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Conformational dependence of the electronic coupling for singlet excitation energy transfer in DNA. An INDO/S study†

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Using the INDO/S method, we study the effects of structural fluctuations on the interaction of singlet excited states in homogeneous poly(dA)-poly(dT) and alternating poly(dAdT) stacks. The coupling for excitation energy transfer (EET) between intra- and inter-strand nucleobases is derived with the fragment excitation difference scheme (Hsu, et al. J. Phys. Chem. C 2008, 112, 1204). In this approach, both Coulomb and short-range contributions to the EET coupling are properly accounted for. 15000 conformations for each nucleobase dimer were considered. Conformational fluctuations of DNA are shown to result in a large variation of the transfer integral. The root mean square coupling values are used to characterize the interaction of π–π* states in DNA. The intra-strand and inter-strand couplings between adenines are found to be significantly smaller than those for thymines. Our findings suggest that (1) EET couplings in DNA are significantly more sensitive to conformational changes of the π stack than is estimated within the dipole–dipole scheme; (2) singlet excitation energy transfer in poly(dA)-poly(dT) should predominantly occur through thymine bases; (3) π–π* excited states in homogeneous stacks are more delocalized than in alternating sequences; (4) structural fluctuations can strongly affect the exciton distribution.

Introduction

DNA excited state dynamics has attracted considerable attention.1,2 Experimental and theoretical studies in this field have been motivated by the desire to understand the high photostability of DNA. One of possible mechanisms used by DNA to protect itself from UV damage is delocalization of electronic excitation, which decreases the possibility of subsequent photochemical reactions. Another related mechanism is fast excitation energy transfer (EET). Despite much effort, (see ref. 1–8 and papers cited therein), many details on excited electronic states in DNA remain unclear. Different hypotheses concerning the photostability of DNA have been discussed.1 Among other factors, the photochemical behavior of DNA is affected by the basepair sequence and the size and conformation of oligo- and polynucleotides, which are closely related to the stacking interaction of nucleobases.1,2

Because the electronic properties of nucleobases are similar, interpretation of spectroscopic measurements for DNA can be quite difficult. Computational modeling may help to distinguish different contributions and to explore the role of electronic and structural factors. The nature of excited states within DNA and related systems has been intensively studied using different theoretical approaches (see for instance, recent papers9–17 and references therein). Recent developments in the theoretical and computational treatment of EET have been reviewed by Scholes18 and Beljonne et al.19

The electronic coupling is a key parameter for describing the delocalization of excited states and the probability of EET.18,19 The coupling of singlet excited states includes the delocalization of excited states and the probability of subsequent energy transfer. The dipole–dipole (DD) scheme provides good estimates when the spatial extension of the transition densities in chromophores is small compared to the inter-chromophore separation, otherwise, quantum mechanical methods must be employed.18,19 When two molecules interact in the excited state, the transition energies split. Within a two state model, the electronic coupling for symmetrical systems is equal to a half of the excited state splitting (both the short- and long-range interactions are included).18–20 For nonsymmetrical systems, however, the half-splitting scheme only provides an upper limit of the coupling. We note that the nucleobases in dimers like A2 or T2 of the ideal A- or B-DNA geometry, are structurally dissimilar and the coupling can be significantly smaller than A/2.15,16 The short and long range interactions in stacked nucleobase dimers have been analyzed using coupled-cluster (RI-CC2) calculations.16

Very recently, Hsu et al.21 introduced a fragment excitation difference (FED) scheme to estimate the EET coupling for both symmetrical and non-symmetrical systems. The FED approach is an elegant extension of the fragment charge difference method22 used to calculate the electronic coupling

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for hole and excess electron transfer. Because electronic excitation can be viewed as the creation of an electron–hole pair, the excited state electron density can be presented as a sum of the attachment and detachment electron densities.\textsuperscript{23} The FED scheme can be used in combination with various quantum chemical methods. In the current study, we employ FED together with the semiempirical method INDO/S,\textsuperscript{24} which describes the excited state properties of organic molecules reasonably well\textsuperscript{25} and is often applied to DNA models.\textsuperscript{10,17,26} Because INDO/S is computationally very efficient, it can be combined with MD simulations. The influence of conformational dynamics on the EET coupling in DNA oligomers was examined within the DD scheme.\textsuperscript{10}

Below we report the results of INDO/S calculations of EET couplings in poly(dA)-poly(dT) and poly(dAdT)\textsubscript{2}. 15 000 snapshots for each nucleobase dimer separated by 1 ps were extracted from MD trajectories provided by Ascona B-DNA Consortium.\textsuperscript{27} We consider the effects of conformational dynamics on the intra- and inter-strand interaction of excited states in DNA.

