THE JOURNAL OF CHEMICAL PHYSICS VOLUME 44, NUMBER 1 1 JANUARY 1966

Theoretical Studies of Transannular Interactions. I. Benzene Excimer Fluorescence and the Singlet States of the Paracyclophanes

MARTIN T. VALA, JR.,* IAN H. HILLIER, STUART A. RICE, AND JOSHUA JORTNER
Department of Chemistry and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

(Received 18 December 1964; revised manuscript received 6 July 1965)

The changes in the electronic transition energies of benzene which occur on dimerization have been calculated. It is shown that the energy-level splittings due to the interactions between neutral-excitation states are too small to explain the observed anomalous emission from concentrated benzene solutions and the absorption spectra of the paracyclophanes. To extend the theory, the eight-electron problem is treated for configurationally interacting neutral-excitation and charge-resonance states. Intermolecular overlap is included in a way consistent with the use of a core potential in the Goeppert-Mayer–Sklar representation. Use is also made of Hückel LCAO molecular orbital wavefunctions and a linear combination of four Slater carbon-atom $2p\pi$ wavefunctions fit to an SCF function. The anomalous emission from benzene solutions can now be understood to arise from transitions from the lowest excimer state of α-level parentage for benzene molecules ~ 3 or ~ 3.3 Å apart when ground-state repulsion is taken into account. The solution absorption spectra of the paracyclophanes are interpreted within this framework of neutral-excitation–charge-resonance configuration interaction. Finally, dimer symmetries different from D_{6h}, have been invesigated in an attempt to understand the absorption spectra of single crystals of [2.2] paracyclophane.

I. INTRODUCTION

When two planar aromatic molecules are parallel and close to one another, it is to be expected that the interactions between the π-electron charge distributions on the two molecules will lead to modifications of the energies and ordering of the electronic states. To date, such interactions have been realized in two classes of experimental conditions.

Forster and Kasper[1,2] observed that the singlet emission spectrum of pyrene in solution consists of a normal vibrationally structured band and a broad structureless band shifted 6000 cm^{-1} to longer wavelengths. From a study of the absorption spectrum and the concentration dependence of the emission spectrum, it was suggested that the structureless luminescence originated from a species formed by the association of an excited molecule and a molecule in its ground state. This species has been named an *excimer*.[3] Since these original observations, singlet excimer emission has been observed in different phases and under a variety of conditions for a large number of aromatic hydrocarbons.[4,5] Of special importance for this work is the observation[6] of excimer fluorescence at 31 750 cm^{-1} from concentrated benzene solutions at room temperature.

Cram and co-workers[7] have synthesized a class of dimers of benzene to which has been given the generic name paracyclophanes. The paracyclophanes are a series of molecules in which two benzene rings are linked together in both *para* positions by $(CH_2)_n$ groups. In some of these molecules, two benzene rings are forced to remain close to one another by connecting methylene bridges of differing length. Both the symmetric and unsymmetric paracyclophanes show characteristic alterations of the absorption spectrum which indicate considerable interaction between the benzene rings.

The theoretical investigation of the nature of the intermolecular interactions in excimers has developed along two lines. Forster proposed two requirements for excimer emission: that the lowest state of the molecule be ^1L_b and that a ^1L_a state lie adjacent to the ^1L_b state.[8,9] It was asserted that the ^1L_a state would be split such that its lower component would lie below the ^1L_b state components. Forster attributed the excimer fluorescence to transitions from the lower ^1L_a component to the (repulsive) ground state. It is now known that the first condition is unnecessary, since 9-methyl anthracene[10] and perylene[11] both exhibit excimer fluorescence despite having a lowest state with symmetry ^1L_a. Moreover, McGlynn and Azumi[12] have shown that the energy-level splittings arising from dipole–dipole inter-

---

* U.S. Public Health Service Predoctoral Fellow. Present address: Department of Chemistry, University of Copenhagen, Copenhagen, Denmark.

[1] T. Forster and K. Kasper, Z. Physik. Chem. (Frankfurt) **1**, 19 (1954).

[2] T. Forster and K. Kasper, Z. Elektrochem. **59**, 976 (1955).

[3] The term excimer, introduced by B. Stevens [Nature **192**, 725 (1961)], is used to denote an excited dimeric species which is stable only in the excited state, and to differentiate this species from photodimers which are stable in the ground state as well as the excited state.

[4] R. Williams, J. Chem. Phys. **28**, 577 (1958).

[5] J. B. Birks, Proc. Roy. Soc. (London) **A280**, 289 (1964); **A277**, 571 (1964).

[6] T. V. Ivanova, G. Mokeeva, and B. Sveshnikov, Opt. Spectry. **12**, 325 (1962) [Opt. i Spektroskopiya **12**, 586 (1962)].

[7] D. J. Cram, N. L. Allinger, and H. Steinberg, J. Am. Chem. Soc. **76**, 6132 (1954).

[8] T. Forster, Pure Appl. Chem. **4**, 121 (1962).

[9] T. Forster, Pure Appl. Chem. **7**, 73 (1963).

[10] J. B. Birks and J. B. Aladekomo, Photochem. Photobiol. **2**, 415 (1963).

[11] J. Tanka, Bull. Chem. Soc. Japan **36**, 1237 (1963).

[12] T. Azumi and S. P. McGlynn, J. Chem. Phys. **41**, 3131 (1964).

actions are too small to explain the observations unless unreasonably small intermolecular separations are assumed.

The second theoretical approach appeals to a low-energy charge-transfer level as the source of eximer emission.[13,14] Charge-transfer levels are, in general, very difficult to locate in systems of the type under discussion. Tanaka[11] has suggested that an absorption band in crystalline perylene at 27 000 cm^{-1} is due to a transition from the ground state to a charge-transfer state, but Hochstrasser[15] has pointed out that the distinction between a vibronic-coupling pattern and a charge-transfer transition is not clear at present. In a very recent paper Pope, Kallmann, and Giachino[16] have presented evidence derived from photoelectric-emission experiments, that the lowest charge-transfer state in several crystals of aromatic molecules is located about 0.3–0.5 eV above the first singlet exciton state.

The most recent theoretical work[17–20] on the origin of excimer emission from large aromatic molecules, other than benzene, has been based on a combination of the two original approaches. That is, the electronic states of the dimer are constructed by using the configurational mixing of neutral excitations and charge-transfer excitations. These investigations have often used computational simplifications such as parameterization of the effective nuclear charge in a Slater orbital exponent,[17] the assumption of D_{2h} symmetry for the excimer state,[17–19] neglect of the core potential,[18] and the use of semiempirical values for the resonance integrals.[18] Because of these approximations, there remain unsatisfactory features in the theoretical analyses which may possibly lead to untrustworthy predictions. An alternative theoretical approach to the problem of trans-annular interactions involves the use of a supermolecule approximation in which the π electrons of the two parallel rings are treated in the LCAO–MO approximation. A treatment of just this form was carried out by Koutecky and Paldus[21] for the case of [2.2] paracyclophane using the semiempirical methods introduced by Pople[22] and by Pariser and Parr.[23] It is difficult to estimate the accuracy of the semiempirical molecular integrals used in this work.

There are, therefore, two alternative descriptions of the excited states of a dimer: one is that of the molecular orbital theory, where all the π electrons of the two interacting systems are included, while in the other the two interacting systems are treated within the framework of exciton theory including neutral exciton states (constructed using the tight-binding approximation) which allow for excitation exchange and charge-transfer exciton states, which allow for intermolecular electron delocalization. It can be shown that for the case of two interacting ethylene molecules the semiempirical Pariser–Parr–Pople scheme is equivalent to the extended-exciton-theory formalism.

In this paper we present a theoretical analysis of the π-electron states of the benzene excimer and of the paracyclophanes, with attention focused on the explanation of the excimer emission spectrum and the several paracyclophane absorption spectra. Of all the complex aromatic hydrocarbons, benzene is the simplest in structure and therefore an investigation of the benzene case is fundamental to an understanding of the forces responsible for excimer formation. However, a complicating feature is introduced by the high symmetry of the benzene molecule, which leads to degeneracy in the highest bonding orbital and in the lowest antibonding orbital. This degeneracy, which must be accounted for in the formulation of inter- and intramolecular transitions, makes benzene a somewhat more complicated case to handle than the higher polyacenes. Dewar and Longuet-Higgins[24] have shown how linear combinations of degenerate wavefunctions can account adequately for electron repulsion in intramolecular neutral-excited-state transitions. Similarly, wavefunctions for intermolecular charge-transfer transitions, in which an electron from one of the highest degenerate bonding orbitals on one molecule is transferred to one of the two lowest degenerate antibonding orbitals on the other molecule, must be constructed from suitable linear combinations of the molecular orbitals involved.

The computations reported herein make use of the formalism developed by Choi, Jortner, Rice, and Silbey[25] in the study of configuration interaction between neutral exciton states and charge-transfer exciton states in molecular crystals. Intermolecular overlap is included in a way consistent with the use of a core potential in the Goeppert-Mayer–Sklar representation. Simple Hückel LCAO molecular wavefunctions are used throughout this paper since it is known that the Hückel functions are not very different from the best available semiempirical configuration-interaction-type wavefunctions. All calculations have been carried out using a carbon $2p\pi$ SCF wavefunction to construct the LCAO molecular orbitals.

II. STATIONARY STATES OF THE DIMER

Since both the benzene excimer and the paracyclophanes contain only two rings, we restrict our attention

---

[13] J. Ferguson, J. Chem. Phys. **28**, 765 (1958).

[14] R. M. Hochstrasser, J. Chem. Phys. **36**, 1099 (1962).

