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Triplet-Exciton Dynamics in Polyadenilic Acid

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In this paper we present the results of a theoretical study of triplet exciton dynamics in single-strand polyadenilic acid. The triplet jump time was related to the intermolecular electron-exchange interactions, and to a semiempirical scattering time. Calculations of the intermolecular interactions were performed for five different structural models for the helical polymer. The theoretical results are consistent with the available experimental triplet energy-transfer data for this system, provided that the structure of single-strand polyadenilic acid is close to that of RNA 11. For this structural model the nearest-neighbor triplet-transfer integrals in polyadenilic acid are $\sim 0.5\ \mathrm{cm}^{-1}$, and the estimated triplet-exciton jump time is $\tau_j \sim 10^{-9}$ sec.

I. INTRODUCTION

The electronic properties of biopolymers are of considerable intrinsic interest. Experimental studies of the electronic states of DNA and its components[1–4] were conducted in an attempt to understand the molecular and electronic mechanisms responsible for photoinduced biological mutagenic effects, which may alter the genetic message of DNA. Optical studies, in particular the changes in the optical rotary dispersion,[5] and in the absorption intensities[6] resulting on the formation of a regular helix are of considerable importance for establishing the conformation of biopolymers. The theoretical interpretation of optical data such as optical rotatory dispersion and hypochromism is fraught with difficulties, as they have to be handled within the framework of second-order perturbation theory. The limited utility of perturbation techniques results from infinite-term summations over intermediate states, and in principle all the excited crystal (or rather polymer) states have to be included.

During the last few years, considerable progress was achieved in the experimental and theoretical studies of exciton spectroscopy and exciton energy transfer in molecular crystals of aromatic molecules.[7] In particular, the nature of intermolecular interactions, energy-level splitting, and energy transfer via triplet excitons in simple molecular crystals, such as naphthalene and anthracene, have been elucidated.[8–16] It is the purpose of this paper to discuss triplet-exciton states in polyadenilic acid, focusing our attention on the interpretation of triplet energy transfer in this system. Energy migration is determined by intermolecular interaction terms, which in the case of triplet-exciton states arise mainly from short-range intermolecular electron-exchange interactions. These exchange integrals are extremely sensitive to the molecular orientation and to the intermolecular distance. Extensive experimental data on triplet-energy migration in single-strand polyadenilic acid were resently obtained by Bersohn, Shulman, Eisinger, and their collaborators.[17–19] At this stage, theoretical studies of triplet-exciton dynamics in this system appear to be of interest. The questions we shall consider are:

(a) How is the triplet jump time related to the intermolecular interactions, and to other parameters which determine triplet-exciton scattering?

(b) How can the triplet-exciton scattering parameters be estimated?

(c) How are the intermolecular interactions affected by the conformation of the biopolymer?

(d) Do the theoretical data provide support to the triplet-exciton model for energy transfer in polyadenine?

The results of the present theoretical study combined with the available experimental data are expected to provide a new method to monitor the nature of the

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helical configuration in polyadenine. It is suggested that triplet energy-transfer data can be applied as useful tools to establish the conformation of some biopolymers.

II. SURVEY OF EXPERIMENTAL DATA

Polyadenine exists in two conformations[20]: an acid form which is a hydrogen-bonded double helix, while the nonprotonated neutral form appears as a single strand. Studies of the radiative decay of excited states can be conducted only in the case of the single strand, as both fluorescence and phosphorescence are quenched in the double-strand form.[19] The following experimental observations were reported:

(a) The single-strand polymer reveals a large degree of base stacking in ethylene glycol–water glasses at 77°K,[18,19] so that the triplet energy-transfer experiments were conducted on an ordered system.

(b) The phosphorescence of polyadenilic acid in glasses at 77°K can be quenched by small quantities (of the order of 1 mole%) of Mn^{2+} ions.[17] These experimental data were interpreted by Bersohn and Isenberg[17] in terms of triplet energy migration.

(c) Quantitative studies[18] of quenching of phosphorescence by divalent paramagnetic ions, i.e., Mn^{2+}, Co^{2+}, and Cu^{2+} (which are bound to the polynucleotide via the phosphate group) provide evidence for the triplet-exciton model in which the diffusion length is of the order of 100 adenine residues. The similar efficiency of different paramagnetic ions may indicate that the quenching process is limited by triplet diffusion. Eisinger and Shulman[18] have interpreted their experimental data in terms of a diffusion theory, which leads to a triplet jump time of $\tau_j = 4\times10^{-4}$ sec, for triplet transfer to a neighboring chromophore.

(d) The estimate of τ_j from the quenching experiments provides an upper limit for the triplet-exciton jump time. Phosphorescence and ESR measurements of the decay time of triplet excitons in polyadenilic acid reveal that the decay times are unaffected by quenching.[18] These results require the rejection of the diffusion-limited model, and were explained by a model in which barriers to diffusion limit the range. Triplet diffusion can take the place along an ordered region of the polymer (which extends over the range of about 100 residues) and τ_j is expected to be shorter than 4×10^{-4} sec.

(e) A lower limit for the triplet-exciton jump time was obtained from an unsuccessful attempt to observe spin–spin motional averaging of the triplet ESR spectrum in polyadenilic acid, as compared to the constituent adenine monophosphate.[18,19] This result leads to the conclusion that $\tau_j > 2\times10^{-10}$ sec.

The beautiful experimental work of Bersohn, Eisinger, Shulman, and their colleagues provides strong evidence for the validity of the triplet-exciton model, where the range of the ordered polymer region, rather than the jump time, limits the diffusion length. The available experimental information reveals that $2\times10^{-10}\text{ sec} < \tau_j < 4\times10^{-4}$ sec. We now proceed to a theoretical study of τ_j.