### Computational details

#### MD trajectories

MD data for 15-basepair double-strand oligomers 5’-G A\textsubscript{13} G-3’ and 5’-G T (AT)\textsubscript{6} G-3’ were downloaded from the website of the Beveridge group.\textsuperscript{28} Overall, benchmark MD trajectories for 39 different DNA duplexes (each oligomer is 15 nucleotide pairs in length) containing 136 unique DNA tetranucleotides were obtained by Ascona B-DNA Consortium,\textsuperscript{27} using a well established protocol: \(T = 300\text{ K},\ P = 1\text{ atm},\ 2\text{ fs} \) integration step, parm94 force field,\textsuperscript{29} TIP3P water molecules,\textsuperscript{30} periodic boundary conditions, cutoff of 9 Å for nonbonded interactions, particle-mesh Ewald algorithm\textsuperscript{31} for treatment of electrostatic interactions. Details on the MD simulation are well described.\textsuperscript{27} To exclude end effects, we consider nucleobases located in the middle of the oligonucleotides (intra-strand dimers A\textsubscript{1}A\textsubscript{2} and T\textsubscript{2}T\textsubscript{3} in the 5’-G A\textsubscript{1} G-3’ duplex and inter-strand dimers A\textsubscript{1}A\textsubscript{2}, A\textsubscript{2}A\textsubscript{3}, T\textsubscript{6}T\textsubscript{24} and T\textsubscript{3}T\textsubscript{24} in 5’-G T (AT)\textsubscript{6} G-3’).

#### Quantum chemical calculations

The excitation energies and electron densities were calculated using the multi-configurational INDO/S method.\textsuperscript{24} Configuration interaction of 144 singly excited states (the active space of 12 HOMOs and 12 LUMOs) was used for each of 15 000 conformations of intra-strand dimers A-A, T-A, T-T, and T-T and inter-strand dimers A/A, A/A, T/T, and T/T. The EET coupling is calculated by the FED method:\textsuperscript{21}

\[
|V| = \frac{\Delta \cdot |x_{mn}|}{\sqrt{(x_{mn} - x_{mn})^2 + 4 \cdot x_{mn}^2}},
\]

where \(\Delta\) is the splitting of the excited states \(m\) and \(n\), \(\Delta = |E_m - E_n|\), and matrix elements \(x_{mn}\) are expressed through the excited-state densities:

\[
x_{mn} = \int_{r \in D} \rho_{ex}^{mn}(r) dr - \int_{r \in A} \rho_{ex}^{mn}(r) dr
\]

\(\rho_{ex}\) is calculated as the sum of the attachment and detachment densities.\textsuperscript{21} We note that FED can be applied to systems with both localized and delocalized excited states. In the limiting case, when donor and acceptor are identical and electronic states are completely delocalized, eqn (1) reduces to \(|V| = \frac{\Delta}{2}\).

Much effort has been put into properly selecting the excited state of interest (each of two states should represent a linear combination of the same local excitations). Usually such a selection is not very difficult when treating only one system. The problem becomes more complicated if many structures have to be considered. There are two conditions to fulfill. First, the states of the same nature, e.g. \(\pi-\pi^*\), should be chosen for all structures extracted from the MD trajectory. Because the order of excited states can change when passing from one snapshot to another, 10 lowest excited states were analyzed for each snapshot. Second, the two-state model should be applicable, i.e. the selected excited states are accurately represented by linear combinations of only two states localized on the individual bases. Let \(L_{ij}\) and \(L_{ji}\) characterize localization of excited state \(\Psi_j\) on sites 1 and 2 (by definition, \(L_{ij} + L_{ji} = 1\) for any system consisting of two sites). We calculated the coupling only for structures, where the excited states of interest, \(\Psi_i\) and \(\Psi_j\), meet the requirement

\[
1 - \delta \leq |L_{ij} + L_{ji}| \leq 1 + \delta
\]

The parameter \(\delta\) defines tolerated deviations from the ideal two state model. At \(\delta = 0.05\) applied throughout this study, condition (3) is satisfied for more than 8800 snapshots for each type of dimers.

