Nonthermal fragmentation of $C_{60}$

H. O. Jeschke
Institut für Theoretische Physik der Freien Universität Berlin, Arnimallee 14, 14195 Berlin, Germany,

M. E. Garcia and J. A. Alonso
Departamento de Física, Universidad de Valladolid, 47011 Valladolid, Spain.
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A theoretical study of the subpicosecond fragmentation of $C_{60}$ clusters in response to ultrafast laser pulses is presented. We simulate the laser excitation and the consequent nonequilibrium relaxation dynamics of the electronic and nuclear degrees of freedom. The first stages of the nonequilibrium dynamics are dominated by a coherent breathing mode followed by the cold ejection of single C atoms, in contrast to the dimer emission which characterizes the thermal relaxation. We also determine the nonequilibrium damage thresholds as a function of the pulse duration.

During the last decade much attention has been paid to the study of the ultrafast fragmentation of molecules and clusters upon excitation with femtosecond laser pulses \[1,2\]. The sub-picosecond relaxation dynamics of the nuclear degrees of freedom, as a typical ultrafast phenomenon, becomes interesting when it presents new features, qualitatively different from the well known thermal relaxation processes. There are many recent examples of such new phenomena in solids, like the cold melting of graphite and silicon \[3,4\], ultrafast desorption \[5\] or femtosecond graphitization of diamond \[6\]. For clusters, the search for ultrafast phenomena presenting nonthermal features is difficult. The reason for that is the lack of well established thermal effects from which ultrafast nonthermal phenomena could be distinguished. This is, however, a very robust thermal phenomenon in cluster physics: the cooling of vibrationally excited $C_{60}$ clusters through emission of carbon dimers \[7,8\]. This remarkable process is closely related to the cage structure and the high stability of fullerenes. On large time-scales, successive and stochastic dimer emission dominates the decay of a hot fullerene. Now, a fundamental question regarding the short-time behavior of fullerenes is whether the dimer-emission is also present in the nonthermal decay of a hot fullerene. Now, a fundamental question regarding the short-time behavior of fullerenes is whether the dimer-emission is also present in the nonthermal decay of a hot fullerene.

The problem and focus in this paper on a particular relaxation mechanism, which results from excitation of many electron-hole pairs on the neutral cluster. This means that, from all possible excitations upon ultrafast absorption of many photons we only consider those involving excited electrons below the continuum states. Thus, we do not consider single or multiple ionization processes, which are, of course, also present. However, from phase-space arguments the processes we take into account in this work should be the most probable ones for not very high laser intensities.

In order to describe the nonthermal dynamics of $C_{60}$ we write down a classical Lagrangian for the atoms, which contains the effect of the electronic system as a many-body potential $\Phi(\{r_{ij}\},t)$:

$$\mathcal{L} = \sum_{i=1}^{N} \frac{m_i}{2} \dot{r}_i^2 - \Phi(\{r_{ij}\},t). \quad (1)$$

Here, a number of $N$ atoms with masses $m_i$ at positions $r_i$ interact through the potential $\Phi(\{r_{ij}\},t)$, which depends on the distances $r_{ij} = |r_i - r_j|$ between the atoms. Thus, the first term of $\mathcal{L}$ is the kinetic energy of the $N$ particles, calculated from the velocities $\dot{r}_i$. $\Phi(\{r_{ij}\},t) = \Phi(H_{el}(\{r_{ij}\}),t)$ is a complicated functional of the electronic Hamiltonian $H_{el}$. The equations of motion for a cluster can immediately be derived through the Euler-Lagrange equations. In the case of the tight-binding (TB) Hamiltonian employed in this work the gradients of the interaction potential $\Phi(\{r_{ij}\},t)$ are not available in a closed form and the equations of motion cannot be integrated analytically. Thus, a numerical pro-
procedure has to be used. We employ the Verlet algorithm in its velocity form [3,4].

