Electronic and Vibrational Exciton Structure in Crystalline Benzene

E. R. Bernstein, S. D. Colson, R. Kopelman, and G. W. Robinson

Citation: The Journal of Chemical Physics **48**, 5596 (1968); doi: 10.1063/1.1668262
View online: http://dx.doi.org/10.1063/1.1668262
View Table of Contents: http://aip.scitation.org/toc/jcp/48/12
Published by the American Institute of Physics

Electronic and Vibrational Exciton Structure in Crystalline Benzene*

E. R. BERNSTEIN,† S. D. COLSON,‡ R. KOPELMAN,§ AND G. W. ROBINSON
Gates and Crellin Laboratories of Chemistry,|| California Institute of Technology, Pasadena, California
(Received 10 April 1967)

The purpose of this paper is to lay a consistent theoretical framework for the discussion of a series of forthcoming experimental papers on the absorption and emission of light by benzene crystals. Emphasis will be placed not only on the usual Davydov splittings but also on $\mathbf{k}\neq\mathbf{0}$ states and band-to-band transitions in neat (pure) crystals, and on orientational effects, site splittings, shifts, and resonance pair spectra in isotopic mixed crystals. The role of translationally equivalent interactions will be discussed. The *interchange-group* concept is used in order to simplify the theoretical analysis. From the four possible interchange groups $\mathbf{D}_2$, $\mathbf{C}_{2v}{}^a$, $\mathbf{C}_{2v}{}^b$, $\mathbf{C}_{2v}{}^c$, the $\mathbf{D}_2$ group is found to be the most convenient for the classification of benzene exciton functions. A differentiation between *static* and *dynamic* interactions is made in the limit of Frenkel excitons, and the concepts of *site distortion energy* and the *ideal mixed crystal* are introduced to aid in this distinction. Data pertaining to site shifts and splittings and resonance and quasiresonance interaction terms for the ${}^1B_{2u}$ electronic exciton band and the vibrational $\nu_{12}(b_{1u})$, $\nu_{15}(b_{2u})$, and $\nu_{18}(e_{1u})$ exciton bands are discussed in order to illustrate briefly the theoretical concepts.

I. INTRODUCTION

The benzene molecule has long served as a prototype for the study of π-electron systems. The benzene crystal has been of similar importance in the study of intermolecular interactions. The experimental investigation of vibrational[1] and electronic[2] transitions in solid benzene paralleled the theoretical development of symmetry considerations[3] and exciton theory[4] for molecular crystals. Several review articles discuss much of this past work.[5] More recently, a powerful approach to the investigation of exciton interactions, first mentioned by Hiebert and Hornig,[6] using off-resonance techniques in isotopic mixed crystals, has been utilized[7] in the study of the electronic exciton structure of benzene.

Certainly for vibrational excitons and probably for those electronic excitons associated with the lowest singlet and triplet states of benzene, the Frenkel limit applies. Even though the theory of Frenkel excitons has been discussed many times before, both in general and with particular reference to the benzene crystal, the presently available literature on this subject has many shortcomings for our purposes. The shortcomings arise especially in discussions of the symmetry classification of the crystal wavefunctions, the Davydov "D term," the approximations leading to closed-form expressions for eigenfunctions and eigenvalues of $\mathbf{k}\neq\mathbf{0}$ states, transition probabilities involving the $\mathbf{k}\neq\mathbf{0}$ states, the meaning of site-group splittings, and the causes of breakdown of oriented-gas-model polarization properties. It is partly for this reason that we undertake to redevelop and extend the subject as it specifically concerns the benzene-crystal problem. In doing this we develop the concepts of the *ideal mixed crystal* and the *site distortion energy* and clarify the meaning of the Davydov D term. We further emphasize the possible shortcomings of a first-order theory.

One of the specific purposes of this paper is to emphasize the importance of discussing exciton interactions in terms of precisely defined exciton coupling constants rather than splittings, band shapes, or over-all bandwidths. While it is possible to derive uniquely these characteristics of the exciton band from the coupling constants, the converse is not generally true. In particular, for the case of benzene, merely giving the splittings among the observed three Davydov components as has been done for both electronic and vibrational bands in no way fixes the magnitude or relative signs of the

* Work supported in part by a Grant from the National Science Foundation, GP-4238.
† Present address: Enrico Fermi Institute for Nuclear Studies, University of Chicago, 5630 Ellis Avenue, Chicago, Ill. 60637.
‡ Present address: Division of Pure Physics, National Research Council, Ottawa 7, Ontario, Canada.
§ Present address: Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48104.
|| Contribution No. 3512.

[1] (a) R. S. Halford and O. A. Schaeffer, J. Chem. Phys. **14**, 141 (1946); (b) R. D. Mair and D. F. Hornig, J. Chem. Phys. **17**, 1236 (1949); (c) A. Früling, Ann. Phys. (Paris) **6**, 26 (1951); (d) S. C. Sirkar and A. K. Ray, Ind. J. Phys. **24**, 189 (1950); (e) S. Zwerdling and R. S. Halford, J. Chem. Phys. **23**, 2221 (1955).

[2] (a) V. L. Broude, V. S. Medvedev, and A. F. Prikhotko, Zh. Eksp. Teor. Fiz. **21**, 665 (1951); (b) V. L. Broude, V. S. Medvedev, and A. F. Prikhotko, Opt. Spektrosk. **2**, 317 (1957); (c) V. L. Broude, Usp. Fiz. Nauk **74**, 577 (1961) [Sov. Phys.—Usp. **4**, 584 (1962)]; (d) V. N. Vatulev, N. I. Sheremet, and M. T. Shpak, Opt. Spektrosk. **16**, 577 (1964) [Opt. Spectrosc. **16**, 315 (1964)]; (e) A. Zmerli, J. Chim. Phys. **56**, 387 (1959).

[3] (a) R. S. Halford, J. Chem. Phys. **14**, 8 (1946); (b) D. F. Hornig, J. Chem. Phys. **16**, 1063 (1948); (c) H. Winston and R. S. Halford, J. Chem. Phys. **17**, 607 (1949); (d) H. Winston, J. Chem. Phys. **19**, 156 (1951); (e) L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

[4] (a) A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill Book Co., New York, 1962); (b) D. Fox and O. Schnepp, J. Chem. Phys. **23**, 767 (1955); (c) D. P. Craig and P. C. Hobbins, J. Chem. Soc. **1955**, 539; (d) D. P. Craig, J. Chem. Soc. **1955**, 2302; (e) D. P. Craig and S. H. Walmsley, Mol. Phys. **4**, 113 (1961); (f) D. P. Craig and J. R. Walsh, J. Chem. Soc. **1958**, 1613; (g) A. S. Davydov, Usp. Fiz. Nauk **82**, 393 (1964) [Sov. Phys.-Usp. **7**, 145 (1964)].

[5] (a) D. S. McClure, Solid State Phys. **8**, 1 (1959); (b) W. Vedder and D. F. Hornig, Advan. Spectry. **2**, 189 (1961); (c) O. Schnepp, Ann. Rev. Phys. Chem. **14**, 35 (1963); (d) D. P. Craig and S. H. Walmsley, in *Physics and Chemistry of the Organic Solid State*, D. Fox, M. M. Labes, and A. Weissberger, Eds. (Interscience Publishers, Inc., New York, 1963), Vol. 1, p. 586; (e) D. A. Dows, *ibid.*, p. 609.

[6] G. L. Hiebert and D. F. Hornig, J. Chem. Phys. **20**, 918 (1952).

[7] G. C. Nieman and G. W. Robinson, J. Chem. Phys. **39**, 1298 (1963).

excitation exchange interactions responsible for this splitting. This is so because one transition from the totally symmetric ground state to one of the Davydov components is dipole-forbidden. It should be further noted that the relative signs of the coupling constants have significance only if the convention used in defining the crystal wavefunctions is given explicitly. The *interchange-group* concept introduced in an earlier paper and discussed briefly in Sec. II is used for this purpose. Not only do the magnitudes and signs of the coupling constants uniquely define the Davydov splittings, but they also give detailed information concerning the directional properties of the excitation exchange interaction. This provides a much more sensitive test of theoretical calculations, which in the past have been compared only to over-all splittings, and thus presents a means of determining the origin of these interactions (i.e., in the case of electronic excitations, mixing with ion-pair exciton states,[8] octopole–octopole interactions,[4b] exchange interactions,[7] etc.).

Using the theory we illustrate, with specific examples from the benzene-crystal spectra, how to extract the exciton coupling constants. The band structure of the $^1B_{2u}$ electronic state and a few ground-state vibrational bands of C_6H_6 are discussed in detail. While the magnitudes and relative signs of the exciton coupling constants (see Sec. II.G) can be obtained from studies with unpolarized light, assignments of each coupling constant to an interaction among a specific set of molecules in the crystal requires that polarization properties of the transitions be known. Because of the difficulty of identification of crystal faces in benzene, in addition to depolarization caused by cracking and straining at low temperatures, polarization assignments are more apt to be unreliable than those in other crystals of aromatic molecules. It is hoped that unambiguous polarized-light experiments can be carried out in the near future, in order that reliable assignments of the coupling constants can be made. In the meantime the earlier polarization assignments of Broude[2e] for the electronic spectrum and those of Zwerdling and Halford[1e] for the infrared spectrum will be employed.

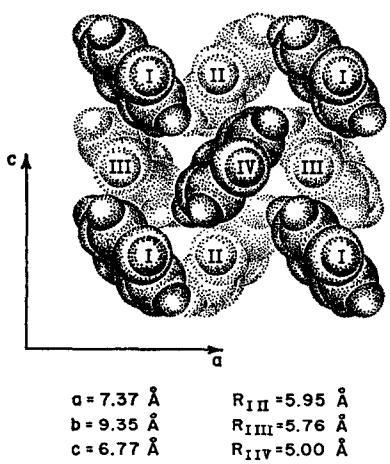

FIG. 1. Diagram of crystalline benzene viewed down the *b* axis. The R_{ij} are the center-to-center distances at 77°K between molecules *i* and *j*.

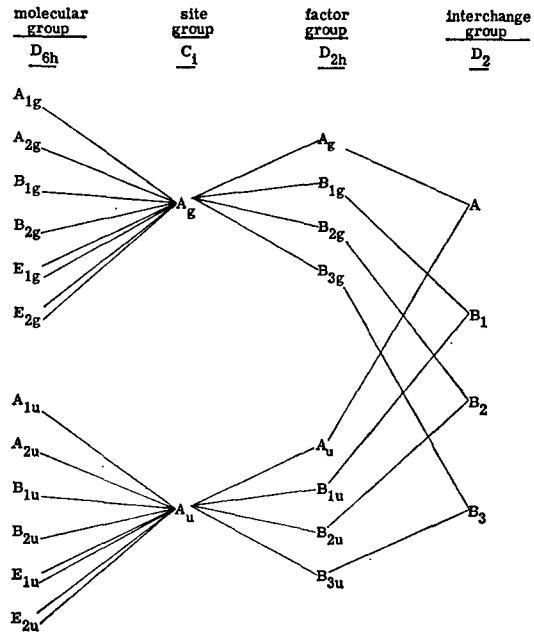

FIG. 2. Correlation among groups pertinent to the benzene crystal.