The EET couplings were also estimated using the DD scheme:

\[
V_{DD} = \frac{\mu_1 \mu_2}{r^3} - \frac{3(|\mu_1|^2 r^2 + |\mu_2|^2 r^2)}{r^3}
\]

Transition dipole moments \(\mu_1\) and \(\mu_2\) of isolated nucleobases are calculated with INDO/S.

#### Intra- and inter-strand nucleobase arrangement

In poly(dA)-poly(dT) stacks, the EET is determined by intra-strand couplings A-A and T-T. In poly (dAdT)\textsubscript{2}, the situation is more complicated.

\[
5' - A_{i-1} - T_1 - A_{i+1} - \cdots - T_{k-1} - A_k - T_{k+1} - 3'
\]

\[
3' - T - A_j - T - \cdots - A - T_1 - A - 5'
\]

Because of the helix structure, the mutual position of nucleobases in intra-strand fragments \(A_{i-1} - T_1\) and \(T_{k-1} - A_{k+1}\) is different. This structural dissimilarity should lead to different coupling values for A-T and T-A. Also, there are two types of inter-strand arrangement of A and T. To distinguish these dimers, we use A/A and A/A for configurations \(A_{i-1} A_i\) and \(A_{i+1} A_k\) respectively, and T/T and T/T for dimers \(T_{k-1} T_{k+1}\) and \(T_{k-1} T_{k+1}\) shown in the Scheme.
Results and discussion

As recently demonstrated, the EET coupling may be very sensitive to conformational changes. For instance, in the thymine dimer, it decreases by a factor of 15 when passing from an A- to a B-DNA conformation. As shown below, the EET coupling changes significantly along MD trajectories. To measure the effective coupling, we use its root mean square \( V_{\text{rms}} \)

\[
V_{\text{rms}} = \sqrt{\langle V^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} V_i^2}
\]

(5)

In line with the Förster theory, the EET rate is determined by the product of the EET coupling squared and the spectral overlap

\[
k = \frac{2\pi}{h} V^2 \int J(\omega) d\omega
\]

(6)

Therefore, \( V_{\text{rms}} \) rather than \( \langle V \rangle \) must be applied to describe EET.

Energy gap fluctuation

The fluctuation of the energy gap between two \( \pi-\pi^* \) excited states in the stack \( \text{A-T} \) is shown in Fig. 1. Statistical evaluation of the QM/MD data provides \( \Delta_{\text{av}} = 0.106 \pm 0.064 \) eV. The high-level calculations predict the gap in adenine dimers to be 0.147 and 0.057 eV for the ideal A- and B-DNA geometries. Because the MD structure of \( 5'-G \text{A}13 \text{G}-3' \) (and other oligonucleotides) is shifted from B- to A-DNA, \( \Delta_{\text{av}} = 0.106 \) eV is in good agreement with the \textit{ab initio} results. For \( T_3 \text{A}_2 \), we found \( \Delta = 0.196 \pm 0.092 \) eV, which is somewhat higher than 0.136 and 0.143 eV obtained for A- and B-type dimers. For inter-strand systems \( \text{A} \text{-} \text{A} \) and \( \text{A} \text{-} \text{T} \), the average values of \( \Delta \) are ca. 0.09 eV, whereas for \( \text{T} \text{-} \text{T} \) and \( \text{T} \text{-} \text{A} \) they are about 0.15 eV.

