm \tfrac{1}{4}, -y \pm \tfrac{1}{4}, z),$$
$$I(-x, -y, -z), \quad \sigma_a(-x, y \mp \tfrac{1}{4}, z \mp \tfrac{1}{4}) = I C_a,$$
$$\sigma_b(x \mp \tfrac{1}{4}, -y, z \mp \tfrac{1}{4}) = I C_b, \tag{6}$$

TABLE I. Atomic positions in a unit cell given in fractions of a, b, c.

Atom[a]	x	y	z
1	-0.1446	-0.0474	-0.0484
2	-0.2931	-0.0205	0.0040
3	-0.2156	0.0301	0.0763
4	-0.2138	-0.0927	0.1290

[a]See Fig. 1 in Ref. 1 for the numbering of atoms in a molecule.

$$\sigma_c\left(x \mp \tfrac{1}{4},\ y \mp \tfrac{1}{4},\ -z\right) = I\,C_c,$$

where x, y, z are the fractional coordinates of a point with a, b, and c as the axes. The two operations distinguished by $\pm$ signs are, in fact, identical because they result in two points separated by a primitive translation $\vec{t}_i$. For example, from Eq. (3) we see that the two C_a operations on a point $(\xi,\ \eta,\ \zeta)$ result in the two points with

$$\xi' = x - y + z,\quad \eta' = -x - y - z \pm 0.5,\quad \zeta' = x + y - z,$$

which are separated by $\vec{t}_2$. The factor group has eight one-dimensional irreducible representations.[9]

The coordinates of atoms in a unit cell are given by Abraham.[8] The four atoms of a molecule are located at the coordinates given in Table I. (See Fig. 1 in Ref. 1 for the numbering of atoms in a molecule.) The other four atoms of the same molecule are related to these four by the operation C_c, Eq. (6) (with $-$ sign), i.e.,

$$x_i = -x_j - \tfrac{1}{4},\quad y_i = -y_j - \tfrac{1}{4},\quad z_i = z_j, \tag{7}$$

where i runs from 5 to 8 and

$$j = 9 - i. \tag{8}$$

The four operations of the factor group E, $C_a(-)$, I, and $\sigma_a(+)$ combined with the four fractional translations $(0,\ 0,\ 0)$, $(0,\ \tfrac{1}{2},\ \tfrac{1}{2})$, $(\tfrac{1}{2},\ 0,\ \tfrac{1}{2})$, and $(\tfrac{1}{2},\ \tfrac{1}{2},\ 0)$ generate all the atomic coordinates of the 16 molecules from the above set of 8. The four molecules in the primitive cell are those obtained by applying the above four factor-group operations to the original set. We shall denote these four molecules by A, B, C, and D, respectively. They transform among one another under the operations of the factor group according to the scheme shown in Table II.

Only the identity E and the twofold rotation axis parallel to the c axis are common to the factor group and the molecular symmetry group D_{4d}. Thus the site group is the point group C_2. The operation C_{2x}, whose axis bisects the bond 1-8, of the molecular group D_{4d} (see Sec. III in Ref. 1) corresponds to C_c rotation of the factor group.

A crystal electronic state, belonging to the irreducible representation Γ of the factor group,

can be formed only from those molecular states belonging to the irreducible representations γ of the molecular symmetry group where the characters χ of the site-group elements in Γ and γ are identical. Therefore, crystal states A_{1g}, B_{1g}, A_{1u}, and B_{1u} are formed from molecular states A_1, B_1, and the first components of E_1, E_2, and E_3 (characters of E and C_2 are both 1); and crystal states B_{2g}, B_{3g}, B_{2u}, and B_{3u} are formed from molecular states A_2, B_2, and the second components of E_1, E_2, and E_3 (characters of E and C_2 are 1 and -1, respectively).

Let $\vec{R}_l$ be the vector from the origin to the center of the primitive cell l, and $\vec{\tau}_A$, $\vec{\tau}_B$, $\vec{\tau}_C$, and $\vec{\tau}_D$ be the vectors from the center of the primitive cell to the centers of the molecules A, B, C, and D, respectively; then a crystal-state wave function (unnormalized) with wave vector $\vec{k}$ and belonging to the irreducible representation Γ of the factor group can be written as

$$\Psi_\Gamma(\vec{k}) = \sum_{x = A,B,C,D} F_{\Gamma x}\,\psi_x(\vec{k}), \tag{9}$$

where $\psi_x(\vec{k})$ is the Bloch sum of the molecular wave functions ϕ,

$$\psi_x(\vec{k}) = e^{i\vec{k}\cdot\vec{\tau}_x} \sum_l e^{i\vec{k}\cdot\vec{R}_l}\,\phi(\vec{r} - \vec{R}_l - \vec{\tau}_x), \tag{10}$$

and the coefficients $F_{\Gamma x}$ can be determined from Table II, in terms of the characters of operations in the factor group, as

$$F_{\Gamma A} = \chi_\Gamma(E) = 1, \qquad F_{\Gamma B} = \chi_\Gamma(C_a) = \pm 1,$$
$$F_{\Gamma C} = \chi_\Gamma(I) = \pm 1, \qquad F_{\Gamma D} = \chi_\Gamma(\sigma_a) = \pm 1. \tag{11}$$

Equation (9), with Eqs. (10) and (11), describes the states of either an excess carrier or an exciton in this molecular crystal, depending on whether ϕ in Eq. (10) is a one-electron MO or a molecular excited state. The former is treated in Sec. III and the latter in Sec. VI.

III. EXCESS-CARRIER ENERGY-BAND STRUCTURE

The energy of an excess carrier in the crystal state Eq. (9) can be written as

TABLE II. Transformation of the four molecules in a primitive cell under the factor-group operations. A prime on a molecule (e.g., B') denotes that the molecule under column E (e.g., A) is transformed into the molecular position B but with the atom i in the position of atom j related by Eq. (8).