II. THEORY

A. Site, Interchange, and Factor-Group Symmetry

The symmetry of crystals can be considered as made up of the following types of operations: (1) *site operations*, describing the local "point" symmetry, where the "point" of interest usually is the center of the molecular building block, and (2) *transport operations*, carrying a given molecular unit into a physically identical location and orientation. The transport operations can be classified further into two categories: (a) the *translational operations*, and (b) the *interchange operations*. The latter includes both proper and improper rotations, screw rotations, and glide reflections. The so-called *static-field* interactions are related to the site symmetry, while the *dynamic* interactions are related to the transport symmetry.[5b] Dynamic interactions have gone under names such as excitation exchange, resonance, or exciton interactions, or by the term "the coupling of oscillators."

In the case of the benzene crystal the space group is $D_{2h}^{15}(P_{bca})$, and there are four molecules per primitive unit cell occupying sites of inversion symmetry[9] (see

[8] R. Silbey, S. A. Rice, and J. Jortner, J. Chem. Phys. **43**, 3336 (1965).

[9] E. G. Cox, Rev. Mod. Phys. **30**, 159 (1958); E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, Proc. Roy. Soc. (London) **A247**, 1 (1958); G. E. Bacon, N. A. Curry, and S. A. Wilson, *ibid.* **A279**, 98 (1964).

TABLE I. Symmetry transformations of the $\mathbf{k}=0$ one-site excitons.

	E	C_2^a	C_2^b	C_2^c	i	σ_a	σ_b	σ_c
$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{IV}}{}^g$
$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{III}}{}^g$
$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{II}}{}^g$
$\alpha_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{I}}{}^g$	$\phi_{\mathrm{IV}}{}^g$	$\phi_{\mathrm{III}}{}^g$	$\phi_{\mathrm{II}}{}^g$	$\phi_{\mathrm{I}}{}^g$
$\phi_{\mathrm{I}}{}^u$	$\phi_{\mathrm{I}}{}^u$	$\phi_{\mathrm{II}}{}^u$	$\phi_{\mathrm{III}}{}^u$	$\phi_{\mathrm{IV}}{}^u$	$-\phi_{\mathrm{I}}{}^u$	$-\phi_{\mathrm{II}}{}^u$	$-\phi_{\mathrm{III}}{}^u$	$-\phi_{\mathrm{IV}}{}^u$
$\phi_{\mathrm{II}}{}^u$	$\phi_{\mathrm{II}}{}^u$	$\phi_{\mathrm{I}}{}^u$	$\phi_{\mathrm{IV}}{}^u$	$\phi_{\mathrm{III}}{}^u$	$-\phi_{\mathrm{II}}{}^u$	$-\phi_{\mathrm{I}}{}^u$	$-\phi_{\mathrm{IV}}{}^u$	$-\phi_{\mathrm{III}}{}^u$
$\phi_{\mathrm{III}}{}^u$	$\phi_{\mathrm{III}}{}^u$	$\phi_{\mathrm{IV}}{}^u$	$\phi_{\mathrm{I}}{}^u$	$\phi_{\mathrm{II}}{}^u$	$-\phi_{\mathrm{III}}{}^u$	$-\phi_{\mathrm{IV}}{}^u$	$-\phi_{\mathrm{I}}{}^u$	$-\phi_{\mathrm{II}}{}^u$
$\phi_{\mathrm{IV}}{}^u$	$\phi_{\mathrm{IV}}{}^u$	$\phi_{\mathrm{III}}{}^u$	$\phi_{\mathrm{II}}{}^u$	$\phi_{\mathrm{I}}{}^u$	$-\phi_{\mathrm{IV}}{}^u$	$-\phi_{\mathrm{III}}{}^u$	$-\phi_{\mathrm{II}}{}^u$	$-\phi_{\mathrm{I}}{}^u$

Fig. 1). The site group is therefore $\mathbf{C}_i$. The four sets of translationally inequivalent molecules corresponding to the four sites per unit cell are labeled I, II, III, IV. Note that the designation of molecules II and IV has been changed from that of Nieman and Robinson[7] (also Fox and Schnepp[4b] and Craig and Walsh[4f]) to agree with the crystallographic work of Cox, Cruickshank, and Smith.[9]

The interchange operations in the benzene crystal are the screw-axis rotations C_2^a, C_2^b, and C_2^c and the glide-plane reflections $\sigma^a(\equiv iC_2^a)$, $\sigma^b(\equiv iC_2^b)$, and $\sigma^c(\equiv iC_2^c)$. Considering the translations as interchange-identity operations E, certain sets of the above-mentioned operations generate groups of order four[10] which we call *interchange groups*. The four interchange operations associated with an interchange group permute the four sets of translationally inequivalent molecules among themselves. There are four possible interchange groups for the benzene crystal: $\mathbf{C}_{2v}{}^a=\{E, C_2^a, \sigma^b, \sigma^c\}$, $\mathbf{C}_{2v}{}^b=\{E, \sigma^a, C_2^b, \sigma^c\}$, $\mathbf{C}_{2v}{}^c=\{E, \sigma^a, \sigma^b, C_2^c\}$, and $\mathbf{D}_2=\{E, C_2^a, C_2^b, C_2^c\}$. The particular set $\{E, C_2^a, C_2^b, C_2^c\}$ is unique in that it has the virtue that the right or left handedness of a coordinate system attached to a site is preserved upon such permutations. We therefore call the set $\mathbf{D}_2$ the *proper interchange group* for the benzene crystal.

The *factor group* $\mathbf{D}_{2h}$ for the benzene crystal is generated as the direct product of the site group and the interchange group, $\mathbf{D}_2\times\mathbf{C}_i$ for the particular case of the proper interchange group. This relationship among site, interchange, and factor-group symmetry holds, however, for all interchange groups, proper as well as improper. The space symmetry of the crystal is generated from the factor-group symmetry and the translational symmetry, or, alternatively, from the site and transport symmetries or the interchange and site-translation symmetry $\mathbf{S}(\alpha^1)$ defined by Vedder and Hornig.[5b] The correlation among the benzene molecular point group and the site, interchange, and factor groups in the benzene crystal is depicted in Fig. 2. It should be noted that the only nontrivial symmetry of the molecule that is carried over to the site, and therefore to the factor and space groups, is inversion.

[10] R. Kopelman, J. Chem. Phys. **47**, 2631 (1967).

B. Generation of Exciton Functions

In the limit of the tight-binding (Frenkel) approximation for a crystal containing N molecules with four molecules per unit cell, we construct antisymmetrized functions representing localized electronic or vibrational excitation f on a particular molecule at a given site in the crystal,

$$\phi_{nq}{}^f=\mathcal{A}\chi_{nq}{}^f\prod_{n'\neq n}^{N/4}\chi_{n'q}{}^0, \tag{1}$$

where $\mathcal{A}$ is the electronic antisymmetrizing operator, n labels the unit cell, q labels the site (I, II, III, IV) in the unit cell, and χ_{nq} is a *crystal-site function* (see below). From these functions one can generate the one-site exciton functions in the Bloch representation,[3e]

$$\phi_q{}^f(\mathbf{k})=(N/4)^{-1/2}\sum_{n=1}^{N/4}\exp(i\mathbf{k}\cdot\mathbf{R}_{nq})\phi_{nq}{}^f, \tag{2}$$

where $\mathbf{R}_{nq}$ denotes the position of the center of a molecule located at the qth site in the nth unit cell with respect to a common crystal origin and $\mathbf{k}$ is the reduced wave vector. It is convenient to write

$$\mathbf{R}_{nq}=\mathbf{r}_n+\boldsymbol{\tau}_{nq}, \tag{3}$$

with $\mathbf{r}_n$ defining some convenient local origin in the nth unit cell and $\boldsymbol{\tau}_{nq}$ being a vector from this local origin to site $q(=\mathrm{I}, \mathrm{II}, \mathrm{III}, \mathrm{IV})$ in this same unit cell. Note that because of translational symmetry $\boldsymbol{\tau}_{nq}$ is identical for all n. Therefore, we shall hereafter drop the subscript n.

Before going further one must be specific about the site numbering. One scheme is as good as another, but it is important to be consistent and always to state explicitly which convention is used, since the appearance of the results depends on the numbering scheme used. Using the operations of the proper interchange group $\mathbf{D}_2$, we define the numbering scheme for benzene as in Table I such that for $\mathbf{k}=\mathbf{0}$,[11] $C_2{}^a\phi_{\mathrm{I}}{}^f(\mathbf{0})\rightarrow\phi_{\mathrm{II}}{}^f(\mathbf{0})$,

[11] These relations do not hold for all values of $\mathbf{k}$; it is obvious that for the general case the interchange operations convert a function belonging to one value of $\mathbf{k}$ into a function belonging to a different value of $\mathbf{k}$. However, besides $\mathbf{k}=0$ there are other special values of nonzero $\mathbf{k}$ where certain of the relationships are valid, i.e., $C_2{}^a\phi_{\mathrm{I}}{}^f(k_a, 0, 0)=\phi_{\mathrm{II}}{}^f(k_a, 0, 0)$. See Ref. 3(e) for a full discussion.

$C_2^b\phi_I^f(\mathbf{0})\rightarrow\phi_{III}^f(\mathbf{0})$, and $C_2^c\phi_I^f(\mathbf{0})\rightarrow\phi_{IV}^f(\mathbf{0})$. In the same way C_2^a "interchanges" sites III and IV, C_2^b "interchanges" sites II and IV, while C_2^c "interchanges" sites II and III. This is the same numbering scheme as used by Cox, but is different from that of Ref. 4b and Ref. 7.

C. The Crystal Hamiltonian

We now proceed to determine the Hamiltonian matrix elements for the specific case of the benzene crystal. The manner in which one divides up the total crystal Hamiltonian H into a zero-order part and a perturbation Hamiltonian part depends upon the representation to be employed. In the tight-binding limit, where excitation is localized primarily at the site, it is convenient to divide H into a one-site Hamiltonian H^0 and an intersite interaction Hamiltonian H':

$$H^0=\sum_{n=1}^{N/4}\sum_{q=1}^{IV}H^0(nq), \tag{4}$$

$$H'=\tfrac{1}{2}\sum_{n=1}^{N/4}\sum_{q=1}^{IV}\sum_{n'=1}^{N/4}\sum_{q'=1}^{IV}(1-\delta_{nn'}\delta_{qq'})H'(nq;n'q'), \tag{5}$$

where $\delta_{nn'}\delta_{qq'}=1$ for $n=n'$ and $q=q'$ simultaneously, and is equal to zero otherwise. The eigenfunctions of $H^0(nq)$ are just the crystal-site functions χ_{nq} introduced in Eq. (1). It should be emphasized that Eq. (4) does not provide for multiple excitations of two or more sites, and therefore places at least a part (for example, the R^{-6} part) of the van der Waals' energy contribution in H'. Mixing with nonlocalized Wannier exciton states or ion-pair states must also come from H' when using the tight-binding representation.

