Ab Initio Time-Domain Study of the Triplet State in a Semiconducting Carbon Nanotube: Intersystem Crossing, Phosphorescence Time, and Line Width

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Supporting Information

ABSTRACT: Motivated by recent experiments (J. Am. Chem. Soc. 2011, 133, 17156), we used nonadiabatic (NA) molecular dynamics implemented within ab initio time-domain density functional theory to investigate the evolution of the excited electronic singlet and triplet states in the (6,4) carbon nanotube (CNT). The simulation simultaneously included the NA electron–phonon interaction and the spin–orbit (SO) interaction and focused on the intersystem crossing (ISC) from the first excited singlet state (S1) to the triplet state (T1) and subsequent relaxation to the ground electronic state (S0). For the first time, the state-of-the-art methodology (Phys. Rev. Lett. 2005, 95, 163001; Phys. Rev. Lett. 2008, 100, 197402) has been advanced to include triplet states. The S1–T1 ISC was calculated to occur within tens of picoseconds, in agreement with the experimental data. This time scale is on the same order as the S1–S0 nonradiative decay time obtained previously for the (6,4) CNT. The homogeneous phosphorescence line width, which can be measured in single-molecule experiments, was predicted to be on the order of 10 meV at room temperature. This value is similar to the fluorescence line widths of CNTs suspended in air. The NA electron–phonon and SO couplings were found to be on the order of 1 meV; however, the former fluctuates much more than the latter, causing the ISC rate to be limited by the SO interaction rather than NA interaction. The electronic energy lost nonradiatively during ISC is deposited into high-frequency optical phonons of the CNT arising from C–C stretching motions. The calculations indicate that ISC can contribute to the radiative energy losses and low photoluminescence quantum yields observed in semiconducting CNTs.

Theoretical estimates of the radiative lifetimes are on the nanosecond time scale, while the nonradiative relaxation has been evaluated to occur within hundreds of picoseconds in perfect CNTs and tens of picoseconds in CNTs with defects.6,7 The observed low quantum yields of photoluminescence (PL) present a great practical difficulty in numerous CNT applications.17–21 Experimental studies have concluded that nonradiative decay mechanisms dominate the relaxation of both bound excitons and free charge carriers in CNTs.5,9–11 The excitonic splitting into bright and dark singlet states, as well as the presence of triplets, complicates the issue further.5,22,23 Static electronic structure calculations using high-level ab initio density functional theory (DFT) and semiempirical Hamiltonians have provided estimated singlet and triplet energies and splittings. Time-domain theoretical studies of the relaxation pathways constitute the next step in elucidating and consolidating the conflicting experimental evidence. Recently, the dynamics of intersystem crossing (ISC) into and out of the lowest-energy triplet excited state of a single-walled CNT has been characterized experimentally in the time domain, motivating the current theoretical work.

Here we present the first ab initio time-domain simulation of ISC between singlet and triplet electronic states in a CNT. We considered optical line widths and nonradiative relaxation times for the transitions from the lowest-energy excited singlet state (S1) to the lowest triplet state (T1) and from T1 to the ground state (S0) (Figure 1). The study was made possible by the

Figure 1. Jablonski diagram showing the nonradiative relaxation processes under investigation. The singlet excited state (S1) decays to the ground state (S0) by NA coupling. Alternatively, S1 undergoes ISC to the lowest triplet state (T1) by a combination of NA and SO couplings, and then another ISC takes T1 to S0.

