Time-Domain Ab Initio Simulation of Energy Transfer in Double-Walled Carbon Nanotubes

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1. INTRODUCTION

Multiwalled carbon nanotubes (MWNTs) are comprised of multiple coaxial nanotube cylinders of various chiralities nested within each other, where the constituent individual tubes can exhibit either semiconducting or metallic behavior. The interlayer distance in such tubes is comparable to the distance between the sheets in graphene, and hence the layers are described with van der Waals forces. The ability to combine nanotubes possessing different electronic and optical properties in one system opens a broad spectrum of potential applications, including electronics, photonics, and sensors.1−7

Numerous experiments have been carried out to investigate the novel properties of the MWNTs and, particularly, DWNTs. Special interest is drawn to the exciton energy transfer between carbon nanotubes, as the size of the quasi-one-dimensional excitons in carbon nanotubes (CNTs) is comparable to the donor−acceptor distance in such systems.8−11 However, only some of the energy transfer processes can be observed experimentally, thus hindering detailed description of the mechanisms involved. Time-dependent theoretical investigation of nonequilibrium dynamics provides a reliable way of taking into account the competing pathways in large nanoscale systems and unveiling the actual exciton relaxation mechanisms.

Ultrafast exciton energy transfer in DWNTs was extensively studied by Koyama and co-workers in ref 13 by means of femtosecond time-resolved luminescence measurements. They have shown that after the initial photoexcitation above the E11 level of the inner tubes a fast (∼170 fs) exciton energy transfer toward the E22 level of the outer tubes takes place, followed by an intraband relaxation to the E11 level. The suggested mechanism of the energy transfer did not involve any dark or charge transfer states, even though many such states are present in the systems under investigation.

In our paper, we aim to elucidate energy transfer pathways in semiconducting DWNTs through an ab initio analysis of their electronic structure, followed by a simulation of nonadiabatic (NA) molecular dynamics (MD) after the initial excitation to the E11 level of the inner tubes. Application of time-domain (TD) density functional theory (DFT) to model the photoinduced energy transfer allows for description of the ultrafast dynamics, by taking into consideration optical transitions, as well as dark and charge transfer states, which cannot be observed experimentally.

We compare energy transfer dynamics occurring in three different sets of coaxial semiconducting carbon nanotube pairs, in order to determine the influence of the chirality and relative energy level distribution on the transfer rates. First, we provide a detailed description of the systems and analyze their electronic structure and corresponding energy transfer pathways. The full and partial densities of states (DOS) are juxtaposed with the charge density distribution of the relevant orbitals. The DOS are examined at different temperatures and
simulation times along the MD trajectory, to fully cover the tube’s behavior and its impact on the following photoexcitation dynamics. We then discuss the absolute and relative positions of the electronic energy levels, as well as the phonon modes that couple the electronic states and accommodate the electronic energy lost during the transfer and relaxation processes. Lastly, we present the results of the real-time nonadiabatic molecular dynamics simulation and present the comprehensive mechanism of photoinduced dynamics occurring in semiconducting DWNTs. The influence of van der Waals interactions on the geometry and the resulting transfer dynamics are also discussed herein.

2. THEORY

The simulations involve a combination of NAMD with TDDFT, used for the description of vibrational and electronic evolutions, respectively. The methodology has been implemented within time-independent DFT codes,14–18 which are capable of adiabatic MD. This strategy moves the majority of the computational efforts into these well-optimized codes, making the calculation very efficient.

2.1. Simulation Methodology. TDDFT is combined with the fewest switches surface hopping (FSSH) technique,19 which satisfies the detailed balance condition to a good approximation,20 thus allowing for calculation of nonradiative relaxation dynamics.19

The electron–nuclear dynamics are described within the TD Kohn–Sham (KS) framework,21–23 which expresses the electron density of the system, \( \rho(t) \), as a sum of the densities of the single-electron KS orbitals, \( \psi_n(r,t) \), occupied by \( N_e \) electrons

\[
\rho(r, t) = \sum_{n=1}^{N_e} |\psi_n(r, t)|^2
\]