Since the translational subgroup of the space group is Abelian, only one-dimensional irreducible representations occur.[12] Thus, as is well known, in the Bloch representation the Hamiltonian matrix describing the energy levels associated with a set of translationally equivalent molecules in a crystal contains no off-diagonal elements. The matrix is therefore diagonal in the reduced wave vector $\mathbf{k}$, each diagonal element being characterized by one specific value of this "quantum number." If only a single nondegenerate excited state of the molecule is considered and if the crystal structure is such that there is only one molecule per unit cell, i.e., if all N molecules in the crystal are translationally equivalent, then the $N\times N$ Hamiltonian matrix simply consists of N diagonal terms of the type $\langle f,\mathbf{k}\,|\,H\,|\,f,\mathbf{k}\rangle$, where f, $\mathbf{k}$ represents the function (and its complex conjugate) of Eq. (2) for a single q, and where $H=H^0+H'$.

If two molecular states, say f' and f'', in such a crystal are considered, then the Hamiltonian matrix consists of $2N$ diagonal terms, $\langle f',\mathbf{k}\,|\,H\,|\,f',\mathbf{k}\rangle$ and $\langle f'',\mathbf{k}\,|\,H\,|\,f'',\mathbf{k}\rangle$. Since in general $\phi_q^f(\mathbf{k})$ need not be an exact eigenfunction of H because of the choice of χ_{nq}^f, there may be "configuration-interaction" terms $\langle f',\mathbf{k}\,|\,H\,|\,f'',\mathbf{k}\rangle$, giving rise to a matrix consisting of N 2×2 blocks along the main diagonal. Many such singly excited configurations $f',f'',f'''\cdots$ may have to be considered. In addition, again depending upon the choice of representation, there may be *multiply excited configurations* of the crystal that must be included for energy or intensity calculations. For example, the doubly excited configurations constructed from localized excitation functions,

$$\phi_{n',n''}^{f'f''}=\mathcal{A}\chi_{n'}^{f'}\chi_{n''}^{f''}\prod_{n\neq n',n''}^{N}\chi_n^0 \tag{6}$$

(for one molecule per unit cell), may be very important in the consideration of van der Waals energies and spectral shifts through the matrix elements $\langle f'f'',\mathbf{k}\,|\,H\,|\,00,\mathbf{k}\rangle$ and $\langle f'f'',\mathbf{k}\,|\,H\,|\,f0,\mathbf{k}\rangle$.

When there are 4 molecules per unit cell (4 different sets of translationally equivalent molecules) and the possibility exists of doubly degenerate molecular states, as in the benzene crystal, the Hamiltonian matrix is a little more complicated. Considering only a single, nondegenerate excited state f, the full $N\times N$ Hamiltonian matrix consists of $\frac{1}{4}N$ 4×4 Hermitian submatrices, each submatrix labeled by a unique $\mathbf{k}$, along the main diagonal. Off-diagonal elements within each submatrix arise because of interactions among the four sets of translationally inequivalent molecules (i.e., among the four *sites*). Matrices of higher order than four would have to be considered if f described a doubly degenerate molecular state (in which case the $\frac{1}{4}N$ submatrices are 8×8) or if interaction of the fth configuration with other singly or multiply excited configurations were to be included.

D. First-Order Frenkel Theory

Using the one-site exciton functions of Eq. (2) as zero-order functions, the first-order Hamiltonian matrix elements for the excited state of crystalline benzene, corresponding to the fth excited state of the molecule, are

$$\mathcal{L}_{qq'}^f(\mathbf{k})=\sum_{n'=1}^{N/4}\exp(i\mathbf{k})\cdot(\boldsymbol{\tau}_{q'}-\boldsymbol{\tau}_q)\exp(i\mathbf{k})\cdot(\mathbf{r}_{n'}-r_n)\times\int\phi_{nq}^{f*}H\phi_{n'q'}^f dR. \tag{7}$$

It is convenient in Eq. (7) to separate the $\mathbf{k}$-independent terms, for which $q=q'$ and $n=n'$, from the $\mathbf{k}$-dependent terms, and write

$$\mathcal{L}_{qq'}^f(\mathbf{k})=(\epsilon^f+D^f)\delta_{qq'}+L_{qq'}^f(\mathbf{k}), \tag{8}$$

[12] (a) E. P. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), p. 59; (b) G. F. Koster, *Space Groups and Their Representations* (Academic Press Inc., New York, 1957), first published in *Solid State Physics*, F. Seitz and D. Turnbull, Eds. (Academic Press Inc., New York, 1957), Vol. 5, pp. 173–256; C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), Chap. 9.

where

$$\epsilon^f = \int \phi_{nq}{}^{f*} H^0 \phi_{nq}{}^f dR, \tag{9}$$

$$D^f = \int \phi_{nq}{}^{f*} H' \phi_{nq}{}^f dR. \tag{10}$$

Using an approximate Hamiltonian matrix, in which certain nonnearest translationally equivalent interactions are assumed negligible,[13] the normalized crystal eigenfunctions $\Psi^{f\alpha}(\mathbf{k})$ may be expressed in terms of the representations α of the $\mathbf{D}_2$ interchange group. They are

$$\Psi^{f\alpha}(\mathbf{k}) = \tfrac{1}{2} \sum_{q=\mathrm{I}}^{\mathrm{IV}} a_q{}^{\alpha} \phi_q{}^f(\mathbf{k}), \tag{11}$$

where the $a_q{}^{\alpha}$ are coefficients corresponding to the αth representation of $\mathbf{D}_2$. For $\alpha = A$, $a_q{}^A = +1, +1, +1, +1$ when $q = \mathrm{I}, \mathrm{II}, \mathrm{III}, \mathrm{IV}$, respectively. Similarly, $a_q{}^{B1} = +1, +1, -1, -1$; $a_q{}^{B2} = +1, -1, +1, -1$; and $a_q{}^{B3} = +1, -1, -1, +1$. It is to be noted that the convenient use of $a_q{}^{\alpha}$ in Eq. (11) in no way implies that the functions $\Psi^{f\alpha}(k)$ are bases for the representations of the interchange group. As we have emphasized earlier,[11] this is true only for special values of $\mathbf{k}$. In the particular case of $\mathbf{k}=\mathbf{0}$ one need not call upon the above approximation, and in our first-order tight-binding limit, the eigenfunctions may be written exactly:

$$\begin{aligned}
\Psi^{fA}(\mathbf{0}) &= \tfrac{1}{2}[\phi_{\mathrm{I}}{}^f(\mathbf{0}) + \phi_{\mathrm{II}}{}^f(\mathbf{0}) + \phi_{\mathrm{III}}{}^f(\mathbf{0}) + \phi_{\mathrm{IV}}{}^f(\mathbf{0})], \\
\Psi^{fB_1}(\mathbf{0}) &= \tfrac{1}{2}[\phi_{\mathrm{I}}{}^f(\mathbf{0}) + \phi_{\mathrm{II}}{}^f(\mathbf{0}) - \phi_{\mathrm{III}}{}^f(\mathbf{0}) - \phi_{\mathrm{IV}}{}^f(\mathbf{0})], \\
\Psi^{fB_2}(\mathbf{0}) &= \tfrac{1}{2}[\phi_{\mathrm{I}}{}^f(\mathbf{0}) - \phi_{\mathrm{II}}{}^f(\mathbf{0}) + \phi_{\mathrm{III}}{}^f(\mathbf{0}) - \phi_{\mathrm{IV}}{}^f(\mathbf{0})], \\
\Psi^{fB_3}(\mathbf{0}) &= \tfrac{1}{2}[\phi_{\mathrm{I}}{}^f(\mathbf{0}) - \phi_{\mathrm{II}}{}^f(\mathbf{0}) - \phi_{\mathrm{III}}{}^f(\mathbf{0}) + \phi_{\mathrm{IV}}{}^f(\mathbf{0})].
\end{aligned} \tag{12}$$

The functions $\Psi^{f\alpha}(\mathbf{0})$ map into *gerade* or *ungerade* functions of the $\mathbf{D}_{2h}$ factor group, depending on whether χ^f is *gerade* or *ungerade*. The complete correlation diagram is given in Fig. 2.

It is important to note that the $\mathbf{k}=\mathbf{0}$ crystal-function transformations under $\mathbf{D}_2$ are independent of the symmetry g or u of the site function χ^f. This is not the case[10] for the other three possible interchange groups, all of which contain two glide-plane reflection operations that change the sign of u functions but not of g functions, if right-handed coordinate systems are used throughout. This is an example of the kind of ambiguity that may arise when an improper interchange group is used. Group theoretically, such improper groups are correct, but they can certainly lead to confusion in practice. In any case, both for those who use the proper interchange group and for those who insist on using improper ones, it is important in molecular-crystal spectroscopy that the convention, whatever it is, be stated explicitly. Even though the difference of results is only a matter of phasing, in order to compare calculated and experimental quantities it *is* important to know just what phase relation is used by any particular author!

It should perhaps be pointed out how *not* to form interchange or factor-group representations. Symmetry elements present in the molecule but absent in the site have no significance in the crystal! Using them to find the interchange or factor-group representations is definitely incorrect in principle and, at best, misleading in practice. This procedure, introduced by Davydov (see p. 43 of Ref. 4a), has consistently given wrong or inconsistent results for the benzene crystal, though usually the results have been correct for systems such as naphthalene and anthracene where there are only two molecules per unit cell. For instance, Davydov (p. 56 of Ref. 4a) gives only a pair of factor-group components (and different ones at that!) for B_{1u} and B_{2u} electronic states of benzene, even though he employs four molecules per unit cell. The reason that Davydov obtained incorrect results for benzene was not, as is often stated,[2e,4b] that he employed the old crystal structure, since that had the correct space group. It was because he tried to make use of the molecular-point-group operations in the crystal, where, except for those preserved by the site, they have no meaning.

In the paper of Fox and Schnepp[4b] an attempt was made to follow Davydov's method of constructing factor-group representations by using molecular-point-group operations. These authors did, however, use carefully selected coordinate systems on each molecule in conjunction with the refined crystal-structure data of Cox.[9] They correctly found four factor-group components for each nondegenerate state of molecular benzene, in agreement with Winston[3d]; but the crystal functions they obtained for the molecular B_{1u} state belonged to different factor-group representations than those for the molecular B_{2u} state! Both B_{1u} and B_{2u} states, and for that matter all u states of benzene, have identical site and factor-group representations and should therefore all be described by the same type of crystal wavefunction insofar as symmetry is concerned. It is easy to see from what we have presented here and in Sec. II.A that the treatment of Fox and Schnepp actually amounts to the use of the $\mathbf{C}_{2v}{}^b$ interchange group for the $^1B_{1u}$ molecular electronic state and the $\mathbf{C}_{2v}{}^c$ interchange group for the $^1B_{2u}$ state. The use of such conventions is mathematically correct, but, unless they are stated explicitly, the meaning of the factor-group wavefunctions and the relative signs (*vide infra*) of the coupling constants become obscure.