Dependence of EET coupling on the \( \pi \)-stack conformation

The arrangement of basepairs in a stack is usually described by six parameters (3 translations \( \text{shift, slide, and rise} \); and three rotations \( \text{tilt, roll, twist} \), see Fig. S1 in the Supporting Information). In ideal B-DNA, \( \text{rise} = 3.38 \) Å, \( \text{twist} = 36^\circ \) and other parameters are zero. By variation of \textit{shift}, \textit{slide}, \textit{rise} and \textit{twist}, nucleobases in the dimer remain coplanar. Let us consider how the coupling depends on these parameters. The structure of DNA \( \pi \)-stacks is quite flexible. Along an MD trajectory, \textit{shift} can typically range from \( -2.3 \) to \( 2.1 \) Å, \textit{slide} from \( -3.6 \) to \( 1.5 \) Å, \textit{rise} from \( 2.5 \) to \( 4.4 \) Å, and \textit{twist} from \( 7^\circ \) to \( 46^\circ \). Fig. 2 compares intra-strand A–A couplings squared computed with the FED and DD schemes. The structures were generated by varying the distance between planes of stacked adenine bases (\textit{rise}). As seen, the FED and DD couplings agree well when \textit{rise} \( \geq \) 6 Å. In line with eqn (4), the coupling decreases as \textit{rise} \( \rightarrow \) 3 Å. In DNA \( \pi \) stacks, \( \text{rise} = 3.4 \pm 0.3 \) Å and in this region, the FED results are significantly smaller than the \( V_{\text{DD}} \) (Fig. 2). Fig. 3 demonstrates the dependence of the intra-strand A–A coupling squared on \( \text{shift, slide and twist} \). As seen, the total coupling \( V \) computed using FED and \( V_{\text{DD}} \) exhibit similarly qualitative behavior, although their absolute values are quite different. The data demonstrated in Fig. 2 and 3 suggests that the EET coupling in DNA is quite sensitive to conformational changes of the \( \pi \) stack, and therefore, averaging over many conformations is required to obtain a reliable value for it.

Thermal fluctuation of the coupling

Now we consider fluctuations of the intra-strand coupling \( \text{A-T} \) along the 15 ns MD trajectory (15000 snapshots separated by 1 ps). As already noted, the coupling was calculated only for systems when the two state model can be applied (eqn (3)). The number of included snapshots depends critically on the parameter \( \delta \); for \( \delta = 0.01, 0.03, 0.05 \) and 0.10, \( N = 2653, 5951, 8838 \) and 13819. The \( V_{\text{rms}} \) value, however, remains almost unchanged, increasing from 0.027 to 0.031 eV. The parameter \( \delta = 0.05 \) was applied for all types of dimers.

As seen from Fig. 4, \( V^2 \) shows an oscillatory behavior and a large variance. There are many conformations, where \( V^2 \) is an order of magnitude greater than \( \langle V^2 \rangle \). The large variation of the coupling is caused by changes both in the internal geometries of the bases and their mutual position. Moreover, the coupling is very responsive to different types of motion (Fig. 3). Because of that, strong EET coupling can be found in quite different structures and it seems difficult to identify a
small region in the conformational space, where the system has large coupling values. The average value of $V^2$ of $8.1 \times 10^{-4} \text{ eV}^2$ corresponds to $V_{\text{rms}} = 0.029 \text{ eV}$. Overall, $V_{\text{DD}}$, eqn (4), is significantly stronger than $V$, eqn (1), its root mean square value of 0.0547, is as twice as large as $V_{\text{rms}}$. Interestingly, the fluctuation of $V_{\text{DD}}$ is remarkably smaller than that of $V$ (Fig. 4). Relatively small effects of thermal fluctuations on $V_{\text{DD}}$ were found also in previous studies.\textsuperscript{10,14} The DD scheme is based on the assumption that the transition dipole moments of donor and acceptor has a fixed length, which is independent of the structure of the complex; the direction of the dipoles is determined by the orientation of the donor and acceptor sites. This approximation works well when the short-range interaction between donor and acceptor is negligible, i.e. at relatively long distances between chromophores. In a DNA \pi stack, the distance between nucleobases is short, $\sim 3.5 \text{ A}$. and the covalent interaction between subunits affects their electronic properties. Because orbital overlap between nucleobases depends strongly on the conformation, structural fluctuations may considerably influence excited state properties, including the transition density.\textsuperscript{10} This means that the matrix element $s_{mn}$ in eqn (1), is very sensitive to the stack geometry. In terms of the $V_{\text{DD}}$ model, the transition moments of nucleobases become sensitive to structural fluctuations of the \pi stack. These effects are however neglected.