E	C_a	C_b	C_c	I	σ_a	σ_b	σ_c
A	B	B'	A'	C	D	D'	C'
B	A	A'	B'	D	C	C'	D'
C	D	D'	C'	A	B	B'	A'
D	C	C'	D'	B	A	A'	B'

$$E_\Gamma(\vec{k}) = \langle \Psi_\Gamma(\vec{k}) | \mathcal{H} | \Psi_\Gamma(\vec{k}) \rangle / \langle \Psi_\Gamma(\vec{k}) | \Psi_\Gamma(\vec{k}) \rangle . \quad (12)$$

The denominator is the normalization integral and, on neglecting the overlap integrals between two MO's centered on different molecules, we have

$$\langle \Psi_\Gamma(\vec{k}) | \Psi_\Gamma(\vec{k}) \rangle = \sum_{lx} \sum_{my} F_{\Gamma x} F_{\Gamma y}$$

$$\times \exp[i\vec{k}(\vec{R}_{lx} - \vec{R}_{my})] \delta_{lm} \delta_{xy}$$

$$= \sum_{lx} F_{\Gamma x}^2 = 4N, \quad (13)$$

where N is the total number of primitive cells, and we have used Eq. (11). The indexes l, m, and n re-

fer to cells, and x, y, and z refer to the molecules in a primitive cell. The following abbreviations are used throughout this paper:

$$\vec{R}_{lx} = \vec{R}_l + \vec{\tau}_x , \quad (14)$$

$$\phi(lx) = \phi(\vec{r} - \vec{R}_l - \vec{\tau}_x). \quad (15)$$

With the Hamiltonian

$$\mathcal{H} = -(\hbar^2/2m) \nabla^2 + \sum_{nz} V_{nz}, \quad (16)$$

where V_{nz} is the potential of a neutral molecule nz, the numerator becomes

$$\langle \Psi_\Gamma(\vec{k}) | \mathcal{H} | \Psi_\Gamma(\vec{k}) \rangle = \sum_{lx} F_{lx}^2 \langle \phi(lx) | - (\hbar^2/2m) \nabla^2 + V_{lx} + {\sum_{nz}}' V_{nz} | \phi(lx) \rangle + \sum_{lx} \sum_{my} F_{\Gamma x} F_{\Gamma y}$$

$$\times \exp[i\vec{k} \cdot (\vec{R}_{lx} - \vec{R}_{my})] \langle \phi(my) | (\hbar^2/2m) \nabla^2 + V_{lx} + V_{my} | \phi(lx) \rangle$$

$$= \sum_{lx} F_{\Gamma x}^2 [\epsilon + {\sum_{my}}' \langle \phi(lx) | V_{my} | \phi(lx) \rangle] + \sum_{lx} {\sum_{my}}' F_{\Gamma x} F_{\Gamma y} \exp[i\vec{k} \cdot (\vec{R}_{lx} - \vec{R}_{my})] \langle \phi(my) | V_{my} | \phi(lx) \rangle ,$$

$$(17)$$

where we have neglected three-molecule integrals, and ϵ is the MO energy of ϕ in an isolated molecule. Noting that the sum over my is independent of lx, and using Eq. (11) again, we have

$$\langle \Psi_\Gamma(\vec{k}) | \mathcal{H} | \Psi_\Gamma(\vec{k}) \rangle = 4N[\epsilon + {\sum_{my \neq 1A}}' \langle \phi(1A) | V_{my} | \phi(1A) \rangle$$

$$+ F_{\Gamma A} {\sum_{my \neq 1A}}' F_{\Gamma y} \langle \phi(my) | V_{my} | \phi(1A) \rangle$$

$$\times \cos(\vec{k} \cdot (\vec{R}_{1A} - \vec{R}_{my}))]. \quad (18)$$

Moving the origin of $\vec{R}$ to $\vec{R}_{1A}$, and noting $F_{\Gamma A} = 1$, we finally have

$$E_\Gamma(\vec{k}) = \epsilon + {\sum_{my \neq 1A}}' \langle \phi(1A) | V_{my} | \phi(1A) \rangle$$

$$+ {\sum_{my \neq 1A}}' F_{\Gamma y} \langle \phi(my) | V_{my} | \phi(1A) \rangle \cos\vec{k} \cdot \vec{R}_{my}. \quad (19)$$

The $\vec{k}$ dependence of the energy appears only in the third term. In terms of $\vec{q}_i$, Eq. (4),

$$\vec{k} = \beta_1 \vec{q}_1 + \beta_2 \vec{q}_2 + \beta_3 \vec{q}_3 , \quad (20)$$

where the β's vary from $-\pi$ to $+\pi$. For a special direction of $\vec{k}$, e.g., in the direction of crystal axis a [see Eq. (5)],

$$\vec{k}_a = \beta_1(\vec{q}_1 + \vec{q}_3) = \alpha \vec{q}_a , \quad (21)$$

where α varies from -2π to 2π.

The intermolecular energy integral

$$W_{AB} = \langle \phi(B) | V_B | \phi(A) \rangle \quad (22)$$

determines the width of the energy band and therefore is important in the discussion of carrier-

transport properties. In Sec. IV, we calculate this quantity with the MO's obtained in Ref. 1.

IV. INTERMOLECULAR ENERGY INTEGRALS

The ith MO, centered on molecule A, is represented by a linear combination of atomic orbitals (LCAO):

$$\phi_i(A) = \sum_{\alpha=1}^{8} \sum_{\mu=1}^{4} f_{i\alpha\mu} \varphi_{A\alpha\mu} . \quad (23)$$