The KS energy, \( E(\psi_n) \), includes the electron kinetic energy, the electron–nuclear attraction, the electron–electron repulsion, and the exchange-correlation energy functional, respectively

\[
E(\psi_n) = \sum_{n=1}^{N_e} \langle \psi_n | K | \psi_n \rangle + \sum_{n=1}^{N_e} \langle \psi_n | V | \psi_n \rangle + \frac{e^2}{2} \int \frac{\rho(r', t) \rho(r, t)}{|r - r'|} d^3r' + E_{XC}(\rho)
\]

Application of the TD variational principle to the KS energy determines the evolution of the electron density via a set of single-electron KS orbitals

\[
i \hbar \frac{\partial}{\partial t} \psi_n(r, t) = H(r, R, t) \psi_n(r, t); \quad n = 1, 2, \ldots, N_e
\]

These equations are coupled through the dependence of the Hamiltonian, \( H(r,R,t) \), on the total electron density. The explicit time dependence of the Hamiltonian stems from the external potential, created by the moving atoms.

The TD one-electron wave functions \( \phi_k^i(r,R_i(t)) \) are expressed in adiabatic KS basis, which is calculated from the current atomic positions \( R_i \), obtained from the adiabatic MD calculations

\[
\psi_n^i(r, t) = \sum_k c_{nk}(t) \phi_k^i(r, R_i(t))
\]

The evolution of the adiabatic coefficients is obtained by inserting eq 4 into eq 3

\[
i \hbar \frac{\partial}{\partial t} c_{nk}(t) = \sum_k c_{nk}(t) (\epsilon_k^i \delta_{jk} + d_{jk})
\]

where \( \epsilon_k^i \) is the energy of the adiabatic state \( k \), and \( d_{jk} \) is the NA coupling between KS orbitals \( j \) and \( k \). The NA coupling is generated through the atomic motion and is calculated numerically as the overlap between the orbitals \( j \) and \( k \) at sequential time steps

\[
d_{jk} = -i\hbar \langle \phi_j | \nabla_{R_k} | \phi_k \rangle = -i\hbar \left( \frac{\partial}{\partial R_k} \right) \phi_k
\]

In the FSSH approach, the expansion coefficients \( c_{nk} \) and NA coupling vector are used to define the transition probabilities between the adiabatic states19

\[
d_{jk} = -2Re(\frac{A_{jk}^a d_{jk}}{A_{jk}^a}) dt \quad A_{jk}^a = c_{j}^a c_{k}^a
\]

The transitions between the states occur in form of “hops” and are computed on the fly for the current ionic configuration. The classical-path approximation, justified for nanoscale materials and implemented within FSSH,24 allows us to use the ground-state trajectory to simulate the photoinduced dynamics at a great computational saving.

Further details of the TDDFT–NAMD approach can be found in refs 21–25. The validity of the method is discussed in ref 26. The exciton basis describes the joint electrons and holes dynamics, as implemented in the PYXAID package.24

2.2. Simulation Details. Each simulation cell shown in Figure 1 consists of two concentric semiconducting carbon nanotubes. Due to the application of the periodic boundary conditions for our calculations, the tubes in each pair are chosen to have unit cells of approximately the same length.

The calculations are carried out with VASP package.14,15 The nonlocal exchange-correlation energy is described with the PBE density functional.27 The projector-augmented wave (PAW) potentials15 are used to treat interactions between the atomic cores and valence electrons. After initial optimization at 0 K, the simulation cells are heated to 300 K, using repeated velocity rescaling, followed by a 2000 fs production run in the microcanonical ensemble, with a 1 fs nuclear time step. The obtained atomic trajectories are used to sample geometry and electronic initial conditions in the NAMD calculations. Since the thermal motions are dominant, the ground-state trajectories provide a good approximation for description of the ion dynamics during the energy transfer events. The nonadiabatic dynamics after the initial excitation to the E_{11} level of the inner tubes is studied for 500 fs in the exciton basis.24

Figure 1. Simulation cells of the DWNT systems optimized at 0 K.
3. RESULTS AND DISCUSSION

In order to obtain an in-depth analysis of the energy transfer dynamics in double-walled carbon nanotubes, three DWCNT systems comprised of pairs of semiconducting carbon nanotubes are investigated: (11,0)@(20,0), (8,4)@(16,8), and (10,0)@(19,0), shown in Figure 1. The (11,0), (8,4), and (10,0) CNTs are referred to as inner tubes of the corresponding pairs. The interlayer distance in these pairs is comparable to that of graphene (0.32–0.42 nm),\(^3\) thus ensuring their significant stability.