III. TRIPLET-EXCITON TRANSFER

Theoretical studies of exciton dynamics[10,14,16] have introduced two limiting descriptions for the microscopic motion of excitons: the coherent motion band model, where plane-wave exciton states are a good zero-order description of the stationary states, and the strong-scattering hopping model, where localized excitations provide a suitable zero-order approximation for the crystal stationary states. Triplet-exciton migration is determined by relatively small intermolecular interactions, so that the rate of triplet-excitation transfer is expected to be small relative to the lattice relaxation time. Triplet-exciton scattering is expected to take place at every lattice site, and thus to destroy the crystal momentum as a good quantum number. In the limit of strong exciton scattering, with a mean free path of the order of lattice spacing, the exciton motion can be analyzed in terms of a random-walk model.[10,14] The applicability of the strong-scattering model for triplet energy transfer was suggested[17] for DNA and for organic crystals.[10,16] These physical arguments are supported by recent model calculations[21] where an exactly soluble model was considered, assuming that the excitation energy at a lattice site as well as the excitation-transfer matrix elements, are random functions of time (because of the lattice vibrations). For the case of triplet-exciton motion in a linear chain, it was demonstrated that an abrupt change from coherent to incoherent motion takes place when the fluctuation in the exciton energy exceeds the exciton bandwidth. When the motion becomes incoherent, the excitation transfer is adequately described as a diffusion process.

We proceed now to consider the random-walk model for triplet excitons in polyadenine applying a constant mean free path (Λ) or a constant mean free time (τ_s) approximation. These parameters are related by

$$\Lambda = \tau_s \langle V^2 \rangle^{1/2}, \tag{1}$$

where $\langle V^2 \rangle^{1/2}$ is the (thermally averaged) rms exciton-group velocity. Our physical strong-scattering model implies, of course, that $\Lambda \lesssim a$ (where a is the lattice spacing) and that the exciton bandwidth is small relative to $\hbar/\tau_s$. Now, the diffusion coefficient is given by

$$D = \tau_s \langle V^2 \rangle, \tag{2a}$$

or, alternatively

$$D = \Lambda \langle V^2 \rangle^{1/2}. \tag{2b}$$

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Application of the random-walk model relates the diffusion coefficient for a one-dimensional (polymer) system to the jump time τ_j by

$$D = a^2/2\tau_j. \tag{3}$$

In the limit of "high" temperatures, which are large compared to the spread of the exciton band, all states are equally populated, so that

$$\langle V^2 \rangle^{1/2} \approx Ma/\hbar, \tag{4}$$

where M is the transfer matrix element between nearest neighbors. The jump time is thus given by

$$\tau_j = \hbar^2/2M^2\tau_s \tag{5a}$$

or

$$\tau_j = a\hbar/2M\Lambda. \tag{5b}$$

Some order-of-magnitude estimates can be made, taking the mean free path to be comparable to the lattice spacing $\Lambda \sim a$. We then obtain[14] the simple result, which is intuitively expected from the uncertainty relation,

$$\tau_j = \hbar/M. \tag{6}$$

The same result will be obtained by taking the scattering time to be equal to the reciprocal bandwidth $\tau_s = \hbar/2M$, or alternatively, from the random-walk energy-transfer model with the density of states assumed to be evenly distributed over the narrow exciton band.[14] This procedure depends on a somewhat arbitrary choice of the exciton scattering parameters.[16] It was recently pointed out[7,16] that Λ and τ_s may be estimated from the exciton optical bandwidth 2Γ, which is determined by the relaxation process,

$$\tau_s = \hbar/2\Gamma, \tag{7a}$$

or

$$\Lambda = \langle V^2 \rangle^{1/2}/2\Gamma \tag{7b}$$

so that

$$\tau_j = \hbar\Gamma/M^2. \tag{8}$$

The self-consistency relation for the applicability of the random-walk model implies that the exciton bandwidth is small, relative to the optical linewidth, $\Gamma \gg M$. Hence, the uncertainty relation (6) provides a lower limit for the jump time.

An approximate estimate for the linewidth Γ may be obtained from experimental data considering the half-linewidth for the optical transition[7,16] to the triplet state in the polymer. The optical linewidth measures the lifetime of a $\mathbf{k} = 0$ exciton state, and it is assumed that the scattering time is the same for all exciton states, or alternatively, that scattering events at different sites are not correlated. Such an assumption implies, of course, that the linewidths are equal for absorption and phosphorescence. The estimate of Γ from the optical linewidth provides an upper limit for the line broadening, or alternatively, a lower limit for the diffusion coefficient. It is not surprising that for the case of triplet-exciton diffusion in crystalline anthracene, the equivalent of Eq. (6)[14] leads to $D = 5 \times 10^{-4}$ cm^2/sec, Eq. (7a) yields[16] $D = 0.2 - 0.9 \times 10^{-4}$ cm^2/sec, while the experimental result[14,16] $D(\text{exptl}) = 2 \times 10^{-4}$ cm^2/sec is located between these two limiting estimates.

An alternative approach to the strong-scattering hopping model may be adopted by considering the very weak coupling limit for energy transfer.[22,23] In this case, excitation transfer takes places between a larger number of quasicontinuum densely spaced levels. For a one-dimensional system, the jump time is given by

$$\tau_j = \hbar/4\pi M^2 F. \tag{9}$$

The spectral overlap integral is

$$F = \int f_a(E) f_p(E)\, dE, \tag{10}$$

where $f_a(E)$ and $f_p(E)$ are the singlet–triplet absorption function and the triplet–singlet phosphorescence function, respectively, each normalized to unity on an energy scale. Comparison of Eqs. (8) and (9) leads to the relation