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implementation\textsuperscript{7,8,28} of the fewest-switches surface hopping (FSSH) technique for simulating coupled electron–phonon dynamics\textsuperscript{29} within time-dependent Kohn–Sham (TDKS) theory.\textsuperscript{10} The current work represents a major advance of the earlier theory because it includes spin–orbit (SO) coupling. Recent theoretical calculations and experimental investigations have shown\textsuperscript{5,31,32} that SO coupling is strong in curved carbon nanostructures and that it can promote transfer of electronic excitation between different spin manifolds. Our simulations predict that \( S_1 \) decays to \( T_1 \) within tens of picoseconds, in agreement with the experimental result.\textsuperscript{5} The magnitudes of the nonadiabatic (NA) electron–phonon and SO electronic couplings are similar; however, the NA coupling fluctuates more than the SO coupling. The fluctuation of the NA coupling is general to both the singlet and triplet manifolds. Nonradiative relaxation within the singlet manifold is accelerated when the NA coupling peaks.\textsuperscript{7} Even though the ISC rate depends simultaneously on the magnitudes of the NA electron–phonon interaction and the SO interaction, our study indicates that it is determined primarily by the latter. The nonperturbative simulation showed that the ISC rate is proportional to the square of the SO coupling, validating a perturbation theory assessment such as the use of Fermi's golden rule. The electronic energy lost during ISC is deposited into high-frequency optical phonons produced by C–C stretching motions. The calculated homogeneous optical line widths of the singlet–triplet transitions are on the order of 10 meV at room temperature. This value is similar to the measured\textsuperscript{14,33} and calculated\textsuperscript{7} line widths of luminescence occurring within the singlet manifold. The predicted participation of the C–C stretching modes in ISC and the phosphorescence line width value can be measured spectroscopically in the future. The reported results indicate that ISC plays an important part in the nonradiative energy losses and low PL yields seen in the experiments.\textsuperscript{14–16}

FSSH\textsuperscript{29} is a technique for evolving a quantum-mechanical (electronic) subsystem coupled to classical-mechanical atomic motion. Ruministic of quantum master equations, it defines instantaneous state-to-state transition rates that depend on the atomic evolution. In contrast to many other quantum–classical schemes, FSSH to a good approximation obeys detailed balance between transitions up and down in energy and leads to thermal equilibrium in the long-time limit. Therefore, it can be used to study relaxation processes. The implementation of FSSH within TDKS electronic structure theory\textsuperscript{50} is described in ref 28, and ref 8 reports the application of FSSH-TDKS to the ultrafast relaxation of high-energy excitations in CNTs. The implementation of a semiclassical correction for decoherence/dephasing within FSSH-TDKS for the study of PL quenching in CNTs by nonradiative relaxation from \( S_1 \) to \( S_0 \) is described in ref 7.

The present study focused on ISC that occurs by a combination of SO coupling, which allows transitions between singlets and triplets, and NA coupling, which is responsible for transfer of the electronic energy released during a singlet–triplet transition to phonons. For this purpose, FSSH-TDKS was advanced to incorporate SO interactions\textsuperscript{54} as detailed in the Supporting Information (SI). The SO coupling induces transitions between different spin states. The \( S_0 \) and \( T_1 \) energies were computed with DFT as the ground-state energies for the singlet and triplet spin symmetries. The NA coupling was computed in the KS basis.\textsuperscript{7,8,28} The SO coupling was obtained by performing the DFT calculations with and without the SO coupling interactions at every time step along the trajectory; the SO coupling was evaluated as half the difference of the singlet–triplet splittings obtained from the two calculations. Additional calculations were performed using the constant SO coupling values reported in the literature.\textsuperscript{51}

The ISC study focused on the semiconducting (6,4) CNT, which has a significantly smaller unit cell than the (6,5) CNT studied experimentally.\textsuperscript{5} A variety of \( S_1–T_1 \) energy splittings have been reported in the literature\textsuperscript{25–27} and we tested a range of possibilities. In our dynamics calculations, \( T_1 \) was 1 eV above \( S_0 \). The average SO coupling between \( T_1 \) and \( S_0 \) in our trajectory calculations was 1.6 meV. This is slightly smaller than the value of 2.4 meV produced in another theoretical study.\textsuperscript{51} To test the importance of the magnitude of the SO coupling, we performed the calculations using each of these values. Since the SO coupling is predicted to be inversely proportional to the CNT diameter,\textsuperscript{31,52} we also used the value of 1.0 meV to evaluate the ISC in larger-diameter CNTs.

