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On the Excited Electronic States of Isotactic Polystyrene and Polyvinylnaphthalene

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A detailed theoretical analysis of the band structure and Davydov splittings in the p and β bands of isotactic polystyrene and polyvinylnaphthalene has been undertaken. It is shown that singlet band splittings are large and have different symmetry characteristics from those of crystalline benzene and naphthalene. The triplet bandwidths are, however, very small. The rate of triplet–triplet annihilation is shown to be considerably less than that characteristic of a monomeric aromatic crystal such as anthracene or naphthalene and therefore phosphorescence from the pure polymer is a distinct possibility. The role of aperiodic potentials on the bandwidths is briefly discussed.

I. INTRODUCTION

THE electronic properties of ordered (and disordered) polymers are of considerable interest for a variety of reasons:

(a) There exist a number of photoinduced biological reactions in which the properties of a particular macromolecule may define the reaction mechanism. For example, energy transfer along the desoxypentose nucleic acid double helix may be involved in the mutagenic reaction resulting from the absorption of high-energy electromagnetic radiation.

(b) On formation of a regular helix from a disordered array there may occur changes in the optical rotatory dispersion and the absorption intensities of certain electronic transitions. These changes in optical properties are of great intrinsic interest. An understanding of the conditions under which they occur and their origin is rendered even more important by the fact that changes in optical properties are often used to monitor the content of helical configuration when such information is required for other investigations.

(c) A helical macromolecule provides an ordered environment for any selected monomeric chromophore. Because of the difference in site symmetry and in interactions between a chromophore in an ordered polymer and in a crystal, optical studies impossible in the crystal may be possible in the ordered polymer. For example, the bandwidth for transfer of triplet excitons is sufficiently large in any pure molecular crystals of aromatic compounds that there is rapid exciton migration leading to efficient triplet–triplet annihilation. In these cases it is impossible to study phosphorescence from the crystal. We show in this paper that the triplet exciton bandwidths in polystyrene and polyvinylnaphthalene are very small (in contrast with crystalline benzene and naphthalene where the bandwidth is of the order of magnitude of 30 cm^{-1})[1] and therefore that triplet exciton migration may be sufficiently slow that phosphorescence can be studied.

Theoretical studies of the electronic properties of helical polymers have been reported by several workers in recent years. From the work of Moffitt, Kirkwood, and Fitts,[2] Tinoco,[3] and Rhodes[4] has come an understanding of the optical rotatory dispersion and hypochromism of the isolated helical macromolecule. In contrast, very little attention has been focused on detailed calculation of energy level splittings, exciton band structure, singlet and triplet energy transfer, and related topics. It is the purpose of this paper to discuss several of these phenomena.

This paper presents a detailed theoretical analysis of the band structure and Davydov splittings in the p band and β band of isotactic polystyrene and polyvinylnaphthalene. These substances have been chosen as prototypes because of the wavefunctions available for complex molecules, the best are for the planar aromatic hydrocarbons. Because of the small overlap of monomeric residue wavefunctions in the polymer a simple product is a good first approximation to the polymer wavefunction. But the small overlap introduces difficulties as well as simplifications, for the tail of the wavefunction must be known with considerable accuracy if meaningful calculations are to be made. We have used both Hückel molecular orbitals and self-consistent field molecular orbitals for the monomer wavefunctions. In each case the atomic basis functions were Hartree–Fock carbon $2p\pi$ orbitals. It is found that the singlet band splittings for the 2000-Å band of isotactic polystyrene and the 2750-Å and 2200-Å bands of isotactic polyvinylnaphthalene are large (400, 1600, and 6800 cm^{-1} respectively). Triplet band splittings were also calculated and found to be two to three orders of magnitude smaller than for the singlet bands

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[1] (a) G. C. Nieman and G. W. Robinson, J. Chem. Phys. **39**, 1298 (1963). (b) J. L. Katz, J. Jortner, S. I. Choi, and S. A. Rice, *ibid.*, p. 1897.

[2] W. Moffitt, J. Chem. Phys. **25**, 467 (1956); W. Moffitt, D. D. Fitts, and J. G. Kirkwood, Proc. Natl. Acad. Sci. U.S. **43**, 723 (1957).

[3] I. Tinoco, Jr., J. Am. Chem. Soc. **82**, 4785 (1960); J. Chem. Phys. **33**, 1332 (1960).

[4] W. Rhodes, J. Am. Chem. Soc. **83**, 3609 (1961).

(the ${}^3B_{1u}$ band in isotactic polystyrene is split 0.46 cm^{-1}). The very small splitting of the triplet band is directly attributable to a very small triplet exchange interaction, which interaction is small because of the large intermonomer separation.

In this paper we do not consider any mixing of ion-pair exciton states with neutral exciton states. The role of such charge-transfer interactions in determining fluorescence and phosphorescence spectra will be considered in a separate publication. The neglect of the influence of charge-transfer states is probably satisfactory for the case of solid polymers since the large distances between chromophores (larger than in the corresponding crystalline benzene and napthalene) considerably reduce the stabilizing polarization energy.

II. GENERAL THEORY

Isolated molecules of isotatic polystyrene and isotactic polyvinylnaphthalene may be considered to be perfect crystals characterized by one-dimensional Brillouin zones. The unit cells of these two polymers contain three and four monomers, respectively. If it is assumed that the electronic states of the polymer arise from the weak binding of nonvibrating monomer electronic states, then the most naïve analysis leads to the expectation that each monomeric band is split into three bands in polystyrene and four bands in polyvinylnaphthalene. By the application of group theoretical arguments this prediction may be refined to include degeneracies and the identification of levels connected by allowed transitions.