[15] R. M. Hochstrasser, J. Chem. Phys. **40**, 2559 (1964).

[16] M. Pope, H. Kallmann, and J. Giachino, J. Chem. Phys. **42**, 2540 (1965).

[17] T. Azumi, A. T. Armstrong, and S. P. McGlynn, J. Chem. Phys. **41**, 3839 (1964).

[18] J. Koutecky and J. Paldus, Tetrahedron **19**, 201 (1963).

[19] J. N. Murrell and J. Tanaka, Mol. Phys. **4**, 363 (1964).

[20] E. Konijnenberg, Doctoral thesis, Free University of Amsterdam, Holland, 1963.

[21] J. Koutecky and J. Paldus, Collection Czech. Chem. Commun. **27**, 599 (1962).

[22] J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953).

[23] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953).

[24] M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A67**, 795 (1954).

[25] S. Choi, J. Jortner, S. A. Rice, and R. Silbey, J. Chem. Phys. **41**, 3294 (1964).

to the possible electronic states of a molecular dimer. We assume, for the present, that the molecules are fixed and nonvibrating. Then, in the zeroth-order approximation, the totally symmetric ground state of the dimer may be represented in the form

$$\Phi^0 = \mathcal{A}_N \phi_1{}^0 \phi_2{}^0, \tag{1}$$

where $\mathcal{A}_N$ is the antisymmetrization operator [for neutral (N) molecules] which exchanges electrons only between molecules, and the superscript (0) refers to the ground electronic state. Similarly, a localized excited-state wavefunction for the dimer is

$$\Psi_{1,2}{}^{0,f} = \mathcal{A}_N \phi_1{}^0 \phi_2{}^f, \tag{2}$$

where $\phi_2{}^f$ represents the fth neutral excited state of Molecule 2. Of course, Eq. (2) does not represent a stationary state of the dimer in that under certain operations of the dimer symmetry group $\Psi_{1,2}{}^{0,f}$ will be transformed into $\Psi_{1,2}{}^{f,0}$. Proper linear combinations of these two localized states are stationary states of the dimer and belong to different irreducible representations of the symmetry group:

$$\Phi_{S,A}{}^f = 2^{-\frac{1}{2}} \{ \Psi_{1,2}{}^{0,f} \pm \Psi_{1,2}{}^{f,0} \}, \tag{3}$$

where the subscripts S and A refer to the symmetric and antisymmetric combinations of localized states.

The inclusion of electron exchange bewteen component molecules of the dimer requires that we consider the stationary charge-transfer wavefunctions of the dimer. Let r denote a highest bonding orbital and t a lowest antibonding orbital. Then the transfer of an electron from the rth orbital of Molecule 1 to the tth orbital of Molecule 2 leads to a wavefunction $R_1{}^{+(r)} R_2{}^{-(t)}$, with the + and − referring to the sign of the ionic charge. The symmetric and antisymmetric charge resonance (CR) states are, in analogy with Eq. (3),

$$R_{S,A}{}^{r \to t} = 2^{-\frac{1}{2}} \{ \mathcal{A}_I R_1{}^{+(r)} R_2{}^{-(t)} \pm \mathcal{A}_I R_1{}^{-(t)} R_2{}^{+(r)} \}, \tag{4}$$

where $\mathcal{A}_I$ denotes the intermolecular antisymmetrization operator for ionized (I) molecules.

III. DETAILS OF THE FORMALISM

A. Dimer Hamiltonian

Turning now to the discussion of the calculation of the energy matrix, we first note that the dimer Hamiltonian may be written:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + V_{12}, \tag{5}$$

where

$$V_{12} = \sum_{I,J} \frac{z_I z_J e^2}{R_{IJ}} - \sum_{I,j} \frac{z_I e^2}{R_{Ij}} - \sum_{J,i} \frac{z_J e^2}{R_{Ji}} + \sum_{j>i} \frac{e^2}{r_{ij}}. \tag{6}$$

Subscript capital letters refer to nuclei and subscript lower-case letters to electrons. The first-order ground-state and excited-state energies are

$$E^0 = e_1{}^0 + e_2{}^0 + \langle \phi_1{}^0 \phi_1{}^0 \mid V_{12} \mid \phi_2{}^0 \phi_2{}^0 \rangle, \tag{7}$$

$$E_{\pm}{}^f = e_2{}^f + e_1{}^0 + \langle \phi_1{}^0 \phi_1{}^0 \mid V_{12} \mid \phi_2{}^f \phi_2{}^f \rangle \pm \epsilon, \tag{8}$$

$$\epsilon = \langle \mathcal{A} \phi_1{}^f \phi_2{}^0 \mid V_{12} \mid \phi_1{}^0 \phi_2{}^f \rangle. \tag{9}$$

The energies appearing in Eqs. (7) and (8) are of three types: the $e_i{}^0$ and $e_i{}^f$ are the ground-state and excited-state energies of free molecules, the terms of the form $\langle \phi_1 \phi_1 \mid V_{12} \mid \phi_2 \phi_2 \rangle$ represent the interaction of the charge distribution of Molecule 1 with that of Molecule 2, and ϵ is the excitation exchange energy.

In the following sections we detail the procedure used in the calculation of the energy splitting term ϵ [Eq. (9)]. We first consider the contribution of the first-order neutral-excitation interactions to the Davydov splitting. As a refinement, the second-order crystal-field-induced mixing of nondegenerate neutral-excitation states is then investigated. It is found that neither of these techniques give predicted splittings which are in agreement with experiment. Finally, the effect of configurational mixing of neutral-excitation and charge-resonance states on the Davydov splitting is explored and found to adequately predict the observed splittings for reasonable intermolecular conformations and separations.

B. First-Order Neutral-Excitation Splitting

The diagonal neutral-excitation integral of interest is

$$J_{12}{}^{f,f} = \langle \phi_1{}^f \phi_2{}^0 \mid V_{12} \mid \phi_1{}^f \phi_2{}^0 \rangle \pm \langle \phi_1{}^f \phi_2{}^0 \mid V_{12} \mid \phi_1{}^0 \phi_2{}^f \rangle, \tag{10}$$

in which the first term contributes only to the band shift. The second term may be broken down into components for, say, the ${}^1B_{1u}(p)$ state of benzene:

$$\begin{aligned} J_{12}{}^{p,p} = \pm \tfrac{1}{2} \{ & \langle \chi_1{}^{2-5} \chi_2{}^0 \mid V_{12} \mid \chi_1{}^0 \chi_2{}^{2-5} \rangle \\ & + \langle \chi_1{}^{2-5} \chi_2{}^0 \mid V_{12} \mid \chi_1{}^0 \chi_2{}^{3-4} \rangle + \langle \chi_1{}^{3-4} \chi_2{}^0 \mid V_{12} \mid \chi_1{}^0 \chi_2{}^{2-5} \rangle \\ & + \langle \chi_1{}^{3-4} \chi_2{}^0 \mid V_{12} \mid \chi_1{}^0 \chi_2{}^{3-4} \rangle \}. \end{aligned} \tag{11}$$

Now, for the singlet-state spin components $S=0$ and $m_s=0$, we have

$$\begin{aligned} \chi^{2-5} = 2^{-\frac{1}{2}} \{ & \mathcal{A}[u_1(1) \bar{u}_1(2) u_2(3) \bar{u}_5(4) u_3(5) \bar{u}_3(6)] \\ & - \mathcal{A}[u_1(1) \bar{u}_1(2) \bar{u}_2(3) u_5(4) u_3(5) \bar{u}_3(6)] \}. \end{aligned} \tag{12}$$

As usual, the subscript refers to the molecular orbital and the bar above denotes Spin β while its absence denotes Spin α. The only nonvanishing terms in the dimer-interaction-potential operator V_{12} are the two electron-repulsion operators. The result of substituting Eq. (12) and its analogs into Eq. (11) is the following:

$$\begin{aligned} J_{1,2}{}^{p,p} = \pm \{ & \langle u_5 u_2 \mid v_5 v_2 \rangle + \langle u_5 u_2 \mid v_4 v_3 \rangle + \langle u_4 u_3 \mid v_5 v_2 \rangle \\ & + \langle u_4 u_3 \mid v_4 v_3 \rangle \} \mp \tfrac{1}{2} \{ \langle u_5 v_5 \mid u_2 v_2 \rangle \\ & + \langle u_5 v_4 \mid u_2 v_3 \rangle + \langle u_4 v_5 \mid u_3 v_2 \rangle + \langle u_4 v_4 \mid u_3 v_3 \rangle \}, \end{aligned} \tag{13}$$

where

$$\langle u_5u_2 \mid v_4v_3 \rangle \equiv \langle u_5(a)u_2(a) \mid r_{ab}^{-1} \mid v_4(b)v_3(b) \rangle \quad (14)$$

and

$$\langle u_5v_4 \mid u_2v_3 \rangle \equiv \langle u_5(a)v_4(a) \mid r_{ab}^{-1} \mid u_2(b)v_3(b) \rangle \quad (15)$$

and the u molecular orbitals are located on Molecule 1 and the v's on Molecule 2.