The phonon-induced pure-dephasing/decoherence times for the \( S_1–T_1 \) and \( T_1–S_0 \) transitions were evaluated by computing the dephasing function \( D(\tau) \), given by\textsuperscript{55}

\[
D(\tau) = \exp\left[ -\frac{i}{\hbar} (\Delta E) \tau \right] \exp\left\{ -\frac{i}{\hbar} \int_0^\tau \Delta E(\tau) \, d\tau \right\} 
\]

where \( \Delta E \) is the energy difference between the states of interest and the angle brackets denote thermal averaging. The dephasing functions are shown in Figure 2. The data were fit to an exponential, which was multiplied by a cosine in the \( T_1–S_0 \) case to capture the oscillatory part (see the SI). The pure-dephasing time calculated for the \( S_1–T_1 \) transition was \( \tau_{ff} = 66 \) fs, while the \( T_1–S_0 \) dephasing was faster (\( \tau_{ff} = 49 \) fs). The same approach produced a pure-dephasing time of 60 fs for the \( S_1–S_0 \) transition,\textsuperscript{36} in agreement with the experimental data.\textsuperscript{36} Dephasing occurs because of fluctuations of the electronic energy levels induced by vibrational motions. The SO coupling has little effect on the dephasing because it is small and nearly constant (see Figure 3a). The oscillation seen in the \( T_1–S_0 \) dephasing function shown in Figure 2 is caused by the optical G mode arising from C–C stretching motions. Radial breathing modes (RBMs) are responsible for the small-amplitude oscillations at longer times in Figure 2. RBMs contribute much more significantly to dephasing in CNTs with defects because defect sites are strongly coupled to RBMs.\textsuperscript{35}

The pure-dephasing times are significantly shorter than the lifetimes determined below. Therefore, in the absence of
inhomogeneous broadening, which can be eliminated by photon-echo or single-molecule experiments, the width of the corresponding optical line (Γ) may be expressed as

$$\Gamma = \frac{1}{\tau_2} = \frac{1}{2\tau_1} + \frac{1}{\tau_3} \approx \frac{1}{2\tau_1}$$

(2)

where τ₂ is the overall dephasing time, τ₃ is the pure-dephasing time, and τ₁ is the lifetime (τ₁ >> τ₂). The homogeneous width of the T₁−S₀ line is 13 meV (Table 1), which is slightly larger than the S₁−S₀ width of 11 meV. The phosphorescence line width can be detected in optical experiments. If needed, the phosphorescence intensity can be increased, for instance, by atomic hydrogen absorption and chemical functionalization, following the strategy used to brighten the lowest-energy singlet exciton. [The calculated singlet-state optical absorption spectrum of the (6,4) CNT is shown in the SI].

Figure 3a shows the evolution of the NA and SO couplings over a representative 100 fs period. Their magnitudes are similar, but the SO coupling is much less sensitive to the atomic motion than the NA coupling. The fluctuation of the NA coupling with time is a general effect. The peaks in the NA coupling accelerate the nonradiative transition between the S₁ and S₀ states. Similar to the case of the S₁−S₀ nonradiative relaxation, the energy lost during ISC is accommodated primarily by the high-frequency C−C stretching motions.

Figure 3b,c presents the simulation results for the S₁−T₁ and T₁−S₀ ISC processes, respectively, obtained using different SO coupling values, including the one calculated in the present work (~1.6 meV; Figure 3a), the literature value (2.4 meV), and the order of magnitude (1.0 meV). If it is assumed that the decay is exponential, as in the experiments, the initial portion of the population versus time curve obtained in the simulation can be fit to P(t) = 1 − exp(−t/τISC) producing the ISC times (τISC) reported in Table 1. τISC is inversely proportional to the square of the SO coupling, as predicted by perturbation theory (e.g., Fermi’s golden rule). Thus, our nonperturbative simulation validates a perturbative treatment.

The S₁−T₁ transition occurs in tens to hundreds of picoseconds, depending on the strength of the SO coupling and the S₁−T₁ energy gap (Table 1). A larger energy gap, in agreement with ref 26, results in a slower transition. Reducing the gap according to the estimates from refs 25 and 27 speeds up the ISC. These time scales agree with the recent experimental data. The S₁−S₀ transfer time evaluated previously for the (6,4) CNT is 150 ps, indicating that the S₁−T₁ ISC can compete with direct S₁−S₀ nonradiative relaxation. Theoretical studies of CNTs that included mixing between singlet and triplet manifolds predicted radiative lifetimes of 30−40 ns. Therefore, the long-lived T₁ state should emit light, enhancing the luminescence quantum yield.