The calculated effective couplings are listed in Table 1. The $V_{\text{DD}}$ values for the intra-strand interactions are by a factor of 2 larger than $V$, while rather good agreement is found for the inter-strand couplings. For the sake of convenience, below we consider only FED couplings. The intra-strand matrix elements are in the range of 0.03–0.06 \text{ eV}. The coupling T–T is found to be the strongest one, 0.058 \text{ eV}; $V(A\text{–}A)$ is smaller by a factor of 2. Quite different values are found for A–T and T–A couplings, 0.046 and 0.036 \text{ eV}. As expected, the inter-strand couplings are weaker than the corresponding intra-strand values. The $V_{\text{rms}}$ values for A/A and A\text{"A} are two times smaller than $V(A\text{–}A)$, the T/T and T\text{"T} couplings are by a factor of 3 smaller than $V(T\text{–}T)$.

Table 1 Root mean square couplings for singlet excitation energy transfer in DNA \pi stacks. The total coupling $V$ and dipolar coupling $V_{\text{DD}}$ are calculated using eqn (1) and (4), respectively

<table>
<thead>
<tr>
<th>Stack\textsuperscript{a}</th>
<th>Type</th>
<th>$V$</th>
<th>$V_{\text{DD}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intra-strand coupling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A\text{–}A\text{B}</td>
<td>A–A</td>
<td>0.0285</td>
<td>0.0547</td>
</tr>
<tr>
<td>T\text{–}T\text{A}</td>
<td>T–T</td>
<td>0.0582</td>
<td>0.0942</td>
</tr>
<tr>
<td>A\text{–}T\text{B}</td>
<td>A–T</td>
<td>0.0463</td>
<td>0.0715</td>
</tr>
<tr>
<td>T\text{–}A\text{B}</td>
<td>T–A</td>
<td>0.0358</td>
<td>0.0653</td>
</tr>
<tr>
<td>Inter-strand coupling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A\text{–}A\text{B}</td>
<td>A/A</td>
<td>0.0113</td>
<td>0.0115</td>
</tr>
<tr>
<td>T\text{–}A\text{B}</td>
<td>A/A</td>
<td>0.0147</td>
<td>0.0228</td>
</tr>
<tr>
<td>T\text{–}T\text{B}</td>
<td>T/T</td>
<td>0.0167</td>
<td>0.0173</td>
</tr>
<tr>
<td>T\text{–}T\text{B}</td>
<td>T/T</td>
<td>0.0196</td>
<td>0.0256</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Structures of A\text{–}A\text{B} and T\text{–}T\text{A} were extracted from the MD trajectory of 5\text{‘}G A\text{13} G\text{3}; all other structures from MD of 5\text{‘}G T (AT)\text{6} G\text{3}.\textsuperscript{28}
The obtained data can be used to estimate probabilities for singlet \( \pi-\pi^* \) excitation energy transfer through \( \pi \) stacks. Assuming that the spectral overlap in eqn (6) for stacked adenines is similar to that for thymines, we suggest that EET in homogeneous poly(dA)-poly(dT) sequences should presumably occur through the dT strand because EET within dA is less probable by a factor of 4 \((V^2 \text{ for } T-T \text{ and } A-A = 3.4 \times 10^{-3} \text{ and } 0.8 \times 10^{-3} \text{ eV}^2)\). In alternating oligomers (dAdT)\(_n\), one may expect that EET will proceed through thymine bases (inter-strand zigzag pathway). As the absorption and fluorescent spectra of T and A are not very different, their spectral overlap should be large enough to make feasible the intra-strand EET through –A–T–A–T– strands.

Couplings of \( n-\pi^* \) excited states are found to be considerably smaller than the of \( \pi-\pi^* \) states interaction.\(^{15,16}\) Our calculations of \( n-\pi^* \) excited states in the TT stack give \( V_{\text{ms}} = 0.44 \times 10^{-3} \text{ eV} \). Thus, the estimated probability for \( n-\pi^* \) exciton transfer is four orders of magnitude smaller than for \( \pi-\pi^* \) EET.