In LCAO molecular orbital theory, the molecular orbitals u_h of aromatic hydrocarbons are represented as linear combinations of carbon atomic $2p\pi$ wavefunctions,

$$u_h = \sum_j C_{jh}\omega^j, \quad (16)$$

where the C_{jh} are the Hückel coefficients (neglecting overlap) for the hth molecular orbital. Using (16), Eq. (14) assumes the form

$$\langle u_5u_2 \mid v_4v_3 \rangle$$
$$= \sum_{i,j,k,l} C_{i5}C_{j2}C_{k4}C_{l3} \langle \omega_1^i(a)\omega_1^j(a) \mid r_{ab}^{-1} \mid \omega_2^k(b)\omega_2^l(b) \rangle. \quad (17)$$

In this calculation three- and four-center integrals are considered to be negligibly small and only two-center integrals ($i=j$, $k=l$) are evaluated. It is convenient to use a linear combination of four Slater-type orbitals fitted to an SCF function for the carbon $2p\pi_z$ electron,

$$\omega^j = r\cos\theta \sum_i a_i(\alpha_i^5/\pi)^{\frac{1}{2}} \exp(-\alpha_i r_j). \quad (18)$$

This procedure guarantees that the behavior in the tail of the carbon $2p\pi_z$ wavefunction will be reasonably accurate. It has been shown by Silbey, Kestner, Jortner, and Rice[26] that this choice of wavefunction gives good agreement with the intermolecular overlap and exchange integrals computed using SCF functions for a carbon–carbon segment.

The two-center integrals between two carbon SCF orbitals located on different molecules were expressed as a linear combination of five atomic integrals for the Coulomb terms: $\sigma\sigma\sigma\sigma$, $\pi\pi\sigma\sigma$, $\sigma\pi\pi\sigma$, $++++$, and $+--+$, in the notation of Kotani *et al.*[27] These integrals were computed using a program from the Laboratory for Molecular Structure and Spectroscopy of The University of Chicago.

C. Crystal-Field Mixing of Neutral-Excitation States

The simplest first-order Davydov theory in which the aggregate band splitting is influenced by only one molecular electronic state is incomplete, even within the framework of the tight-binding approximation, since the mixing of other excited molecular states with the initial state may take place. The effect of this mixing is to redistribute the intensity and energy in the various energy levels (see Sec. IV).

The relevant off-diagonal matrix element under consideration here is

$$J_{1,2}^{f,g} = \tfrac{1}{2} \langle \phi_1^f\phi_2^0 \pm \phi_1^0\phi_2^f \mid V_{12} \mid \phi_1^g\phi_2^0 \pm \phi_1^0\phi_2^g \rangle, \quad (19)$$

where f and g denote two different excited molecular states. In a more convenient form,

$$J_{1,2}^{f,g} = \Gamma_{1,2}^{f,g} + \Delta_{1,2}^{f,g}, \quad (20)$$

$$\Gamma_{1,2}^{f,g}$$
$$= \pm\tfrac{1}{2}\{ \langle \phi_1^f\phi_2^0 \mid V_{12} \mid \phi_1^0\phi_2^g \rangle + \langle \phi_1^0\phi_2^f \mid V_{12} \mid \phi_1^g\phi_2^0 \rangle \}, \quad (21)$$

$$\Delta_{1,2}^{f,g} = \tfrac{1}{2}\{ \langle \phi_1^f\phi_2^0 \mid V_{12} \mid \phi_1^g\phi_2^0 \rangle + \langle \phi_1^0\phi_2^f \mid V_{12} \mid \phi_1^0\phi_2^g \rangle \}. \quad (22)$$

It may be readily shown that the matrix component $\Delta_{12}^{f,g}$ vanishes. This is due to the pairing property of molecular orbitals in alternant hydrocarbons and to the retention of only two-center integrals. Evaluation of the off-diagonal energy-exchange component $\Gamma_{1,2}^{f,g}$, for the $^1B_{2u}(p)$ and $^1E_{1u}(\beta, \beta')$ states of molecular benzene gives

$$\Gamma_{1,2}^{p,\beta'} = \pm\tfrac{1}{4}\{ \langle (\chi_1^{3-4}+\chi_1^{2-5})\chi_2^0 \mid V_{12} \mid \chi_1^0(\chi_2^{3-4}-\chi_2^{2-5}) \rangle$$
$$+ \langle \chi_1^0(\chi_2^{3-4}+\chi_2^{2-5}) \mid V_{12} \mid (\chi_1^{3-4}-\chi_1^{2-5})\chi_2^0 \rangle \}, \quad (23)$$

which reduces to

$$\Gamma_{1,2}^{p,\beta'} = \pm\{ \langle u_4u_3 \mid v_4v_3 \rangle - \langle u_2u_5 \mid v_2v_5 \rangle \}$$
$$\mp\tfrac{1}{2}\{ \langle u_4v_4 \mid u_3v_3 \rangle - \langle u_2v_2 \mid u_5v_5 \rangle \}. \quad (24)$$

These matrix elements were calculated (neglecting three- and four-center terms) using Hückel wavefunctions.

D. Location of the Charge-Transfer State

The energy of the charge-transfer state relative to the ground state of the dimer may be calculated from

$$E(\mathrm{CT}) = \mathrm{I.P.} - \mathrm{E.A.} + G, \quad (25)$$

where I.P. and E.A. are the ionization potential and the electron affinity of the free molecule, and G is the Coulomb interaction between positive and negative ions. The values of I.P.−E.A. for benzene quoted in the literature are 11.0 [28] and 10.66 eV,[29] and due to this uncertainty the calculations have been performed with a series of values of this quantity. The Coulomb interaction G between positive and negative ions was calculated by assuming a charge distribution given by the Hückel molecular orbitals. For ion-pair separations of 2.0 Å or greater, the four possible combinations of

---

[26] R. Silbey, N. Kestner, J. Jortner, and S. A. Rice, J. Chem. Phys. **42**, 444 (1965).

[27] M. Kotani, E. Ishiguro, K. Hijikata, T. Nakamura, and A. Amemiya, J. Phys. Soc. Japan **8**, 463 (1953).

[28] R. M. Hedges and F. A. Matsen, J. Chem. Phys. **28**, 950 (1958).

[29] J. R. Hoyland and L. Goodman, J. Chem. Phys. **36**, 12, 21 (1962).

degenerate-bonding molecular orbitals and degenerate-antibonding molecular orbitals lead to the same values of G.

Equation (25) is strictly applicable only to the gas phase. In solution, the polarization of the surrounding medium (P) should be taken into account. In the calculations reported herein we have not specifically taken this quantity into account, as the uncertainty in its value, coupled with that of (I.P.−E.A.), results in the energy of the charge-transfer state being an adjustable parameter.

The on-diagonal matrix element which mixes different charge-resonance states is set equal to zero in this work since these are, at best, higher-order effects and therefore small in magnitude compared to neutral-excitation and charge-resonance-state mixing.

E. Configuration Mixing of Charge-Resonance and Neutral-Excitation States

As the intermolecular separation between the benzene molecules in the dimer is decreased, the possibility of intermolecular electron exchange is increased and the importance of the off-diagonal charge-resonance–neutral-excitation mixing matrix element is enhanced. In the calculation of these elements it is assumed that the molecular wavefunctions are undistorted by the interaction between the excited- and ground-state molecules or by the interaction between positive and negative ions, and that these wavefunctions are well represented by the simple Hückel molecular orbital functions. The introduction of core potentials simplifies the calculation of the matrix elements considerably. However, one must be careful in the definition of the core and interaction potentials, since the electron occupation numbers of orbitals are different in the neutral-excited molecular pair and in the ion pair. In order to consider all the possible interactions in a benzene dimer it is necessary to solve an eight-electron problem. This complication arises from the degeneracy of the highest filled bonding orbitals in benzene; in the higher polyacenes only four electrons need be considered. The wavefunctions for the neutral-excited singlet state and the charge-transfer states are:

$$\phi_1^{n\rightarrow n+\Delta i}\phi_2^0 = 2^{-\frac{1}{2}}\{\mathcal{A}_N[u_m(1)\bar{u}_m(2)u_n(3)\bar{u}_{n+\Delta i}(4)v_m(5)\bar{v}_m(6)v_n(7)\bar{v}_n(8)] - \mathcal{A}_N[u_m(1)\bar{u}_m(2)\bar{u}_n(3)u_{n+\Delta i}(4)v_m(5)\bar{v}_m(6)v_n(7)\bar{v}_n(8)]\}, \tag{26}$$

$$R_1^{+(n)}R_2^{-(n+\Delta j)} = 2^{-\frac{1}{2}}\{\mathcal{A}_I[u_m(1)\bar{u}_m(2)u_n(3)\bar{v}_{n+\Delta j}(4)v_m(5)\bar{v}_m(6)v_n(7)\bar{v}_n(8)] - \mathcal{A}_I[u_m(1)\bar{u}_m(2)\bar{u}_n(3)v_{n+\Delta j}(4)v_m(5)\bar{v}_m(6)v_n(7)\bar{v}_n(8)]\}, \tag{27}$$

$$R_1^{-(n+\Delta j)}R_2^{+(n)} = 2^{-\frac{1}{2}}\{\mathcal{A}_I[u_m(1)\bar{u}_m(2)u_n(3)\bar{u}_n(4)v_m(5)\bar{v}_m(6)v_n(7)\bar{u}_{n+\Delta j}(8)] - \mathcal{A}_I[u_m(1)\bar{u}_m(2)u_n(3)\bar{u}_n(4)v_m(5)\bar{v}_m(6)\bar{v}_n(7)u_{n+\Delta j}(8)]\}, \tag{28}$$

where m, n represent Molecular Orbitals 2 or 3; $\Delta i=2$ or 3 for m, $n=2$, and 1 or 2 for m, $n=3$. The quantity Δj is similarly defined. The core Hamiltonian $\mathcal{H}_{1,2}^c$ for Molecules 1 and 2 is defined to be

$$\mathcal{H}_1^c = V_1^c + 2J_1^1 - K_1^1, \tag{29}$$

$$\mathcal{H}_2^c = V_2^c + 2J_2^1 - K_2^1, \tag{30}$$

where V_1^c and V_2^c are the core potentials of Molecules 1 and 2 (i.e., the bare nuclear potential screened by the Hartree field of the sigma electrons). J_1^s and K_1^s are the Coulomb and exchange operators for Molecular Orbital s on the 1st molecule:

$$J_1^s v_l'(1) = \int [|u_s(2)|^2/r_{12}] d\tau_2 v_l'(1), \tag{31}$$

$$K_1^s v_l'(1) = \int [u_s(2)v_l'(2)/r_{12}] d\tau_2 u_s(1), \tag{32}$$

where v' may equal u or v, and l may equal m or n. The reader should note that the core defined herein contains the π electrons from the lowest bonding molecular orbital of benzene in addition to the sigma electrons. The eight-electron dimer Hamiltonian is:

$$\mathcal{H} = \sum_{i=1}^{8}\{T_i + \mathcal{H}_1^c(i) + \mathcal{H}_2^c(i) + \sum_{i>j} r_{ij}^{-1}\}, \tag{33}$$

where the T_i are the kinetic-energy operators. The mixing elements between the various symmetry-adapted states

TABLE I. Symmetry-adapted dimer wavefunctions.

