First-Principles Simulations of Chemical Reactions in an HCl Molecule Embedded inside a C or BN Nanotube Induced by Ultrafast Laser Pulses

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We show by first-principles simulations that ultrafast laser pulses induce different chemical reactions in a molecule trapped inside a nanotube. A strong laser pulse polarized perpendicular to the tube axis induces a giant bond stretch of an encapsulated HCl molecule in semiconducting carbon nanotube or in a BN nanotube. Depending on the initial orientation of the HCl molecule, the subsequent laser-induced dynamics is different: either complete disintegration or rebonding of the HCl molecule. Radial motion of the nanotube is always observed and a vacancy appears on the tube wall when the HCl is perpendicular to the tube axis. Those results are important to analyze confined nanochemistry and to manipulate molecules and nanostructures encapsulated in organic and inorganic nanotubes.

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The photophysical and photochemical properties of single-walled carbon nanotubes (SWCNTs) have attracted a lot of interest recently [1–4] almost 20 years after the identification of chiral structures of carbon nanotubes (CNTs) [5,6]. The nanometer space inside SWCNTs has been used to fill nanotubes with metals [7] and molecules [8–10]. The rich variety of chemical properties and the modifications of those induced by the tube-wall confinement have opened a new avenue of research linked to the one-dimensional nanoconfined chemistry. SWCNTs could be used to control molecular self-assembly which is a key in nanotechnology. Photochemistry in those confined spaces was observed for photoharvesting chromophores inside CNTs [11] and their carrier dynamics were analyzed by optical spectroscopy [12]. Understanding the confinement effect in the photophysics and photochemistry of encapsulated molecules is of fundamental and practical interest.

In this Letter, we propose using a short and intense laser pulse to control the photochemistry of molecules inside carbon and BN nanotubes. The benefit of trapping molecules inside CNTs is to increase the cross section of the photoirradiation compared to those in gas phase. To theoretically simulate the photochemical dynamics in such nanospace we should take into account depolarization [13–15] or enhancement [16] of the optical electric field (E field) depending on the optical frequency. A first-principles approach is needed, which has motivated the work in the Letter. We chose an HCl molecule as a test case and found significant expansion or dissociation of the molecule depending on the molecular orientation inside an (8,0) carbon nanotube or inside an (8,0) BN nanotube under irradiation of strong and short laser pulse.

Photochemical reactions can be treated within time-dependent density functional theory (TDDFT) [17].

TDDFT using the simplest local-density approximation (TDLDA) was applied to study the dynamics of metal clusters and isolated molecules [18,19] in the presence of a strong laser pulse. We extended this type of TDLDA approach to photochemistry in the nanospace inside SWCNTs. Dynamics of the HCl molecule inside semiconducting nanotubes was calculated under the pulse laser with wavelength of 800 nm and the full width at half maximum as 2 fs. These conditions make duration time of the pulse only 4 fs and make the pulse shape strongly asymmetric in the direction of the alternating optical E field as shown in Fig. 1. Such a short pulse is indeed experimentally available [20]. We remark that the TDDFT approach can also be applied with longer laser pulses of weaker intensity [21].

We employed the TDLDA for computing real-time propagation of electron wave functions [22] using the Suzuki-Trotter formula [23,24] coupled with the classical molecular dynamics within the Ehrenfest approximation [25]. To express valence wave functions, we used the plane-wave basis set with the cutoff energy of 60 Ry while the interaction of valence electrons and ions was expressed

FIG. 1 (color online). Pulse shape considered in the current simulation. The dotted line denotes the Gaussian envelope function of the pulse. The maximum field intensity is 12 V/Å.

by the soft pseudopotentials [26] with separable form [27]. As for the exchange-correlation functional, the local-density approximation (LDA) using the functional form [28] fitted to the numerical data for isotropic electron gas [29] was employed. We also used the PBE [30] functional and concluded that LDA shows enough accuracy in describing the relative total energies dependent on the molecular orientations [31]. The size of the unit cell corresponds to the double cell size of the (8,0) tube in the tube axis, and the Γ point was taken for the momentum space integration. This corresponds to taking Γ and X points for the primitive cell of the zigzag tube [35]. When we performed the molecular dynamics, conservation of the internal total energy plus kinetic energies of ions minus work done by optical E field [36] was confirmed. This indicates the numerical stability of the calculation [37].

