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Response of C_{60} and C_n to ultrashort laser pulses

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In this paper we introduce a method for realistic simulations of nonadiabatic processes, including the interaction of light with matter. Calculations of the response of C_{60} and carbon chains to laser pulses demonstrate that even rather subtle features are correctly described. For example, in C_{60} the pentagonal-pinch mode is dominant at low fluence, the breathing mode is dominant at high fluence, and dimers are preferentially emitted during photofragmentation. In carbon chains, on the other hand, trimers tend to be broken off. After collisional fragmentation, the remnants of a C_{60} molecule tend to reform their bonds, yielding new 5, 6, or 7 membered rings.

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The interaction of matter with ultrashort and ultraintense laser pulses is a current frontier of science. New discoveries often result from the ability to explore a new regime. Here one explores both extremely short time scales (below one hundred femtoseconds) and extremely high intensities (above one terawatt per square centimeter). The usual approximations of theoretical physics and chemistry break down under these conditions, and both electrons and atoms exhibit new kinds of behavior.

In a broader context, many processes in physics, chemistry, and biology involve the interaction of electromagnetic radiation with complex molecules and materials. Traditional treatments of this problem involve the Born-Oppenheimer approximation (in which the electrons are assumed to adiabatically follow the motion of the nuclei), the Franck-Condon principle (in which the nuclei are regarded as frozen during each electronic transition), and Fermi's golden rule (which is based on both first-order perturbation theory and the premise that the field varies harmonically on a long time scale). These assumptions may be difficult to employ for a complex system, and they are not necessarily valid for ultraintense and ultrashort laser pulses. In the most general case, one needs reliable numerical simulations.

Time-dependent density-functional theory[1] is now well established and has been successfully used to calculate photoabsorption spectra and excitation energies of atoms and small molecules. However, one would like a complementary approach which is suitable for larger systems and multiphoton processes.

Here we introduce a method for realistic simulations of the interaction of light with matter, which combines the virtues of tight-binding electron-ion dynamics (TED) (Refs. 2–5) and density-functional-based tight-binding (DFTB).[6,7] (There are also connections with time-dependent density-functional theory[1] and other density-functional-based schemes,[8,9] which we will discuss in a longer article.) The essential ideas are as follows.

Both the effective one-electron Hamiltonian and the effective repulsive forces between ion cores are accurately determined in local-density-functional calculations. That is we employ the DFTB ansatz, which can be seen as a stationary approximation to DFT,[7] and which has been found to yield accurate results in a variety of different systems, including molecules, clusters, solids, and surfaces.[6,7]

Dynamical problems are treated with a series of techniques fully described in Refs. 3 and 5: The electron dynamics is determined from the time-dependent Schrödinger equation; the dynamics of the ion cores is determined from a generalized Hellmann-Feynman theorem, which can also be interpreted as a generalized Ehrenfest theorem;[2] the electrons are coupled to the radiation field through a time-dependent Peierls substitution;[3,10] the motion of the ions is solved using a velocity Verlet algorithm, which conserves phase space; and the evolution of the electron states is solved with a generalized Cayley algorithm, based on a Dyson-like expansion of the time-evolution operator,[5] which conserves probability and preserves orthogonality.

We mention that this method—density-functional-based tight-binding electron-ion dynamics (DFTED)—is inherently an $O(N)$ method once the initial state has been specified. It is thus well-suited to large systems such as complex materials and biological molecules.

The system emphasized in this paper, C_{60}, is already rather substantial, since it has 240 valence electrons, described by a Schrödinger equation which must be solved with a time step of $\sim$50 attoseconds. It is also a good test of the reliability of the method, since the features of its response to laser pulses in different regimes of intensity and duration exhibit a number of interesting subtleties which will be explored below.