Dimer Symmetry

$$\left.\begin{array}{l} 2^{-\frac{1}{2}}(\phi_1^P\phi_2^0+\phi_1^0\phi_2^P) \\ 2^{-1}(R_1^{+(3)}R_2^{-(4)}+R_1^{+(2)}R_2^{-(5)}+R_1^{-(4)}R_2^{+(3)}+R_1^{-(5)}R_2^{+(2)}) \end{array}\right\}$$

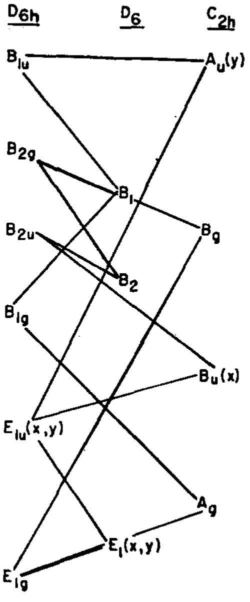
$$\left.\begin{array}{l} 2^{-\frac{1}{2}}(\phi_1^P\phi_2^0-\phi_1^0\phi_2^P) \\ 2^{-1}(R_1^{+(3)}R_2^{-(4)}+R_1^{+(2)}R_2^{-(5)}-R_1^{-(4)}R_2^{+(3)}-R_1^{-(5)}R_2^{+(2)}) \end{array}\right\}$$

$$\left.\begin{array}{l} 2^{-\frac{1}{2}}(\phi_1^a\phi_2^0+\phi_1^0\phi_2^a) \\ 2^{-1}(R_1^{+(2)}R_2^{(4)}-R_1^{+(3)}R_2^{-(5)}+R_1^{-(4)}R_2^{+(2)}-R_1^{-(5)}R_2^{+(3)}) \end{array}\right\}$$

$$\left.\begin{array}{l} 2^{-\frac{1}{2}}(\phi_1^a\phi_2^0-\phi_1^0\phi_2^a) \\ 2^{-1}(R_1^{+(2)}R_2^{-(4)}-R_1^{+(3)}R_2^{-(5)}-R_1^{-(4)}R_2^{+(2)}+R_1^{-(5)}R_2^{+(3)}) \end{array}\right\}$$

$$\left.\begin{array}{l} 2^{-\frac{1}{2}}(\phi_1^\beta\phi_2^0+\phi_1^0\phi_2^\beta) \\ 2^{-\frac{1}{2}}(\phi_1^{\beta'}\phi_2^0+\phi_1^0\phi_2^{\beta'}) \\ 2^{-1}(R_1^{+(2)}R_2^{-(4)}+R_1^{+(3)}R_2^{-(5)}+R_1^{-(4)}R_2^{+(2)}+R_1^{-(5)}R_2^{+(3)}) \\ 2^{-1}(R_1^{+(3)}R_2^{-(4)}-R_1^{+(2)}R_2^{-(5)}+R_1^{-(4)}R_2^{+(3)}-R_1^{-(5)}R_2^{-(2)}) \end{array}\right\}$$

$$\left.\begin{array}{l} 2^{-\frac{1}{2}}(\phi_1^\beta\phi_2^0-\phi_1^0\phi_2^\beta) \\ 2^{-\frac{1}{2}}(\phi_1^{\beta'}\phi_2^0-\phi_1^0\phi_2^{\beta'}) \\ 2^{-1}(R_1^{+(2)}R_2^{-(4)}+R_1^{+(3)}R_2^{-(5)}-R_1^{-(4)}R_2^{+(2)}-R_1^{-(5)}R_2^{+(3)}) \\ 2^{-1}(R_1^{+(3)}R_2^{-(4)}-R_1^{+(2)}R_2^{-(5)}-R_1^{-(4)}R_2^{+(3)}+R_1^{-(5)}R_2^{-(2)}) \end{array}\right\}$$



(Table I) may be broken down into components for, say, the $B_{2u}(\alpha)$ neutral state, and the B_{2u} charge-resonance state, viz.,

$$\begin{aligned}\tfrac{1}{4}\{&\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(2)}R_2^{-(4)}\rangle+\langle\chi_1^0\chi_2^{2-4}\,|\,\mathcal{H}\,|\,R_1^{-(4)}R_2^{+(2)}\rangle+\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(4)}R_2^{+(2)}\rangle\\ &+\langle\chi_1^0\chi_2^{2-4}\,|\,\mathcal{H}\,|\,R_1^{+(2)}R_2^{-(4)}\rangle-\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(3)}R_2^{-(5)}\rangle-\langle\chi_1^0\chi_2^{2-4}\,|\,\mathcal{H}\,|\,R_1^{-(5)}R_2^{+(3)}\rangle\\ &-\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(5)}R_2^{+(3)}\rangle-\langle\chi_1^0\chi_2^{2-4}\,|\,\mathcal{H}\,|\,R_1^{+(3)}R_2^{-(5)}\rangle-\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(2)}R_2^{-(4)}\rangle\\ &-\langle\chi_1^0\chi_2^{3-5}\,|\,\mathcal{H}\,|\,R_1^{-(4)}R_2^{+(2)}\rangle-\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(4)}R_2^{+(2)}\rangle-\langle\chi_1^0\chi_2^{3-5}\,|\,\mathcal{H}\,|\,R_1^{+(2)}R_2^{-(4)}\rangle\\ &+\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(3)}R_2^{-(5)}\rangle+\langle\chi_1^0\chi_2^{3-5}\,|\,\mathcal{H}\,|\,R_1^{-(5)}R_2^{+(3)}\rangle+\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(5)}R_2^{+(3)}\rangle\\ &+\langle\chi_1^0\chi_2^{3-5}\,|\,\mathcal{H}\,|\,R_1^{+(3)}R_2^{-(5)}\rangle\}.\end{aligned}\tag{34}$$

In the above equation we note that the matrix element

$$\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(3)}R_2^{-(5)}\rangle$$

is identical with

$$\langle\chi_1^0\chi_2^{2-4}\,|\,\mathcal{H}\,|\,R_1^{-(5)}R_2^{+(3)}\rangle.$$

Similar relations hold for the other matrix elements. For the evaluation of the charge-transfer-state mixing with the neutral α and neutral p excitation states there are a number of other matrix elements which must be considered. The following relations between these mixing matrix elements greatly simplify their computation:

$$\begin{aligned}&\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(3)}R_2^{-(4)}\rangle\Rightarrow\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(2)}R_2^{-(5)}\rangle,\\ &\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(4)}R_2^{+(3)}\rangle\Rightarrow\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(5)}R_2^{+(2)}\rangle,\\ &\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(2)}R_2^{-(5)}\rangle\Rightarrow\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{+(3)}R_2^{-(4)}\rangle,\\ &\langle\chi_1^{3-5}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(5)}R_2^{+(2)}\rangle\Rightarrow\langle\chi_1^{2-4}\chi_2^0\,|\,\mathcal{H}\,|\,R_1^{-(4)}R_2^{+(3)}\rangle.\end{aligned}\tag{35}$$

The evaluation of the terms on the right-hand side of Eq. (35) may be formed from Eqs. (40)–(43) by interchanging Index 4 and 5, and 3 and 2.