We tested the toughness of the carbon (8,0) nanotube against the short pulse shown in Fig. 1. The nanotube was found to survive when the maximum field strength was 12 V/Å: the nanotube showed giant anisotropic oscillation in the radial direction; see Fig. 2. However, the nanotube broke when an E -field strength was 13.6 V/Å. Such high intensity of the E field is experimentally accessible. For example, the laser intensity I available by experiment for 5 fs duration is 4×10^{15} W/cm² [38], with corresponding electric field $E = 17.4$ V/Å according to the formula $I = 1/2\epsilon_0 c E^2$, where ϵ_0 and c are the dielectric function of vacuum and velocity of light, respectively. Reference [39] reported that metallic nanotubes tend to be destroyed by laser power lower than 1 mW/ μ m². However, in that case, the additional chemical functionalization was needed, and thus revisiting that experiment with use of ultrashort laser pulse with higher intensities would shed light on the role of chemical functionalization for the selectivity in destroying metallic tubes.

Next, we systematically checked the dynamics of HCl molecules irradiated with the same shape and strength of the pulse as Fig. 1. Several molecular orientations with respect to the tube axis were tested, while in all cases the

polarization vector of the pulse was set perpendicular to the tube axis. According to the LDA calculations, the HCl molecule is exothermically incorporated inside the carbon (8,0) nanotube with energy gained about 0.3 eV per HCl molecule with the most favored molecular orientation, i.e., perpendicular to the tube axis. Since two HCl molecules (HCl dimer) were found to be unstable inside the carbon (8,0) tube [40], we focus our attention on a single HCl molecule in this work. Meanwhile, the orientation parallel to the tube axis is metastable with 0.19 eV higher total energy, but still the HCl molecule is trapped exothermically. Another orientation tilted 53° from the most stable orientation shown in Fig. 3 with $t = 0$ fs costs only 0.019 eV per molecule; thus, it is very likely that the molecular orientation distributes beyond this tilted angle below room temperature.

Taking this tilted geometry as a snapshot, we have investigated the dynamics of the HCl molecules upon irradiation of the pulse shown in Fig. 1. Since the rotation takes the time far beyond picoseconds, the initial velocity of the HCl molecule is negligibly small compared to the velocity induced by the laser pulse. Figure 3 shows the dynamics. After the decay of the pulse, the H atom started to leave the Cl atom and was reflected by the tube wall. At the end of the simulation the H atom had a kinetic energy of 1.8 eV with the internuclear H-Cl distance larger than 3.3 Å, putting in evidence the complete fragmentation of the HCl molecule. On the other hand, the Cl atom did not obtain considerable kinetic energy. The radius of the nanotube was expanding within this simulation. Afterwards the tube should start to shrink as shown in Fig. 2.

We also tested the HCl dynamics starting from the most stable geometry (ground state configuration) where the molecular orientation is perpendicular to tube axis. As shown in Fig. 4, the H atom again left from Cl, but moved back after the reflection from the tube wall. The incident angle of the H atom to the tube wall was just 90°; this collision caused replacement of the target carbon atom at $t = 43.6$ fs. Because of asymmetric distortion in the radial direction, the replacement finally propagated to the edge of

FIG. 2. Deformation of the (8,0) carbon nanotube under the pulse of Fig. 1 with polarization perpendicular to tube axis. The polarization direction is indicated by the open arrow.

FIG. 3 (color online). Dynamics of an HCl molecule with the pulse shown in Fig. 1 starting with a tilted orientation inside (8,0) carbon nanotube. Gray (blue small) and light gray (light green and bigger) balls denote H and Cl atoms, respectively, while other gray balls are C atoms. Front atomic structures of the nanotube wall are omitted in this figure to make the HCl molecule visible. Gray (blue) arrows are guides for eyes to follow trajectory of the H atom. Direction of the polarization of the pulse is indicated by the open arrow.