One last thing should be pointed out. The use of projection operators[14] does indeed guarantee that the crystal functions are eigenfunctions, but does not specify a convention, unless the phases of the functions used in this method are explicitly identified with certain interchange operations.[10]

[13] (a) S. D. Colson, R. Kopelman, and G. W. Robinson, J. Chem. Phys. **47**, 27 (1967); (b) S. D. Colson, D. M. Hanson, R. Kopelman, and G. W. Robinson, J. Chem. Phys. **48**, 2215 (1968).

[14] Ref. 12(a) p. 118.

E. Site Functions

For small site distortions like those for crystalline benzene, distinguishing between site functions and molecule functions is not expected to make large differences in energy. It is, however, extremely important to differentiate between site functions and free-molecule functions when considering intensities and polarization properties of transitions. A breakdown of the oriented-gas model for intensities can occur because of site distortion even in the absence of large energy perturbations by intersite interactions. The oriented-gas model, for example, would be obviously inappropriate in cases where a weak or forbidden gas-phase transition is greatly enhanced in the crystal. Such enhancement can occur even though the intermolecular forces causing the intensity enhancement are so weak that they do not cause a measurable breakdown of the first-order Frenkel limit with respect to energy.

Unfortunately, the concept of the site function as introduced by Winston and Halford[3c] and further discussed by Winston[3d] is somewhat ambiguous. These authors envisioned the distortion at the site as arising from a general "crystal field." This sort of language is convenient for many problems, and in particular for the discussion of the vibrational states of crystals, with which Winston and Halford were primarily concerned. For the vibrational problem it is easy to separate crystal-field effects in H^0 from interaction terms in H'. One merely considers in H^0 a molecule in the crystal where not only the nuclei but also the electrons have been distorted. This leads to different equilibrium nuclear positions and different (intramolecular) force constants than in the free molecule; H', which also has the symmetry of the site, is written in terms of intermolecular force constants coupling these distorted molecules. For the electronic exciton problem, however, the crystal-field idea does not allow a very clear separation of H^0 and H'. Which intermolecular interaction terms in H should be considered part of the "crystal field," and which should be included in H'?

Three possible choices of electronic basis functions $\chi_{nq}{}^f$ come to mind: (1) the $\chi_{nq}{}^f$ could be eigenfunctions of a free, undistorted benzene molecule, (2) $\chi_{nq}{}^f$ could be eigenfunctions of a distorted benzene molecule in some "average field" of all the other molecules in the crystal, or (3) $\chi_{nq}{}^f$ could be eigenfunctions of a free benzene molecule whose nuclear framework has been distorted to match that of the molecule in the crystal.

The first choice is undesirable since the symmetry of the terms in H^0 are higher than that of the crystal site. Terms in H' would then have to contain the effect of the nuclear distortion on the electronic energies in addition to the usual interaction terms. The advantage of this approach, however, lies in the relative simplicity of the basis functions, and is therefore the one that has been used in theoretical calculations. It should be emphasized that the higher-order effects of configuration interaction and van der Waals energy must be taken care of separately in this approach. Thus, a strictly first-order theory may be inadequate to explain "shifts" and other contributions to the crystal energies. Such contributions are expected to be particularly important for electronic excitation. We shall not consider this model here since one of our objectives is to emphasize the consequences of the low symmetry of the crystal-site functions.

The second type of basis function may lead to the kind of ambiguity mentioned earlier, since terms in H^0 representing the "crystal field" contain intermolecular interelectronic interactions usually included in H'. It would be desirable to choose H^0 to be an "effective Hamiltonian" such that the eigenvalues $\langle 0 \mid H^0 \mid 0 \rangle$ and $\langle f \mid H^0 \mid f \rangle$ already include $\mathbf{k}$-independent configuration-interaction and van der Waals terms. However, such an effective Hamiltonian cannot be written down in terms of one-site functions as in Eq. (4), and to include multi-site functions in H^0 would destroy the useful Frenkel exciton formalism upon which the above theoretical results are based. We therefore abandon this extreme approach in the case of vibrational and low-lying electronic states of benzene, which we feel lie very close to the Frenkel limit.

To employ a less extreme crystal-field model, where only one-site terms appear in H^0, is possible, but difficult to prescribe precisely. Qualitatively, the electrons and nuclei at the site are distorted by some effective electrical field caused by the rest of the crystal, the field being chosen so as to minimize contributions from higher-order effects. The van der Waals terms and terms arising from configuration interaction with, say, Wannier or ion-pair states of the crystal must be taken into account separately by perturbation theory.

A still less extreme crystal-field model would be the third one above—the distorted-nuclei model. It would again give rise to van der Waals and configuration-interaction contributions, since the electronic eigenfunctions of a free molecule, even though its nuclei have been distorted, are not necessarily equivalent to eigenfunctions of any of the zero-order Hamiltonians in the second model. Thus, the distorted-nuclei model gives rise to the same kind of energy contributions as the $\mathbf{D}_{6h}$ model, but the value of each energy contribution differs for the two models. In addition, the $\mathbf{k}$-dependent energies differ for the various models. Just as in other problems, individual terms in a total energy expression have different values depending upon what representation is used, and the terms add up to the true total energy only in the highest order of approximation.

F. Band Energies

The $\mathbf{k}$-dependent energies of the exciton band can be obtained in closed form to first-order in crystal-site wavefunctions from the approximate Hamiltonian matrix discussed in Ref. 13. This first-order energy, expressed in a manner similar to the original Davydov

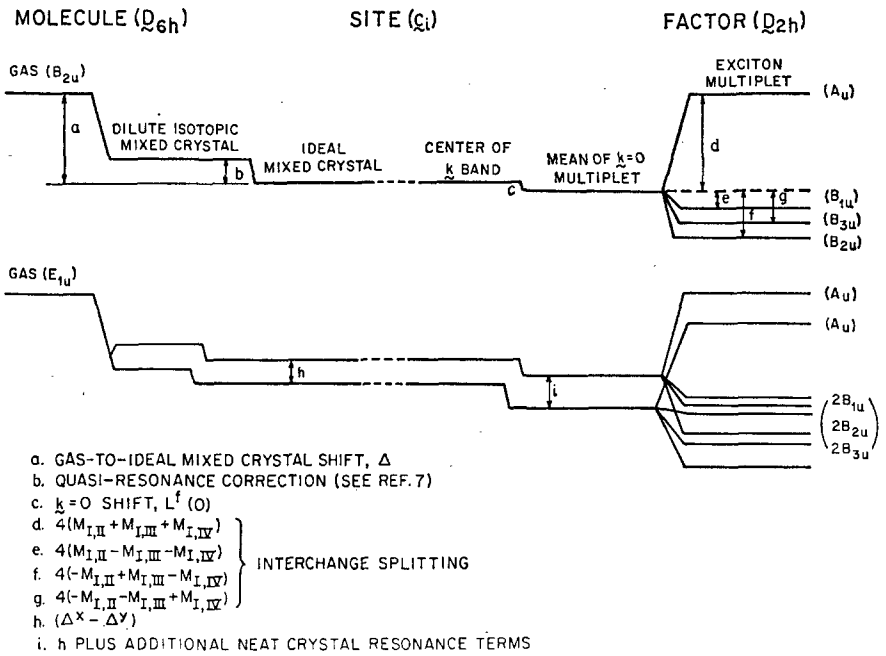

FIG. 3. Schematic exciton structure—benzene.

form,[4a] is

$$E^{f\alpha}(\mathbf{k})\equiv\mathcal{E}^{f\alpha}(\mathbf{k})-\mathcal{E}^0=\epsilon+D+L^{f\alpha}(\mathbf{k}). \quad (13a)$$

When higher-order effects are taken into account Eq. (13a) becomes

$$E^{f\alpha}(\mathbf{k})=\epsilon+D+L^{f\alpha}(\mathbf{k})+W+w(\mathbf{k}). \quad (13b)$$

In these equations $\mathcal{E}^{f\alpha}(\mathbf{k})$ and $\mathcal{E}^0$ are, respectively, the excited and ground-state energies of the crystal; $\epsilon=\epsilon^f-\epsilon^0$, where ϵ^f and ϵ^0 are the excited and ground-state energies of a molecule at the site whose eigenfunctions $\chi_{nq}{}^f$ are specified by some particular site representation; $D=D^f-D^0$ is a $\mathbf{k}$-independent band-shift term, and $L^{f\alpha}(\mathbf{k})$ is the $\mathbf{k}$-dependent energy associated with the αth irreducible representation of the interchange group. The quantities ϵ^f and D^f were defined in Sec. II.D; ϵ^0 and D^0 are analogously defined except that ground-state site functions $\phi_{nq}{}^0$ are employed. To first order, the $\mathbf{k}$-dependent energy $L^{f\alpha}(\mathbf{k})$, which is of primary importance in the consideration of the Frenkel exciton-band structure, is a function of the $\mathbf{k}$-dependent matrix elements $L_{qq'}{}^f(\mathbf{k})$ defined in Sec. II.D:

$$L^{f\alpha}(\mathbf{k})=L^f(\mathbf{k})+a_{\mathrm{II}}{}^{\alpha}L_{\mathrm{I\,II}}{}^f(\mathbf{k})+a_{\mathrm{III}}{}^{\alpha}L_{\mathrm{I\,III}}{}^f(\mathbf{k})+a_{\mathrm{IV}}{}^{\alpha}L_{\mathrm{I\,IV}}{}^f(\mathbf{k}). \quad (14)$$

We have dropped the subscripts on the diagonal element $L_{qq}{}^f(\mathbf{k})$, since the approximation[13] from which Eq. (14) is derived rests on the fact that

$$L_{\mathrm{I\,I}}{}^f(\mathbf{k})=L_{\mathrm{II\,II}}{}^f(\mathbf{k})=L_{\mathrm{III\,III}}{}^f(\mathbf{k})=L_{\mathrm{IV\,IV}}{}^f(\mathbf{k}) \quad (15)$$

for each $\mathbf{k}$. Equation (15) is not an approximation, of course, for some special values of $\mathbf{k}$ such as $\mathbf{k}=\mathbf{0}$.[4g] The quantities W and $w(\mathbf{k})$ in Eq. (13b) represent the contributions from higher-order $\mathbf{k}$-independent shift terms and higher-order $\mathbf{k}$-dependent energies, respectively.

Rather than specifying any particular representation in this paper, for the purpose of fitting the experimental data we shall simply adopt the form of Eqs. (13a) and (13b) with the understanding that the theoretical values of the parameters depend upon the particular representation chosen.