Consider now the application of the formalism of exciton theory[5] to the cases under study. Because of the weak interaction and very small overlap of the monomeric wavefunctions ϕ, the zeroth-order ground-state wavefunction of the polymer will be taken to have the form

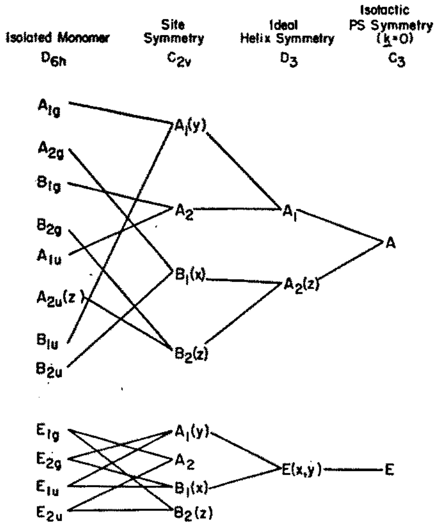
$$\Phi^0=\mathcal{A}\prod_{m,\beta}\phi_{m\beta}^0, \tag{1}$$

where the superscript (0) denotes the ground state and the indices m, β denote the unit cell (m) and the site within the unit cell (β). One-site exciton functions are defined to have the form

$$\Psi_{n\alpha}^f=\mathcal{A}\phi_{n\alpha}^f\prod_{m\beta}{}'\phi_{m\beta}^0, \tag{2}$$

where $\mathcal{A}$ is the antisymmetrization operator equal to $\sum_P(-1)^P P$ (here P permutes electrons between molecules), the $n\alpha$th monomeric subunit is excited to the fth isolated molecule state, and the prime indicates that the product includes all N monomers of the helix *except the* $n\alpha$th. To obtain a wavefunction representing a stationary excited state of the polymer a suitable linear combination of one-site exciton functions must be taken.

TABLE I. Correlation table for isotactic polystyrene.



The choice of proper linear combination coefficients is determined by the requirement that the polymer wavefunction transform as one of the irreducible representations of the site group (the group whose elements describe the symmetry of the monomeric subunit). In the solid state, isotactic polystyrene is a single stranded helical polymer with three monomers per unit cell, unit cell repeat distance of 6.65 Å, and with the phenyl ring planes tilted 20° from the horizontal and twisted 13° about the axis connecting the phenyl ring to the polymer backbone.[6] Because of large repulsive forces acting between overlapping rings, in isotactic polyvinylnaphthalene there are four monomers to the unit cell, a repeat distance of 8.10 Å, and the angle of twist about the axis connecting the naphthyl group to the polymer is increased to 68° (from 13°).[7] Since the monomeric subunits of both polymers lie in a plane neither perpendicular not parallel to the helix axis, $\pi-\pi^*$ transitions which are polarized in the plane of the ring will have components both along the helix (z) axis and the plane (xy) normal to it.

When a benzene ring with symmetry D_{6h} is attached to a polymer backbond to form polystyrene, the site symmetry becomes C_{2v}. The basis functions for isotactic polystyrene must belong to one of the irreducible representations A or E of the helix group C_3. The correlation table (Table I) shows this process diagrammatically: in forming symmetrized basis functions for the entire helix, the irreducible representations of the site group go over into the irreducible representations

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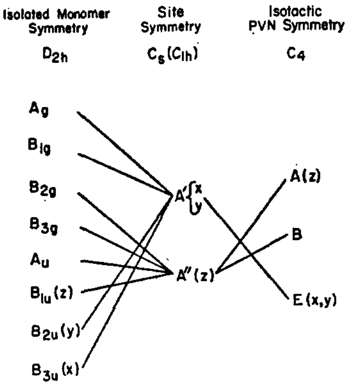
[5] (a) A. S. Davydov, Zh. Eksperim. i Teor. Fiz. **18**, 210 (1948). (b) A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill Book Company, Inc., New York, 1962).

[6] G. Natta and P. Corradini, Makromol. Chem. **16**, 77 (1955); Nuovo Cimento Suppl. **15**, 68 (1960).

[7] P. Corradini and P. Ganis, Nuovo Cimento, Suppl. **15**, 104 (1960).

TABLE II. Correlation table for isotactic polyvinylnaphthalene.



of the helix. The correlation table only presents the symmetry species of the helix for the factor group representation ($\mathbf{k}=0$). The third column lists the irreducible representations of a helix whose side groups lie in a plane perpendicular to the helix axis. This condition is relaxed in the last column, which describes the prevailing configuration in the polymers under discussion.

There are only two irreducible representations in the factor group of an isotactic polymer of pitch three (i.e., three monomers per unit cell). Two bands are predicted, one doubly degenerate and one nondegenerate, transitions to each of which are allowed, since at least one of the transition dipole moment operators transforms as each of the two levels. In Table II a similar correlation analysis is given for isotactic polyvinylnaphthalene (PVN). In this case there are three irreducible representations of the helix factor group, two of which are nondegenerate and one doubly degenerate: transitions are allowed to only two of these levels. Our simple predictions from Davydov theory for the number of bands are indeed correct when degeneracies are accounted for.

To form the helix wavefunctions we take a linear combination of the one-site excitons

$$\Phi_{k,l}{}^{f}=(1/N^{\frac{1}{2}})\sum_{n,\alpha}a_{n\alpha}{}^{k,l}\Psi_{n\alpha}{}^{f},\tag{3}$$

where

$$(1/N)\sum_{n\alpha}(a_{n\alpha}{}^{kl})^{*}a_{n\alpha}{}^{kl}=1\tag{4}$$

and the $a_{n\alpha}{}^{kl}$ must transform as one of the irreducible representations of the helix group. From the work of Rhodes[8] it is readily shown that

$$a_{n\alpha}{}^{kl}=\exp\left\{2\pi i\left[\frac{kn}{M}+\frac{k\alpha}{PM}+\frac{l\alpha}{P}\right]\right\},\tag{5}$$

where P is an integer equal to 3 for isotactic polystyrene and 4 for isotactic polyvinylnaphthalene, k is the magnitude of the lattice wave vector, l labels the band, and M is the number of unit cells in the helix. Clearly $PM=N$. The introduction of (5) into (3) followed by normalization leads to

$$\Phi_{kl}{}^{f}=\frac{1}{(PM)^{\frac{1}{2}}}\sum_{n\alpha}\exp\left\{2\pi i\left[\frac{kn}{M}+\frac{k\alpha}{PM}+\frac{l\alpha}{P}\right]\right\}\Psi_{n\alpha}{}^{f}.\tag{6}$$