Before turning to the DFTED simulations, let us review our previous results[4] using the well-constructed semiempirical tight-binding model of Xu *et al.*[11] Even though it was fitted to a data base which does not include fullerenes, this model already provides a surprisingly good treatment of the most robust properties of C_{60}. For example, the lengths of the single and double bonds are predicted quite accurately, as are the frequencies of the $A_g(1)$ breathing mode and $A_g(2)$ pentagonal-pinch mode. Furthermore, in our simulations with this model[4] the breathing mode was correctly found to be dominant at high fluence. There were two major deficiencies, however, which involved rather subtle features of the interaction of laser pulses with this fullerene: Monomers, rather than dimers, tended to be evolved during photofragmentation, and the pentagonal-pinch mode was never excited with any appreciable amplitude.

In short, the model of Xu *et al.* is very good, but does not do a perfect job of describing the dynamics of electrons and atoms when the molecule responds to an intense laser pulse on an ultrashort time scale. Since density-functional theory (DFT) provides an accurate first-principles description of total energies, one expects that a DFT-based method will be more reliable than even the best semiempirical tight-binding models. The results shown below demonstrate that DFTED does in fact capture the important subtleties that are missed by semiempirical TED.

First let us consider the ground-state properties of C_{60} within the present DFTB scheme: The calculated lengths of the double bond and single bond are, respectively, 1.397 and 1.449 Å, in close agreement with the measured values of 1.402 and 1.462 Å. There is an overbinding for the carbon-carbon bonds of approximately 0.4 eV, and the vibrational frequencies are typically a few percent (as high as 15%) above the measured values. These results can already be considered a success, however, because the parameters are obtained from first-principles calculations rather than being fit to experiment. In addition, the calculated HOMO-LUMO gap is 1.81 eV, which is remarkably close to the measured value of 1.9 eV.[12] The ordering and degeneracy of the molecular levels are also in good agreement within ~ 10 eV of the HOMO level. These features are important for problems such as those considered here, which involve the excitation of large fractions of the valence electrons to higher energy levels through multiphoton processes.

Now let us turn to the dynamical simulations, beginning with the results for relatively low fluence, in which the molecule remains intact but various optically-active vibrational modes can be excited. Figure 1 shows the response of a C_{60} molecule, initially at 0 K, when it is subjected to 10 fs FWHM laser pulses with a central photon energy of 2.0 eV. The Fourier power spectrum was obtained by taking the Fourier transform of the velocity autocorrelation function over an interval of 1 ps following the completion of the laser pulse. The most noticeable feature is the excitation of the two fully symmetric modes: the $A_g(1)$ breathing mode at 535 cm^{-1} and $A_g(2)$ pentagonal-pinch mode at 1600 cm^{-1}.

Note that the pentagonal-pinch mode is now excited with appreciable amplitude. There is in fact remarkable qualitative and quantitative agreement with the experimental results of Dexheimer *et al.*[13] Moreover, it is known from experiment that the pentagonal-pinch mode dominates the Raman spectrum for C_{60},[14] in agreement with the low-fluence results of Fig. 1.

At a fluence of 0.16 $\mathrm{KJ/m^2}$, the breathing mode is found to be completely dominant. This result is in excellent agreement with the experimental results of Fleischer *et al.*[15] In addition, the decrease in relative amplitude for the pentagonal-pinch mode with increasing fluence agrees with the measurements of Meletov *et al.*[16]