$$\Gamma = (4\pi F)^{-1}. \tag{11}$$

The triplet-exciton optical linewidth was observed for crystalline anthracene from the excitation spectrum for singlet–triplet transition monitored by recording the delayed fluorescence intensity, as a function of the energy of the exciting light.[16] These experimental data lead to $\Gamma \approx 70$ cm^{-1} for anthracene. On the other hand, Eq. (11) leads to $\Gamma \approx 100$ cm^{-1} for this system. Delayed fluorescence was not observed from polyadenilic acid and the excitation spectrum for the polymer phosphorescence was not yet determined. Until these data become available, we shall adopt the anthracene spectral value for polyadenilic acid and set $\Gamma = 70$ cm^{-1}. This estimate is not inconsistent with the polymer phosphorescence spectrum. Some rough numerical estimates are now in order: for $M = 1$ cm^{-1}, we get from Eq. (8) $\tau_j \approx 3.5 \times 10^{-10}$ sec, while $\hbar/M \approx 5 \times 10^{-12}$ sec. For $M \approx 0.1$ cm^{-1}, $\tau_j = 3.5 \times 10^{-8}$ sec, while $\hbar/M \approx 5 \times 10^{-11}$ sec. Turning our attention now to the experimental data summarized in Sec. II, we can deduce that the transfer integrals in polyadenilic acid should not exceed 0.5–1.0 cm^{-1}.

IV. TRIPLET MATRIX ELEMENTS

Only nearest-neighbor transfer integrals have to be considered as long-range Coulomb interactions are negligible for triplet states. The dominant electronic contribution arises from intermolecular exchange interactions[8,10]

$$K_{n1,m\mu} = \langle (\mathcal{A} - 1)\varphi_{n1}{}^f \varphi_{m\mu}{}^0 \mid V_{n1,m\mu} \mid \varphi_{n1}{}^0 \varphi_{m\mu}{}^f \rangle, \tag{12}$$

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where φ_{kl}^i is the electronic molecular wavefunction at the kl site in the ith electronic state (0 and f correspond to the ground state and to the triplet state, respectively), $V_{n1,m\mu}$ is the intermolecular interaction potential, and $\mathcal{A}$ corresponds to the intermolecular antisymmetrization operator.

We shall now consider the molecular wavefunctions. A number of calculations were performed on the excited electronic states of purines and pyrimidines[24–28] using the semiempirical Pariser–Parr SCF CI scheme. The recent data of Pullman *et al.*[25–27] yield good results for the zero-field splitting parameters and the excitation energies for the first triplet state of the nucleic bases. The π-electron charge distributions reported in that work are in good agreement with the theoretical data of Kuprevich.[28]

The molecular wavefunctions are now represented in the π-electron approximation

$$\varphi^f=\sum_I d_I\phi^{k\to l};\qquad I\equiv(kl),\tag{13}$$

where $\phi^{k\to l}$ corresponds to the one-electron excitation from the orbital k to the orbital l. Neglecting the effects of configuration interaction on the ground state and considering only the contribution of two-center intermolecular-exchange terms, the intermolecular electron-exchange integrals are displayed in the form[10]

$$K_{n1,m\mu}{}^f=-\sum_I\sum_{I'}\sum_i\sum_j d_Id_{I'}C_i{}^kC_j{}^{k'}C_i{}^lC_j{}^{l'}\times\langle w_{m\mu}{}^i(1)w_{n1}{}^j(1)\mid r_{12}{}^{-1}\mid w_{m\mu}{}^i(2)w_{n1}{}^j(2)\rangle\tag{14}$$

where $C_i{}^k$ corresponds to the single-configuration SCF molecular orbital coefficient for the kth MO (u^k) on the ith atom, while $w_{m\mu}{}^i$ represents the ith atomic orbital of the molecule $m\mu$.

It will be useful to now consider the hidden approximations involved in the calculation of the intermolecular interactions for the lowest triplet-exciton state of polyadenilic acid.

(a) A single molecular electronic configuration was considered, as the contribution of crystal-field mixing between different triplet states is expected to be negligible.[10]

(b) We have restricted ourselves to the tight binding approximation disregarding the mixing between Frenkel triplet-exciton states and charge-transfer states.[29] This approximation seems to be justified for a polymer, since the stabilization of the charge-transfer states by polarization interactions is expected to be lower than in a three-dimensional molecular crystal.

(c) In the derivation of Eq. (14) it was assumed that the molecular orbitals located on adjacent molecules are orthogonal. As the intermolecular overlap integrals are quite small (of the order 10^{-2}–10^{-4}), the Löwdin orthogonalization procedure can be applied. Using the procedure described previously,[10] the nonorthogonality corrections were calculated. As expected,[10] the nonorthogonality corrections were found to be small (of the order of 10%–20% of the exchange terms). Only nonorthogonality correction terms between π orbitals were evaluated, and orthogonalization effects coupling σ and π orbitals were not considered.

(d) Three- and four-center terms have been neglected in the calculation of the exchange integrals.

(e) The atomic orbitals appearing in Eq. (14) were represented in terms of carbon atom SCF $2p$ atomic wavefunctions.[10] The same atomic wavefunction was used for the carbon and the nitrogen atoms at large distances. In view of our meager knowledge of the behavior of molecular wavefunctions at large distances, this seems to be a reasonable zero-order approximation.

We now turn our attention to the molecular wavefunctions. We shall consider the wavefunction calculated by Pullman *et al.*[30] for the first triplet state of adenine. A cursory examination of this SCF CI wavefunction indicates that an appreciable contribution arises from the single configuration $\phi^{6\to7}$, which is characterized by a weight factor of 0.81. We have carried out calculations using three types of wavefunctions: the single-configuration SCF wavefunction of Tanaka and Nagakura[24] and of Pullman,[30] and the SCF CI wavefunction of Pullman.[30] The electron-exchange integrals calculated using the Pullman single-configuration SCF wavefunction[30] differ from the results obtained with the Pullman SCF CI wavefunction by about a numerical factor of 2–3. The results obtained using the Pullman SCF CI wavefunction and the Tanaka–Nagakura function do not differ by more than a numerical factor of 2.