Given Eq. (6) and the helix Hamiltonian

$$\mathcal{H}=\sum_{n\alpha}[\mathcal{H}_{n\alpha}+\sum_{m\beta\neq n\alpha}V_{n\alpha,m\beta}]\tag{7}$$

with $V_{n\alpha,m\beta}$ the interaction energy operator between monomers $n\alpha$ and $m\beta$, and $\mathcal{H}_{n\alpha}$ the Hamiltonian of the isolated monomer, application of the first-order perturbation theory to obtain the eigenvalues of

$$\mathcal{H}\Phi_{kl}{}^{f}=E\Phi_{kl}{}^{f}\tag{8}$$

leads to the energy E^{f} of the excited state of the helix and a system of algebraic equations for determining the band structure. Upon subtraction of the ground-state energy, we obtain the excitation energy of the polymer:

$$\Delta E^{f}=\Delta E_{m\beta}{}^{f}+D_{m\beta}{}^{f}+\epsilon^{f}(k,l),\tag{9}$$

where

$$\Delta E_{m\beta}{}^{f}=E_{m\beta}{}^{f}-E_{m\beta}{}^{0}\tag{10}$$

is the excitation energy of one molecule, $D_{m\beta}{}^{f}$ is the Davydov "crystal shift," and $\epsilon^{f}(k,l)$ characterizes the band structure. In explicit form, the secular equation is

$$[\sum_{n\alpha}M^{f}{}_{n\alpha,m\beta}a_{n\alpha}{}^{kl}-\epsilon^{f}(k,l)a_{m\beta}{}^{kl}]=0,\tag{11}$$

where

$$M^{f}{}_{n\alpha,m\beta}=J^{f}{}_{n\alpha,m\beta}+K^{f}{}_{n\alpha,m\beta}.\tag{12a}$$

Considering only the fth excited state, the excitation transfer matrix element is

$$J^{f}{}_{n\alpha,m\beta}=\langle\phi_{m\beta}{}^{f}\phi_{n\alpha}{}^{0}\mid V_{n\alpha,m\beta}\mid\phi_{m\beta}{}^{0}\phi_{n\alpha}{}^{f}\rangle\tag{12b}$$

and the excitation and electron exchange matrix element is

$$K^{f}{}_{n\alpha,m\beta}=\langle(\mathcal{A}-1)\phi_{m\beta}{}^{f}\phi_{n\alpha}{}^{0}\mid V_{n\alpha,m\beta}\mid\phi_{m\beta}{}^{0}\phi_{n\alpha}{}^{f}\rangle.\tag{12c}$$

Equation (11) when solved for $\epsilon^{f}(k,l)$ leads to the following band structure formulas:

polystyrene:

$$\epsilon^{f}(k,l)=\sum_{\alpha=0}^{2}\exp\{2\pi i[(k\alpha/3M)+\tfrac{1}{3}l\alpha)]\}$$
$$\times\sum_{n=0}^{M}{}'\exp\{2\pi i(kn/M)\}M^{f}{}_{n\alpha,00},\tag{13a}$$

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[8] W. Rhodes, J. Chem. Phys. **37**, 2433 (1962).

polyvinylnaphthalene:

$$\epsilon^f(k,l)=\sum_{\alpha=0}^{3}\exp\{2\pi i[(k\alpha/4M+\tfrac{1}{4}l\alpha)]\}$$

$$\times{\sum_{n=0}^{M}}'\exp\{2\pi i(kn/M)\}M^f{}_{n\alpha,00}, \quad (14a)$$

where the primes indicate omission of the term $M^f{}_{00,00}$.

Using Eqs. (13a) and (14a) the first-order splitting in the absorption spectrum (at $\mathbf{k}=0$) may be readily calculated. For polystyrene:

$$\epsilon^f(0,0)=2{\sum_{n=0}^{M}}'M^f{}_{n0,00}+2\sum_{n=0}^{M}(M^f{}_{n1,00}+M^f{}_{n2,00}),$$

$$\epsilon^f(0,\pm1)=2{\sum_{n=0}^{M}}'M^f{}_{n0,00}-\sum_{n=0}^{M}(M^f{}_{n1,00}+M^f{}_{n2,00}), \quad (13b)$$

Here an arbitrary monomer is selected and labeled as the 0, 0th: zeroth unit cell, zeroth site position. Thus, the Davydov splitting (at $\mathbf{k}=0$) is

$$\Delta\epsilon^f=3\sum_{n=0}^{M}(M^f{}_{n1,00}+M^f{}_{n2,00}). \quad (13c)$$

For polyvinylnaphthalene:

$$\epsilon^f(0,0)=2{\sum_{n=0}^{M}}'(M^f{}_{n0,00}+M^f{}_{n1,00}+M^f{}_{n2,00}+M^f{}_{n3,00}),$$

$$\epsilon^f(0,\pm1)=2{\sum_{n=0}^{M}}'(M^f{}_{n0,00}-M^f{}_{n2,00}),$$

$$\epsilon^f(0,2)=2{\sum_{n=0}^{M}}'(M^f{}_{n0,00}-M^f{}_{n1,00}+M^f{}_{n2,00}-M^f{}_{n3,00}), \quad (14b)$$

and the splitting between the two allowed components ($l=0$ and $l=\pm1$) is

$$\Delta\epsilon^f=2\sum_{n=0}^{M}(2M^f{}_{n2,00}+M^f{}_{n1,00}+M^f{}_{n3,00}). \quad (14c)$$

It is noted from Eqs. (13c) and (14c) that only matrix elements between translationally inequivalent chromophores contribute to the Davydov splitting, while interactions between translationally equivalent monomers contribute to the band shift.