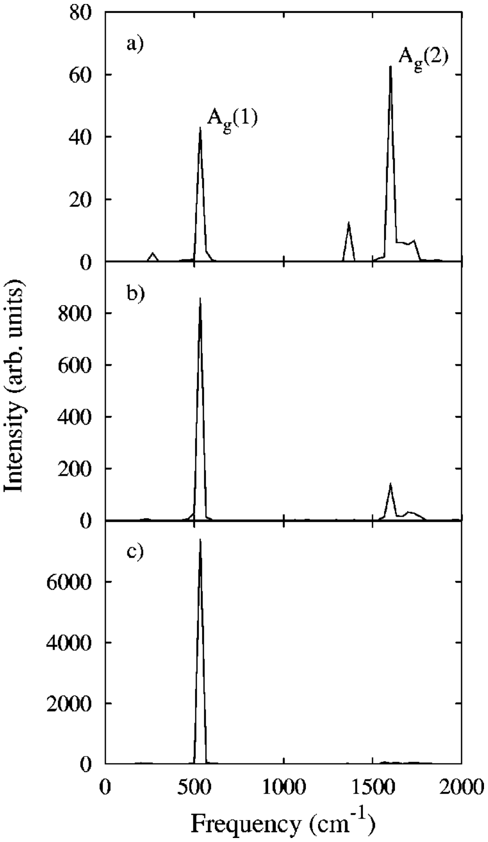

FIG. 1. Vibrational spectrum of C_{60} after being subjected to a 10 fs FWHM, 2.0 eV laser pulse with a fluence of (a) 0.06 $\mathrm{KJ/m^2}$, (b) 0.10 $\mathrm{KJ/m^2}$, and (c) 0.16 $\mathrm{KJ/m^2}$.

The dominance of the breathing mode at high intensity has a simple physical interpretation: There are two fully symmetric modes which can support a displacive excitation of coherent phonons, but only the breathing mode allows the atoms to move away from one another in response to the weaker excited-state bonding.

Now we turn to the still higher fluences which produce photofragmentation, for which representative snapshots from DFTED simulations are shown in Figs. 2–4. Figure 2 shows results for a C_{60} molecule, initially at a temperature of 300 K, which is subjected to a 35 fs, 2.0 eV laser pulse with a fluence of 1.17 $\mathrm{KJ/m^2}$. (The polarization vector points out of the page, and the pulse duration is the same as in Tchaplyguine *et al.*[17] Both the initial C_{60} molecule and the fragments are taken to be charge neutral in the present simulations.) This was the lowest fluence for which we could obtain fragmentation within one picosecond, and it causes 13.7% of the valence electrons to be promoted into excited states. There are two particularly striking features in Fig. 2: The first is the dramatic opening of both ends of the fullerene, accompanied by the breaking of many bonds. The second is the release of a dimer (at $t=952$ fs) with a kinetic energy of 0.25 eV, which is slightly more than half the value reported for the experiments of Hohmann *et al.*[18] Following emission of the dimer, the remaining 58 atoms tend to move back toward one another and reform bonds with both hexagons and pentagons. However, complete reformation of a closed

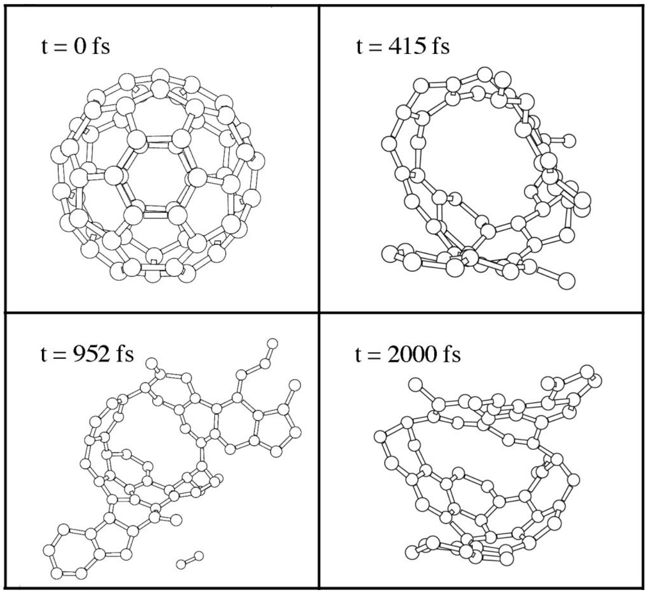

FIG. 2. Photofragmentation of C_{60} following a 35 fs FWHM, 2.0 eV laser pulse with a fluence of 1.17 KJ/m^2.