We use the indexes i, j, k to specify a MO; α, β, γ to specify an atom; and μ, ν, ω to specify an atomic orbital. The potential of a neutral molecule B is given by[10]

$$V_B = \sum_r (-z_r e^2/r_\gamma) + \sum_{j=occ} (2J_j - K_j), \quad (24)$$

where Z_γ is the nuclear charge of atom γ in B, and

$$\langle \phi_i | J_j | \phi_k \rangle = \langle \phi_i \phi_j | e^2/r_{12} | \phi_k \phi_j \rangle$$

$$\equiv (\phi_i \phi_k | \phi_j \phi_j), \quad (25)$$

$$\langle \phi_i | K_j | \phi_k \rangle = \langle \phi_i \phi_j | e^2/r_{12} | \phi_j \phi_k \rangle$$

$$\equiv (\phi_i \phi_j | \phi_j \phi_k). \quad (26)$$

Substituting Eqs. (23)–(26) into Eq. (22), we have

$$W_{AB} = \langle \phi_i(A) | V_B | \phi_{i(B)} \rangle$$

$$= e^2 \sum_{\alpha\mu} \sum_{\beta\nu} f_{i\alpha\mu} f_{i\beta\nu} \{\sum_\gamma (-z_\gamma) \langle \varphi_{A\alpha\mu} | 1/r_\gamma | \varphi_{B\beta\nu} \rangle$$

$$+ \sum_{j=occ} \sum_{\alpha'\mu'} \sum_{\beta'\nu'} f_{j\alpha'\mu'} \, f_{j\beta'\nu'}$$

$$\times [2(\varphi_{A\alpha\mu} \varphi_{B\beta\nu} | \varphi_{B\alpha'\mu'} \varphi_{B\beta'\nu'})$$

$$- (\varphi_{A\alpha\mu}\varphi_{B\beta'\nu'} | \varphi_{B\alpha'\mu'} \varphi_{B\beta\nu})]\}. \qquad (27)$$

By neglecting three-center integrals, the nuclear potential term becomes

$$\sum_{\gamma} (- Z_{\gamma}) \langle \varphi_{A\alpha\mu} | 1/r_{\gamma} | \varphi_{B\beta\nu} \rangle$$

$$= - Z \langle \varphi_{A\alpha\mu} | | 1/r_{\beta} | \varphi_{B\beta\nu} \rangle , \qquad (28)$$

the nuclear charge Z being the same (6) for all atoms in S_8. The Coulomb term can be approximated as

$$2\sum_j \sum_{\alpha'\mu'} \sum_{\beta'\nu'} f_{j\alpha'\mu'} f_{j\beta'\nu'} (\varphi_{A\alpha\mu} \varphi_{B\beta\nu} | \varphi_{B\alpha'\mu'} \varphi_{B\beta'\nu'}) = 2\sum_j \sum_{\alpha'\mu'} f_{j\alpha'\mu'} \left(\sum_{\beta'\nu'} f_{j\beta'\nu'} S_{\alpha'\mu'\beta'\nu'} \right) (\varphi_{A\alpha\mu} \varphi_{B\beta\nu} | \varphi_{B\alpha'\mu'} \varphi_{B\alpha'\mu'})$$

$$= 2\sum_{\mu'} \left[\sum_j f_{j\beta\mu'} \left(\sum_{\beta'\nu'} f_{j\beta'\nu'} S_{\alpha'\mu'\beta'\nu'} \right) \right] (\varphi_{A\alpha\mu} \varphi_{B\beta\nu} | \varphi_{B\beta\mu'} \varphi_{B\beta\mu'}) = 2\sum_{\mu'} Q_{\mu'\mu'} (\varphi_{A\alpha\mu} \varphi_{B\beta\nu} | \varphi_{B\beta\mu'} \varphi_{B\beta\mu'}), \qquad (29)$$

where $S_{\alpha\mu\beta\nu}$ is the overlap integral between the atomic orbitals μ on α and ν on β, and the modified charge-density matrix,

$$Q_{\mu\omega} = \sum_{j=occ} f_{j\alpha\mu} \left(\sum_{\beta\nu} f_{j\beta\nu} \, S_{\alpha\omega\beta\nu} \right), \qquad (30)$$

which, in case of S_8, is independent of α by symmetry (Table III). The exchange term is similarly approximated as

$$\sum_j \sum_{\alpha'\mu'} \sum_{\beta'\nu'} f_{j\alpha'\mu'} f_{j\beta'\nu'} (\varphi_{A\alpha\mu} \varphi_{B\beta'\nu'} | \varphi_{B\alpha'\mu'} \varphi_{B\beta\nu}) = \sum_j \sum_{\alpha'\mu'} f_{j\alpha'\mu'} \sum_{\beta'\nu'} f_{j\beta'\nu'} S_{\beta\nu\alpha'\mu'} (\varphi_{A\alpha\mu} \varphi_{B\beta'\nu'} | \varphi_{B\beta\nu} \varphi_{B\beta\nu})$$

$$= \sum_{\nu'} \left[\sum_j f_{j\beta\nu'} \left(\sum_{\alpha'\mu'} f_{j\alpha'\mu'} S_{\beta\nu\alpha'\mu'} \right) \right] (\varphi_{A\alpha\mu} \varphi_{B\beta\nu'} | \varphi_{B\beta\nu} \varphi_{B\beta\nu})$$

$$= \sum_{\nu'} Q_{\nu'\nu} (\varphi_{A\alpha\mu} \varphi_{B\beta\nu'} | \varphi_{B\beta\nu} \varphi_{B\beta\nu}). \qquad (31)$$

The hybrid integrals in Eqs. (29) and (31) are calculated with the Mulliken approximation[11] as

$$(\varphi_{A\alpha\mu}\varphi_{B\beta\mu} | \varphi_{B\beta\mu'} \varphi_{B\beta\mu'})$$

$$= \tfrac{1}{2} S_{\alpha\mu\beta\nu} [(\varphi_{A\alpha\mu} \varphi_{A\alpha\mu} | \varphi_{B\beta\mu'} \varphi_{B\beta\mu'})$$

$$+ (\varphi_{B\beta\nu} \varphi_{B\beta\nu} | \varphi_{B\beta\mu'} \varphi_{B\beta\mu'})]$$

$$= \tfrac{1}{2} S_{\alpha\mu\beta\nu} [1/R_{\alpha\beta} + (\nu\nu | \mu'\mu')], \qquad (32)$$

where the one-center–two-electron integral $(\nu\nu | \mu'\mu')$ can be obtained from the Hartree-Fock atomic calculation,[12] and the values for sulfur are given in Table III. The last step in the approximation is justified because α and β are on different molecules and $R_{\alpha\beta} > 3.5$ Å.