We have finally to relate the electronic exchange integrals to the transfer terms. The weak vibronic coupling scheme is obviously applicable in this case[7] and the pure electronic terms have to be modified by a Franck–Condon vibrational overlap factor $\langle\chi^{00}\mid\chi^{fi}\rangle^2$, where χ^{00} and χ^{fi} correspond to the vibrational wavefunction in the ground vibronic state and in the ith

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

[30] A. Pullman (private communication). The molecular wavefunction for the first triplet state is given in the form:

$$0.90\phi^{6\to7}+0.135\phi^{5\to7}-0.02\phi^{3\to7}+0.057\phi^{2\to7}+0.03\phi^{1\to7}-0.077\phi^{6\to8}+0.1787\phi^{5\to8}+0.002\phi^{7\to8}+0.0125\phi^{3\to8}-0.045\phi^{2\to8}+0.012\phi^{1\to8}+0.03\phi^{6\to9}-0.1344\phi^{5\to9}+0.125\phi^{7\to9}-0.219\phi^{3\to9}-0.067\phi^{2\to9}-0.03\phi^{1\to9}+0.038\phi^{6\to10}-0.056\phi^{5\to10}+0.07\phi^{4\to10}+0.036\phi^{3\to10}+0.06\phi^{2\to10}-0.046\phi^{1\to10}.$$

vibronic component of the fth electronic state, respectively. Triplet energy transfer in the $f0$ vibronic state is determined by

$$M=K\langle\chi^{00}\mid\chi^{f0}\rangle^2, \tag{15}$$

where K is the nearest-neighbor exchange term. From the relative intensities in the phosphorescence spectrum of polyadenilic acid,[18] we estimate the relevant Franck–Condon vibrational overlap factor $\langle\chi^{00}\mid\chi^{f0}\rangle^2\approx 0.25$.

V. SPECULATIONS ON THE STRUCTURE OF SINGLE-STRAND POLYADENILIC ACID

The calculation of the intermolecular exchange integrals requires the experimental information concerning the structure of the polymer. The structure of single-strand polyadenilic acid is at present unknown. It may be conjectured that the structure of single-strand poly A is similar to that experimentally established for the double-strand structures of DNA or RNA. However, such a general statement is inadequate, as the intermolecular interaction terms are very sensitive to the separation and in particular to the relative orientation of the bases. In view of the lack of experimental data concerning the single-strand poly A, we have used the following structural models.

(a) The DNA (DNA model 1),[31,32] where the bases are taken to be perpendicular to the helix axes.

(b) The DNA model 3 (DNA3),[31,32] where the bases are weakly tilted, while the helical constants are the same as for the previous structure.

(c) The double-strand poly A (PAA),[33] where the bases are more tilted than before, the structure being more extended with a translation $R(z)=3.8$ Å and an eightfold rotation axis.

(d) The RNA 10-fold (RNA10) and 11-fold (RNA11) structures.[34] These differ from the former structures in that the atomic coordinates of the purine residues are located away from the helix axis, while the translations between the base pairs are somewhat shorter.

In Table I, we present the relevant helical parameters for the biopolymers, which serve as models for the single-strand poly A. We also display the electron-exchange term K, the orthogonality correction terms O, calculated using these five different structural models. From these results, it is apparent that the transfer times τ_j calculated for the structures of DNA1, DNA3, and PAA structures are too short to account for the experimental data.[19] For the RNA11 structure, both the Tanaka–Nagakura SCF function and the Pullman SCF CI function lead to $\tau_j\approx 10^{-9}$ sec. This result obtained for the structure of RNA11 is close to

TABLE I. Intermolecular electron-exchange interaction and triplet jump time in polyadenilic acid.

			Pullman SCF				Pullman SCF CI			Tanaka–Nagakura SCF		
Structural model	$R(z)$ (Å)	θ (deg)	$K^{(1)}$ [a] (cm^{-1})	$O^{(1)}$ [b] (cm^{-1})	$M^{(1)}$ [c] (cm^{-1})	$\tau_j^{(1)}$ [d] (sec)	$K^{(2)}$ [e] (cm^{-1})	$M^{(2)}$ (cm^{-1})	$\tau_j^{(2)}$ (sec)	$K^{(3)}$ [f] (cm^{-1})	$M^{(3)}$ (cm^{-1})	$\tau_j^{(3)}$ (sec)
DNA1	3.36	36°	−26.9	0.9	−6.72	8.2×10^{-12}	−25.1	−6.27	9.4×10^{-12}	−14.5	−3.61	2.8×10^{-11}
DNA3	3.36	36°	−17.1	2.0	−4.27	2.0×10^{-11}	−18.7	−4.67	1.7×10^{-11}	−18.6	−4.65	1.1×10^{-11}
PAA	3.80	45°	−6.1	2.0	−1.53	1.6×10^{-10}	−10.5	−2.63	5.3×10^{-11}	−6.86	−1.72	1.2×10^{-10}
RNA10	3.0	36°	−16.1	1.8	−4.02	2.3×10^{-11}	−18.4	−4.59	1.7×10^{-11}	−10.6	−2.64	5.3×10^{-11}
RNA11	2.73	32.7°	−7.4	0.3	−1.84	1.1×10^{-10}	−2.47	−0.62	9.7×10^{-10}	−1.32	−0.35	3.2×10^{-9}

[a] $K^{(1)}$ is the electron-exchange interaction calculated using Pullman's single-configuration $\phi^{6\rightarrow7}$ molecular wavefunction for adenine.[30]

[b] $O^{(1)}$ is the orthogonality intermolecular correction calculated using Pullman's single-configuration $\phi^{6\rightarrow7}$ molecular wavefunction.[30]

[c] $M^{(i)}\approx 0.25\,K^{(i)}$ $(i=1, 2, 3)$.

[d] $\tau_j^{(i)}$ is the $(i=1, 2, 3)$ jump time calculated from Eq. (8) with $\Gamma\approx 70$ cm^{-1}.

[e] $K^{(2)}$ is the electron-exchange interaction calculated using Pullman's SCF CI molecular wavefunctions, Ref. 30.