Up to this point no attention has been given to the nonorthogonality of the neutral and ion-pair wavefunctions on different molecular centers. The wavefunction of a neutral-excited state on one chromophore is not, in general, orthogonal to an ionized state on another chromophore. As a rule, it is important to account for the overlap of these wavefunctions in an energy calculation since neglect of overlap may lead to alterations of considerable magnitude and, therefore, to unreliable results. One of the simplest and most efficient orthogonization schemes is the symmetric orthogonization method of Löwdin.[30] Following Löwdin's scheme as applied by Silbey *et al.*[31] to the study of Davydov splittings in molecular crystals, we define a set of wavefunctions ϕ_i which are characterized by small overlap. Then

$$\phi_i'=\phi_i-\tfrac{1}{2}\sum_j\phi_jS_{ji}+\tfrac{3}{8}\sum_{k,l}\phi_kS_{kl}S_{li}-\cdots, \qquad (36)$$

where

$$S_{kl}=\langle\phi_k\mid\phi_l\rangle-\delta_{kl} \qquad (37)$$

from which

$$\mathcal{H}_{ik}'=\mathcal{H}_{ik}-\tfrac{1}{2}\sum_j\{S_{ij}\mathcal{H}_{jk}+\mathcal{H}_{ij}S_{jk}\}+\cdots. \qquad (38)$$

Higher-order terms in the overlap S may be neglected since the overlap is assumed to be small. Then, for off-diagonal matrix elements which are much smaller than the diagonal elements, we may write

$$\mathcal{H}_{ik}'=\mathcal{H}_{ik}-S_{ik}\mathcal{H}_{kk}+\tfrac{1}{2}S_{ik}(\mathcal{H}_{kk}-\mathcal{H}_{ii}). \qquad (39)$$

The last term in this expression is neglected for the states under consideration here. Thus, each term in Eq. (35) must be modified by a nonorthogonality correction; e.g., the first term in Eq. (35) becomes

$$\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid R_1^{+(3)}R_2^{-(4)}\rangle-\langle\chi_1^{3-5}\chi_2^0\mid R_1^{+(3)}R_2^{-(4)}\rangle\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid\chi_1^{3-5}\chi_2^0\rangle.$$

The terms on the right-hand side of Eq. (35) may be formed from the terms on the left-hand side by interchanging Index 4 and 5 and vice versa in the following equations. The derivation of the following formulas is due to Silbey.[32]

$$\begin{aligned}\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid R_1^{+(3)}R_2^{-(4)}\rangle-\langle\chi_1^{3-5}\chi_2^0\mid R_1^{+(3)}R_2^{-(4)}\rangle\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid\chi_1^{3-5}\chi_2^0\rangle&=\langle v_4\mid V_n^{\mathrm{GMS}}-\sum_{i=1}^{3}K_n^i+2K_m^3-J_m^3\mid u_5\rangle\\&\quad-\langle v_4\mid u_5\rangle\langle u_5\mid 2K_m^3-J_m^3\mid u_5\rangle-\sum_{i=1}^{3}\langle v_4\mid u_i\rangle\langle u_i\mid 2K_m^3-J_m^3\mid u_5\rangle+\sum_{i=1}^{3}\langle v_i\mid u_5\rangle\langle v_i\mid J_m^3\mid v_4\rangle\\&\quad+\sum_{i=1}^{3}\{\langle u_1\mid v_i\rangle\langle u_1u_5\mid v_4v_i\rangle+\langle u_2\mid v_i\rangle\langle u_2u_5\mid v_4v_i\rangle-\langle u_3\mid v_i\rangle\langle u_3u_5\mid v_4v_i\rangle\},\end{aligned} \qquad (40)$$

$$\begin{aligned}\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid R_1^{-(4)}R_2^{+(3)}\rangle-\langle\chi_1^{3-5}\chi_2^0\mid R_1^{-(4)}R_2^{+(3)}\rangle\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid\chi_1^{3-5}\chi_2^0\rangle&=2\langle u_3u_5\mid u_4v_3\rangle-\langle u_5u_4\mid u_3v_3\rangle\\&\quad+\langle u_3\mid v_3\rangle\langle u_4\mid -2K_m^3\mid u_5\rangle-2\sum_{i=1}^{3}\{\langle u_i\mid v_3\rangle\langle u_4u_i\mid u_3u_5\rangle+\langle u_4\mid v_i\rangle\langle u_3u_5\mid v_3v_i\rangle\\&\quad-\tfrac{1}{2}\langle v_3\mid u_i\rangle\langle u_4u_5\mid u_3u_i\rangle-\tfrac{1}{2}\langle u_3\mid v_i\rangle\langle u_4u_5\mid v_3v_i\rangle\},\end{aligned} \qquad (41)$$

$$\begin{aligned}&\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid R_1^{+(2)}R_2^{-(5)}\rangle-\langle\chi_1^{3-5}\chi_2^0\mid R_1^{+(2)}R_2^{-(5)}\rangle\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid\chi_1^{3-5}\chi_2^0\rangle\\&\quad=2\langle u_3u_5\mid u_2v_5\rangle-\langle v_5u_5\mid u_2u_3\rangle-\sum_{i=1}^{3}\{\langle u_5\mid v_i\rangle\langle u_2u_3\mid v_5v_i\rangle+\langle v_5\mid u_i\rangle\langle u_2u_3\mid u_5u_i\rangle\}\\&\quad\quad-2\sum_{i=1}^{3}\{\langle v_5\mid u_i\rangle\langle u_5u_3\mid u_2u_i\rangle+\langle u_2\mid v_i\rangle\langle u_5u_3\mid v_5v_2\rangle\},\end{aligned} \qquad (42)$$

$$\begin{aligned}&\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid R_1^{-(5)}R_2^{+(2)}\rangle-\langle\chi_1^{3-5}\chi_2^0\mid R_1^{-(5)}R_2^{+(2)}\rangle\langle\chi_1^{3-5}\chi_2^0\mid\mathcal{H}\mid\chi_1^{3-5}\chi_2^0\rangle\\&\quad=-\langle u_3\mid V_m^{\mathrm{GMS}}-\sum_{i=1}^{3}K_m^i-2K_m^5+J_m^5\mid v_2\rangle+\sum_{i=1,2,5}\langle v_2\mid u_i\rangle\langle u_3\mid -J_m^2\mid u_i\rangle-\sum_{i=1}^{3}\langle v_i\mid u_5\rangle\langle u_3u_5\mid v_2v_i\rangle\\&\quad\quad+\sum_{i=1,2}\langle v_2\mid u_i\rangle\langle u_3\mid J_m^5-K_m^5\mid u_i\rangle+\sum_{i=1}^{3}\langle v_i\mid u_3\rangle\langle v_2\mid J_m^5-J_m^3\mid v_i\rangle.\end{aligned} \qquad (43)$$

---

[30] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).
[31] R. Silbey, J. Jortner, and S. A. Rice, J. Chem. Phys. **42**, 1515 (1965).
[32] R. Silbey, Ph.D. thesis, University of Chicago, 1965.

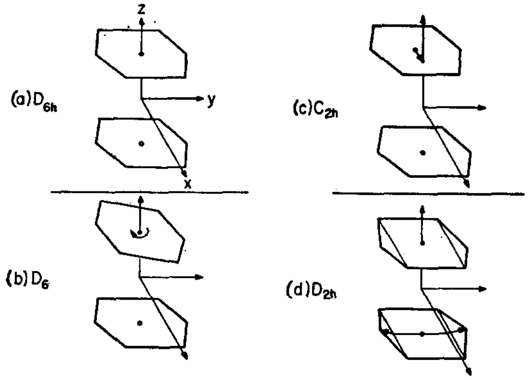


FIG. 1. Schematic representation of various configurations of dimers composed of D_{6h} monomers.

The remaining eight matrix elements may be generated by exchanging Index 2 and 3, and Index 4 and 5 on Molecule 2 only, in Eqs. (40)–(43). In these equations, V_1^{GMS} is the Goeppert-Mayer–Sklar potential

$$V_1^{\mathrm{GMS}}=V_1^c+\sum_{s=1}^{3}2J_1^s, \tag{44}$$

and involves the screening of the core by the Hartree field of the π electrons. The computation of the several integrals given in Eqs. (40)–(43) has been outlined previously.[25]

IV. SELECTION RULES AND SYMMETRY

The benzene molecule is planar and hexagonal (point group D_{6h}) with a carbon–carbon bond length of 1.397 Å. Two of the benzene near-ultraviolet transitions to the states ${}^1B_{2u}$ (38 000 cm^{-1}) and ${}^1B_{1u}$ (48 000 cm^{-1}) are symmetry forbidden but are observed experimentally, being vibronically induced.[33] It is believed that the transition to the ${}^1B_{2u}(\alpha)$ state is polarized along the short (x), (bond-bisecting) molecular axis, and that to the ${}^1B_{1u}(p)$ state is polarized along the long (y), (atom-bisecting) molecular axis. The third benzene transition in the ultraviolet, ${}^1E_{1u}\leftarrow A_{1g}$, occurs at 54 500 cm^{-1} and is polarized in the molecular (x, y) plane In this paper we consider a dimer composed of two identical benzene molecules, and consider only the above $\pi\rightarrow\pi^*$ transitions. The dimer symmetry D_{6h} in which the two molecules lie parallel to each other in a sandwich fashion [Fig. 1(a)] has been the model for the excimers of higher polyacenes most studied by other workers. The model of the symmetric paracyclophanes consisting of such an arrangement with the benzene rings joined by methylene bridges, strictly belongs to the group D_{2h}. However, the additional methylene units are not included in our approximation, and thus the paracyclophanes may be treated as belonging to the group D_{6h}. Although the perfect sandwich symmetry is the one which has been most considered as a possibility for excimer formation by other workers, at present there appear to be no arguments on energetic grounds to limit the symmetry to this arrangement. There is direct structural evidence for deviations from D_{2h} symmetry in the cases of the [2.2] and [3.3] paracyclophanes, and, in addition, it is difficult to reconcile the observed absorption and fluorescence spectra of single crystals of [2.2] paracyclophane with a perfect sandwich structure. We also consider the dimers of D_6 symmetry consisting of two benzene rings, one of which has been rotated about its z axis [Fig. (1b)], and of C_{2h} symmetry in which the two rings do not lie directly above one another [Fig. 1(c)]. In addition, we consider a D_{2h} dimer in which the aromatic rings are deformed from the regular D_{6h} symmetry into a symmetrical boat form of symmetry C_{2v} [Fig. 1(d)]. These three dimer models have been selected for a detailed study from the numerous possible configurations, as there is evidence for their occurrence and they can lead to interpretations of the complex crystal spectra of [2.2] paracyclophane.