Similarly, we have

$$(\varphi_{A\alpha\mu}\varphi_{B\beta\nu'} | \varphi_{B\beta\nu} \varphi_{B\beta\nu})$$

$$= \tfrac{1}{2} S_{\alpha\mu\beta\nu'} [1/R_{\alpha\beta} + (\nu'\nu' | \nu\nu)]. \qquad (33)$$

Substituting Eqs. (28), (29), and (31)–(33) into Eq. (27), we have

$$W_{AB} = e^2 \sum_{\alpha\mu} \sum_{\beta\nu} f_{i\alpha\mu} f_{i\beta\nu}$$

$$\times \{(- Z) \langle \varphi_{A\alpha\mu} | 1/r_{\beta} | \varphi_{B\beta\nu} \rangle + \sum_{\mu'} (Q_{\mu'\mu'} S_{\alpha\mu\beta\nu}$$

$$- \tfrac{1}{2} Q_{\mu'\nu} S_{\alpha\mu\beta\mu'})[1/R_{\alpha\beta} + (\nu\nu | \mu'\mu')]\}. \qquad (34)$$

This integral decreases rapidly with the increase

TABLE III. One-center–two-electron integrals $(\mu\mu/\nu\nu)$ for sulfur (in eV) and the modified charge-density matrix Q Eq. (30) for an S_8 molecule.

$(\mu\mu/\nu\nu)$ [a]	$3s$	$3px$	$3py$	$3pz$
$3s$	14.29	13.00	13.00	13.00
$3px$		12.50	10.80	12.70
$3py$			14.86	10.34
$3pz$				12.96
$Q_{\mu\nu}$ [b]				
$3s$	0.6004	0.1230	0.0	0.2094
$3px$	0.1439	0.9249	0.0	−0.0579
$3py$	0.0	0.0	0.6100	0.0
$3pz$	0.2400	−0.0582	0.0	0.8647

[a]Deduced from F^0 (3s, 3s), F^0 (3s, 3p), etc., in Ref. 9.

[b]Calculated from the MO's in Ref. 1.

in the distance between the two molecules A and B. We have calculated the integrals between the molecule $1A$ (Sec. II) and the 15 molecules listed in Table IV. The contributions from atom pairs separated by more than 6.5 Å have been ignored. The results for the five upper occupied MO's and the four lower empty MO's are given in Table V. All intermolecular integrals are of the order of 0.1 eV or less. Contrary to the suggestions of Gibbons,[2] the integrals between the occupied MO's (mostly consisting of lone pairs) are not always much larger than those between the empty MO's (mostly consisting of σ hybrids). Rather, it seems that a more important factor is the total symmetry of the MO. For example, MO 22, which is a totally symmetric orbital (A_1), gives a large W_{AB} for molecules 8 and 9 (nearest neighbors of the reference molecule), while MO 24, which is of symmetry $E_3(xz)$, gives a large value of W_{AB} for molecule 3, which is not nearest geometrically. For the same molecule (say the nearest-neighbor molecule 9), the more symmetric MO 25 (A_2) gives a larger value of W_{AB} than the less symmetric MO 23 and MO 24 (E_3).

Substituting these values of W_{AB} in Eq. (19), we obtain the band structure. Each band splits into four branches, corresponding to four irreducible representations of the factor group (Sec. II). The band structures with $\vec{k}$ in the directions of the crystal axes are shown in Fig. 2 for three hole bands and two electron bands of lowest energies. The vibrational overlap (see Sec. V) is assumed to be unity. All bandwidths are found to be of the same order of magnitude. The widest hole band (generated from MO 22) is only about three times wider than the electron bands. It is unlikely that such a small difference will lead to a completely different behavior in electron and hole transports.

In the derivation of the expression [Eq. (34)], for W_{AB}, we have assumed that the overlap integral between the vibrational wave functions of the neutral molecule and the molecular anion (or cation) is unity. If this is not so, the quantities W_{AB}, and hence the bandwidths, are reduced by a factor

TABLE IV. Fifteen molecules nearest to the reference molecule $1A$. R_{lx} is the vector to the center of molecule in fractions of a, b, and c, with the center of molecule $1A$ as the origin.

Mol.	Type	Prim. cell			R_{lx}		
Ref.	A	0	0	0	0.0	0.0	0.0
1	A	0	1	$\bar{1}$	-0.5	0.5	0.0 } Equiv.[a]
2	A	0	$\bar{1}$	1	0.5	-0.5	0.0
3	B	0	0	0	0.0	0.0	-0.33
4	B	0	1	0	0.0	0.5	0.17 } Equiv.
5	B	$\bar{1}$	0	1	0.0	-0.5	0.17
6	B	0	0	1	0.5	0.0	0.17 } Equiv.
7	B	$\bar{1}$	1	0	-0.5	0.0	0.17
8	C	0	0	0	0.25	0.25	-0.08 } Equiv.
9	C	$\bar{1}$	0	0	-0.25	-0.25	-0.08
10	C	$\bar{1}$	1	$\bar{1}$	-0.75	0.25	-0.08 } Equiv.
11	C	0	$\bar{1}$	1	0.75	-0.25	-0.08
12	D	0	0	$\bar{1}$	-0.25	0.25	-0.25 } Equiv.
13	D	0	$\bar{1}$	0	0.25	-0.25	-0.25
14	D	0	0	0	0.25	0.25	0.25 } Equiv.
15	D	$\bar{1}$	0	0	-0.25	-0.25	0.25

[a]The two molecules are equivalent as far as the integral Eq. (34) is concerned.

equal to the square of the vibrational overlap S_{vib}.[10,13,14] In this case we are dealing with the transport of small polarons.[13,14]