The preceding discussion has been concerned with the Davydov splitting and band structure due to only one molecular electronic state. A more complete theory must include the crystal field induced mixing of other excited molecular states into the state f under consideration. To this end the Hamiltonian, Eq. (7), must be diagonalized using a basis set $\Phi_{k,l}{}^g$ where the indices g refer to all the excited monomeric states. The diagonal elements are calculated from Eqs. (9), (11), and (12). The off-diagonal elements are

$$\mathcal{H}_{fg}=\langle\Phi_{k,l}{}^f\mid\mathcal{H}\mid\Phi_{k,l}{}^g\rangle, \quad (15a)$$

$$\mathcal{H}_{fg}=\sum_{m,\beta\neq00}\exp\left\{2\pi i\left(\frac{km}{M}+\frac{k\beta}{PM}+\frac{l\beta}{P}\right)\right\}\Gamma_{00,m\beta}{}^{f,g}$$

$$+\sum_{l,\sigma\neq00}\Delta_{00,l\sigma}{}^{f,g}, \quad (15b)$$

where

$$\Gamma_{00,m\beta}{}^{f,g}=\tfrac{1}{2}\{\langle\phi_{00}{}^f\phi_{m\beta}{}^0\mid V_{00,m\beta}\mid\phi_{m\beta}{}^g\phi_{00}{}^0\rangle$$

$$+\langle\phi_{00}{}^g\phi_{m\beta}{}^0\mid V_{00,m\beta}\mid\phi_{m\beta}{}^f\phi_{00}{}^0\rangle\} \quad (15c)$$

$$\Delta_{00,m\beta}{}^{f,g}=\tfrac{1}{2}\{\langle\phi_{00}{}^f\phi_{l\sigma}{}^0\mid V_{00,l\sigma}\mid\phi_{00}{}^g\phi_{l\sigma}{}^0\rangle$$

$$+\langle\phi_{00}{}^0\phi_{l\sigma}{}^f\mid V_{00,l\sigma}\mid\phi_{00}{}^0\phi_{l\sigma}{}^g\rangle\}. \quad (15d)$$

III. NUMERICAL CALCULATIONS

In order to evaluate the interaction matrix element $M^f{}_{n\alpha,m\beta}$, it is necessary to specify both the intermonomeric potential and the monomeric wavefunctions.

The intermonomeric pair potential is

$$V_{n\alpha,m\beta}=\sum_{I,J}\frac{z_Iz_Je^2}{R_{IJ}}-\sum_{I,j}\frac{z_Ie^2}{R_{Ij}}-\sum_{J,i}\frac{z_Je^2}{R_{Ji}}+\sum_{i>j}\frac{e^2}{r_{ij}}, \quad (16)$$

where I and J refer to the nuclei in the different monomers $n\alpha$ and $m\beta$, and i refers to the electrons on $n\alpha$ and j to the electrons on $m\beta$.

The monomer units were assumed to benzene and naphthalene in polystyrene and polyvinylnaphthalene, respectively. The monomeric wavefunctions for the singlet states were taken to be antisymmetrized products of Hückel molecular orbitals, and the semiempirical configuration interaction wavefunctions of Pariser.[9] In Table III the relevant molecular states and wavefunctions used in these calculations are tabulated.

The interaction matrix element, $M^f{}_{n\alpha,m\beta}$, upon which the first order of Davydov splitting is dependent may be written in terms of the molecular wavefunctions. For the $^1B_{1u}(p)$ state of benzene monomer in polystyrene, the component integrals $J^p{}_{n\alpha,m\beta}$ and $K^p{}_{n\alpha,m\beta}$ are

$$J^p{}_{n\alpha,m\beta}=\langle u_4{}^{m\beta}u_3{}^{n\alpha}\mid u_4{}^{n\alpha}u_3{}^{m\beta}\rangle$$

$$+\langle u_4{}^{m\beta}u_3{}^{n\alpha}\mid u_5{}^{n\alpha}u_2{}^{m\beta}\rangle+\langle u_5{}^{m\beta}u_2{}^{n\alpha}\mid u_4{}^{n\alpha}u_3{}^{m\beta}\rangle$$

$$+\langle u_5{}^{m\beta}u_2{}^{n\alpha}\mid u_5{}^{n\alpha}u_2{}^{m\beta}\rangle,$$

$$\langle u_4{}^{m\beta}u_3{}^{n\alpha}\mid u_4{}^{n\alpha}u_3{}^{m\beta}\rangle$$

$$\equiv\langle u_4{}^{m\beta}(a)u_3{}^{n\alpha}(a)\mid r_{ab}{}^{-1}\mid u_4{}^{n\alpha}(b)u_3{}^{m\beta}(b)\rangle, \quad (17)$$

$$K^p{}_{n\alpha,m\beta}=-\tfrac{1}{2}\{\langle u_4{}^{m\beta}u_4{}^{n\alpha}\mid u_3{}^{n\alpha}u_3{}^{m\beta}\rangle$$

$$+\langle u_4{}^{m\beta}u_5{}^{n\alpha}\mid u_3{}^{n\alpha}u_2{}^{m\beta}\rangle+\langle u_5{}^{m\beta}u_4{}^{n\alpha}\mid u_2{}^{n\alpha}u_3{}^{m\beta}\rangle$$

$$+\langle u_5{}^{m\beta}u_5{}^{n\alpha}\mid u_2{}^{n\alpha}u_2{}^{m\beta}\rangle,$$

$$\langle u_4{}^{m\beta}u_4{}^{n\alpha}\mid u_3{}^{n\alpha}u_3{}^{m\beta}\rangle$$

$$\equiv\langle u_4{}^{m\beta}(a)u_4{}^{n\alpha}(a)\mid r_{ab}{}^{-1}\mid u_3{}^{n\alpha}(b)u_3{}^{m\beta}(b)\rangle, \quad (18)$$

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[9] R. Pariser, J. Chem. Phys. **24**, 250 (1956).