For the determination of the interaction potential $\Phi(\{r_{ij}\}, t)$ between the atoms we employ an Hamiltonian $H$ that consists of a tight-binding (TB) part $H_{\text{TB}}$ for the electronic system, the other part being a repulsive potential $\phi(r_{ij})$ that takes care of the repulsion between the ionic cores:

$$H = H_{\text{TB}} + \sum_{i<j} \phi(r_{ij})$$

with

$$H_{\text{TB}} = \sum_{m} \epsilon_{m} n_{m} + \sum_{ij} t_{ij}^{\eta} c_{i}^{\eta \dagger} c_{j}^{\eta}.$$  

Here, $n_{m}$ represents the occupation number operator for the orbital $\eta$ of atom $i$, $c_{i}^{\eta \dagger}$ and $c_{j}^{\eta}$ are fermion creation and annihilation operators, and the hopping matrix element has been abridged by $t_{ij}^{\eta}$. For the description of carbon, the 2$s$, 2$p_{x}$, 2$p_{y}$ and 2$p_{z}$ orbitals are taken into account. The angular dependence of the hopping matrix element is treated following the work of Slater and Koster [15], while for the radial part of $t_{ij}^{\eta}$ and for the distance dependence of the repulsive potential $\phi(r_{ij})$ we employ the form proposed by Xu et al. [16].

Diagonalization of the Hamiltonian of Eq. (3) yields the energy spectrum $\{\epsilon_{m}(\{r_{ij}(t)\})\}$ of the material and thus allows for the calculation of the potential energy

$$\Phi(\{r_{ij}(t)\}, t) = \sum_{m} n(\epsilon_{m}, t) \epsilon_{m} + \sum_{i<j} \phi(r_{ij}).$$  

Here, $n(\epsilon_{m}, t)$ is a time-dependent distribution of the electrons over the energy levels $\epsilon_{m}$. Initially, it is given by a Fermi-Dirac distribution $n^{0}(\epsilon_{m}) = 2/(1 + \exp((\epsilon_{m} - \mu)/k_{B}T))$ at a given electronic temperature $T_e$. Its time dependency that is caused by the absorption of an ultrashort laser pulse and by subsequent thermalization is calculated according to

$$\frac{dn(\epsilon_{m}, t)}{dt} = \int_{-\infty}^{\infty} d\omega \ g(\omega, t-\Delta t) \left\{ n(\epsilon_{m} - \hbar\omega, t-\Delta t) + n(\epsilon_{m} + \hbar\omega, t-\Delta t) - 2n(\epsilon_{m}, t-\Delta t) \right\} - \frac{n(\epsilon_{m}, t) - n^{0}(\epsilon_{m})}{\tau_{1}}.$$  

Here, the laser pulse is characterized by an intensity function $g(\omega, t)$ which describes the distribution of intensity over time and energies. Thus, the electronic distribution $n(\epsilon_{m}, t)$ is at each time step folded with the current laser intensity function $g(\omega, t)$. This means that at each time step, the occupation of an energy level $\epsilon_{m}$ changes in proportion to the occupation difference with respect to levels at $\epsilon_{m} - \hbar\omega$ and at $\epsilon_{m} + \hbar\omega$. We model the complex processes of electron-electron collisions, that lead to an equilibration of the electronic system, by a rate equation of the Boltzmann type for the distribution $n(\epsilon_{m}, t)$. Thus, with a time constant $\tau_{1}$, the distribution $n(\epsilon_{m}, t)$ approaches a Fermi-Dirac distribution $n^{0}(\epsilon_{m})$ at a high electronic temperature $T_e$. As we are not aware of a measured relaxation time in C_{60}, we use $\tau_{1} = 10$ fs, a value that was reported for GaAs [7].

Now we can determine the forces which are needed for the solution of the equations of motion by calculating the gradient of the time-dependent potential $\Phi(\{r_{ij}(t)\}, t)$ of Eq. (4):

$$\mathbf{f}_{k}(\{r_{ij}(t)\}, t) = -\sum_{m} n(\epsilon_{m}, t) (m|\nabla_{k} H_{\text{TB}}(\{r_{ij}(t)\})|m) - \sum_{i<j} \nabla_{k} \phi(r_{ij}),$$

where $\nabla_{k} \equiv \partial/\partial r_{k}$ and $|m\rangle$ is the eigenvector of $H$ corresponding to eigenvalue $\epsilon_{m}$. In this equation, a term which follows from the gradient of the occupations $n(\epsilon_{m}, t)$ has been neglected. In Eq. (6) the Hellman-Feynman theorem has been used. It is important to keep in mind that we are actually using a generalization of the adiabatic principle when we consider TB energy levels with time-dependent fractional occupation numbers $n(\epsilon_{m}, t)$. Note that a calculation of the true nonadiabatic evolution of electronic wave functions is at present only possible for two or three degrees of freedom, while this work studies the time evolution of $3N = 180$ degrees of freedom in the case of C_{60}.