The symmetry-adapted stationary states for these dimer groups are now considered. The localized neutral excited states of the benzene dimer in the Hückel approximation[34] are

$$\phi_i^{\alpha}\phi_j^{0}=2^{-\frac{1}{2}}(\chi_i^{2-4}-\chi_i^{3-5})\chi_j^{0}, \tag{45}$$

$$\phi_i^{p}\phi_j^{0}=2^{-\frac{1}{2}}(\chi_i^{2-5}+\chi_i^{3-4})\chi_j^{0}, \tag{46}$$

$$\phi_i^{\beta,\beta'}\phi_j^{0}=\begin{Bmatrix}2^{-\frac{1}{2}}(\chi_i^{2-4}+\chi_i^{3-5})\chi_j^{0}\\ \\ 2^{-\frac{1}{2}}(\chi_i^{2-5}-\chi_i^{3-4})\chi_j^{0}\end{Bmatrix}, \tag{47}$$

in which χ_i^{2-4} represents an electronic transition in Molecule i from Bonding Molecular Orbital Number 2 to Antibonding Molecular Orbital Number 4. Correspondingly, the different localized charge-transfer states are

$$\begin{array}{ll}R_i^{+(2)}R_j^{-(4)},\ R_i^{+(2)}R_j^{-(5)}, & R_i^{+(3)}R_j^{-(4)},\ R_i^{+(3)}R_j^{-(5)},\\ R_i^{-(4)}R_j^{+(2)},\ R_i^{-(5)}R_j^{+(2)}, & R_i^{-(4)}R_j^{+(3)},\ R_i^{-(5)}R_j^{+(3)}.\end{array} \tag{48}$$

By application of the Wigner projection operator[35,36] to the above basis functions, symmetry-adapted stationary states for each dimer group may be formed. These results for the three dimer symmetries D_{6h}, D_6, and C_{2h} are shown in Table I. When the symmetry is reduced from D_{6h} to D_6 by rotation of one benzene unit about the z axis, the states of B_{1u} and B_{1g}, and B_{2u} and B_{2g} symmetry will mix. In the dimer of C_{2h} symmetry, in

---

[33] J. Platt and H. B. Klevens, Chem. Rev. **41**, 301 (1947).

[34] J. Pople, Proc. Phys. Soc. (London) **68**, 81 (1955).

[35] E. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), p. 118.

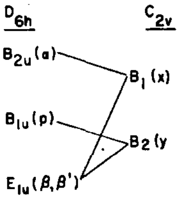
[36] H. Eyring, J. Walter, and G. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1957), p. 172.

which the benzene monomers do not lie directly above one another, the transitions to the B_{1u} and B_{2u} states, which were forbidden in the D_{6h} monomer, become allowed.

In Table II are depicted the symmetry-adapted wavefunctions for a D_{2h} dimer composed of boatlike benzene monomers of C_{2v} symmetry. In the monomer, the α and p states are connected to the ground state by allowed transitions when the molecule is distorted in this manner. The corresponding transitions to the symmetric dimer states of α and p parentage (B_{3u} and B_{2u}) are also allowed in this D_{2h} dimer.

TABLE II. Symmetry-adapted wavefunctions of D_{2v} dimer composed of C_{2v} bent benzenes.

Monomer Symmetries



Dimer Wavefunctions	$\underline{D_{2h}}$
$2^{-\frac{1}{2}}(\phi_1^{3-4}\phi_2^0+\phi_1^0\phi_2^{3-4})$ $2^{-\frac{1}{2}}(\phi_1^{2-5}\phi_2^0+\phi_1^0\phi_2^{2-5})$ $2^{-\frac{1}{2}}(R_1^{+(3)}R_2^{-(4)}+R_1^{-(4)}R_2^{+(3)})$ $2^{-\frac{1}{2}}(R_1^{+(2)}R_2^{-(5)}+R_1^{-(5)}R_2^{+(2)})$	$B_{2u}(y)$
$2^{-\frac{1}{2}}(\phi_1^{3-4}\phi_2^0-\phi_1^0\phi_2^{3-4})$ $2^{-\frac{1}{2}}(\phi_1^{2-5}\phi_2^0-\phi_1^0\phi_2^{2-5})$ $2^{-\frac{1}{2}}(R_1^{+(3)}R_2^{-(4)}-R_1^{-(4)}R_2^{+(3)})$ $2^{-\frac{1}{2}}(R_1^{+(2)}R_2^{-(5)}-R_1^{-(5)}R_2^{+(2)})$	B_{3g}
$2^{-\frac{1}{2}}(\phi_1^{2-4}\phi_2^0+\phi_1^0\phi_2^{2-4})$ $2^{-\frac{1}{2}}(\phi_1^{3-5}\phi_2^0+\phi_1^0\phi_2^{3-5})$ $2^{-\frac{1}{2}}(R_1^{+(2)}R_2^{-(4)}+R_1^{-(4)}R^{+(2)}$ $2^{-\frac{1}{2}}(R_1^{+(3)}R_2^{-(5)}+R_1^{-(5)}R_2^{+(3)}$	$B_{3u}(x)$
$2^{-\frac{1}{2}}(\phi_1^{2-4}\phi_2^0-\phi_1^0\phi_2^{2-4})$ $2^{-\frac{1}{2}}(\phi_1^{3-5}\phi_2^0-\phi_1^0\phi_2^{3-5})$ $2^{-\frac{1}{2}}(R_1^{+(2)}R_2^{-(4)}-R_1^{-(4)}R^{+(2)}$ $2^{-\frac{1}{2}}(R_1^{+(3)}R_2^{-(5)}-R_1^{-(5)}R_2^{+(3)}$	B_{2g}

V. NUMERICAL CALCULATIONS AND RESULTS

The dependence of the neutral singlet-excitation-state splitting on the intermolecular separation for a dimer of D_{6h} symmetry is illustrated in Fig. 2. The ${}^1B_{2u}(\alpha)$ molecular state does not split under first-order interaction because of the pairing property of corresponding lowest antibonding and highest bonding molecular orbitals in alternant hydrocarbons. The ${}^1E_{1u}$ molecular state is split significantly more than the ${}^1B_{1u}$ band, which is to be expected in first order on the basis of the relative oscillator strengths (0.69 to 0.18). Crystal-field mixing of these neutral-excitation states is zero in this symmetry. These small energy-level splittings cannot account for the observed anomalous fluorescence band 6000 cm^{-1} to the red of the normal fluorescence.

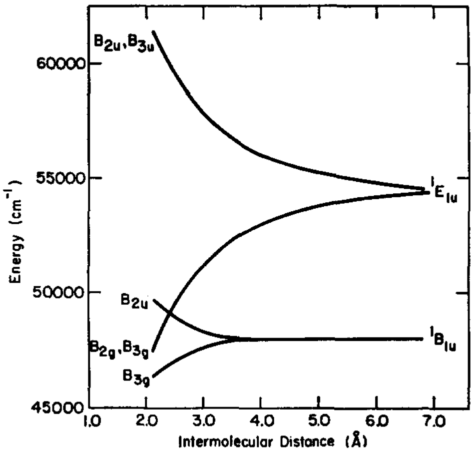


FIG. 2. First-order Davydov splitting of the neutral-excitation states ${}^1B_{1u}(p)$ and ${}^1E_{1u}(\beta,\beta')$ of molecular benzene as a function of intermolecular separation in the D_{6h} dimer. The molecular ${}^1B_{2u}(\alpha)$ state, which is not shown here, does not split in this approximation.

The contribution of the charge-resonance (CR) states to the ${}^1B_{2u}(\alpha)$, ${}^1B_{1u}(p)$, and ${}^1E_{1u}(\beta', \beta)$ state splittings was determined as a function of intermolecular separation in the D_{6h} symmetry. The calculational scheme employs the diagonalization of the energy matrices of the individual dimer-group representations separately. This technique is preferable to a perturbation scheme since the charge-resonance and some of the neutral-excitation levels become almost degenerate for certain intermolecular separations. Figures 3 and 4 show the

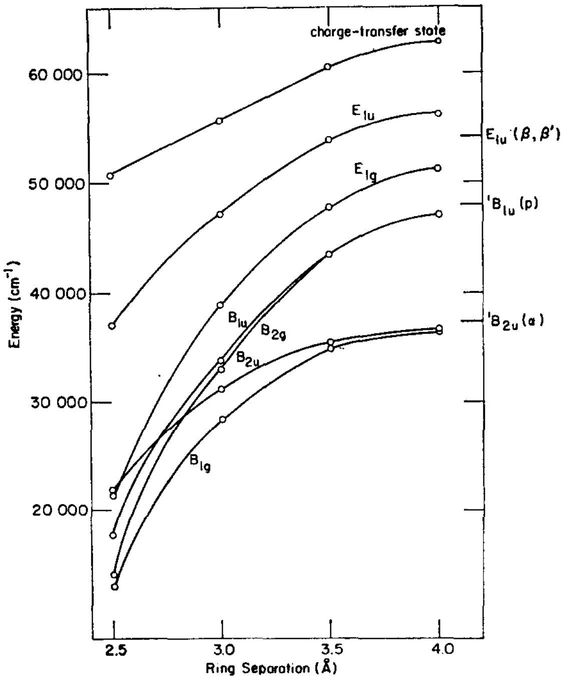


FIG. 3. Energies of D_{6h} dimer as a function of interplanar distance. Low-energy components of states of ${}^1B_{2u}$, ${}^1B_{1u}$, and ${}^1E_{1u}$ molecular-benzene parentage.

TABLE III. Effect of varying charge-transfer-state energy (D_{6h} dimer with ring separation of 3 Å).