V. VIBRONIC INTERACTION IN SULFUR

An expression for the vibrational overlap S_{vib} has been given by Hutchisson,[15] and Siebrand[14] has related the expression to a parameter γ in the polaron theory[13]

$$(S_{vib})^2 = f(\gamma) e^{-\gamma}, \qquad (35)$$

where $f(\gamma)$ is a polynomial of γ depending on the vibrational quantum states, and γ is the ratio of the polaron binding energy E_b to the energy of a vibrational quantum $\hbar \omega$:

$$\gamma = E_b / \hbar \omega. \qquad (36)$$

The polaron binding energy E_b can be represented by the molecular quantities as

$$E_b = \tfrac{1}{2} k (\Delta q)^2, \qquad (37)$$

TABLE V. Intermolecular integrals in eV.

| Rep.	MO	Mol. 1	Mol. 3	Mol. 5	Mol. 7	Mol. 9	Mol. 11	Mol. 13	Mol. 15
$E1$-1	20	0.0081	0.0047	-0.0051	-0.1541	0.1424	-0.0065	-0.0017	0.0963
$E1$-2	21	-0.0182	0.0092	-0.0848	0.0124	0.1345	-0.0328	0.0371	-0.0447
$A1$	22	0.0100	-0.0060	-0.0338	-0.1174	-0.3677	-0.0196	0.0155	-0.0546
$E3$-1	23	-0.0671	-0.0068	-0.0639	-0.0163	-0.0311	-0.0179	-0.0131	-0.0157
$E3$-2	24	0.0075	0.1557	-0.0412	0.0125	-0.0613	0.0016	-0.0521	-0.0354
$A2$	25	-0.0062	0.0059	-0.0391	0.0566	0.1026	-0.0072	-0.0299	-0.0299
$B2$	26	0.0278	-0.0276	0.0228	-0.0591	0.1249	0.0220	-0.0504	-0.0205
$E1$-1	27	0.0195	0.0228	-0.0363	0.0300	-0.2032	-0.0109	0.0131	-0.1142
$E1$-2	28	-0.0170	0.0285	-0.0095	-0.0037	-0.1841	0.0173	0.0552	-0.0131
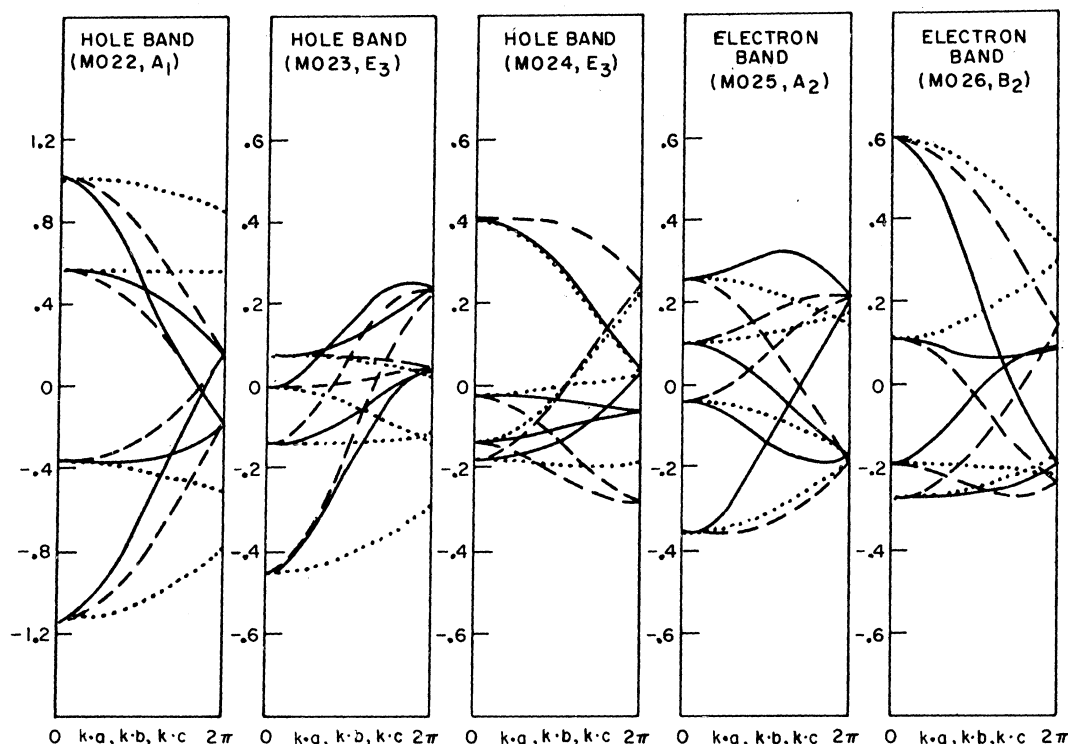
FIG. 2. Excess hole and electron bands of orthorhombic sulfur, with wave vectors $\vec{k}$ along the crystal axes a (full line), b (broken line), and c (dotted line). Vibrational overlap is 1.

where k is the force constant and Δq is the difference in the nuclear configurations of a neutral molecule and a molecular ion with an excess electron (or hole).

A semiquantitative estimate of the quantity Δq for a S_8 molecule can be obtained from the MO's in Ref. 1 as follows.

We define a quantity $B_{\alpha\beta}$, the bond charge between atoms α and β, by

$$B_{\alpha\beta} = \sum_{i=occ} N_i \sum_{\mu,\nu} f_{i\alpha\mu} f_{i\beta\nu} S_{\alpha\mu\beta\nu}, \qquad (38)$$

where N_i is the number of electrons occupying the MO ϕ_i [Eq. (23)], the f's are the LCAO coefficients, and $S_{\alpha\mu\beta\nu}$ is the overlap integral between atomic orbital (AO) $\alpha\mu$ and $\beta\nu$. This quantity is analogous to the bond order in the π electron theory of organic molecules.[16] The latter has been proved to be inversely proportional to the bond lengths. The difference of the bond orders of a molecular ion and a neutral molecule has been used to estimate the vibrational overlaps of aromatic hydrocarbons.[17] Although it is not simple to establish a quantitative relation between the change in the nuclear configuration Δq and the change in $B_{\alpha\beta}$ for a three-dimensional molecule, there is no doubt that a large change in $B_{\alpha\beta}$ implies a large Δq.