TABLE III. Monomer wavefunctions.

State	Wavefunction[a]	Energy (cm^{-1})	Reference
Benzene			
$^1B_{1u}(p)$	$(2)^{-\frac{1}{2}}(\phi^{2-5}+\phi^{3-4})$	48 000	Pople[b]
$^1E_{1u}(\beta\beta')$	$\left\{\begin{array}{l}(2)^{-\frac{1}{2}}(\phi^{2-5}-\phi^{3-4})\\(2)^{-\frac{1}{2}}(\phi^{2-4}+\phi^{3-5})\end{array}\right.$	54 500	Pople[b]
$^3B_{1u}(^3p)$	$(2)^{-\frac{1}{2}}(\phi^{3-4}+\phi^{2-5})$	29 500	Pople[b]
Naphthalene			
$^1B_{2u}(p)$	ϕ^{5-6}	34 500	Pople[b]
	$\left\{\begin{array}{l}\ \ 0.96682\phi^{5-6}+0.23643\phi^{4-7}\\-0.07683\phi^{3-8}-[0.04265/(2)^{\frac{1}{2}}](\phi^{4-10}+\phi^{1-7})\\+0.02432\phi^{2-9}-0.03226\phi^{1-10}\end{array}\right.$		Pariser[c]
$^1B_{1u}(\beta)$	$(2)^{-\frac{1}{2}}(\phi^{4-6}+\phi^{5-7})$	45 500	Pople[b]
	$\left\{\begin{array}{l}[0.95369/(2)^{\frac{1}{2}}](\phi^{4-6}+\phi^{5-7})\\ [-0.20707/(2)^{\frac{1}{2}}](\phi^{5-10}+\phi^{1-6})+[0.21818/(2)^{\frac{1}{2}}](\phi^{3-9}+\phi^{2-8})\end{array}\right.$		Pariser[c]
$^3B_{2u}(^3p)$	ϕ^{5-6}	21 300	Pople[b]
	$\left\{\begin{array}{l}\ \ 0.91929\phi^{5-6}+0.20507\phi^{4-7}\\+0.27354\phi^{3-8}+[0.03217/(2)^{\frac{1}{2}}](\phi^{4-10}+\phi^{1-7})\\+0.17192\phi^{2-9}+0.08625\phi^{1-10}\end{array}\right.$		Pariser[c]

[a] The wavefunctions ϕ^{i-j} are antisymmetrized excited states in which one electron is excited from Orbital i to Orbital j. The molecular orbitals are labeled in order of increasing energy.

[b] J. A. Pople, Proc. Phys. Soc. (London) **A68**, 81 (1955) and references cited therein.

[c] R. Pariser, J. Chem. Phys. **24**, 250 (1956).

where u_h^γ is the hth molecular orbital on monomer γ. The molecular orbitals u_h^γ are represented as linear combinations of carbon atom $2p_z$ wavefunctions.

$$u_h^\gamma=\sum_j C_{jh}w_\gamma^j, \tag{19}$$

where the C_{jh} are Hückel coefficients without overlap for the hth molecular orbital. (Hoyland–Goodman coefficients[10] were used in the triplet case.) Using these orbitals a component of the Coulomb matrix element $J^p{}_{n\alpha,m\beta}$ becomes:

$$\langle u_5^{m\beta}u_2^{n\alpha}\mid u_4^{n\alpha}u_3^{m\beta}\rangle=\sum_{i,j,k,l}C_{i5}C_{j2}C_{k4}C_{l3}$$
$$\times\langle w_{m\beta}^i(a)w_{n\alpha}^j(a)\mid r_{ab}^{-1}\mid w_{n\alpha}^k(b)w_{m\beta}^l(b)\rangle. \tag{20}$$

In this calculation all terms involving more than two-center integrals have been neglected.[11] It is expected[12] that three- and four-center integral contributions will be small. Correction terms introduced by the orthogonalization of molecular orbitals located on different monomers have also been neglected. 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.*[13] The exchange terms were expressed in terms of six atomic integrals: $\sigma\sigma\sigma\sigma$, $\pi\pi\sigma\sigma$, $\pi\sigma\pi\sigma$, $\pi\sigma\sigma\pi$, $++++$, and $+--+$, in the same notation. These 11 integrals were computed using a program supplied by the Laboratory for Molecular Structure and Spectroscopy of The University of Chicago.

Since the interaction matrix element involves essentially long-range intermolecular interactions, the behavior of the carbon $2p_z$ wavefunction at large distances from the nucleus is of considerable importance. It has been shown by Katz *et al.*[14] that using a Slater orbital with an orbital exponent, $\zeta=1.625$ a.u. is seriously inadequate for exchange integrals since it drastically underestimates the magnitude of the tails of the wavefunctions. To overcome this difficulty, a linear combination of 4 Slater-type orbitals were fitted empirically to a SCF wavefunction for carbon $2p_z$ electron.

$$w_\gamma^j=r\cos^k\sum_i a_i(\alpha_i^5/\pi)^{\frac{1}{2}}\exp(-\alpha_i r_j). \tag{21}$$

Further details and parameters may be found in Katz *et al.*[14] To gain greater accuracy, this linear combination was used for both Coulomb and exchange integrals in this calculation.