The nonradiative decay of T₁ to S₀ was found by our calculations to occur within hundreds of picoseconds, depending on the SO coupling strength and the T₁−S₀ energy gap (Table 1). At low SO coupling, the T₁ lifetime exceeded 1 ns. Shifting the T₁−S₀ energy difference from 1.05 to 1.30 eV increased the triplet lifetime by ~20%. The experimental value for the T₁ excited state lifetime of the (6,5) CNT extends into microseconds. This discrepancy could be resolved by reducing the T₁−S₀ SO coupling strength by 2 orders of magnitude. It should be noted that the SO coupling decreases with increasing CNT diameter, nearly vanishing for graphene. At the same time, reducing the SO coupling for the S₁−T₁ transition strongly increases the S₁−T₁ transition time. One could potentially reconcile the theoretical and experimental results for the S₁−T₁ and T₁−S₀ transitions simultaneously by both reducing the SO coupling and either decreasing the S₁−T₁ energy gap or introducing higher-lying triplet states that are close in energy to S₁.

Our results suggest that phonon-assisted ISC can be an important nonradiative decay channel in CNTs. SO coupling in traditional carbon systems is weak. For instance, it has been predicted to be vanishingly small in graphene. In contrast, efficient ISC mechanisms lead to a near-unity transfer of excited singlet states to long-lived triplet states in C₆₀ with an experimental rate constant of 5 × 10⁹ s⁻¹. Since theoretical calculations have predicted that the SO coupling in small-diameter CNTs is as great as or greater than that in fullerenes, it is not surprising that conversion from singlets to triplets may be efficient in CNTs. Our study considered only the transitions between the lowest singlet states and the lowest triplet state, excluding the full triplet state manifold. The inclusion of additional triplet states should increase the overall ISC rate.

### Table 1. Singlet−Triplet Pure-Dephasing Times (τff), Fluorescence Line Widths (Γ), and ISC Times (τISC) for the (6,4) CNT

<table>
<thead>
<tr>
<th>transition</th>
<th>ΔE (eV)</th>
<th>τff (fs)</th>
<th>Γ (meV)</th>
<th>τISC (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁−T₁</td>
<td>0.35</td>
<td>66</td>
<td>9</td>
<td>362/139/62.2</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td></td>
<td>97.3/39.7/16.7</td>
<td></td>
</tr>
<tr>
<td>T₁−S₀</td>
<td>1.05</td>
<td>49</td>
<td>13</td>
<td>1082/430/189</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td></td>
<td>1392/548/238</td>
<td></td>
</tr>
</tbody>
</table>

*At SO couplings of 1.0/1.6/2.4 meV.

![Image](https://example.com/image.png)

**Figure 3.** (a) Comparison of the magnitudes of the NA and SO couplings for the T₁−S₀ transition over a 100 fs trajectory window. (b, c) Evolution of the final state populations for the S₁−T₁ and T₁−S₀ transitions, respectively, corresponding to the 0.35 and 1.05 eV energy gaps (see Table 1).
Embedding the CNT in a matrix and providing other interactions with the environment would provide additional phonon modes to induce NA coupling and facilitate the relaxation. A matrix can distort the CNT, increasing its curvature and thus the SO coupling. Similarly, defects increase the local curvature and therefore the SO coupling, and they also create stronger NA coupling because of the more localized nature of excitations and phonon modes associated with defects. Thus, a host material and defects should accelerate ISC.

In conclusion, we have performed the first ab initio time-domain simulation of ISC in a CNT and calculated the phosphorescence line width. The calculated $S_1 \rightarrow T_1$ ISC time agrees with the recent experimental data, and the line width can be measured in future experiments and compared with our prediction. We have identified the phonon modes that accommodate the electronic energy lost during ISC and shown that the electron–phonon and SO interactions have the same order of magnitude. Our results suggest that the $S_1 \rightarrow T_1$ ISC can provide an efficient nonradiative relaxation pathway in small-diameter CNTs. The rate of ISC can diminish in larger-diameter nanotubes as a result of the decrease in the SO coupling with increasing diameter and the dependence of the ISC rate on the square of the SO coupling. The $S_1 \rightarrow T_1$ ISC should definitely be considered when investigating the origin of the small yields of luminescence observed experimentally, even for larger-diameter nanotubes.

ASSOCIATED CONTENT

Supporting Information

Further calculation details, including a description of incorporating SO interactions into the FSSH-TDKS theory, fitting of the pure-dephasing functions shown in Figure 2, and an optical absorption spectrum of the (6,4) CNT at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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