3.1. Electronic Structure. The first two systems follow the relative energy level distribution discussed in the experimental work:\(^3\) the first excitation energy, \(E_{11}\), of the inner tube (1.1–1.2 eV) is slightly larger than \(E_{22}\) of the outer tube (1.0–1.2 eV). Such energy alignment should lead to an ultrafast energy transfer from the inner tubes to the outer ones, followed by a quick intratube relaxation from \(E_{22}\) to \(E_{11}\), as shown in Figure 2. This energy band distribution in the tubes discussed in the experiment by Koyama et al.\(^3\) leads the authors to focus on the optically bright states when discussing the observed energy transfer, omitting dark or charge transfer states. The influence of the tube chirality on the calculated transfer rates is highlighted through a comparison of a fully zigzag system, (11,0)@(20,0), to a system comprised of chiral tubes, (8,4) @(16,8).

The third system, (10,0)@(19,0), is chosen such that the \(E_{11}\) energy of the inner tube lies between the \(E_{11}\) and \(E_{22}\) energies of the outer tube. This system is used to study energy transfer from the \(E_{11}\) level of the inner tube in a DWCNT system, when the transfer to the \(E_{22}\) level of the outer tube is unlikely due to a high energy barrier.

Optical properties of CNTs are often discussed in terms of electronic transitions within their one-dimensional DOS. Optical transitions occur between corresponding sharp peaks (Van Hove singularities, vHs) of conduction, \(\nu_c\) and valence, \(\nu_v\) bands, which are characteristic for one-dimensional systems. The energy gaps between \(\nu_{1j}\) and \(\nu_{1j}\), \(\nu_{2j}\) and \(\nu_{2j}\), etc. are denoted as \(E_{11}, E_{22}\), etc., respectively. The symmetric transitions have strong optical activity. Crossover transitions, \(E_{ij}\), between \(\nu_{1i}\) and \(\nu_{1j}\) for different \(i\) and \(j\) are dipole-forbidden.

The electronic structure of DWCNTs strongly depends on the curvature of the comprising tubes and the distance between them.\(^3\) It was shown that the increase in the interwall coupling, which arises due to overlap of the \(\pi\)-electron subsystems, leads to the decrease in the energy gap in semiconducting pairs of DWNTs.\(^3\) The strong intertube interaction can also affect the overall field-effect characteristics of the tubes via screening, with the tubes exhibiting neither pure semiconducting nor pure metallic behavior.\(^3\)

A system of interacting tubes is described with total DOS,\(^4\) which can be decomposed into partial DOS (pDOS) that are assigned to each individual tube. In the case of strongly coupled systems, intertube interaction should lead to significant changes in pDOS profiles compared to the DOS of the isolated tubes. Along with optical and crossover transitions, energy transfer in a system of several tubes can involve charge transfer (CT) events. Spectroscopic techniques measure transitions between optically active states, \(E_{\text{th}}\), in which an exciton is localized over a pair of vHs with the same indices (\(e.g., c_1 \rightarrow v_1, c_2 \rightarrow v_2\), etc.) belonging to the same tube. Crossover transitions, \(E_{ij}\), involve vHs with different indices (\(e.g., c_1 \rightarrow v_2, c_2 \rightarrow v_1\), etc.), but the exciton still corresponds to only one tube. Charge transfer in a system of two tubes leads to excitons that delocalized between the tubes and involve any combination of the indices of the conduction band singularities of one tube and the valence band singularities of the other tube (for example, \(c_1 \rightarrow v_{ij}', c_2 \rightarrow v_{ij}'\), etc., where the superscript refers to the first or the second tube).

Our calculations show that inclusion of the intertube interaction at absolute zero does not lead to significant changes in the DOS profile of the (11,0)@(20,0) DWNT, and the partial densities of states of the two interacting tubes closely resemble a superposition of total DOSs of the two equilibrated noninteracting tubes. At this temperature, a DWNT is comprised of perfectly round coaxial cylinders, as shown in Figure 1.