FIG. 4. Dynamics of the HCl molecule starting with the most stable geometry in (8,0) carbon nanotube. The polarization direction of the optical E field of the pulse, shown in Fig. 1, is indicated by the open arrow. The creation of a vacancy is denoted by a solid arrow in the last snapshot.

the laterally expanded top making a vacancy as denoted by the arrow at $t = 108.90$ fs. This dynamics may cause degradation of the nanotube. However, the small energy difference with respect to the orientation of the HCl molecule should lower the probability of this event at room temperature compared to at absolute zero.

The role of the CNT governing the dynamics of the HCl molecule was analyzed. We plotted the time evolution of the Kohn-Sham expectation values in the (8,0) tube throughout the simulation shown in Fig. 2. At very early time of pulse irradiation, the order of occupied and empty bands is alternated and this alternation tends to dissolve indicating recovery of electronic ground state. The corresponding plot for the HCl dynamics in the CNT was also investigated, and the same trend was observed [41]. This manifests no interference between the electronic excitations of the (8,0) tube and the HCl molecule.

Still, the dynamics of the HCl molecule inside the (8,0) tube is governed by the mechanical confinement. The minimum distance between a C atom of the wall and the ejected H atom from the molecules is $1.31 \text{ \AA}$ in Fig. 4, causing strong reflection, while this distance is much longer at $1.84 \text{ \AA}$ in Fig. 3, at the tilted molecular orientation. The interaction could be stronger if the (8,0) tube did not show radial oscillation by pulse. The reflection depending on the molecular orientation makes one expect complete disintegration of an HCl molecule with the molecular axis parallel to the tube axis.

We thus also tested this orientation with the pulse shown in Fig. 1, although this orientation is metastable as mentioned before. The corresponding dynamics of H-Cl bond lengths for HCl molecules, which are, respectively, isolated, encapsulated in (8,0) carbon, and in (8,0) BN nanotubes, are shown in Fig. 5. Surprisingly, the disintegration did not take place inside nanotubes. The suppressed disintegration can merely be understood by the E -field screening of the (8,0) nanotube.

FIG. 5 (color online). The time evolution of H-Cl bond lengths, respectively, in isolated, in carbon (8,0) tube, and in BN (8,0) tube. In all cases, the molecular orientation is parallel to tube axis with polarization of optical E field perpendicular to the tube axis.

The presence of the HCl molecule inside CNT makes the analysis of the E field very complicated in contrast to Ref. [16]. Instead, we focused on initial velocity of the H-Cl elongation as a measure of pulse intensity. When the molecular orientation was tilted and perpendicular to tube axis, the initial velocities of H-Cl elongation were found to be the same as those of isolated HCl molecules. Meanwhile as denoted in Fig. 5, the initial velocity is slower with the parallel molecular orientation. Such dependence of the screened pulse can be attributed to the polarized nature of the HCl molecule.

Furthermore, it is also surprising that the velocity of H-Cl elongation inside the (8,0) BN nanotube is much smaller than that in the (8,0) carbon tube indicating larger screening in the (8,0) BN tube. This is an unexpected result from the lower dielectric constant of the wide gap of the (8,0) BN tube [42]. Therefore, we interpret the higher screening of this short pulse in the (8,0) BN tube as stemming from a high-energy component in the Fourier transformed pulse which hits optical transition at the (8,0) BN tube that has a much higher strength than that in the (8,0) carbon nanotube [43,44].

In conclusion, we showed that dynamics of HCl molecules encapsulated in nanotubes under irradiation with a short laser pulse with polarization vector perpendicular to the tube axis leads to dissociation or significant expansion depending on the molecular orientations [45]. H atoms obtained significantly high kinetic energy upon pulse laser irradiation, while Cl atoms remained immobile. This fact hints at efficient hydrogen extraction from any kind of hydrogenated molecules.

Finally, the current computational approach based on the TDDFT will be applicable for controlling dynamics with designed shape and intensity of laser pulse for future research for both equilibrium and nonequilibrium regimes of phenomena.

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