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[10] J. R. Hoyland, Thesis No. 61–6790, University Microfilms, Inc., Ann Arbor, Michigan, 1961; J. R. Hoyland and L. Goodman, J. Chem. Phys. **36**, 12 (1962).

[11] In the off-diagonal matrix element H_{fg} it may be shown that the $\Delta_{00}{}^{f,g}$ term equals zero when only two-center integrals are considered. This result arises from the pairing of molecular orbitals in alternant hydrocarbons.

[12] Order of magnitude estimates by Silbey *et al.* [J. Chem. Phys. (to be published)] based on the Mulliken approximation indicate a contribution of order 10% for *crystals* of naphthalene and anthracene.

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

[14] J. L. Katz, S. A. Rice, S. I. Choi, and J. Jortner, J. Chem. Phys. **39**, 1683 (1963).

Convergence in the sum over intermonomer interaction matrix elements was accomplished after 18 monomer residues in the case of polystyrene and after 16 in polyvinylnaphthalene. Convergence in the triplet exciton case was complete after essentially one unit cell in both polymers. Since spin–orbit coupling was neglected, the short range of the exchange integrals accounts for this rapid convergence.

In Table IV the Davydov splittings and energy level shifts in the region of optical interest, $\mathbf{k}=0$, are sketched. At the left are the free monomer states with their appropriate group theoretical symmetry designations and experimental energies. The first-order Davydov splittings are then diagrammed, followed by the splittings due to crystal field induced mixing of the first-order states. It is noted that the crystal field induced mixing has the greatest effect on the splitting of the p band of both the polymers. Figures 1 and 2 show the complete band structure for isotactic polystyrene and polyvinylnapthalene, respectively.

TABLE IV. Energy level shifts and Davydov splitting in isotactic polystyrene and polyvinylnapthalene.

MONOMER State	Energy	POLYMER State	Allowed Transition	First Order Level Splitting	Crystal Field Induced Shifts	Davydov Splitting
Benzene		**Polystyrene**				
		$A(l=+0)$	Yes	$+4760\ \mathrm{cm}^{-1}$	$+5200\ \mathrm{cm}^{-1}$	
		$E(l=\pm1)$	Yes	$+2580\ \mathrm{cm}^{-1}$	$+2580\ \mathrm{cm}^{-1}$	
$^1E_{1u}$	$54{,}500\ \mathrm{cm}^{-1}$	$E(l=\pm1)$	Yes	$-213\ \mathrm{cm}^{-1}$	$-215\ \mathrm{cm}^{-1}$	
		$A(l=+0)$	Yes	$-2256\ \mathrm{cm}^{-1}$	$-2240\ \mathrm{cm}^{-1}$	
$^1B_{1u}$	$48{,}000\ \mathrm{cm}^{-1}$	$A(l=+0)$	Yes	$+40\ \mathrm{cm}^{-1}$		
		$E(l=\pm1)$	Yes	$-25\ \mathrm{cm}^{-1}$	$-27\ \mathrm{cm}^{-1}$	$409\ \mathrm{cm}^{-1}$
					$-436\ \mathrm{cm}^{-1}$	
Naphthalene		**Polyvinylnaphthalene**				
		$B(l=+2)$	No	$+3884\ \mathrm{cm}^{-1}$	$+3967\ \mathrm{cm}^{-1}$	
		$E(l=\pm1)$	Yes	$+2618\ \mathrm{cm}^{-1}$	$+2644\ \mathrm{cm}^{-1}$	$6826\ \mathrm{cm}^{-1}$
$^1B_{3u}$	$45{,}500\ \mathrm{cm}^{-1}$					
		$A(l=+0)$	Yes	$-4362\ \mathrm{cm}^{-1}$	$-4182\ \mathrm{cm}^{-1}$	
		$A(l=+0)$	Yes	$+1786\ \mathrm{cm}^{-1}$	$+1598\ \mathrm{cm}^{-1}$	$1635\ \mathrm{cm}^{-1}$
$^1B_{2u}$	$34{,}500\ \mathrm{cm}^{-1}$	$E(l=\pm1)$	Yes	$-8\ \mathrm{cm}^{-1}$	$-37\ \mathrm{cm}^{-1}$	
		$B(l=+2)$	No	$-638\ \mathrm{cm}^{-1}$	$-723\ \mathrm{cm}^{-1}$	

Splittings and shifts have been calculated for only the $^1B_{1u}(p)$ and $^1E_{1u}(\beta, \beta')$ bands of polystyrene and the $^1B_{2u}(p)$ and $^1B_{3u}(\beta)$ bands of polyvinylnaphthalene. Because of the well-known pairing of molecular orbitals in alternant hydrocarbons, the interaction matrix elements of the $^1B_{2u}(\alpha)$ state of the benzene monomer in polystyrene and the $^1B_{1u}(\alpha)$ state of the naphthalene monomer in polyvinylnaphthalene are zero. This is true for two-center integrals involving Hückel as well as Pariser configuration interaction wavefunctions. The splittings in these bands are expected to be small: configurational mixing of change-transfer exciton states into neutral exciton states may be of considerable importance.

It should be noted that the results discussed thus far are for the entire electronic band and do not include effects of vibrational motion. The effects of vibrational–electronic coupling are considered in the next section.