3.2. Thermal Fluctuations. At the higher temperature, 300 K (Figure 3), atomic motions of carbon atoms affect the
Figure 4. Charge densities in the (11,0)@(20,0) DWNT at zero temperature (top row) and along the MD trajectory at room temperature (middle and bottom rows). Here, $\nu^\prime$, $\nu^\prime\prime$, $\nu^\prime\prime\prime$ refer to the first, second, and third Van Hove singularities in the conduction (valence) band of the combined system, respectively.

electronic structure of the tubes. The DWNTs exhibit both radial expansion/contraction as well as in-plane vibrations of the carbon atoms. These motions are characteristic to CNTs and are often analyzed using Raman spectra. In the case of DWNTs, the outer tubes are more flexible and undergo larger radial motion than the inner tubes. However, the resulting effect of the net fluctuation of the electronic energy is smaller than that of the inner tubes, due to the averaging over a larger number of atoms comprising the tube.

The mean calculated values of the excitation energies are in a good agreement with the experimental data and thus confirm the validity of the models used here.

The strength of the intratube interaction varies with the fluctuation in the geometries of the tubes, thus allowing multiple realizations of the relative energy alignment. In the ideal case (based on the assumption made in the experiment), the Fermi level should be surrounded by two vHs arising due to the outer tube, immediately followed by the corresponding vHs peaks for the inner tube. However, due to the notable structural variability of the tubes, the magnitudes and relative positions of the energy levels undergo changes strong enough to establish new energy transfer pathways. Figure 3 shows one of the potential scenarios along the MD trajectory, which agrees with the experimentally suggested distribution. Other calculated realizations of DOS include cases, when the first vHs of the inner tube overlaps with either first or second singularities of the outer tube. These situations open channels for crossover and charge transfer transitions, which compete with the outer tube. These situations open channels for crossover transfer dynamics.

Consequently, one should expect only a slight difference in the corresponding one-dimensional DOS as well as in the resulting transfer dynamics.

3.3. van der Waals Interactions. In order to test the influence of van der Waals interactions on the geometry and dynamics of the DWNTs, the DFT-D2 method of Grimme is employed. The simulation shows that inclusion of van der Waals interactions slightly decreases the range of thermal atomic fluctuations at room temperature. However, the difference is insignificant and nearly indistinguishable (Figure 5). This is because the repulsive term in the intertube interaction is more important than the attractive term.

3.4. Phonon Modes. In order to analyze the phonon modes that couple to the electronic transitions involved in the photoexcitation dynamics, we report the Fourier transform (FT) and the autocorrelation function (ACF) of the gap, $\Delta E_{11}$, between the two lowest excitation energies, $E_{11}$, of the (11,0) and (20,0) nanotubes (Figure 6).

CNTs are characterized by two types of vibrational modes, as detected in the Raman spectra. Radial breathing modes, RBMs, have frequencies around 100–350 cm$^{-1}$. The frequency of the G-mode is around 1580 cm$^{-1}$. While RBMs stem from radial expansion/contraction of the atoms, and hence depend on the
tube’s diameter, the G-mode arises from in-plane vibrations of the carbon atoms and hence is found at the same frequency for all the tubes. The defect-induced D-mode and its second overtone, $G'$, are not found on the theoretically obtained FT plots for single wall CNTs, as the model tubes possess perfect structure.

For DWNTs with a weak coupling, Raman spectra closely resemble a combination of the spectra of the individual tubes. The diameter dependence of the RBM leads to a number of low frequency peaks, stemming from both the inner and the outer tubes, as they are characterized by different diameters (Figure 6). Additional low-frequency peaks might be attributed to a special case of RBM, the bundling mode. The high-frequency G-mode does not participate actively in the energy transfer between the inner and outer CNTs, even though it is active in electronic energy relaxation within individual CNTs. The high-frequency local mode has little effect on the relative energies of the photoexcited states in the two CNTs, while RBMs induce energy fluctuations by inducing fluctuations in CNT cylindrical shape and diameter.