The calculated values of $B_{\alpha\beta}$ for a neutral molecule (24 occupied MO) and the change in $B_{\alpha\beta}$, $\Delta B_{\alpha\beta}(i)$, when an extra electron $(i > 24)$ or a hole $(i \leqslant 24)$ is present in the MO i, are shown in Fig. 3. In general, an extra electron in S_8 creates a larger change in $B_{\alpha\beta}$ than an extra hole does. This is reasonable because an extra electron goes into MO's, which are mostly of σ hybrids and therefore have large densities along the bonds, whereas an extra hole goes into MO's of largely lone-pair hybrids which have less densities along the bonds.

The $\Delta B_{\alpha\beta}$ for a molecular anion with an extra electron in the lowest empty MO 25 is a factor of 3.6 larger than that of a cation with an extra hole in the highest occupied MO (23 or 24) (the average $\Delta B_{\alpha\beta}$ over the eight bonds, -0.015, being used). If there is a direct proportionality between ΔB and Δq, then the polaron binding energy $E_b(e)$ associated with the anion will be a factor of $(3.6)^2 = 13$ larger than that associated with the cation $E_b(h)$; consequently,

$$\gamma \text{ (electron)} \approx 13\gamma \text{ (hole)}. \qquad (39)$$

Since the effect of vibronic coupling is important only when $\gamma > 1$, and because of the exponential dependence Eq. (35), a factor of 13 in γ could reduce the bandwidth by more than five orders of magnitude.
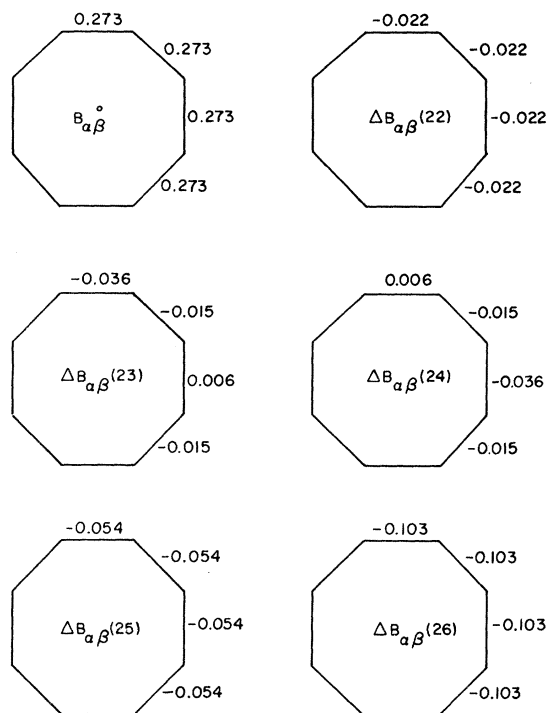
FIG. 3. Bond charges of neutral S_8 molecule $B^0_{\alpha\beta}$ and the changes in the bond charges $\Delta B_{\alpha\beta}(i)$ when an extra electron ($i > 24$) or an extra hole ($i \leq 24$) is placed in MO i. The quantities are symmetric with respect to the center of the octagon.

In naphthalene and anthracene, because of the special characteristics of alternant hydrocarbons,[16] the changes in bond orders when an electron is added to or removed from the neutral molecule are equal (and opposite in signs). Thus both electron and hole have equal vibronic couplings, and since the electronic intermolecular energy integrals are of the same order of magnitude,[10] we expect the electron and the hole mobilities to be of the same order of magnitude. This is in agreement with the experimental findings.[6]

Another example of the effect of different vibronic coupling is in the phtholocyanines. Copper phthalocyanine[5] has been observed to have a mobility of about 100 cm²/V sec, approximately three orders of magnitude larger than that of metal-free phthalocyanine. The large mobility in copper phthalocyanine was attributed to the presence of the copper $3d$ orbitals which provides an out-of-plane interaction with the neighboring molecule.[5] However, a calculation[18] similar to those performed for metal-free phthalocyanine[19] indicates that the intermolecular electronic interaction in both copper and metal-free phthalocyanines are of the same order of magnitude. An alternative and more con-

vincing explanation for the large difference in the mobilities of the two phthalocyanines can be given as follows: In copper phthalocyanine, the highest occupied MO consists of mostly the copper $3d$ orbital and is half-filled.[20] Therefore, either an electron is added to or removed from the molecule, the change in the bond charge $\Delta B_{\alpha\beta}$ is that contributed from the MO mostly localized at the center of the molecule. On the other hand, both the highest occupied and the lowest empty MO's of metal-free phthalocyanine[21] are delocalized π orbitals spread almost uniformly over the molecule. An extra hole or electron in such orbitals would give rise to a larger change in the bond charge, and therefore, larger change in the nuclear configuration. Thus we expect the polaron binding energy E_b to be larger for metal-free phthalocyanine than for copper phthalocyanine. The difference of three orders of magnitude in the mobilities can easily be accounted for by the exponential dependence of the bandwidths on E_b.

Therefore, we conclude that the difference of orders of magnitude in mobilities can be more easily accounted for by the difference in the polaron binding energies, or equivalently, in the vibronic couplings, than by the difference in electronic-intermolecular overlaps.

VI. NONCONDUCTING OPTICAL ABSORPTION

Another interesting point in the transport properties of orthorhombic sulfur is the existence of a nonconducting optical-absorption band near 4 eV.[2] Spear and co-workers[2] have interpreted it as due to "localized excitons," without commenting why such excitons are "localized."

In molecular crystals, the formation of molecular excitons is the primary process of optical absorption,[22] and such excitons are believed to be the precursors of the mobile charges.[23] Therefore, excitons do not account for the nonconducting absorption unless they are localized at a molecular site, so that they cannot propagate to an imperfection where they dissociate.