If the higher-order $\mathbf{k}$-dependent terms $w(\mathbf{k})$ are negligible, as they will be in the case where perturbing bands are far removed from the Frenkel exciton band under study, the simple form of $L^{f\alpha}(\mathbf{k})$ discussed in the preceding sections is preserved. We shall assume this to be the case for vibrational as well as low-lying electronic excitations in crystalline benzene, and shall show in this and subsequent papers that such an assumption does not conflict with experimental evidence. Even though the higher-order $\mathbf{k}$-dependent terms must be ignored to preserve the simple form of our equations, for the purpose of fitting experimental data all the higher-order $\mathbf{k}$-independent shift terms, such as the van der Waals terms, may be included without difficulty. Neglecting the $w(\mathbf{k})$, we rewrite Eq. (13b) as

$$E^{f\alpha}(\mathbf{k})=\tilde{\epsilon}+L^{f\alpha}(\mathbf{k})+\Delta, \quad (16)$$

where

$$\Delta=\epsilon-\tilde{\epsilon}+D+W.$$

Some of these energy contributions for mixed crystals and for $\mathbf{k}=\mathbf{0}$ states of neat crystals are illustrated schematically in Fig. 3 for both degenerate and nondegenerate states of molecular benzene. The quantity $\tilde{\epsilon}$ is just the gas-phase excitation energy. In some of our

future papers it will be convenient to introduce a "site distortion energy" $P=\epsilon-\bar{\epsilon}$. In Eq. (16) the quantities $L^{f\alpha}(\mathbf{k})$ and Δ can be imagined by the experimentalist as the $\mathbf{k}$-dependent energy and site-shift term that give the best fit to the observed exciton-band energies relative to the free-molecule energy, and by the theorist as quantities to be calculated using first- and higher-order perturbation theory starting with the best available site functions $\chi_{nq}{}^{f}$. It is possible further to decompose Δ for degenerate states into a shift term and an intrasite resonance shift contribution. This approach will be taken in a future paper from this laboratory concerning crystal-site effects for the benzene system.[15] Knowing $E^{f\alpha}(\mathbf{k})$ and $\bar{\epsilon}$, experiments can generally[16] shed light only on the over-all values of $L^{f\alpha}(\mathbf{k})$ and Δ, not on the source of these terms.

It is necessary to make a final comment upon the D term in Δ. The reader should note that the D term does not contain contributions from site states other than the ground and particular excited state with which one is dealing, and is representation-dependent. There has been some ambiguity in the literature about this D term. Some workers, while using a definition of D similar to ours and free-molecule basis functions, have tried to equate it to the total experimental gas-to-crystal band shift for the transition. This, of course, is a highly erroneous kind of correlation, particularly for electronic excitations, because of the possible presence of relatively large second-order shift terms and the difference between D at the site and D calculated with molecular functions. In some cases, but not benzene, there is also the possible presence of large $\mathbf{k}=\mathbf{0}$ shift terms $L^{f}(\mathbf{0})$, that cause the mean value of the $\mathbf{k}=\mathbf{0}$ Davydov components not to be related to the mean energy of the whole band. Still other workers have tried to equate the entire gas-to-crystal shift to the $\mathbf{k}=\mathbf{0}$ shift terms. The reader should note that the shifts in neat (the term *neat* is used here to mean unadulterated; the term *pure* is used in reference to chemical impurities) crystals, in isotopic mixed crystals, and in chemical mixed crystals (i.e., benzene in hexane) are often all of similar size and direction. The effect of resonance interactions is nearly lost in the second case and completely lost in the latter case, indicating that resonance interactions must give a relatively minor contribution to the shift. For some molecular-crystal transitions, where the exciton interactions are strong, such correlations between experimental and theoretical band-shift terms may be more nearly correct than for the benzene transitions discussed here. However, even in these cases neglect of site distortion energy and in particular second-order contributions to Δ is probably not justified.

[15] E. R. Bernstein (unpublished).

[16] This point is discussed by T. Thirunamachandran, Ph.D. thesis, University College, London, 1961. He points out that the importance of the octopole–octopole interactions in determining the Davydov splitting can be evaluated by determining the polarizations of the benzene exciton components.

G. Coupling Constants and Davydov Splittings

Some earlier papers[4b,4f,7] concerned with the exciton structure of crystalline benzene expressed first-order energies in terms of coupling constants M_a, M_b, M_c, $M_{\mathrm{I\,II}}$, $M_{\mathrm{I\,III}}$, and $M_{\mathrm{I\,IV}}$, dropping the superscript f, whence

$$\begin{aligned} L^{f}(\mathbf{0}) &= 2M_a(\mathbf{0})+2M_b(\mathbf{0})+2M_c(\mathbf{0}), \\ L_{\mathrm{I\,II}}{}^{f}(\mathbf{0}) &= 4M_{\mathrm{I\,II}}(\mathbf{0}), \\ L_{\mathrm{I\,III}}{}^{f}(\mathbf{0}) &= 4M_{\mathrm{I\,III}}(\mathbf{0}), \\ L_{\mathrm{I\,IV}}{}^{f}(\mathbf{0}) &= 4M_{\mathrm{I\,IV}}(\mathbf{0}), \end{aligned} \tag{17}$$

there being an identical set of translationally equivalent interactions along each positive and negative crystallographic direction a, b, and c and a set of four identical interactions between any molecule and its translationally inequivalent neighbors. While Ref. 7 considered the M's in Eq. (17) to be nearest-neighbor interactions, they are really summed quantities over all members of each set in accordance with Eq. (7). Since translationally equivalent interactions lying skew to the crystallographic axes have been omitted,[13] the energy contribution $L^{f}(\mathbf{0})$ in Eqs. (17) is approximate even for $\mathbf{k}=\mathbf{0}$. However, for the ${}^{1}B_{2u}$ and ${}^{3}B_{1u}$ electronic states of benzene, and undoubtedly also for vibrational states of benzene, the approximation is an excellent one because of the smallness of the omitted terms (*vide infra*).

For the particular case of $\mathbf{k}=\mathbf{0}$, the resulting four energy levels associated with each nondegenerate molecular state are the Davydov components. These are important, since they are the only ones that can be reached by interaction with radiation from the $\mathbf{k}=\mathbf{0}$ ground state of the crystal. In terms of the coupling constants and with respect to a common origin, $\bar{\epsilon}+\Delta+L^{f}(0)$, the $\mathbf{k}=\mathbf{0}$ energies and polarizations relative to the crystallographic axes are

$$\begin{aligned} E(A) &= 4(+M_{\mathrm{I\,II}}+M_{\mathrm{I\,III}}+M_{\mathrm{I\,IV}}), \\ E(B_1) &= 4(+M_{\mathrm{I\,II}}-M_{\mathrm{I\,III}}-M_{\mathrm{I\,IV}}), && \| a, \\ E(B_2) &= 4(-M_{\mathrm{I\,II}}+M_{\mathrm{I\,III}}-M_{\mathrm{I\,IV}}), && \| b, \\ E(B_3) &= 4(-M_{\mathrm{I\,II}}-M_{\mathrm{I\,III}}+M_{\mathrm{I\,IV}}), && \| c, \end{aligned} \tag{18}$$

where it is understood that the $M_{qq'}$'s refer to $\mathbf{k}=\mathbf{0}$. These equations are exact for the Frenkel model. It should be noted that the mean value $\bar{\epsilon}+\Delta+L^{f}(\mathbf{0})$ of the Davydov components lies at the mean value $\bar{\epsilon}+\Delta$ of the exciton band only in the case where all $\mathbf{k}$-dependent translationally equivalent interactions are negligible. $L^{f}(\mathbf{0})$ will be referred to as the $\mathbf{k}=\mathbf{0}$ shift (or the *translational shift*). This point is important in the analysis of isotopic mixed-crystal data, since it is $\bar{\epsilon}+\Delta$, not $\bar{\epsilon}+\Delta+L^{f}(\mathbf{0})$, that determines the position of the guest energy levels in the ideal case (*vide infra*).

H. Site-Group Splitting and the Ideal Mixed Crystal

Direct manifestation of the reduction in symmetry of molecular quantities in the site is the site-group splitting.

Symmetry arguments show that degenerate states of the molecule often map into nondegenerate irreducible representations of the site group. This is true in benzene, where the molecular symmetry is much higher than the site symmetry (see Fig. 2). Degeneracies present in the molecular state can therefore be removed by the site. The splitting has been called *site-group splitting*[3a] and has been primarily studied in the vibrational spectrum of molecular crystals. Site splitting is certainly not limited to vibrations alone, but is probably not a very useful concept for degenerate electronic states where vibronic interactions are also present.

In order to be able to discuss site-group splitting without complications due to interchange group splitting it is suggested that site-group splitting be defined phenomenologically as the splitting obtained for the guest in an *ideal mixed crystal.* The ideal mixed crystal is defined as one in which: (a) the guest is infinitely dilute, (b) the only difference between guest and host is one of isotopic substitution, (c) guest and host have the same symmetry and dimensions, (d) quasiresonance interactions between guest and host are negligible, and (e) the effects of isotopic substitution on Δ can be neglected. Isotopic mixed crystals approximate fairly closely this definition for most vibrational states but not necessarily for electronic states (see Sec. IV). Small correction terms to be discussed later can be applied to bring the isotopic mixed crystal even closer to the concept of the ideal mixed crystal in those cases where it is an appropriate approximation. The phenomenological definition of the ideal mixed crystal brings into agreement, as closely as is thought possible, the observed vibrational site-group splitting in isotopic mixed crystals and the original idea[3a] that site-group splitting is the result of the static-field ($\mathbf{k}$-independent) interactions at the site. In the ideal mixed crystal the site-group splitting of a degenerate-gas-phase band will therefore be quantitatively identical to the difference in the Δ terms of the originally degenerate components. Symbolically this can be written as $(\Delta_x-\Delta_y)$, where x and y designate the degenerate components.

In the neat crystal there are additional resonance contributions to the splitting of free-molecule degenerate states. Excitation exchange interactions will couple not only site-group components of one kind (say x) among different sites, but may also couple site-group components of different kinds (x and y) among the various sites. The last statement is certainly true when both "kinds" belong to the same site-group species (benzene!), but is true also in some cases where the two "kinds" belong to different site-group species.[17] In other words, degenerate or nearly degenerate levels present after the static interactions have been introduced may be further coupled together by the dynamic ($\mathbf{k}$-dependent) interactions in the neat crystal or by quasiresonance interactions in the mixed crystal. This statement holds whether the near degeneracy arises from site-group splitting or from accidental degeneracies present in the system. The latter case when applied to vibrational levels resembles Fermi resonance.[18] It is different from typical Fermi resonance in that the effect is an intermolecular one and that anharmonicities of the usual type need not be present to effect the interaction.