As can be seen from Figure 6 (inset), the correlation of the changes in difference between the $E_{11}$ energies of the tubes is rather poor and decreases rapidly. The initial decay occurs within 75 fs, and only a single strong recurrence is seen at about 250 fs. The rapid decay of the autocorrelation function is easily rationalized by participation of a broad range of RBMs in the energy transfer between the inner and outer tubes.

3.5. Nonadiabatic Dynamics. NAMD was carried out taking into account different scenarios of charge density distribution over the orbitals, as well as various initial geometrical configurations. In all the cases, the initial excitation corresponds to the $S_1$ level of the inner tube. The data were then averaged over the ensembles of initial conditions. Figure 7 shows the population of the $S_1$ level of the inner tubes (black line) and combined contributions from $S_1$ and $S_2$ level populations of the outer tubes (red line).

For the (11,0)@(20,0) system (Figure 7a), different initial configurations result in a relatively wide distribution of the possible transfer rates (up to 50 fs deviation from the average), although the overall relaxation profile remains the same. This points to a significant dependence of the dynamics on the initial conditions. The $S_2$ level of the outer tube (20,0) almost does not participate in the transfer, and the energy transfer toward the $S_1$ level defines the dynamics at the <0.5 ps time scale. For the (8,4)@(16,8) DWNT, the rate distribution is much narrower (with deviations of up to 20 fs), and most of the transfer occurs toward the $S_2$ level, rather than the $S_1$ level of the outer tube (Figure 7b).
As can be seen from Figure 7, neither of the shown scenarios depicts complete relaxation dynamics taking place in the systems: almost immediately after the initial excitation, the contributions of the populations within one relaxation path do not add up to unity. This indicates that dark and charge transfer states play a significant role in the relaxation along with optically active $S_{\text{inner}} \Rightarrow S_{\text{outer}}$ transitions.

The simulated intertube transfer is in excellent agreement with the experimental data. For the (11,0)@(20,0) DWNTs the average transfer time is about 220 fs; in the (8,4)@(16,8) pair the transfer takes about 70 fs; in the (10,0)@(19,0) system the inner tube is quenched at approximately 100 fs (Figure 7c). Consequently, the vicinity of the $S_i$ level of the acceptor tube to the $S_j$ level of the donor tube, as in the (11,0)@(20,0), and (8,4)@(16,8) DWNTs, does not guarantee a significant acceleration in the transfer rates of the photogenerated excitons, compared to the systems where this condition is not satisfied, as in the (10,0)@(19,0) carbon nanotube pair (Figure 2).

4. CONCLUSIONS

Photoinduced exciton relaxation dynamics in the three sets of semiconducting DWNTs were studied by means of TDDFT–NAMD. The nonequilibrium dynamics simulations of exciton transfer from inner to outer CNTs reveal strong dependence on the geometrical configuration of the system during the photoexcitation. The investigated DWNTs exhibit distinctive expansion/contraction at room temperature, which is only slightly suppressed by the inclusion of the van der Waals forces. Geometrical distortions alter the relative alignment of energy levels and modulate intertube interactions, thus opening a range of channels for exciton relaxation. For the systems where the $S_j$ level of the acceptor tube lies immediately below the $S_i$ level of the donor tube, the experimental results suggest that the exciton transfer should occur in such order: $S_{\text{donor}} \Rightarrow S_{\text{acceptor}} \Rightarrow S_{\text{acceptor}}$. Due to the limitations of the time-resolved luminescence spectroscopy, the suggested mechanism implies that the impact of dipole-forbidden crossover transitions and charge transfer states is negligible. Such an assumption leads to an incomplete picture. Our calculations show that additional relaxation pathways arise due to optically dark states. The relaxation is facilitated primarily by low-frequency, RBM modes of CNTs since these modes have the strongest effect on the CNT shape and intertube coupling. Photoinduced exciton relaxation in DWNTs is an intricate process, which depends strongly on the combination of the alignment of the CNT energy levels, the magnitude of the intertube interaction, and the geometry fluctuation. These calculations allow explicating and untangling the relaxation dynamics taking place in semiconducting DWNTs and their multilayered counterparts.

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