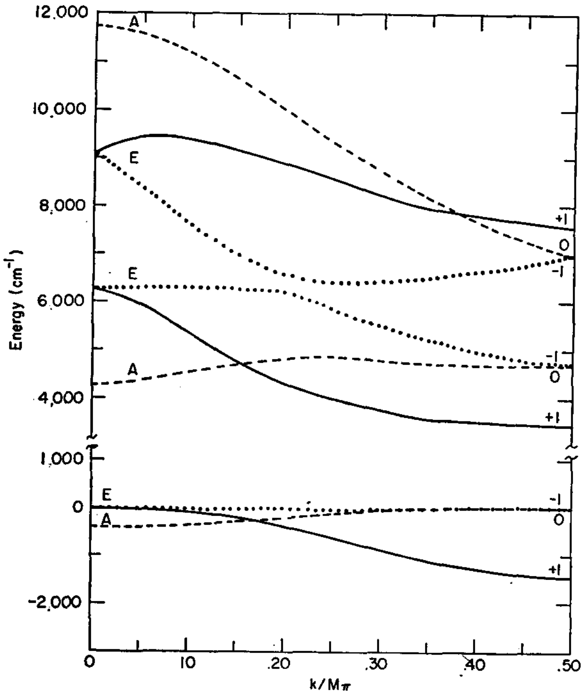

FIG. 1. Band structure of isotactic polystyrene. The letters to the left refer to the band symmetry representation of the helix group. The numbers to the right are the band labels l [see Eqs. (13) and (14)]. The ordinate shows only relative energies; the zero energy band is the E component of the P (2000-Å) band in polystyrene.

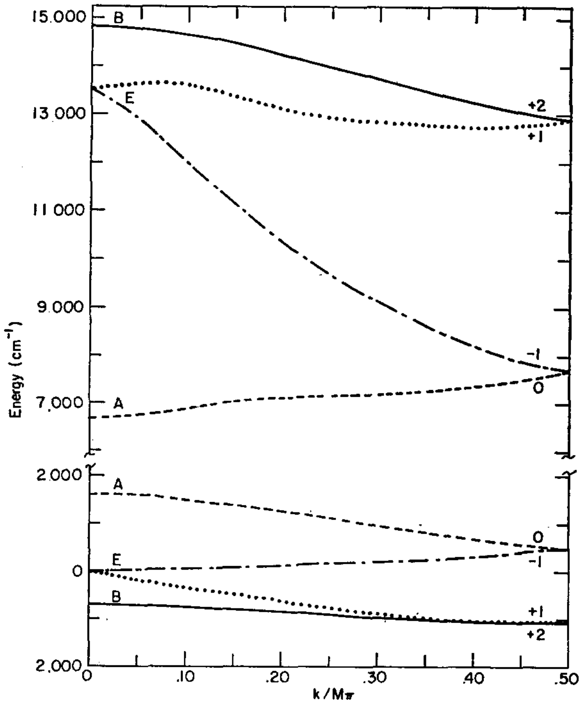

FIG. 2. Band structure of isotactic polyvinylnaphthalene. The E component of the P (2750-Å) band of PVN lies at the zero of energy.

IV. VIBRATIONAL COUPLING EFFECTS

Throughout the previous discussion we have assumed that the Davydov splitting is large relative to the vibrational spacing. In this strong coupling limit there will be two well-separated absorption peaks. In the other limit, the weak coupling limit, the Davydov splitting is amall compared to the vibrational spacing and instead of starting with the total electronic wavefunction a different formalism must be used. In the weak coupling limit we take the molecular wavefunctions in vibronic form

$$\phi_{m\beta}{}^{f,v_i}=\phi_{m\beta}{}^{f}\chi_{m\beta}{}^{v_i}, \tag{22}$$

where $\chi_{m\beta}{}^{v_i}$ is a vibrational wavefunction for the $m\beta$th molecule in the v_ith vibrational state. If the functions defined by Eq. (15) are used as the basis for calculating the matrix elements of the intermolecular potential, the integrals are all modified as follows:

$$\begin{aligned}\langle \mathcal{A}\phi_{n\alpha}{}^{f,v_i}\phi_{m\beta}{}^{0,0} \mid V_{n\alpha,m\beta} \mid \phi_{n\alpha}{}^{0,0}\phi_{m\beta}{}^{f,v_i}\rangle &= \langle \mathcal{A}\phi_{n\alpha}{}^{f}\phi_{m\beta}{}^{0} \mid V_{n\alpha,m\beta} \mid \phi_{n\alpha}{}^{0}\phi_{m\beta}{}^{f}\rangle \\ &\quad \times \langle \chi_{n\alpha}{}^{v_i} \mid \chi_{n\alpha}{}^{0}\rangle\langle \chi_{m\beta}{}^{v_i} \mid \chi_{m\beta}{}^{0}\rangle. \end{aligned} \tag{23}$$

It is seen that in the weak coupling limit, the total electronic matrix element is multiplied by a vibrational overlap factor, being otherwise unmodified from the matrix element in the strong coupling limit.

From the figures displayed in Table IV it is clear that the splittings in the ${}^1B_{3u}$ and ${}^1B_{2u}$ states of the naphthalene residue represent strong coupling, as do those for the ${}^1E_{1u}$ state of the benzene residue. However, the splitting of the ${}^1B_{1u}$ states of the benzene residue is better represented as a weak coupling case.

It is now necessary to comment on the magnitude of the computed matrix elements, since this will influence the validity of the deduction made in the preceding paragraph. It is well known that the available wavefunctions often lead to an overestimate of the transition dipole moments of aromatic molecules. For example, the Pariser functions overestimate the transition moment from the ground state for the $P({}^1B_{2u})$ state of naphthalene by a factor of about 2.5, and the $\beta({}^1B_{3u})$ state by a factor of about 1.2. For the case of benzene no easy comparison is possible because some of the transitions of interest are formally forbidden in the lowest order. Now, it might be asserted that the computed matrix elements should be scaled by a factor $f_{\text{exptl.}}/f_{\text{theoret.}}$ where f is the oscillator strength. From the data displayed in Table III it is clear that such an alteration would not change our description of the splittings since they would remain individually large enough to still require description in the strong (or weak) coupling limit. Therefore, the most important qualitative feature of the calculated splittings is independent of the error made in computing transition moments.