The essence of the last paragraph is that *whenever site-group splitting and interchange-group splitting are expected together, the total effect cannot be handled even conceptually as a simple superposition of two independent effects.* For the benzene crystal, the full 8×8 submatrix must be considered. Since there are in this case 10 independent off-diagonal coupling constants, their values are not determinable from the limited experimental data obtainable. A separation of the two effects would be justified as a first approximation only if: (a) the site-group interaction is an order of magnitude larger than the resonance interactions, (b) the site-group components are of different symmetry (see, however, Ref. 17), or (c) the resonance interactions are much larger than the site-group splitting. Except for the first two cases, the so-called site-group splitting in a neat crystal will contain contributions not only from the phenomenological site-group splitting in the ideal mixed crystal, but also from resonance interactions usually discussed within the space group.

The ideal mixed crystal is also a useful concept for discussing nondegenerate states. If, for a real mixed crystal, the deviations from the idealizing conditions can be evaluated quantitatively, the mean value $\bar{\epsilon}+\Delta$ of the exciton band can be found from the mixed-crystal energy. This technique allows one to evaluate $L'(\mathbf{0})$ if the mean value $\bar{\epsilon}+\Delta+L'(\mathbf{0})$ of the Davydov components is independently known. Similarly, if $L'(\mathbf{0})$ is known to be negligible, the mean value of the Davydov components can be equated to $\bar{\epsilon}+\Delta$. For the case of benzene vibrations where $L'(\mathbf{0})$ is expected to be small, this provides a technique for finding the position of the "forbidden" Davydov component. These concepts were utilized by Nieman and Robinson[7] for the determination of the Davydov structure of the lowest excited electronic states of the benzene crystal.

III. EXPERIMENTAL METHODS AND RESULTS

The experiments of Nieman and Robinson[7] on the $^1B_{2u}$ electronic[19] exciton band were repeated. These

[17] This will happen when one or more symmetry operations of different, physically equivalent sites are not parallel. This points out the usefulness of the interchange group, as some interactions "allowed" by the interchange group appear to be forbidden by the factor group. This apparent contradiction arises because similar but nonparallel operations of different sites may all map into the same class of operations of the factor group. It should be remembered that the site group is only isomorphous with a subgroup of the factor group, not identical with it.

[18] R. Kopelman, J. Chem. Phys. **44**, 3547 (1966), and references therein.

[19] As the molecular symmetry is not conserved in the site, the use of D_{6h} designations for the symmetry of crystal states is not really correct. However, we will retain the notation here merely as a convenient labeling device.

TABLE II. Some u vibrational levels of C_6H_6 (in cm^{-1}).

Symmetry	Gas[a]	C_6H_6 in C_6D_6[b]	Neat crystal[b]	Polarization and symmetry[c]
			1030.0	
			1032.5	
		1034.8	1033.3	
$e_{1u}(\nu_{18})$	1037	1038.6	1034.6	
			1038.9	
			1039.8	
$b_{1u}(\nu_{12})$				
	1010	1011.3	1006.9	c B_{3u}
			1008.6	b B_{2u}
			1009.7	a B_{1u}
			1142.5	c B_{3u}
$b_{2u}(\nu_{15})$	1146	1146.9	1148.6	a B_{1u}
			1150.3	b B_{2u}

[a] S. Brodersen and A. Langseth, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 1, 1 (1959). The last two values are derived from combination bands.

[b] Our measurements.

[c] S. Zwerdling and R. S. Halford, J. Chem. Phys. 23, 2221 (1955).

results will be discussed briefly to illustrate the theory and to derive the exciton coupling constants using the D_2 interchange group. Infrared transitions in neat and isotopic mixed-benzene crystals were also studied, and a few of these spectra will be discussed for further illustration.

The deuterated benzene was obtained from Merck, Sharp, and Dohme, Ltd., Canada, and was vacuum distilled before use. The C_6H_6 was obtained from Phillips Petroleum Co. (99.89 mole % pure) and was used without further purification. The neat crystals for the infrared experiments were made by placing liquid benzene between two CsI windows, which were pressed together in a sample holder. The holder was made from brass and was fitted with indium in order to apply firm, uniform pressure to the soft salt windows. A few drops of benzene were placed on the CsI window, and the sample holder was assembled and attached to the bottom of a "cold-finger" helium Dewar in a dry-nitrogen atmosphere. The Dewar was then assembled, and the sample was frozen to liquid-nitrogen temperature (77°K) while the Dewar was being evacuated. At this temperature one could see through the sample, and even upon subsequent cooling to 4.2°K the sample remained clear. Sample thickness, estimated from measurements of absolute absorption intensities[20] in the infrared, was about 5–10 μ. For the ultraviolet experiments a technique similar to that used by Nieman and Robinson[7] was employed.

FIG. 5. Infrared spectrum of the $e_{1u}(\nu_{18})$ fundamental of neat C_6H_6 at 4.2°K.

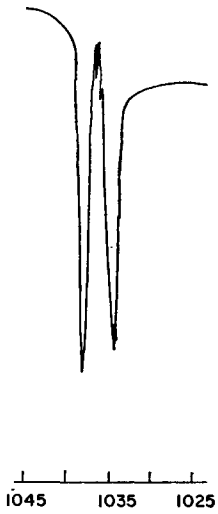

FIG. 4. Infrared spectrum of the $e_{1u}(\nu_{18})$ fundamental of 1% C_6H_6 in C_6D_6 at 4.2°K, showing 3.8 cm^{-1} site-group splitting.

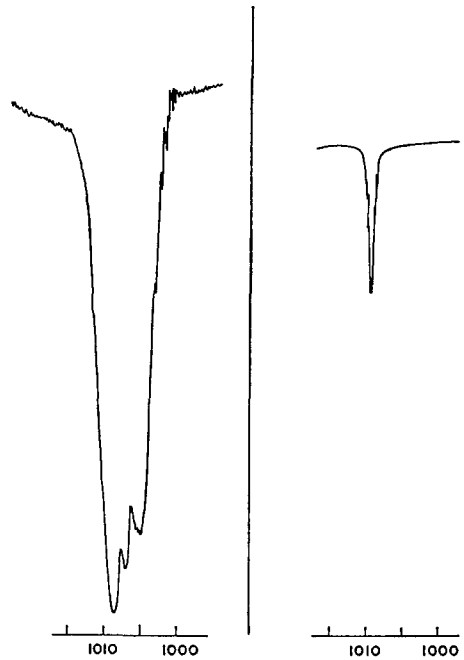

FIG. 6. Infrared spectra of the $b_{1u}(\nu_{12})$ fundamental of neat C_6H_6 and 1% C_6H_6 in C_6D_6 at 77°K.

[20] W. B. Person and C. A. Swenson, J. Chem. Phys. 33, 233 (1960); J. L. Hollenberg and D. A. Dows, J. Chem. Phys. 39, 495 (1963).

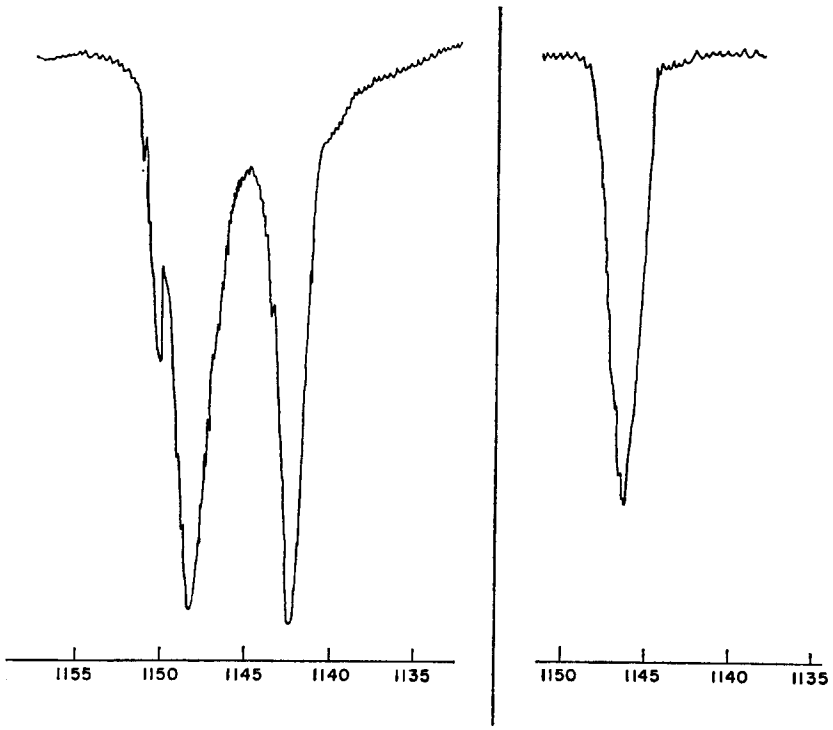

FIG. 7. Infrared spectra of the $b_{2u}(\nu_{15})$ fundamental of neat C_6H_6 and 1% C_6H_6 in C_6D_6 at 77°K.

The concentration of the isotopic mixed samples was about 1% guest in 99% host. This low concentration was used in order that complete isolation of the guest in the host crystalline lattice could be effected. For the detection of infrared absorption this required the use of larger, less convenient sample thicknesses than those used in past work. The thicker samples were made with a 0.050-in. indium wire gasket placed between the CsI windows. When compressed, this spacing was approximately 0.75–1.0 mm thick. The gasket was not made into a closed circle, allowing an entrance into which the liquid sample could be introduced. However, indium "tails", with which the sample holder could be sealed after it filled with benzene, were left attached. The well-mixed[21] sample was then placed in the holder, sealed, and solidified as discussed above. After cooling to 77°K the sample was heavily cracked, although it was possible to see through some portions of it. Some of the infrared spectra were taken at 77°K and some at 4.2°K, with no apparent differences observed. These data are presented in Table II and in Figs. 4–7. The neat-crystal infrared spectra are virtually identical with those already reported in the literature.[20]

[21] Poorly mixed samples of 1% guest in 99% host and a well-mixed sample of higher concentration were studied. The absorptions were not as sharp as those of the low-concentration isotopic mixed crystals, and some lines even exhibited residual splittings. This tends to indicate that, in general, mixed-crystal studies designed to eliminate guest–guest interactions should be carried out at guest concentrations of less than 2%. The concentrated (5–10%) mixed-crystal spectra of J. L. Hollenberg and D. A. Dows, J. Chem. Phys. **39**, 495 (1963), appear much like the above-mentioned poorly mixed samples.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

As explained in Sec. II, in order to understand fully molecular crystalline interactions, it is advantageous to study both neat and isotopic mixed crystals. With the data obtained from mixed crystals it is often possible to isolate and to study separately crystalline interactions arising from different "sources." By varying the isotopic substitution, guest energy states in such samples can be brought into near resonance with host levels. Providing there are no complications arising from a breakdown of the ideal-mixed-crystal concept, it is not only possible to gain knowledge about the static-field interactions, but also about the dynamic interactions.