I.P.−E.A. (eV)	Dimer states (cm^{-1})					
	B_{1u}	B_{2g}	B_{2u}	B_{1g}	E_{1u}	E_{1g}
10	30 200	29 400	29 300	26 000	41 800	35 100
11	33 900	33 100	31 300	28 400	47 200	38 900
12	36 700	36 000	32 600	30 000	51 100	41 500

states of α, p, and (β', β) parentage for a dimer of D_{6h} symmetry for inter-ring distances between 2.5 and 4.0 Å, the value of I.P.−E.A. being taken as 11 eV. At distances greater than 3 Å, the order of the states is as in the isolated benzene molecule. The lowest state is thus of α parentage, and the anomalous fluorescence at ~30 000 cm^{-1} from concentrated solutions of benzene may be assigned to emission from the $^1B_{1g}$ state for an intermolecular separation of ~3.1 Å. At small inter-ring distances (3 Å and less) the mutual separation of the four states of α and p parentage is reduced, and at these distances this calculation is not sufficiently accurate to unequivocally assign the order of the states. For example, at 3 Å, the separation of the B_{2u} and B_{2g} states is calculated to be ~1 800 cm^{-1}. An accuracy of this magnitude can certainly not be claimed for an approximate calculation of this type. We return to this point when discussing the crystal spectrum of [2.2] paracyclophane. Owing to the uncertainty in the value of the energy of the charge-transfer state, we have investigated the effect of varying I.P.−E.A. [Eq. (25)]. In Table III are presented results for a D_{6h} dimer, with ring separation 3 Å, I.P.−E.A. being taken in the range 10–12 eV. It can be seen that this has a pronounced effect on the energy levels, and in effect, introduces an adjustable parameter in interpreting experimental data.

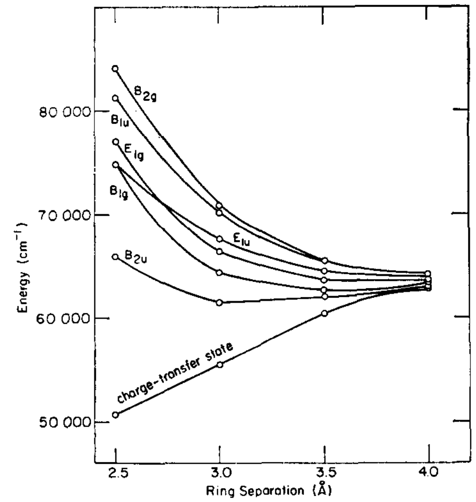


FIG. 4. Energies of D_{6h} dimer as a function of interplanar distance. High-energy components of states of $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ molecular-benzene parentage.

VI. ULTRAVIOLET SPECTRA OF THE PARACYCLOPHANES

The anomalous absorption bands of the paracyclophanes can be considered as the analogs of the fluorescence bands of the benzene excimer. The absorption spectra of concentrated benzene solutions (and of crystalline benzene) do not contain any anomalous absorption bands because the ground-state repulsion between the chromophores keeps them well separated. Anomalous absorption bands are found in the absorption spectra of the small paracyclophanes,[7] since the methylene bridges guarantee the proximity of the rings. In this interpretation, the forces active in excimer formation from an excited- and a ground-state molecule are also responsible for the band splittings in the absorption spectra of the paracyclophanes.

In Fig. 5 the absorption spectra of the [2.2] and [3.3] paracyclophanes, as reported by Cram, Allinger, and Steinberg, are shown.[7] The crystal and molecular structures of both these compounds have been determined.[37,38] In both cases the benzene rings are slightly distorted from their normal planar configuration into a symmetrical boat form. In addition, in [3.3] paracyclophane, the two rings do not lie directly above one another. In [2.2] paracyclophane the maximum and minimum ring-to-ring distances have been found to be 3.09 and 2.75 Å, respectively. In the [3.3] paracyclophane the corresponding distances are 3.31 and 3.14 Å. It has been shown that the decrease in symmetry brought about by these distortions from D_{6h} symmetry may affect the selection rules, making transitions forbidden in D_{6h}, allowed in the new symmetry group. In the discussion of the solution spectra of the paracyclophanes a D_{6h} configuration is assumed. (In reality, the group of the symmetric paracyclophane is, of course, D_{2h}, but our calculations do not distinguish between these.)

The solution spectrum of [2.2] paracyclophane at room temperature reveals broad structureless absorption bands showing no vibrational structure with peaks at 310, 290, 260, and 225 mμ. From the results presented in Fig. 3 for the D_{6h} model with inter-ring separation of 3–3.1 Å we can assign the first band to the transition

---

[37] K. Lonsdale, H. J. Milledge, and K. V. K. Rao, Proc. Roy. Soc. (London) **A255**, 82 (1960).

[38] P. K. Gantzel and K. N. Trueblood, Acta Cryst. **18**, 958 (1965).

TABLE IV. Energy levels of D_{2h} dimer composed of bent-benzene (C_{2v}) dimers (I.P.−E.A.=11 eV).

D_{6h} Dimer (ring separation 3 Å) dimer states (cm^{-1})				D_{2h} Dimer, dimer states (cm^{-1})			
B_{1u}	B_{2g}	B_{2u}	B_{1g}	B_{2u}	B_{3g}	B_{3u}	B_{2g}
33 900	33 100	31 300	28 400	33 300	29 800	31 600	28 500

to a B_{1g} state (α parentage), the second band to the transition to the B_{2u} state (α parentage), the third band to the transition to the B_{1u} state (p parentage), and the fourth band to transitions to states of β parentage. Although the calculated energies are rather too small on the whole, the low-energy onsets of the absorption bands roughly corresponding to the 0–0 transitions are quite well reproduced by these calculations which pertain to a dimer consisting of two planar molecules (see Fig. 5). Since the rings in the [2.2] paracyclophane are known to be bent by about 13°,[37] calculations for this configuration, using the crystallographically determined ring separation, have been performed. The symmetry-adapted wavefunctions for this D_{2h} dimer have been previously discussed and are displayed in Table II. The energy matrices of the dimer-group representations were diagonalized using the configuration-interaction matrix elements, and configuration energies for bent benzene tabulated by Allinger *et al.*[39] The results of this computation are compared with that for the D_{6h} dimer with inter-ring separation of 3 Å in Table IV. It is apparent that the ring bending affects the B_{2g} state most strongly, depressing it below the B_{2u} state. The low-energy band might conceivably consist of the two forbidden transitions to the B_{1g} state (α parentage) and the B_{2g} state (p parentage). The solution spectra are rather uninformative regarding the nature of these symmetry-forbidden transitions which can arise from vibronic coupling effects, or from molecular distortion. To obtain this information we now study the crystal spectrum of [2.2] paracyclophane as determined by Ron and Schnepp.[40]

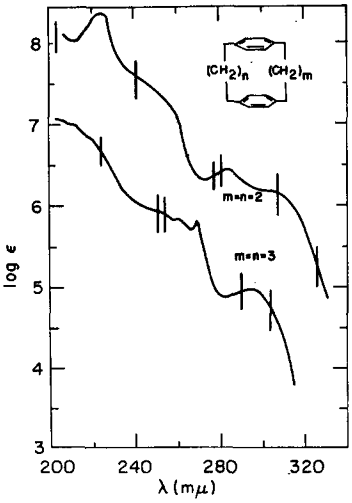


FIG. 5. Ultraviolet absorption spectra of [2.2] and [3.3] paracyclophanes.[7] The positions of the calculated energy levels from Fig. 3 for interplanar separations of 3.1 and 3.3 Å, respectively, are superposed on the spectra.

The crystal structure of [2.2] paracyclophane is tetragonal with a D_{4h} [37] space group, and Molecular Site Group D_{2h}. These are two molecules per unit cell. The molecules are arranged in the unit cell with the long (y) dimer axis parallel to the unique tetragonal axis and the molecular planes (the dimeric xy planes) perpendicular to one another within the unit cell. Fortunately for our interpretation, no crystal Davydov splitting is possible in this orientation. Two types of thin crystals were used by Ron and Schnepp: the isotropic crystals had the face perpendicular to the unique axis developed and gave extinction between crossed polaroids for all orientations, whereas the anisotropic crystal face was not identified, but between crossed polaroids the crystals exhibited extinction for two perpendicular directions. Spectra of both crystals were taken at 20.4°K and exhibited much vibrational fine structure on a continuous absorption background whose intensity rose steadily with increasing energy. The isotropic crystal spectrum, whose broad continuous background begins to rise in intensity at a higher energy than the anisotropic spectrum, is polarized perpendicular to the tetragonal axis and therefore along the short axis of the dimer molecules. The anisotropic spectrum, which contains the isotropic spectrum, is polarized in directions both perpendicular and parallel to the unique crystal axis, i.e., along the short (x) and long (y) dimer axes, respectively. The 0–0 transition at 30 361 cm^{-1} is long axis polarized. This observation was puzzling since it was felt that the 0–0 band originated from transitions to α excitation states which are polarized along the short molecular axis. This work has recently been extended by Ron and Schnepp, and the following additional observation recorded:

(1) The 0–0 line is observed in the crystal spectrum at 30 361 cm^{-1}, followed by a long progression with 236-cm^{-1} spacing, corresponding to the breathing mode of the two rings. This transition is long axes polarized.

(2) The assignment of the 0–0 line is unambiguous in view of the successful measurement of the fluorescence spectrum. The fluorescence spectrum is long axis polarized and the progression is evidently the mirror image of the parallel component in the absorption spectrum. No short-axes component was observed in the fluorescence spectrum.

---

[39] N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, J. Am. Chem. Soc. 85, 1171 (1963).