[f] $K^{(3)}$ is the electron-exchange interaction calculated using the Tanaka–Nagakura single-configuration $\phi^{6\rightarrow7}$ molecular wavefunction for adenine.[24]

[31,32] R. Langridge, D. A. Marvin, W. E. Seeds, and H. R. Wilson, J. Mol. Biol. **2**, 38 (1960). In Model 1, the base pairs are 4 Å nearer the helix axis than in the Crick model.

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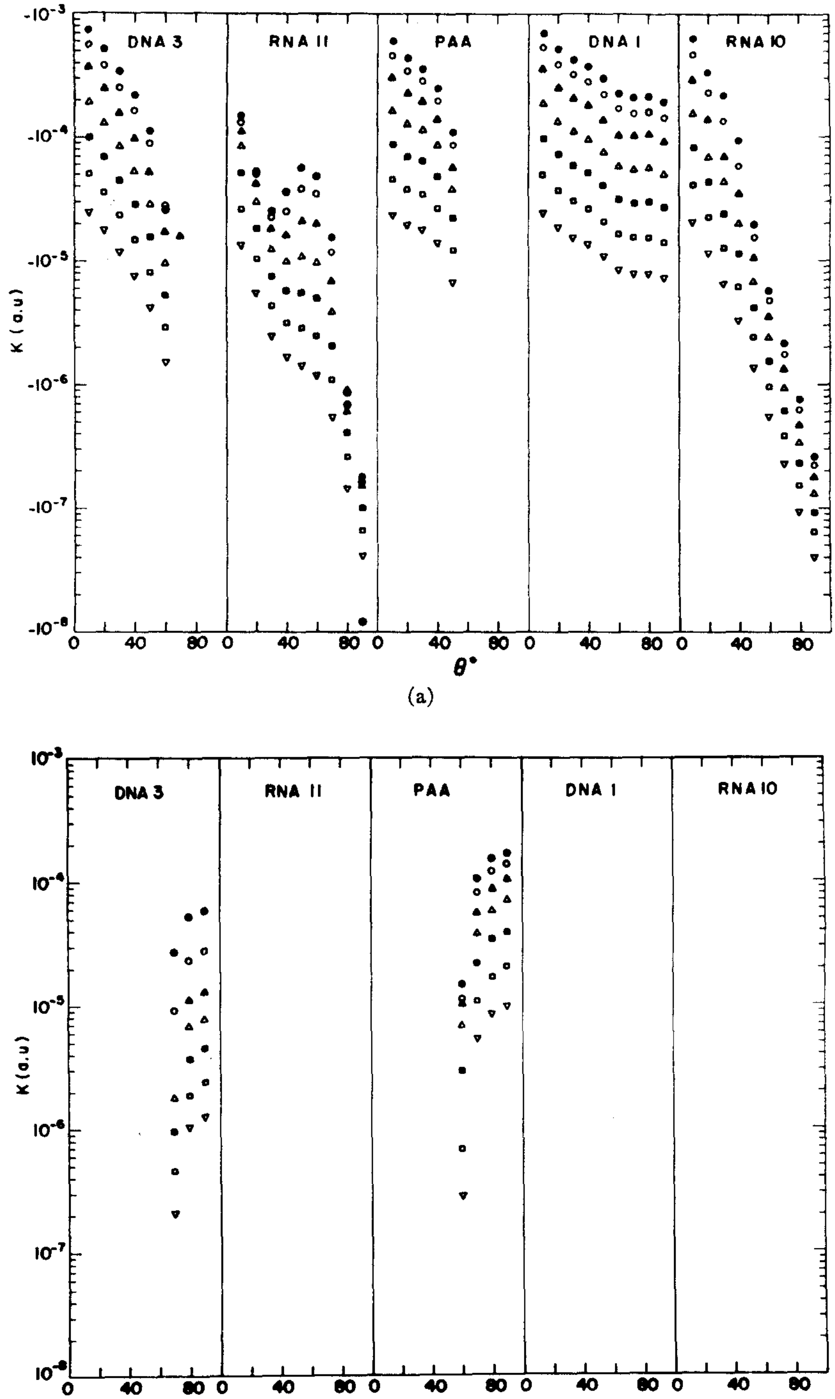
[34] S. Arnott, M. H. F. Wilkins, W. Fuller, and R. Langridge, J. Mol. Biol. **27**, 535 (1967).



(a)

(b)

FIG. 1. The dependence of the intermolecular electron-exchange integrals K on the helix parameters θ and $R(z)$ for five different models (see text) which determine the coordinates of the reference molecule. θ is given in degrees. The energies K are given in atomic units (10^{-5} a.u. $=2.26$ cm^{-1}). These calculations were performed using a single-configuration molecular wavefunction of Pullman.[30] The translations along the axis are: ●, $R(z)=5.0$ a.u.; ○, $R(z)=5.5$ a.u.; ▲, $R(z)=6.0$ a.u.; △, $R(z)=6.5$ a.u.; ■, $R(z)=7.0$ a.u.; □, $R(z)=7.5$ a.u.; ▽, $R(z)=8.0$ a.u. (a) Range of negative K values. (b) range of positive K values.

the upper limit of the transfer integral M derived from experiment.[19]

The structure of the single-strand polyadenilic acid may be somewhat more extended than that corresponding to the double-strand RNA11. Some indirect experimental evidence is available which indicates that the formation of stacking interactions in single-strand polyadenilic acid is accompanied by an increase in the degree of the extension of the molecule. Luzzani's work indicates that the mass per unit length of neutral polyadenilic acid is exactly one-half that of the double-strand PAA structure.[35] Hydrodynamic evidence for a