Now we present the results for the fragmentation of C_{60} clusters, which show important differences between thermal and nonthermal response. As experiments usually provide only electron-emission spectra or mass spectra of ionized fragments on long time scales, this theoretical investigation is complementary to the experimental results in the sense that it can clarify mechanisms and time evolution of the damage in the clusters during the first stages of the relaxation process.

A typical fragmentation process is shown in the structure snapshots of Fig. 1, which corresponds to an absorbed energy $E_{0} = 3.5$ eV/atom from a $\tau = 80$ fs laser pulse. While 40 fs after the pulse maximum, the cluster is still intact, already 50 fs later, the structure has been torn open and we can see carbon atoms and chains dangling from the remainders of the C_{60} cage. Again 50 fs later the emission of three carbon monomers is observed. This emission of monomers is the dominant initial fragmentation mechanism we obtain for femtosecond laser pulses. In the further subpicosecond dynamics of the main fragment four more monomers are emitted. Carbon atoms that have moved far away from the remaining cluster are
not shown in the subsequent panels. At $t = 440$ fs, a coil of carbon chains has formed. They stabilize to form three independent chains of 15, 16, and 22 atoms. This fragmentation product is similar to the linked chain structure found as a result of thermal bond breaking [8]. The C$_{16}$ cluster has a closed ring structure. Note that, apart from the process shown in Fig. 1, other relaxation mechanisms are possible. For instance, an absorbed energy of 3.5 eV/atom could be enough to ionize the cluster several times. We stress again that we only consider excitations below the continuum. In the experiments, however, both kind of mechanisms are present.

In Fig. 2, snapshots of a C$_{60}$ cluster isomerization as a consequence of the absorption of $E_0 = 2.3$ eV/atom from a $\tau = 5$ fs laser pulse are shown. This value of the absorbed energy is close to the damage threshold of $t_d = 2.1$ eV/atom and thus the isomerization process takes place on a fairly long time scale of a few hundred fs. At $t = 200$ fs after the laser pulse maximum the first breaking of bonds is taking place. This damage to the cluster develops over the following 400 fs into a chain of carbon atoms that is attached at both ends to the original molecule.

We have analyzed the nonthermal fragmentation of C$_{60}$ clusters for a large range of pulse durations and absorbed energies. We observed that a certain thermalization of the atomic degrees of freedom starts to occur at $t_{th} \approx 3$ ps after the pulse maximum. Therefore we define the threshold for nonthermal fragmentation as the maximal absorbed energy for which no fragmentation occurs for $t \leq t_{th}$. In Fig. 3 we show the dependence of the threshold for nonthermal fragmentation as a function of the pulse duration. The fragmentation threshold was found to vary only slightly with pulse duration. For pulses of $\tau = 5$ fs to $\tau = 300$ fs duration the threshold is around $t_{th} = 2.1$ eV/atom. We expect that after redistribution of the energy deposited in the cluster, thermal fragmentation may take place later even for energies be-
low the threshold $t_{th}$.

FIG. 3. Nonthermal fragmentation threshold for C$_{60}$ clusters as a function of laser pulse duration. In the range from $\tau = 5$ fs to $\tau = 300$ fs, no clear dependence of the threshold on pulse duration is observed. A damage threshold of $t_d = 2.1 \pm 0.2$ eV can be attributed to the entire range of pulse durations.

As mentioned above, it has been found experimentally that carbon dimers as products of the thermal fragmentation of C$_{60}$ dominate the fragmentation spectra [7]. Calculations have been reported [8] which show that heating of C$_{60}$ to a temperature of $T = 5600$ K leads to a fragmentation of C$_{60}$ by the emission of a dimer C$_2$. In order to test the validity of the nonequilibrium fragmentation of C$_{60}$, we thermalized C$_{60}$ clusters to a temperature $T = 5600$ K. We also find that the thermal fragmentation process is a dimer emission on a time scale of several picoseconds. In order to visualize the differences between thermal and nonthermal fragmentation, we now analyze the different trajectories with the help of the atomic equivalence indices [19,20]. These quantities, which are instructive for the characterization of the vibrational excitation and structural changes in C$_{60}$, are defined by

$$\sigma_i(t) = \sum_j |r_i(t) - r_j(t)|,$$

(7)