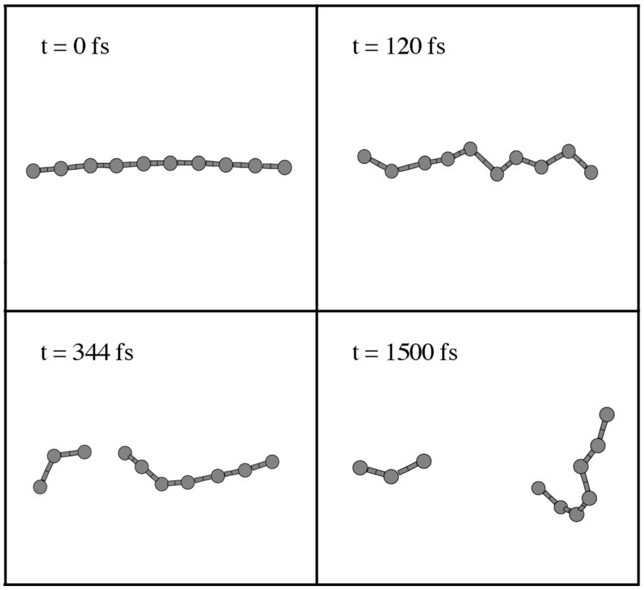

FIG. 4. Photofragmentation of C_{10} chain following a 20 fs FWHM, 2.7 eV laser pulse with a fluence of 1.6 KJ/m^2.

structure is not observed, since there is still a large population of electrons in excited states at the end of the simulation.

For a still higher fluence of 1.24 KJ/m^2, represented by Fig. 3, we observe that the cage begins to break apart at $t = 299$ fs, with the emission of both a dimer and a trimer. (In this case, the polarization vector is horizontal and in the plane of the page.) Experimentally, it is well established that C_{60} should normally fragment with the emission of even numbered clusters,[17] as in Fig. 2. In the present case, however, the cage continues to open up, and at $t = 998$ fs another dimer is emitted. It is apparent that the remaining cluster is structurally unstable, and the atoms continue to move apart. At $t = 2000$ fs, two corannulene-like structures of 29 and 24 atoms are connected by only one bond. One therefore expects that they will eventually separate (on a 10^6 femtosecond time scale) rather than reform as a stable odd-numbered cluster with greater than 32 atoms.

Further results for C_{60} will be presented elsewhere. Let us now turn to a representative simulation for a C_n cluster with $n < 32$—specifically a C_{10} chain. Figure 4 shows the photofragmentation of a 10 atom neutral carbon chain initially at 300 K, by a laser pulse with a FWHM duration of 20 fs, a photon energy centered at 2.7 eV, and a fluence of 1.6 KJ/m^2. In this case 16.5% of the valence electrons were promoted to excited states. The figure shows that this level of excitation causes a change in the bonding, leading to a highly

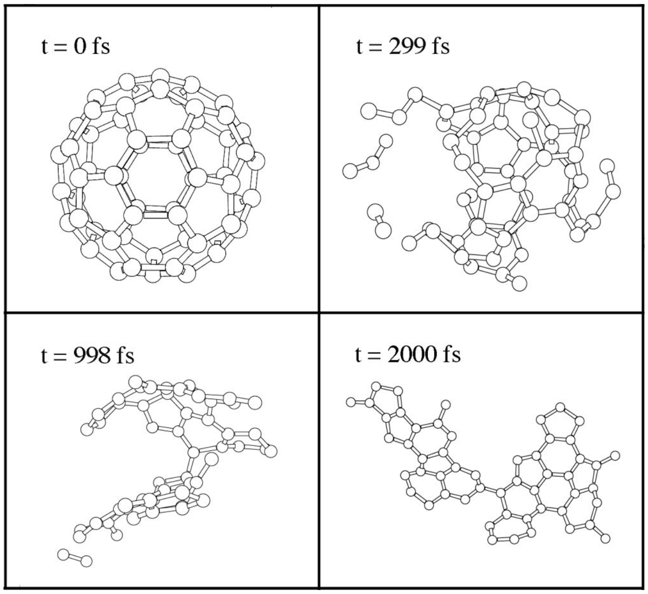

FIG. 3. Photofragmentation of C_{60} following a 35 fs FWHM, 2.0 eV laser pulse with a fluence of 1.24 KJ/m^2.