In general, because of the small but finite intermolecular forces, a crystal state, in which some one selected molecule is excited, is not a stationary solution of the crystal Schrödinger equation. The correct solutions are states corresponding to a delocalization of the excitation over all molecules in the crystal and can be represented by the wave function equations (9) and (10) with $\phi(\vec{r} - \vec{R}_l - \vec{\tau}_x)$ representing a state in which the molecule at cell l, site x, is excited:

$$\phi(\vec{r} - \vec{R}_l - \vec{\tau}_x) = \chi^*_{lx} \prod_{my \neq lx}{}' \chi_{my}, \tag{40}$$

where χ^* and χ represent an excited-state and the

ground-state wave functions, respectively.[24] The energy of this crystal state can be written as[22,24]

$$E_\Gamma(\vec{k}) = E_G + \Delta E + \sum_{mylx}{}' \{\langle \chi_{lx}^* \chi_{my} | V_{lx,my} | \chi_{lx}^* \chi_{my} \rangle$$

$$- \langle \chi_{lx} \chi_{my} | V_{lx,my} | \chi_{lx} \chi_{my} \rangle + F_{\Gamma y}$$

$$\times \exp[i\vec{k} \cdot \vec{R}_{my}] \langle \chi_{lx}^* \chi_{my} | V_{lx,my} | \chi_{lx} \chi_{my}^* \rangle\}, \quad (41)$$

where Γ is the irreducible representation of the state, E_G is the ground-state energy, ΔE is the excitation energy in an isolated molecule and $V_{lx,my}$ is the intermolecular-pair interaction potential. The first two terms in the curly bracket contribute to the shift of the "center of gravity" from the excitation energy of the isolated molecule, and the last term contributes to the splitting of states belonging to different irreducible representations (Davydov splitting). The latter is also a measure of the effectiveness of the transfer of the excitation from molecule A to molecule B by the interaction V_{AB}, hence the name excitation-transfer matrix element[25]:

$$T_{AB} = \langle \chi_A^* \chi_B | V_{AB} | \chi_A \chi_B^* \rangle. \quad (42)$$

The potential V_{AB} can be written as

$$V_{AB} = \sum_{K,L} \frac{Z_K Z_L e^2}{r_{KL}} - \sum_{K,j} \frac{Z_K e^2}{r_{Kj}} - \sum_{L,i} \frac{Z_L e^2}{r_{Li}} + \sum_{i,j} \frac{e^2}{r_{ij}}, \quad (43)$$

where K and L denote the nuclei in molecules A and B, respectively, and i and j denote the electrons in A and B, respectively.

Assuming that the nuclear part and the electronic part of the wave functions are separable, and that the excited-state and the ground-state electronic parts are strictly orthogonal, we see the first three terms of Eq. (43) have no contribution to the integral Eq. (42). If the excited state χ^* results from the excitation of an electron from the MO η to MO ξ, and if the overlap between the ground-state and the excited-state vibrational wave functions is S_{vib}, then the fourth term in Eq. (43) gives

$$T_{AB} = (S_{vib})^2 \langle \xi_A \eta_B | e^2/r_{12} | \eta_A \xi_B \rangle$$

$$= (S_{vib})^2 (\xi_A \eta_A | \xi_B \eta_B). \quad (44)$$

As in Sec. IV, the integral over MO's can be expanded into sums of integrals over atomic orbitals by expressing the MO's, ξ and η, as LCAO or linear combination of hybrid orbitals (LCHO), Eq. (23):

$$\xi_A = \sum_\alpha \sum_\mu f_{\xi \alpha \mu} \, \varphi_{A\alpha\mu}, \quad (45)$$

$$\eta_B = \sum_\beta \sum_\nu f_{\eta \beta \nu} \, \varphi_{B\beta\nu}, \quad \text{etc.} \quad (46)$$

Then, we have

$$(\xi_A \eta_A | \xi_B \eta_B) = \sum_{\alpha \mu} \sum_{\beta \nu} f_{\xi \alpha \mu} f_{\eta \beta \nu} \sum_{\alpha' \mu'} \sum_{\beta' \nu'} f_{\xi \alpha' \mu'}$$

$$\times f_{\eta \beta' \nu'} (\varphi_{A\alpha\mu} \, \varphi_{A\beta\nu} | \varphi_{B\alpha' \mu'} \, \varphi_{B\beta' \nu'}). \quad (47)$$

Using Mulliken's approximation,[11] Eq. (47) becomes

$$(\xi_A \eta_A | \xi_B \eta_B) = \sum_{\alpha \mu} [f_{\xi \alpha \mu} \sum_{\beta \nu} f_{\eta \beta \nu} S_{\alpha \mu \beta \nu}]$$

$$\times \sum_{\alpha' \mu'} [f_{\xi \alpha' \mu'} \sum_{\beta' \nu'} f_{\eta \beta' \nu'} S_{\alpha' \mu' \beta' \nu'}]$$

$$\times (\varphi_{A\alpha\mu} \, \varphi_{A\alpha\mu} | \varphi_{B\alpha' \mu'} \, \varphi_{B\alpha' \mu'}). \quad (48)$$

In the last factor of Eq. (48), the atoms α and α' belong to two different molecules and are separated by more than 3.5 Å. It is a good approximation to replace the Coulomb integral by the Coulomb energy of two electronic charges separated by the interatomic distance $R_{\alpha\alpha'}$:

$$(\varphi_{A\alpha\mu} \, \varphi_{A\alpha\mu} | \varphi_{B\alpha' \mu'} \, \varphi_{B\alpha' \mu'}) \approx e^2/R_{\alpha\alpha'}. \quad (49)$$

Then, Eq. (48) reads

$$(\xi_A \eta_A | \xi_B \eta_B) = e^2 \sum_{\alpha, \alpha'} \frac{g_{\xi\eta\alpha} g_{\xi\eta\alpha'}}{R_{\alpha\alpha'}}, \quad (50)$$

where

$$g_{\xi\eta\alpha} = \sum_\mu (f_{\xi \alpha \mu} \sum_{\beta \nu} f_{\eta \beta \nu} S_{\alpha \mu \beta \nu}) \quad (51)$$

can be evaluated for each pair of MO's, ξ and η, from the MO coefficients and overlap matrix elements in Ref. 1. Of particular interest are the g values for $\xi = $MO 25 and $\eta = $MO 22. As we have mentioned in Sec. VII in Ref. 1, MO 25 (A_2) consists of only the σ hybrids a and b with coefficients equal and opposite in signs (see Table I in Ref. 1). Therefore, for $\xi = 25$

$$g_{\xi\eta\alpha} = f_{\xi \alpha a} \sum_{\beta \nu} f_{\eta \beta \nu} (S_{\alpha a \beta \nu} - S_{\alpha b \beta \nu}). \quad (52)$$