where $r_i(t)$ is the position of atom $i$. Thus, the set of coordinates of the C$_{60}$ cluster yields at each time $t$ a set of 60 atomic equivalence indices $\sigma_i(t)$. For every atom, $\sigma_i$ contains the structural information of its surroundings. Degeneracies of the $\sigma_i(t)$ are related to the symmetry of the molecule. In the case of an undamaged C$_{60}$ molecule the high symmetry of the structure leads to a time development of all atomic equivalence indices in a narrow bundle. The atomic equivalence indices corresponding to a trajectory of a C$_{60}$ molecule at a temperature of $T = 5600$ K are shown in Fig. 4 (a). The amplitudes of the oscillations of the single atomic equivalence indices $\sigma_i$ are approximately $A = 22$ Å, compared to $A \approx 7$ Å in the case of a C$_{60}$ cluster at $T = 300$ K. Single atomic equivalence indices with values of 330 Å or more correspond to a dangling chain of carbon atoms that have torn themselves free from the closed cage of the molecule. These atomic equivalence indices do not show harmonic oscillations as most of the $\sigma_i$ of the molecule. In the right side of Fig. 4 (a), the emission of a carbon dimer C$_2$ can be seen, corresponding to the two approximately parallel $\sigma_i$ lines with rapidly increasing magnitude. Note that the emission process is purely thermal; the number of electrons thermally excited above the Fermi level was always below 1 %.
FIG. 4. Atomic equivalence indices $\sigma_i(t)$ for C$_{60}$ clusters. (a) Thermal fragmentation at a temperature $T = 5600$ K. The abscissa indicates the absolute time of the trajectory after heating. At $t = 6.8$ ps the first irreparable damage has developed and can be seen here as the single atomic equivalence indices with values $\sigma_i > 330$ Å far above the average $\sigma_i(t)$. They correspond to carbon chains dangling from the surface of the cluster. At $t = 7920$ fs the emission of a carbon dimer C$_2$ can be observed as two rapidly increasing atomic equivalence indices. (b) Isomerization in response to a $\tau = 5$ fs laser pulse. The time evolution of the atomic equivalence indices corresponds to the same trajectory as the snapshots in Fig. 3. Immediately after the laser pulse maximum at the time $t = 0$ the cluster expands strongly. At $t = 50$ fs the coherent motion of the cluster atoms dissolves into a broad spectrum of individual movements. Atomic equivalence indices with values above $\sigma_i \simeq 320$ Å correspond to chains of atoms that are dangling at the surface of the original cage structure. (c) Fragmentation in response to a $\tau = 80$ fs laser pulse. The $\sigma_i$ evolution corresponds to the cluster in Fig. 3. An energy $E_0 = 3.5$ eV/atom was absorbed from the pulse. The time $t = 0$ fs corresponds to the peak of the laser pulse.

In order to illustrate the dramatic qualitative differences between thermal and nonthermal fragmentation we show in Fig. 4 (a) atomic equivalence indices $\sigma_i(t)$ corresponding to the ultrafast isomerization of C$_{60}$ upon excitation with a laser pulse of $\tau = 5$ fs (see Fig. 3). Beginning at the peak of the very short laser pulse at $t = 0$ fs, the cluster expands strongly. However, this coherent motion is quickly resolved into an incoherent oscillation of the $\sigma_i$. Then, $\sigma_i$ lines with large values emerge at $t = 120$ fs and they do not oscillate harmonically. This indicates damage of the closed cage structure. The range of the $\sigma_i$ values widens for subsequent times in accordance with the formation of a protruding carbon chain that was already mentioned in the description of Fig. 3.

Fig. 4 (c) shows the time development of atomic equivalence indices $\sigma_i(t)$ during the fragmentation of C$_{60}$ (see Fig. 3). During the comparatively long laser pulse of $\tau = 80$ fs duration, the cluster exhibits a coherent breathing mode, but shortly after the pulse maximum at $t = 0$ fs a strong expansion of the cluster is observed. In this case the energy deposited in the cluster was so high that the disintegration sets in already at $t = 70$ fs, recognizable by the rapidly increasing distances between the atomic equivalence indices $\sigma_i(t)$. The fact that only a small part of the $\sigma_i$ lines stay relatively close to each other corresponds to the fact that a very open linear chain structure has formed in Fig. 3.

Summarizing, we have shown that the excitation of C$_{60}$ with femtosecond pulses gives rise to a nonthermal response which is qualitatively different from the well known thermal emission of dimers. Since we consider only electronic excitations below the continuum states, a comparison of our with existing experimental results based on detection of ionic fragments is difficult. However, experimental fragment mass spectra [12] show clearly the existence of fragments of different sizes and a particularly large peak for C$^+$, which would confirm our simulations. In order to check that single ionization does not affect the main predictions of this work we have performed calculations on C$_{60}^+$ clusters and we obtain essentially the same nonthermal fragmentation thresholds.

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