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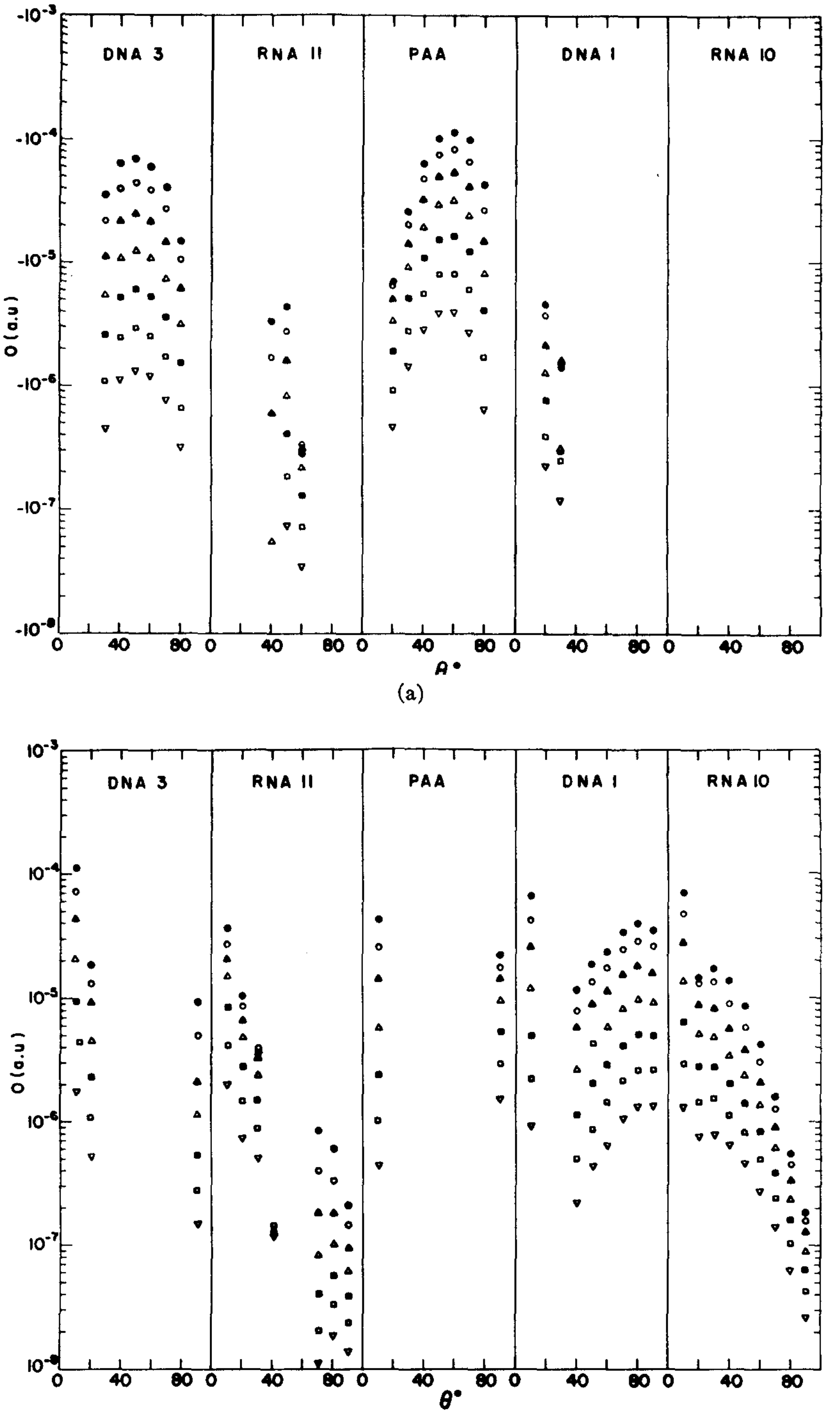

(a)

(b)

FIG. 2. The dependence of the nonorthogonality corrections for intermolecular π–π overlap on the helix parameters. Energies are given in atomic units. Calculations were performed using a single-configuration molecular wavefunction of Pullman.[30] Notation is the same as in Fig. 1. (a) Range of negative O values. (b) Range of positive O values.

highly extended structure of neutral poly A was also reported recently by Eisenberg and Felsenfeld.[36] In order to test the dependence of the M terms on the helical constants, we have performed further calculations of the intermolecular interactions, varying the helical parameters. The atomic coordinates of a reference molecule were assumed to be those given by one of the model structures, while the helical parameters θ and $R(z)$ were varied. These results are displayed in Figs. 1–3 for a single-configuration SCF molecular wavefunction of Pullman, in Fig. 4 for the SCF CI molecular wavefunction, and in Fig. 5 for the Tanaka–Nagakura wavefunction. We notice that the DNA model leads consistently to too high values for the

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[36] H. Eisenberg and G. Felsenfeld, J. Mol. Biol. 30, 17 (1967).