Before going on to the experimental data on benzene it is well to discuss some of the approximations that will be made. The approximations as they apply to the vibrational and lower electronic states of benzene concern: (1) the applicability of the lowest-order approximation for the quasiresonance shift, (2) the correctness of the ideal-mixed-crystal concept, and (3) the limited need for inclusion of configuration interaction.

The quasiresonance shift takes into account the effects of interactions between guest states and host states in a mixed crystal. Neglecting the width of host exciton bands relative to their separation from a guest state, Nieman and Robinson[7] give for the quasiresonance shift

$$\delta \approx 4\beta^2/\Delta E, \tag{19}$$

where

$$\beta^2 \approx M_{\mathrm{I\,II}}^2 + M_{\mathrm{I\,III}}^2 + M_{\mathrm{I\,IV}}^2 + \tfrac{1}{2}(M_a^2 + M_b^2 + M_c^2)$$

and ΔE is the energy difference between the guest state and the mean of the host exciton band. The approximate result given in Eq. (19) can also be obtained from more general considerations, as discussed by Body and Ross[22] [see Eqs. (25) and (26) of their paper] or in the earlier work of Koster and Slater.[23]

From a finite model-crystal calculation, Nieman[24] found that Eq. (19) is a surprisingly good representation of the actual electronic quasiresonance shifts for C_6H_6, C_6H_5D, $C_6H_4D_2$, $C_6H_3D_3$, in a C_6D_6 host, *providing the crystal is sufficiently large.* Even for the case of $C_6H_4D_2$, which lies only about 66 cm^{-1} below the mean of the C_6D_6-host exciton band, the approximation is still good to within a few percent. The reason the approximation is good, even when the guest state lies close to the bottom of the exciton band, is that the density of states for a macroscopic crystal having intermolecular interactions like those in benzene is extremely small near the bottom of the exciton band and reaches a fairly sharp maximum

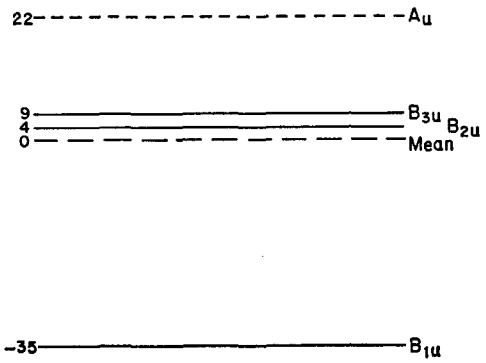

FIG. 8. Davydov structure of the $^1B_{2u}$ electronic state of C_6H_6 using data of Colson. The mean lies at 37 838 cm^{-1}.

near the middle of the band.[13b] Therefore, a preponderance of the states perturbing the guest state are very far away, and for such remote states the simple perturbation result holds. Thus, Eq. (19) can be used with confidence for electronic quasiresonance shifts for most of the benzene isotopes. For vibrational quasiresonance shifts, the host exciton bands are so narrow and the guest–host separations are generally so large that the approximation is again a very good one. The beauty of Eq. (19) is that, providing the ideal-mixed-crystal concept is a good one, the quasiresonance shifts are simply related to the M values. This is not the case for the more general expressions, even when the density-of-state function is known.

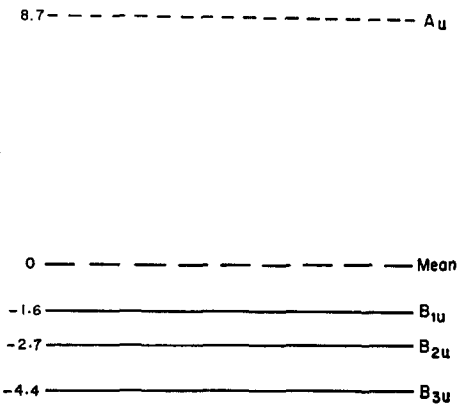

FIG. 9. Vibrational Davydov structure of the $b_{1u}(\nu_{12})$ band of C_6H_6. The mean lies at 1011.3 cm^{-1}.

The second approximation whose validity we shall discuss is the use of the ideal-mixed-crystal concept. *A priori*, one is not certain whether this concept is a useful one or not. Nieman and Robinson[7] used it in their early paper on quasiresonance shifts in the lowest excited singlet and triplet states of benzene. However, recent work by Colson[25] has shown this approximation to be quite erroneous for the singlet state ($^1B_{2u}$) because of an apparent dependence of Δ on deuterium substitution. In view of this, a new analysis by Colson was made, and it was found that the mean of the Davydov components was very close actually to the original value given by Broude,[2c] not to the Nieman and Robinson value. The details of this work are discussed in Colson's paper.[25] Presumably the same kind of breakdown of the ideal-mixed-crystal concept occurs for the lowest triplet ($^3B_{1u}$) state of benzene, so the conclusions reached earlier by Nieman and Robinson[7] about the position of the forbidden (A_u) Davydov component and the width of the triplet exciton band are nullified. Interestingly, the ideal-mixed-crystal concept is quite valid for dilute guest–host mixtures of naphthalene-h_8 and naphthalene-d_8. It is also a valid concept for vibrational states, as indicated by some recent calculations of Bernstein.[26]

The third approximation to be discussed concerns configuration interaction. For vibrations, interaction

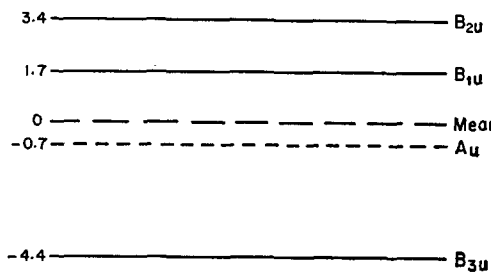

FIG. 10. Vibrational Davydov structure of the $b_{2u}(\nu_{15})$ band of C_6H_6. The mean lies at 1146.9 cm^{-1}.

[22] R. G. Body and I. G. Ross, Australian J. Chem. **19**, 1 (1966).
[23] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).
[24] G. C. Nieman, Ph.D. thesis, California Institute of Technology, Pasadena, Calif., 1965. Nieman used the larger coupling constants of Nieman and Robinson.[7] Use of the now apparently correct, smaller M values (Ref. 25) would cause the approximation to be even better.
[25] S. D. Colson, J. Chem. Phys. **48**, 3324 (1968).
[26] E. R. Bernstein (unpublished).

TABLE III. Various contributions to the energy[a] of some exciton states.

State	Gas-to-mixed-crystal[b] shift	Quasiresonance shift	Static-field term (Δ)	The "k=0 shift" $[L'(0)]$[d]	β	Exciton coupling constants[e] M		
						I, II	I, III	I, IV
$^1B_{2u}$	−248.0±1	0.3[c]	−248.0±1	0±4	+5.3±1	−1.55±0.50	−3.93±0.50	−3.28±0.50
$b_{1u}(\nu_{12})$	+1.3±0.5	∼0.0	+1.0±1	∼0.0	+1.7±0.3	+0.89±0.2	+0.75±0.2	+0.54±0.2
$b_{2u}(\nu_{15})$	+0.9±0.5	∼0.0	+1.0±1	∼0.0	+0.5±0.3	+0.12±0.2	+0.34±0.2	−0.64±0.2

[a] In cm^{-1}.

[b] C_6H_6 in C_6D_6 values. For the vibrational states, there is an additional uncertainty in the gas-phase values since they were derived from combination bands.

[c] Obtained from β of Colson, Ref. 25. This correction is so small that it can be safely ignored.

[d] Upper-limit estimate.

[e] Electronic and vibrational polarization assignments taken from V. L. Broude, Usp. Fiz. Nauk **74**, 577 (1961) [Sov. Phys.—Usp. **4**, 584 (1962)], and S. Zwerdling and R. S. Halford, J. Chem. Phys. **23**, 2221 (1955), respectively. See also R. Kopelman, J. Chem. Phys. **47**, 3227 (1967).

between different states of the crystal do occur in special cases (inter- and intramolecular Fermi resonance). These interactions are easy to deal with when they do occur, since the mixing causes intensity and frequency anomalies that can be directly observed in both perturbed and perturbing levels. Consequently, the perturbations are often simply interpretable. For electronic states the interactions are larger. The perturbing states can thus be far away (and unobservable), yet still exert measurable influence on the state being studied.

In benzene, configuration interaction in the $^1B_{2u}$ state of the crystal is known to be present, since this is the mechanism by which the (0, 0) intensity is derived. But while the effect of configuration interaction on the intensity is impressive, the effect on the energy of the $^1B_{2u}$ exciton band is very small as can be seen by the following semiempirical estimate, which assumes that all the intensity of the 0, 0 band and totally symmetric progressions is caused by configurational mixing between the $^1B_{2u}$ state and the $^1E_{1u}$ state.

The maximum of the $^1E_{1u}\leftarrow{}^1A_{1g}$ transition lies near 56 000 cm^{-1}, and its oscillator strength is 0.44 for the transition to each degenerate component.[27] Photoelectric intensity measurements carried out in our laboratory have shown that the intensity derived from the 0, 0 band and totally symmetric progressions in the $^1B_{2u}\leftarrow{}^1A_{1g}$ transition of crystalline benzene comprises no more than $\frac{1}{5}$ the intensity of the vibronically active transitions. Taking the latter to be of roughly the same strength in the solid as in the gas $[f(\text{gas})=0.0014]$ would then yield, roughly speaking, $f\approx 0.00028$ for the oscillator strength of the part derived from configuration interaction. The coefficient b for interaction between the $^1B_{2u}$ state and each component of the doubly degenerate $^1E_{1u}$ state is given by the following expression:

$$b=[f(\text{perturbed})\nu(^1E_{1u}\leftarrow{}^1A_{1g})/f(^1E_{1u}\leftarrow{}^1A_{1g})\times\nu(^1B_{2u}\leftarrow{}^1A_{1g})]^{1/2}, \quad (20)$$

where

$$b=\langle{}^1E_{1u}\mid H_{\text{CI}}\mid{}^1B_{2u}\rangle/[E(^1E_{1u})-E(^1B_{2u})].$$

The energy shift associated with the perturbation is

$$\delta E=-b^2[E(^1E_{1u})-E(^1B_{2u})], \quad (21)$$

which yields $\delta E\approx -15$ cm^{-1} when $E(^1B_{2u})$ is taken to be ∼40 000 cm^{-1} and assuming that the $^1B_{2u}$ state can mix with only half the doubly degenerate $^1E_{1u}$ state, as is the usual case, at least for certain types of interactions.[28] δE is smaller by a factor of 2 if the entire oscillator strength $f=0.88$ of the $^1E_{1u}\leftarrow{}^1A_{1g}$ is used. Thus, as much as 5% of the band-shift term Δ can arise from $^1E_{1u}$ mixing at the site. (Δ will be seen shortly to be −248 cm^{-1}.) However, the effect of configuration interaction on the relative energies of the $\mathbf{k}$ states within the band can only become appreciable when the $^1E_{1u}$ exciton bandwidth is comparable to the energy difference between the $^1E_{1u}$ and $^1B_{2u}$ states. We consider this to be unlikely in view of theoretical results on the $^1E_{1u}$ state of crystalline benzene[8] and therefore conclude that the effect of this type of configuration interaction on the $^1B_{2u}$ exciton band shape or Davydov splitting is minimal.