**Localization of excited states**

As suggested in previous studies, \( \pi-\pi^* \) excited states in DNA should be delocalized.\(^{10,14,17}\) Our calculations show that the exciton distribution in \( \pi \) stacks is sensitive to conformational changes. Fig. 5 demonstrates how the lowest \( \pi-\pi^* \) excited state is delocalized over adenine dimers depending on the stack structure. Indexes \( L_1 \) and \( L_2 \) are displayed for 110 consecutive snapshots extracted from the MD trajectory of 5'-G A\(_{13}\) G-3'). As seen, the localization indexes change by passing from one structure to another, however, in all structures the excited state remains essentially delocalized. The statistical evaluation for the A\(_7\)A\(_8\) stack provides the following data. The mean value \( \langle L_1-L_2 \rangle = 0.011 \) suggests that, nucleobases A\(_7\) and A\(_8\) are almost equivalent, \( \langle L_1 \rangle \approx \langle L_2 \rangle \approx 0.5 \). The excited state delocalization may be described by the mean absolute value \( \langle |L_1-L_2| \rangle \). If the state is completely delocalized in all configurations then \( \langle |L_1-L_2| \rangle = 0 \); in the case that the excited state is strongly localized, \( \langle |L_1-L_2| \rangle = 1 \). For A\(_7\)A\(_8\), we found \( \langle |L_1-L_2| \rangle = 0.40 \). It suggests that ~70% of the excited state is localized on one site and 30% on the other (see Fig. 5). For the dimer T\(_{23}\)T\(_{24}\), we obtained \( \langle L_1-L_2 \rangle = -0.13 \) and \( \langle |L_1-L_2| \rangle = 0.41 \). These data indicate that the excited state density distribution in the dimer is similar to that in A\(_7\)A\(_8\), while T\(_{24}\) and T\(_{23}\) are slightly different. In contrast, the excited states in inter-strand dimers are found to be more localized. In the A/A stack, \( \langle L_1-L_2 \rangle = -0.02 \), which means that in the average, A\(_7\) and A\(_8\) are equivalent; \( \langle |L_1-L_2| \rangle = 0.79 \) suggests that ~90% of the exciton is localized on one site and 10% on the other (see Fig. 5). A comparable situation is also in A/A, T/T and T/T stacks. According to our calculations, the \( n-\pi^* \) states in T\(_{23}\)T\(_{24}\) are essentially confined to single bases \( \langle |L_1-L_2| \rangle = 0.89 \) corresponds to the delocalization degree of ~5%).

Crespo-Hernandez et al. found that the transient absorption signals decay for alternating (AT)\(_9\)-(AT)\(_9\) duplexes (lifet ime 50 ps) is faster than for A\(_{18}\)T\(_{18}\) (lifetime 150 ps).\(^{4}\) Our data on the delocalization of the \( \pi-\pi^* \) excited states are in agreement with those experimental findings.

It should be noted that calculated electronic coupling can be affected by a heterogeneous environment. Recently, a combined QM/MM method has been introduced to study EET in condensed phases.\(^{33}\) Its application to the perylene diimide dimer showed that the EET coupling increases by ~10–15% when polar surroundings are accounted for.\(^{33}\) Such corrections may also be expected for EET couplings listed in Table 1.

**Conclusions**

Using the FED scheme,\(^{21}\) we calculated intra-strand and inter-strand electronic couplings of singlet \( \pi-\pi^* \) excited states of adenine and thymine nucleobases in homogeneous poly(dA)-poly(dT) and alternating poly(dAdT)\(_n\) stacks and studied the effects of structural fluctuations on the couplings. The FED couplings, including both Coulomb and short-range interactions, were compared with estimates derived from the dipole–dipole scheme. 15,000 structures for each of 8 different dimers were considered.
We have found that EET couplings in DNA are significantly more sensitive to conformational changes in the π stack than are predicted by the dipole–dipole model. The effective couplings of π–π* excited states in stacked thymines are nearly twice as large as in A stacks. Because of that, singlet excitation energy transfer in poly(dA)–poly(dT) should dominantly occur through thymine bases. The π–π* excitations are found to be quite delocalized in homogeneous strands, while they are more localized in alternating sequences. In contrast, n–π* excitons are strongly localized on a single nucleobase and have a very small probability of migrating. Localization of π–π* excited states is sensitive to the stack structure and exhibits oscillating behavior along the MD trajectory.

Acknowledgements

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28. http://humphry.chem.wesleyan.edu:8080/MDDNA The data were downloaded in June 2007. See also http://www.scfbio-itd.res.in/research/dnasimulation.htm for some information about the ABC project.