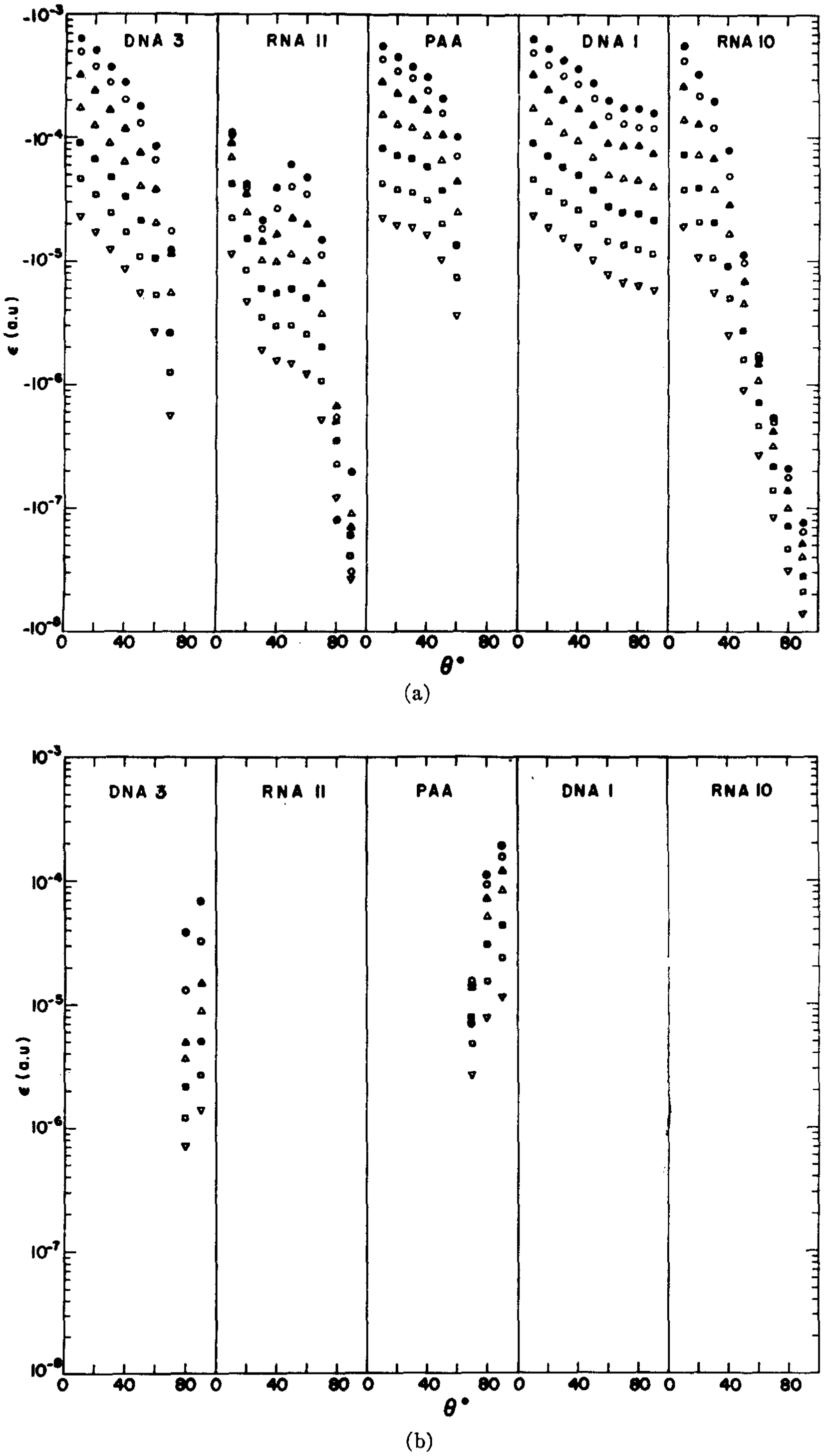

FIG. 3. The dependence of the intermolecular electron exchange interactions corrected for nonorthogonality on the helix parameters. Results are for a single-configuration molecular wavefunction of Pullman.[30] Energies are given in atomic units. Notation is the same as in Fig. 1. (a) Range of negative ε values; (b) range of positive ε values.

interaction term. The DNA3 and PAA structures require a rather drastic increase of the helical angle, the screw axis has to be reduced to a sixfold axis (from a 10- and an eightfold axis in DNA3 and in PAA, respectively). The structure of RNA11 extended to $R(z)\sim 3$–3.5 Å (while the helical angle is kept fixed) yields M values which are consistent with the experimental jump times (see Figs. 4 and 5). Obviously, the calculations of the exchange terms are not accurate enough to monitor the helical constants to a better accuracy.

From the results we conclude that:

(a) The nonorthogonality corrections for the polymer configurations which are of physical interest do not exceed 20% of the electron-exchange terms. How-

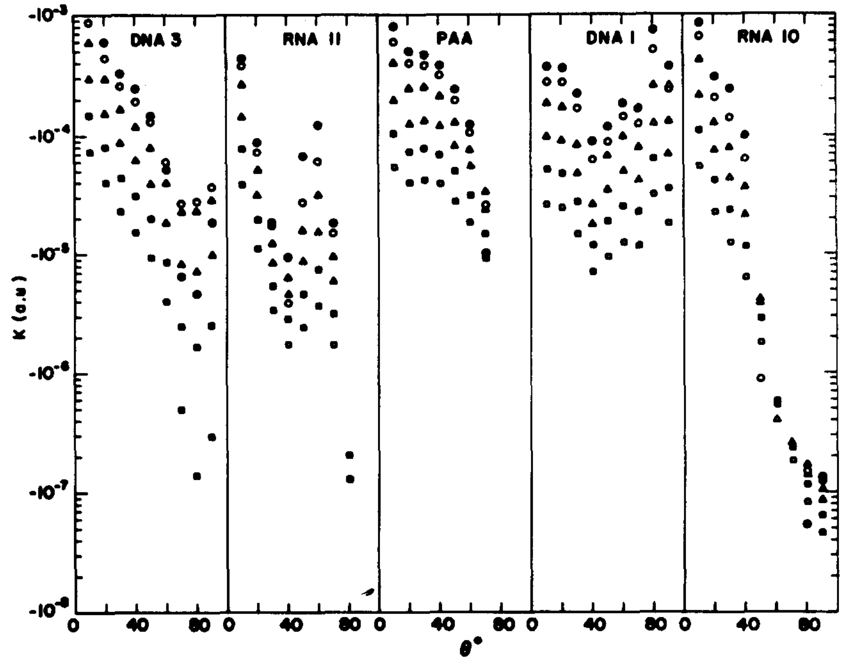

FIG. 4. The dependence of the intermolecular electron-exchange interactions on the helix parameters in poly A. Calculations performed using the SCF CI molecular wavefunction of Pullman.[30] Energies are in atomic units. Notation is the same as in Fig. 1.

ever, when the exchange interactions are low (for large tilting angles) these nonorthogonality corrections are appreciable. The latter contributions may be of interest for understanding barriers for triplet diffusions.