We now proceed with a discussion of some selected experimental results to illustrate the theoretical formulation presented in the paper.

A. C_6H_6 Electronic Band—$^1B_{2u}$

In neat crystalline C_6H_6, the 0–0 line of the $^1B_{2u}$–$^1A_{1g}$ transition has been observed both in absorption and emission. Because of the interchange-group selection rules for these processes[13] ($\Delta\mathbf{k}=\mathbf{0}$; $B_1\leftrightarrow B_2$; $B_1\leftrightarrow B_3$; $B_2\leftrightarrow B_3$; $A\leftrightarrow B_1$, B_2, B_3), only the $\mathbf{k}=\mathbf{0}$ components of the B_1, B_2, and B_3 bands can be observed for transitions involving the totally symmetric ($\mathbf{k}=\mathbf{0}$, A_g) ground state of the crystal. Thus, the $E(A)$ level, or alternatively the mean value of the Davydov components, must be located by an indirect method to obtain the M values of Eq. (17).

The 0–0 component in emission is found to be coincident within 5 cm^{-1} with the lowest-interchange-group

[27] V. J. Hammond and W. C. Price, Trans. Faraday Soc. **51**, 605 (1955).

[28] W. Moffitt, J. Chem. Phys. **22**, 320 (1954).

component observed in absorption. From the selection rules one can therefore conclude that the lowest-interchange component has B symmetry and that its $\mathbf{k}=\mathbf{0}$ level is at or very near the bottom of the band. If a state of B_u symmetry were not the lowest factor-group component, or if the $\mathbf{k}=\mathbf{0}$ level were not its lowest state, we would not have observed the 0–0 transition in emission, but because of the $\Delta\mathbf{k}=\mathbf{0}$ selection rule would have observed only transitions terminating in vibrational exciton bands of the ground electronic state.[13] Without making polarization studies, it is impossible to assign this state further to any one of the three possible B levels (B_{1u}, B_{2u}, B_{3u}). The assignment of the lowest level to one of the B_u levels is consistent with the conclusions reached by Nieman and Robinson.[7]

As mentioned above, in order to obtain the M values from the experimental data, either the position of the A level or the mean value of the Davydov components must be known. If isotopic-mixed-benzene crystals approached the ideal-mixed-crystal limit, the method of Nieman and Robinson[7] could be used. That is, the mean of the Davydov components could be found from isotopic-mixed-crystal data by using the technique outlined in the last paragraph of Sec. II.H. We do not do this here because of the inapplicability of the ideal-mixed-crystal approximation for the electronic states of benzene discovered by Colson.[25]

Another way of determining the mean value of the Davydov components was first suggested by Broude.[20] This method requires knowledge of the frequency of a nontotally symmetric vibration in the upper electronic state of the crystal. (Vibronic exciton splittings associated with such vibrations are small.) Then by simple subtraction from an observed vibronic level in the crystal spectrum, the mean energy of the exciton band can be found. Broude used the ν_6' vibration (gas phase, 523 cm^{-1}) to obtain

$$\bar{\epsilon}+\Delta=37\,835\ \text{cm}^{-1}$$

for the (0, 0) band of the $^1B_{2u}\leftarrow{}^1A_{1g}$ transition of crystalline benzene. Even though the method has various uncertainties, as discussed by Nieman and Robinson,[7] it apparently gives very good results. Colson,[25] using a different vibronic line, for instance, obtains,

$$\bar{\epsilon}+\Delta=37\,838\ \text{cm}^{-1}.$$

Together with the gas-phase 0–0 transition energy[29] (38 086 cm^{-1}), the site-shift term $\Delta=-248$ cm^{-1}. Thus we find the average $\mathbf{k}$-independent crystal binding energy to be about 6% larger for an excited-state molecule in the normal crystal than for a ground-state molecule in the normal crystal.[30]

Neglect of the translationally equivalent interactions seems to be warranted since: (1) the nearest-neighbor intermolecular distances for these interactions are 0.82–3.4 Å larger than the largest translationally inequivalent nearest-neighbor distance (see Fig. 1), (2) density-of-state measurements[13b] are not consistent with large translationally equivalent interaction energies, and (3) observed selection rules[13a] imply that such interactions are small. Therefore, the term $L'(0)$ of Eq. (17) can be neglected, and $\bar{\epsilon}+\Delta$ becomes the mean energy of the Davydov components. Using Colson's value[25] of $\bar{\epsilon}+\Delta$, which is probably slightly more accurate than Broude's, and using Broude's polarization assignments for the Davydov components (B_{1u}, B_{3u}, B_{2u} in increasing order of energy), one obtains for the translationally inequivalent coupling constants

$$M_{\text{I II}}=-1.55\ \text{cm}^{-1},$$

$$M_{\text{I III}}=3.93\ \text{cm}^{-1},$$

$$M_{\text{I IV}}=3.28\ \text{cm}^{-1}.$$

These M values are considerably smaller than the ones reported earlier by Nieman and Robinson[7] and lead to a value of $\beta=5.3$ cm^{-1} and a position of the forbidden $A_u(\mathbf{k}=\mathbf{0})$ level at 37 860 cm^{-1}. A schematic representation of the energies of the Davydov components for the $^1B_{2u}$ state is given in Fig. 8. The data are summarized in Table III.

B. Ground-State Ungerade Vibrations

Ungerade vibrations can be observed in infrared absorption. In the gas phase only a_{2u} and e_{1u} vibrations are dipole-allowed within the $\mathbf{D}_{6h}$ symmetry group of benzene. In the crystal, because of the loss of exact $\mathbf{D}_{6h}$ symmetry, a partial relaxation of the selection rules occurs, and vibrations of original molecular symmetry a_{2u}, b_{1u}, b_{2u}, e_{1u}, and e_{2u} are observed. One degenerate (e_{1u}) and two nondegenerate vibrations (one b_{1u} and one b_{2u}) will be discussed in detail below.

Degenerate Vibrations

We have defined site-group splitting as the splitting that occurs in degenerate vibrations of guest molecules in an ideal mixed crystal. Calculations[26] indicate that for vibrational states of benzene the ideal-mixed-crystal concept is very closely approached by an isotopic mixed crystal in which the guest–host quasiresonance interactions are reduced to a minimum (i.e., for our case, C_6H_6 guest in a C_6D_6 host or vice versa). Such a definition essentially eliminates contributions from resonance interactions to the observed site splitting. Using the C_6H_6 in C_6D_6 mixed crystal, a 3.8-cm^{-1} site-group splitting for the e_{1u} vibration ν_{18} is observed (see Fig. 4). Since the Davydov splitting for nondegenerate ungerade vibrations is about 10 cm^{-1}, a quantitative separation of site-group and interaction-group effects for degenerate vibrations in the neat crystal does not appear

[29] J. H. Callomon, T. M. Dunn, and I. M. Mills, Phil. Trans. Roy. Soc. London **A259**, 499 (1966).

[30] The heat of sublimation for benzene is about 3800 cm^{-1}. G. Milazzo, Ann. Chim. (Rome) **46**, 1105 (1956).

possible. The neat-crystal spectrum of the $e_{1u}(\nu_{18})$ band is given in Fig. 5.

Nondegenerate Vibrations

For these vibrations, in which no site-group splitting occurs, the mixed-crystal data can be used, as in the case of the $^1B_{2u}$ electronic band, to aid in the interpretation of the pure-crystal spectrum. Dilute-mixed-crystal experiments,[15] using hosts of isotopically modified benzene other than C_6H_6 and C_6D_6, indicate that the quasiresonance corrections are negligible (less than 1 cm^{-1}) and that Δ is small and independent of isotopic substitution of the host. Recent calculations of the Davydov structure of benzene vibrational bands[26,31] that are successful in predicting the correct order of magnitude of the over-all splittings would predict negligible interactions between the translationally equivalent molecules. Thus, as a first approximation we assume the mean value of the Davydov components in the pure crystal to be the value of that vibration in the isotopic mixed crystal. With this assumption the three observed B levels allow a calculation of the complete interchange-group structure (see Figs. 9 and 10). Using the polarization results of Zwerdling and Halford,[1e,32] one can then find $M_{\mathrm{I\ II}}$, $M_{\mathrm{I\ III}}$, and $M_{\mathrm{I\ IV}}$ for both the $b_{2u}(\nu_{15})$ and $b_{1u}(\nu_{12})$ vibrational bands. The calculated energies, M values, and β values [Eq. (19)] are given in Table III. Data to be reported later[33] show that the interchange-group structures corresponding to the same normal mode in crystals of C_6H_6 and C_6D_6 are nearly identical.

From the calculated β values it is now possible to check the assumption that the quasiresonance correction to the mixed-crystal data, used to obtain the band centers, is indeed small. Applying Eq. (19) one finds that the quasiresonance correction is less than the experimental error, as was assumed. A discussion of the interaction terms will be given elsewhere.[15,26,33]

V. SUMMARY

The major points made in this paper are:

(1) The concept of the *interchange group* is introduced and is applied to the molecules in the primitive unit cell. This group provides a convenient and unambiguous way of discussing the relative signs of the exciton coupling constants.

(2) The *site-distortion energy* P and *band-shift term* Δ are introduced, and together with the D term are discussed relative to the experimental band shift.

(3) It is emphasized that *site wavefunctions* $\chi_{nq}{}^{j}$, and not molecular wavefunctions, are the ones of greater significance.

(4) *Static* and *dynamic* interactions are distinguished and are associated, respectively, with $\mathbf{k}$-independent and $\mathbf{k}$-dependent terms of the Davydov-energy equation. These interactions are associated with site operations and transport operations, respectively.

(5) The *ideal mixed crystal* is defined, and its importance in the determination of site splittings, band shifts, and forbidden Davydov components is emphasized.

(6) The exciton structure of molecular degenerate, or nearly degenerate, states cannot be described simply as site-group splitting plus interchange-group splitting. We have therefore used the term *site-group splitting* to describe the splitting of molecular-degenerate state associated with guest molecules in an *ideal mixed crystal.*

(7) To illustrate the foregoing theoretical ideas, experimental data are interpreted for the $^1B_{2u}$ electronic exciton band and for a few vibrational exciton bands in the electronic ground state.

[31] I. Harada and T. Shimanouchi, J. Chem. Phys. **44**, 2016 (1966).

[32] R. Kopelman, J. Chem. Phys. **47**, 3227 (1967).

[33] E. R. Bernstein and G. W. Robinson (unpublished).