[40] A. Ron and O. Schnepp, J. Chem. Phys. 37, 2540 (1962).

TABLE V. Energy levels for dimer distorted by rotation about z axis ($D_{6h}\rightarrow D_6$). (I.P.−E.A.=11 eV; ring separation 3 Å.)

Angle of rotation (°)	Dimer states (cm^{-1})					
	B_{1u}	B_{2g}	B_{2u}	B_{1g}	E_{1u}	E_{1g}
0	33 900	33 100	31 300	28 400	47 200	38 900
10	34 100	33 800	30 900	28 700	47 300	38 100

(3) A second electronic transition was observed with an origin at 30 741 cm^{-1}, characterized by a progression with 232-cm^{-1} spacing, and polarized along the short molecular axis. The different vibrational spacing in this transition and the absence of fluorescence from this state support the assignment of Ron and Schnepp in which the two different components of the absorption spectrum represent transitions to two different electronic states. These experimental data also provide unambiguous evidence that the first electronic transition (to the B_{1g} electronic state) is a pure electronic transition and is not vibronically induced.

Two puzzling features remain to be explained:

(a) The polarizations of the transitions.

(b) The relaxation of the selection rules required to explain these purely electronic transitions.

The theoretical calculations presented herein can be adequately reconciled with the experimental results of Ron and Schnepp by invoking the hypothesis originally introduced by Ron and Schnepp,[40] i.e., that in the case of [2.2] paracyclophane a small rotation of one molecule (by about 3°–5°) about the perpendicular z axis prevents cancellation of the total transition moment for the B_{1g} and B_{2g} states and thereby introduces a component along the long dimer axis for the B_{1g} state (of α parentage) and a nonvanishing component along the short dimer axis for the B_{2g} state of p parentage. The same conclusions have been reached by Ron and Schnepp from an analysis of the experimental data.[41]

In Table V are displayed the results of a computation for such a D_6 dimer in which one benzene ring is twisted about the z axis by 10°. It is evident that the energy levels are very little affected by such a distortion. Indeed, it is not considered that such a change as shown in Table V is significant within the framework of the approximations used in the calculation. These small deviations from dimer D_{6h} symmetry have little effect on the neutral-excitation splittings, and certainly do not account for the large shifts observed experimentally.

The energy states for the D_{6h} dimer, with ring separation 3.3 Å, together with the solution absorption spectra of the [3.3] paracyclophane are shown in Fig. 5. As with the [2.2] paracyclophane, satisfactory agreement with experiment is obtained.

VII. DISCUSSION

The calculations presented in this paper show that neither the anomalous emission from concentrated benzene solution, nor the absorption spectra of the paracyclophanes, can be interpreted within the framework of conventional exciton theory considering only the interaction of neutral-excited states. Charge-transfer states have been successful in interpreting the crystal spectra of a number of aromatic hydrocarbons, and there is some experimental evidence for their existence. Their interaction with neutral-exciton states leads to states which can successfully interpret both these observations, considering the unavoidable approximation inherent in such a calculation. In this calculation the repulsive forces present in the ground-state dimer have been neglected. Ground-state repulsive energies of the order of 0.2–0.3 eV at interplanar separations of about 3.0–3.5 Å are thought to adequately represent aromatic excimer systems.[42] If a repulsive energy of this order of magnitude is taken into account, the anomalous fluorescence from benzene solutions is predicted to occur for an interplanar separation of ∼3.3 Å (see Fig. 3), the emission still occurring from a state of α parentage (B_{1g}). Calculations based on the extended Hückel treatment of Hoffmann[43] indicate a stable excimer at an interplanar separation of ∼3.4 Å,[44] which agrees well with the calculation presented here. A similar approximation underlies the interpretation of the paracyclophane spectra, and the introduction of the ground-state repulsion will make the calculated transition energies smaller than those observed experimentally. A more detailed calculation of the ground-state repulsion is not considered to be of value when the semiquantitative nature of the calculation is remembered. To avoid consideration of the ground-state repulsion term, we may compare the separation of the lowest two absorption bands with the value calculated. For [2.2] paracyclophane, the separation of the peaks of these bands (assigned in our calculation to transitions to the B_{1g} and B_{2u} states, respectively) is observed to be 3000 cm^{-1} (Fig. 5); the corresponding calculated value for rings separated by 3 Å is 2900 cm^{-1} (Fig. 3). This good agreement between experiment and our approximate calculation is very pleasing. We have not made detailed quantitative estimations of the intensities of the absorption bands of the paracyclophanes. Indeed, it may seem incongruous that the lowest transition in the [2.2] paracyclophane is assigned to the B_{1g} state in the D_{6h} dimer which will have zero transition moment (Table

---

[41] A. Ron and O. Schnepp, J. Chem. Phys. **44**, 19 (1966).

[42] J. B. Birks and L. G. Christophorou, Proc. Roy. Soc. (London) **A277**, 571 (1964).

[43] R. Hoffman, J. Chem. Phys. **39**, 1397 (1963).

[44] D. B. Chesnut, C. J. Fritchie, and H. E. Simmons, J. Chem. Phys. **42**, 1127 (1965).

I). However, the calculations presented here show that slight distortions from this ideal symmetry have little effect on the energy levels, but may affect the intensity of the transitions. Thus, the B_{1g} state in D_{6h} may borrow intensity from the B_{1u} state when the symmetry of the dimer is reduced to D_6.

Turning to the crystal spectra of [2.2] paracyclophane, we consider that no calculation possible at the present time can confidently predict the observed transitions separated by only 380 cm^{-1}, and the results reported here are no exception. Our calculations do provide reasonable suggestions as to the origin of these transitions, which can satisfactorily account for the polarization directions, and the low intensities. The distortions from D_{6h} symmetry which we have considered do not affect the assignment of the lowest transitions (B_{1g}), which may become allowed in the symmetry group of the distorted dimer. It is not possible to assign the origin of the second transition, for our calculations strongly suggest that the order of the B_{2u} and B_{2g} states *may* invert when the dimer is composed of boat-shaped monomers. For the [3.3] paracyclophane, we consider that such an inversion of these levels with a calculated separation of ~5000 cm^{-1} is unlikely, and predict that the two lowest transitions in this compound (unmeasured as yet) are both of α-state parentage.

ACKNOWLEDGMENTS

We are grateful to Dr. A. Ron and Professor O. Schnepp for many valuable discussions and for prepublication information. It was the study of their experimental work which stimulated our analysis of the paracyclophane spectrum.

We wish to thank the U.S. Public Health Service and the Directorate of Chemical Sciences of the Air Force of Scientific Research for financial support. We have also benefited from the use of facilities provided by the Advanced Research Projects Agency for materials research at the University of Chicago.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 44, NUMBER 1 1 JANUARY 1966

First Differential Ionization Efficiency Curves for Fragment Ions by Electron Impact

F. H. DORMAN*

C.S.I.R.O. Chemical Research Laboratories, Melbourne, Australia

(Received 6 July 1965)

Electron-impact dissociations which yield an ion pair have been studied, by examination of first-differential ionization efficiency curves. No evidence has been found for the occurrence of recently postulated reactions $RH\rightarrow R^{+}+H^{-}$ in hydrocarbons.

INTRODUCTION

USING second-differential ionization efficiency (I.E.) curves a study has been made by the author of direct-ionization electron-impact dissociations,[1–3] that produce positive ions and neutral fragments only. Ion-pair dissociations, however, can be more conveniently studied by first-differential I.E. fragment-ion curves. This is because the threshold laws for the probability of excitation by electron impact[4] lead to simple peak shapes in the first-differential I.E. curves for ion-pair processes. On a simple theory the I.E. curve is a step function for a single-electron, impact-induced ion-pair process,[5] if there is no Franck–Condon broadening, and hence a delta function in the first derivative. When there is energy spread in the ionizing electron beam, the first differential[6] ionization-probability curve will become a peak of the same half-width, in the present case 0.6–0.8 eV. If there is more than one level within this range, the first-differential peak will be broader. The problem of separating the Franck–Condon-type broadening is not considered here. For processes not involving kinetic energy, the amount may not be very significant.

Of the three ion-pair processes examined,[4] using the first-differential electron-impact I.E. curves of the positive fragment ions, $CO\rightarrow C^{+}+O^{-}$, $I_2\rightarrow I^{+}+I^{-}$, $O_2\rightarrow O^{+}+O^{-}$, photon-impact data confirmed the latter two.[7,8] There have been few examinations of the nega-

---

* Division of Chemical Physics, C.S.I.R.O. Chemical Research Laboratories, Melbourne, Australia.

[1] F. H. Dorman, J. Chem. Phys. **41**, 2857 (1964).

[2] F. H. Dorman, J. Chem. Phys. **42**, 65 (1965).

[3] F. H. Dorman, J. Chem. Phys. **43**, 3507 (1965).

[4] F. H. Dorman, J. D. Morrison, and A. J. C. Nicholson, J. Chem. Phys. **32**, 378 (1960).

[5] J. D. Morrison, J. Appl. Phys. **28**, 1409 (1957).

[6] Experimentally, differentials are measured rather than derivatives. The slight increase in apparent energy spread that this leads to is not important here for similar ionizing-voltage increments.

[7] J. D. Morrison, H. Hurzeler, M. G. Inghram, and H. E. Stanton, J. Chem. Phys. **33**, 821 (1960).

[8] C. A. McDowell, *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), Fig. 6, p. 411. The peak at 17.3 eV is the same, although there is disagreement above 19 eV for the higher processes. For the 17.3-eV peak only, see also F. A. Elder, D. Villarejo, and M. G. Inghram, J. Chem. Phys. **43**, 758 (1965).