Applying a reflection with respect to a plane through the atom α and the molecular axis (σ_α), the hybrid αa and αb interchange, and $\beta \nu$ becomes $\gamma \omega$, where $\omega = b, a, c, d$, respectively, for $\nu = a, b, c, d$. Thus

$$(S_{\alpha a \beta \nu} - S_{\alpha b \beta \nu}) = (S_{\alpha b \gamma \omega} - S_{\alpha a \gamma \omega}). \quad (53)$$

Now if $\eta = 22$, which is totally symmetric (A_1), then $f_{\eta \beta \nu} = f_{\eta \gamma \omega}$ and Eq. (52) can be written as

$$g_{\xi\eta\alpha} = f_{\xi \alpha a} \sum_{\beta \nu} [f_{\eta \gamma \omega} (S_{\alpha b \gamma \omega} - S_{\alpha a \gamma \omega})]_{\beta \nu}. \quad (54)$$

Since there is one-to-one correspondence between $\beta \nu$ and $\gamma \omega$, Eq. (54) reads

$$g_{\xi\eta\alpha} = f_{\xi \alpha a} \sum_{\gamma \omega} f_{\eta \gamma \omega} (S_{\alpha b \gamma \omega} - S_{\alpha a \gamma \omega}) = -g_{\xi\eta\alpha} \equiv 0 \quad (55)$$

for $\xi = 25$, $\eta = 22$. Substituting in Eqs. (50) and (44), we see that within the accuracy of the approximation Eq. (49), the excitation-transfer matrix element T_{AB} corresponding to the excitation from

MO 22 to MO 25 (Ref. 1) between any two molecules A and B, is always zero. Thus, the excitation $(22 \rightarrow 25)$ on any molecule can be localized on the original site. This probably is the localized excited state leading to the observed nonconducting optical absorption.[2]

According to the MO calculation in Ref. 1, the excitation energy, $\Delta E\ (22 \rightarrow 25) = 3.07$ eV, is smaller than any other molecular transition energies except one, $\Delta E\ (23, 24 \rightarrow 25)$, which is also symmetry forbidden. The difference between this energy value and that of the nonconducting absorption (4.03 eV) probably arises from both the shift in crystal energy level from that of an isolated molecule and the electron correlation.

The argument leading to the existence of a localized excited state, Eqs. (52)–(55), depends only on the symmetry properties of the puckered eight-atom ring, and is independent of the nature of sulfur atoms or crystal. Therefore, the same argument applies to Se_8 ring molecule, a constituent of vitreous selenium in which nonconducting optical absorption has been observed.[7]

[1] I. Chen, preceding paper, Phys. Rev. B **2**, 1053 (1970).

[2] A. R. Adams and W. E. Spear, J. Phys. Chem. Solids **25**, 1113 (1964); W. E. Spear and A. R. Adams, *ibid.* **27**, 281 (1966); D. J. Gibbons and W. E. Spear, *ibid.* **27**, 1917 (1966); P. K. Ghosh and W. E. Spear, J. Phys. C **1**, 1347 (1968); B. E. Cook and W. E. Spear, J. Phys. Chem. Solids **30**, 1125 (1969).

[3] S. A. Rice and J. Jortner, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic, New York, 1965), p. 63.

[4] C. R. Westgate and G. Warfield, J. Chem. Phys. **46**, 94 (1967).

[5] G. H. Heilmeier and S. E. Harrison, Phys. Rev. **132**, 2010 (1963); G. Delacote and M. Schott, Phys. Status Solidi **2**, 1460 (1962).

[6] R. G. Kepler, Phys. Rev. **119**, 1226 (1960).

[7] J. L. Hartke and P. J. Regensburger, Phys. Rev. **139**, A970 (1965).

[8] S. C. Abrahams, Acta Cryst. **8**, 661 (1955); A. Caron and J. Donohue, *ibid.* **14**, 548 (1961).

[9] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon, New York, 1960), p. 450.

[10] R. Silbey, J. Jortner, S. Rice, and M. T. Vala, J. Chem. Phys. **42**, 733 (1965); **43**, 2925 (1965).

[11] R. S. Mulliken, J. Chim. Phys. **46**, 497 (1944).

[12] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).

[13] T. Holstein, Ann. Phys. (N. Y.) **8**, 325 (1959); **8**, 343 (1959).

[14] W. Siebrand, J. Chim. Phys. **40**, 2223 (1964); **40**, 2231 (1964); **41**, 3574 (1964).

[15] E. Hutchisson, Phys. Rev. **36**, 410 (1930).

[16] A Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, (Wiley, New York, 1962).

[17] E. F. McCoy and I. G. Ross, Australian J. Chem. **15**, 573 (1962).

[18] I. Chen (unpublished).

[19] I. Chen, J. Chem. Phys. **51**, 3241 (1969).

[20] I. Chen, M. Abkowitz, and J. H. Sharp, J. Chem. Phys. **50**, 2237 (1969).

[21] I. Chen, J. Mol. Spectry. **23**, 131 (1967).

[22] A. S. Davydov, *Theory of Molecular Excitons*, translated by M. Kasha and M. Oppenheimer (McGraw-Hill, New York, 1962).

[23] D. M. J. Compton, W. G. Schneider, and T. C. Waddington, J. Chem. Phys. **27**, 160 (1957); **28**, 741 (1958).

[24] D. Fox and O. Schnepp, J. Chem. Phys. **23**, 767 (1965).

[25] R. Silbey, J. Jortner, and S. Rice, J. Chem. Phys. **42**, 1515 (1965).