V. EXCITON-EXCITON ANNIHILATION

One of the most interesting uses to which helical polymers may be put is the study of phosphorescence from the monomer in an ordered environment. In many instances, pure crystals of the molecule equivalent to the side group do not display phosphorescence because of the very efficient triplet–triplet annihilation reaction. The product of this reaction, an excited singlet, gives rise to a delayed fluorescence. Because the interactions between residues on the polymer are less than the interactions in a crystal of a similar compound, it may be possible to cut the rate of triplet–triplet annihilation to a level wherein phosphorescence can compete with annihilation.

For the triplet states, the only relevant matrix elements arise from exchange interactions. Following Jortner, Choi, Katz, and Rice[15] we set the rate of encounter of two excitons equal to

$$\mathcal{R}=zn_t^2/2N\tau_{n\alpha}, \tag{24}$$

where z is the number of nearest neighbors, n_t the concentration of triplet excitons, N the density of of residues, and $\tau_{n\alpha}$ is given by

$$\frac{1}{\tau_{n\alpha}}=\sum_{m\beta}\left(\frac{2\pi}{\hbar}\right) \mid \langle \phi_{m\beta}{}^{f}\phi_{n\alpha}{}^{0} \mid V_{n\alpha,m\beta} \mid \phi_{n\alpha}{}^{f}\phi_{m\beta}{}^{0}\rangle \mid^2 \times \int f(E)F(E)dE, \tag{25}$$

where $F(E)$ and $f(E)$ are the normalized $S\rightarrow T$ absorption and the normalized $T\rightarrow S$ phosphorescence function, respectively.

Alternatively, we may consider the annihilation reaction to occur between two diffusing triplet excitons, whereupon

$$\mathcal{R}=(n_t^2\langle R\rangle/3)\sum_{n\alpha}W_{n\alpha,m\beta}R^2_{n\alpha,m\beta}, \tag{26}$$

where $\langle R\rangle$ is an average monomer spacing, $R_{n\alpha,m\beta}$ is the distance between $n\alpha$ and $m\beta$ and $W_{n\alpha,m\beta}$ is the frequency of jumps of length $R_{n\alpha,m\beta}$, i.e., $W_{n\alpha,m\beta}=\tau^{-1}{}_{n\alpha,m\beta}$. Calculations based on either of these rate equations lead to the same numerical results (within the precision with which we are concerned).

In Table V are listed the triplet matrix elements of importance. With the values displayed in Table V, it is found that

$$\begin{aligned}\mathcal{R}_{tt}&=10^{-16}n_t^2\ \text{cm}^{-3}\ \text{sec}^{-1} \qquad \text{(PS)},\\ \mathcal{R}_{tt}&=10^{-14}n_t^2\ \text{cm}^{-1}\ \text{sec}^{-1} \qquad \text{(PVN)},\end{aligned} \tag{27}$$

which should be compared with the value $2.1\times10^{-11}n_t^2$ cm$^{-3}\cdot$sec^{-1} calculated for crystalline anthracene. Thus, for comparable triplet exciton concentrations, the rate of triplet–triplet annihilation in PS and PVN is several

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[15] J. Jortner, S. Choi, J. L. Katz, and S. A. Rice, Phys. Rev. Letters 7, 323 (1963).

orders of magnitude less than that for crystalline anthracene. Since the annihilation rate in anthracene should be typical, to order of magnitude, of crystals of aromatic molecules, we conclude that there is a distinct possibility of observing phosphorescence from polymers under conditions wherein phosphorescence from the corresponding monomer crystal cannot be seen.

VI. DISCUSSION

The calculations presented in this paper are a necessary preliminary to the study of the electronic states of disordered polymers. From these calculations we can deduce the following about isotactic PS and PVN.

(1) The expected singlet band splittings are large and have symmetry characteristics considerably different from those of crystalline benzene and naphthalene.

(2) The triplet bandwidth is extremely small and therefore the rate of triplet–triplet annihilation is several orders of magnitude less than that characteristic of a typical aromatic crystal (anthracene).

(3) Despite inadequacies in the available molecular wavefunctions it is concluded that the predicted Davydov splittings are best described in the strong coupling limit for a number of the transitions. It is interesting that in the isotactic polymer a transition may be an example of the strong coupling case, whereas the same transition in the crystal corresponds to the weak coupling case (e.g., ${}^1B_{2u}$ state of naphthalene in PVN and the pure crystal).

(4) Because of the narrowness of the triplet exciton band, it is conceivable that interaction with vibrations can lead to a localized state.

When the regularity of the potential field is destroyed (as is the case in an atactic polymer) the techniques which lead to a band structure of the type discussed herein can no longer be used. It is still possible to construct polymer wavefunctions from a linear combination of molecular orbitals, but now the lack of symmetry prevents the construction of a simple phase factor which successively transforms one molecular wavefunction into another. Two limiting cases are of interest:

TABLE V. Triplet matrix elements and splitting.

	$M_{n\alpha,m\beta}^J$ (eV)	$\Delta\epsilon^J$ (cm^{-1})
(a) Polystyrene residue		
1	1.82×10^{-5}	0.46
2	5.58×10^{-7}	
3	-6.52×10^{-7}	
(b) Polyvinylnaphthalene residue		
1	1.58×10^{-4}	2.60
2	3.0×10^{-7}	
3	3.2×10^{-6}	
4	0	

(a) When the potential is nearly periodic (i.e., isotactic or syndiotactic except for an isolated chromophore) it may be possible to generate a set of localized states. Aside from the intrinsic interest which these states have, if properly located they may act as energy traps.

(b) When the potential corresponds to a disordered configuration (i.e., an atactic polymer) it is necessary to average over a representative ensemble of disordered systems to obtain the observable electronic structure. While there is expected to be considerable broadening of the energy levels (corresponding to $\mathbf{k}=0$ in the isotactic polymer) it is still possible to have localized states which may act as energy traps. The study of the various relationships between these levels, the level width and the corresponding levels in the regular case will be the subject of a separate paper.

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