(b) The electron-exchange interactions are strongly affected by the nature of the (approximate) molecular wavefunction. For the Pullman wavefunctions, the inclusion of CI appreciably modifies the K terms. The situation here is similar to that encountered in the treatment of singlet exciton states, using the Pariser–Parr SCF CI wavefunction.[10] The consistency of the results using different molecular wavefunctions (Pullman's SCF CI and Tanaka–Nagakura SCF) inspires some confidence concerning the reliability of our numerical results.

(c) As the K terms are strongly dependent on the relative configuration of the purine bases, triplet energy-transfer data may be useful in monitoring the structure of helical biopolymers.

VI. DISCUSSION

In this paper, we have presented model calculations of the intermolecular electron-exchange interactions in a helical polymer, in an attempt to provide evidence

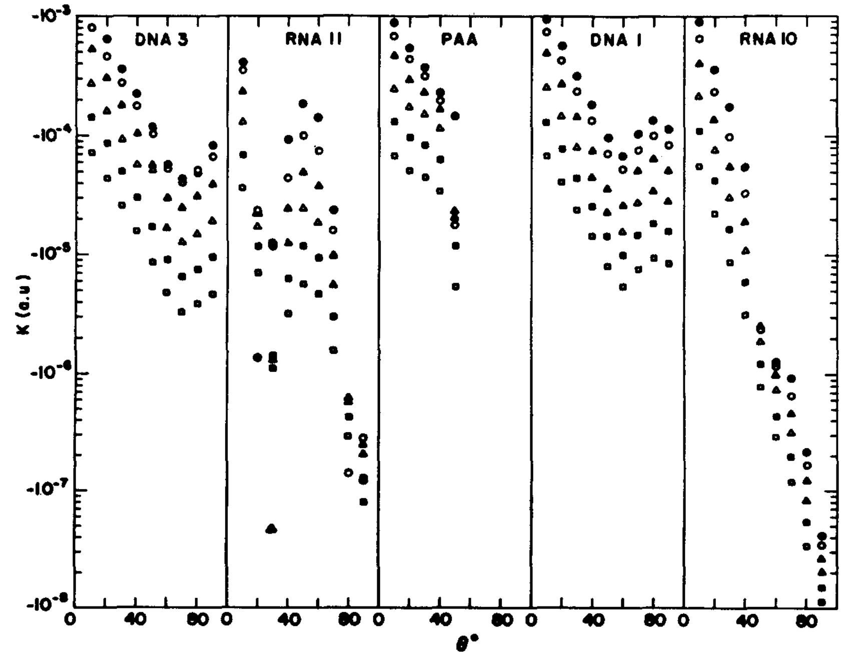

FIG. 5. The dependence of the intermolecular electron-exchange interactions on the helix parameters in poly A. Calculations performed using the single-configuration molecular wavefunction of Tanaka and Nagakura.[24] Energies are in atomic units. Notation is the same as in Fig. 1.

for the structure of single-strand poly A from triplet energy-transfer experiments. It should be stressed that in view of the approximations involved in the present treatment, the accuracy of the absolute values of the transfer matrix elements is rather poor. As the jump time is determined by M^{-2}, the theoretical τ_j values reported herein are accurate only within one order of magnitude. It should be noted, however, that the same computational methods[10] were quite successful in predicting the absolute magnitudes of the Davydov splittings in the first triplet states of molecular crystals such as naphthalene and anthracene.[11,12,16] It can be inferred, therefore, that the present calculations provide a reliable estimate of the relative magnitude of the intermolecular interaction terms for different structural models of the helical polymer. The assignment of the RNA11 structure for the single-strand poly A is consistent with some very recent crystallographic determinations of the structure of poly (A+U) and of poly (I+C). In both cases, the structure is identical with that of RNA and is 11-fold.[37]

The following comments are in order:

(a) The triplet transfer parameters for poly A should be compared now with the well-established data available for molecular crystals. For crystalline anthracene $M \sim 2.5\ \text{cm}^{-1}$ as inferred from the Davydov splitting[12,16] and $\tau_j \sim 5\times10^{-12}$ sec as estimated from the triplet diffusion coefficient.[14,15] The poly A results are $M \sim 0.5\ \text{cm}^{-1}$ and $\tau_j \sim 10^{-9}$ sec. The difference between the jump times in the anthracene crystal and in poly A can be adequately rationalized.

(b) The triplet jump time in the strong scattering random walk is determined by M^{-2}, rather than by M^{-1}, as might have been inferred from the uncertainty broadening of a localized triplet state. Hence, the upper limit estimated herein for the M term in poly A, $M \sim 0.5\ \text{cm}^{-1}$, is by one order of magnitude higher than the previous estimate of Shulman *et al.*[19]

(c) The triplet jump time in poly A [τ_j (theory) $\approx 10^{-9}$ sec] is close to the experimental lower limit ($\tau_j \sim 2\times10^{-10}$ sec) estimated by Shulman *et al.*[19]

(d) The results of this study provide theoretical support to the suggestion of Shulman and Eisinger that the triplet diffusion length in poly A is limited by the range of the ordered polymer regions, rather than by the triplet jump time.

(e) Triplet energy transfer is dominated by near-neighbor interactions, so that long-range coherence effects are not involved. The observation of barriers to the triplet diffusion which limit the exciton migration[18] should be interpreted in terms of a drastic decrease in the transfer integrals. From the data of Figs. 1–4, we notice that the tilting of a single adenine base by a large angle θ will lead to an extremely low intermolecular interaction term. Such a local perturbation will limit the diffusion range. This conclusion is consistent with a previous theoretical study of triplet excitons in polystyrene.[38]

ACKNOWLEDGMENTS

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[37] W. B. Gratzer (private communication).

[38] M. T. Vala, R. Silbey, S. A. Rice, and J. Jortner, J. Chem. Phys. 41, 2846 (1964).