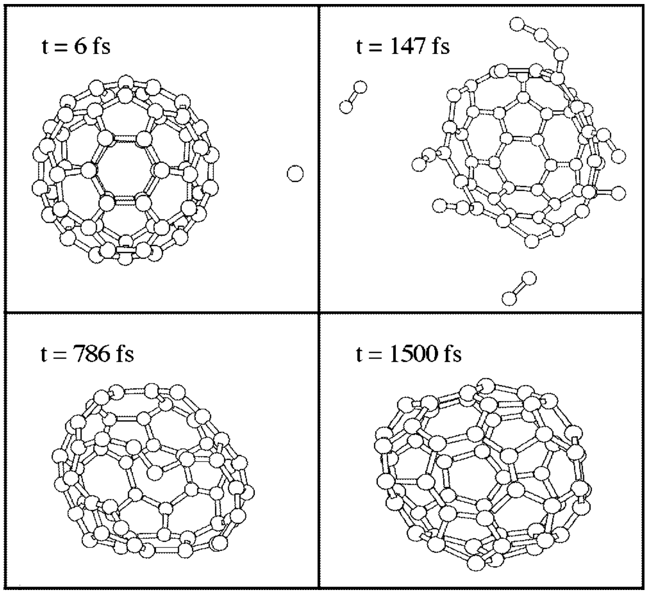

FIG. 5. Nonadiabatic collision of a 155 eV carbon atom with a C_{60} molecule.

kinked chain. At $t=344$ fs, a trimer breaks away from the remaining chain of seven atoms. This outcome is quite significant, because it is observed experimentally that fragmentation of small clusters involves emission of C_3 rather than C_2 units.[18] This same phenomenon was observed in a simulation for a C_7 chain, and results for other C_n will be presented elsewhere.

Finally, we turn to atomic collisions, which can also be a useful test of nonadiabatic models. The first panel of Fig. 5 shows a representative trajectory in a DFTED simulation: A 155 eV projectile carbon atom impinges on a buckyball with a initial temperature of 300 K. The impact is at the center of a hexagon-hexagon bond, with zero impact parameter, and the resulting violent collision promotes 5.2% of the valence electrons into excited states. The virtual camera is then rotated 90° to the left, about a vertical axis passing through the center of the fullerene, in order to reveal the most interesting features of the collision. At $t=147$ fs, we see that the backside of the cage has already reformed, and that two dimers have been released. (The release of dimers in collisional experiments with C_{60} has been widely observed. See, for example, Welling *et al.*[19]) The projectile atom is out of the picture at this point, since it requires only 23 fs to pass through the buckyball. At $t=786$ fs, atoms have bridged the large opening created by the impact on the near side of the cage. At $t=1500$ fs, the remaining 56 atoms have joined to form a new closed-cage structure, whose prominent features include the formation of a seven-membered ring accompanied by a extra pentagon. Seven-membered rings have been previously proposed as likely features in lower-mass fullerenes by Murry *et al.*,[20] based on results of *ab initio* quantum-chemical calculations, and they may also play a role in the stability of larger fullerenes.[21]

The above results represent a nontrivial level of success for the method introduced in this paper. DFTED captures even rather subtle effects, such as the relative amplitudes of vibrational modes after excitation through multiphoton processes at high intensity. It also yields correct results for violent processes at still higher intensities, such as the photofragmentation of fullerene molecules and smaller C_n clusters. We conclude that this method provides a reliable and versatile approach to microscopic studies of the interaction of light with matter.

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