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Nonthermal fragmentation of C_{60}

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Abstract

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 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. © 2002 Elsevier Science B.V. All rights reserved.

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 subpicosecond 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. There 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]. 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 relaxation of C_{60} after an ultrafast excitation, or if other mechanisms become dominant. In this Letter we show that the dimer emission is not present in the nonthermal response of C_{60} immediately after excitation by an intense femtosecond pulse. Instead, the energy absorbed from the laser pulse concentrates first on a breathing mode and part of it is then rapidly transferred to single C atoms, which leave the cluster before any kind of thermalization of the atomic degrees of freedom can take place. We will refer to this process as ‘cold’ fragment emission.

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Recently, several experiments on femtosecond excitation of fullerenes have been performed [9–12]. Experimental results suggest that, as expected, the long-time relaxation is dominated by dimer emission. However, no clear conclusions can be drawn about the fragmentation behavior at very short times. Since such illumination by intense femtosecond pulses involves absorption of many photons by the cluster, many different electronic excitations are created, which lead to different relaxation processes and relaxation products. As a consequence experimental results yield a superposition of thermal and nonthermal fragmentation, (multiple) ionization effects and even Coulomb explosion. Due to the complexity of the problem an exact treatment of the excitation and relaxation processes is not possible. Therefore we simplify the problem and focus in this Letter on a particular relaxation mechanism, which results from excitation of many electron–hole pairs on the neutral or singly ionized cluster. This means that from all possible excitations upon ultrafast absorption of many photons we do not consider multiple ionization processes, which are, of course, also present. However, as we conclude from phase-space arguments that the processes without ionization of the C_{60} molecule should contribute considerably to the relaxation dynamics for not very high laser intensities, we concentrate on the effect of excitations below the continuum.

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 $\Phi(\{r_{ij}\},t)$:

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

Here, a number of N atoms with masses m_i at positions $\mathbf{r}_i$ interact through the potential $\Phi(\{r_{ij}\},t)$, which depends on the distances $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ between the atoms. Thus, the first term of $\mathscr{L}$ is the kinetic energy of the N particles, calculated from the velocities $\dot{\mathbf{r}}_i$. $\Phi(\{r_{ij}\},t) = \Phi(H_{\mathrm{el}}(\{r_{ij}\}),t)$ 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 procedure has to be used. We employ the Verlet algorithm in its velocity form [13,14].

For the determination of the interaction potential $\Phi(\{r_{ij}\},t)$ between the atoms we employ a Hamiltonian H that consists of a TB part H_{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:

$$H = H_{\mathrm{TB}} + \sum_{i<j} \phi(r_{ij}) \tag{2}$$

with

$$H_{\mathrm{TB}} = \sum_{i\eta} \epsilon_{i\eta} n_{i\eta} + \sum_{\substack{ij\eta\vartheta \\ j\neq i}} t_{ij}^{\eta\vartheta} c_{i\eta}^{+} c_{j\vartheta}. \tag{3}$$

Here, $n_{i\eta}$ represents the occupation number operator for the orbital η of atom i, $c_{i\eta}^{+}$ and $c_{j\vartheta}$ are fermion creation and annihilation operators, and the hopping matrix element has been abridged by $t_{ij}^{\eta\vartheta}$. For the description of carbon, the 2s, $2p_x$, $2p_y$ and $2p_z$ 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 $t_{ij}^{\eta\vartheta}$ 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

$$\Phi(\{r_{ij}(t)\},t) = \sum_m n(\epsilon_m,t)\epsilon_m + \sum_{i<j} \phi(r_{ij}). \tag{4}$$

Here, $n(\epsilon_m,t)$ is a time-dependent distribution of the electrons over the energy levels ϵ_m. Initially, it is given by a Fermi–Dirac distribution $n^0(\epsilon_m) = 2/(1+\exp\{(\epsilon_m-\mu)/k_{\mathrm{B}}T_{\mathrm{e}}\})$ at a given electronic temperature T_{e}. Since our purpose is not the calculation of the absorption cross-section but the description of laser-induced structural changes, our approach for calculating the time dependence of $n(\epsilon_m,t)$ consists in assuming that the excitations responsible for the absorption, whatever character they have, decay very fast and give rise to a non-equilibrium electronic distribution, which itself thermalizes and rapidly converges to an equilibrium one at a high electronic temperature [17]. This is described by

$$\frac{\mathrm{d}n(\epsilon_m,t)}{\mathrm{d}t} = \int_{-\infty}^{\infty} \mathrm{d}\omega\, g(\omega,t-\Delta t)\{[n(\epsilon_m-\hbar\omega,t-\Delta t) + n(\epsilon_m+\hbar\omega,t-\Delta t) - 2n(\epsilon_m,t-\Delta t)]\} - \frac{n(\epsilon_m,t)-n^0(\epsilon_m)}{\tau_1}. \quad (5)$$

Here, the laser pulse is characterized by an intensity function

$$g(\omega,t) = \hat{I}_0 \exp\left\{ -\frac{4\ln 2\,(t-t_0)^2}{\tau^2} - \frac{[f\tau(\omega-\omega_0)]^2}{16\ln 2} \right\}, \quad (6)$$

which describes the distribution of intensity over time and energies. Our derivation of Eqs. (5) (first term) and (6), which is based on the Liouville-von-Neumann equation for the density matrix, is similar to that given by Akulin and Karlov [18] and will be described in detail elsewhere [19]. The collision term in Eq. (5) can be derived using non-equilibrium Green's functions [20]. For energies ω given in eV and the pulse duration τ in fs, the factor f is $10^{-15}e/h$. 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 ϵ_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 τ_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 [21].

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) and applying the Hellman–Feynman theorem:

$$\mathbf{f}_k(\{r_{ij}(t)\},t) = -\sum_m n(\epsilon_m,t)\langle m|\nabla_k H_{\mathrm{TB}}(\{r_{ij}(t)\})|m\rangle - \sum_{i<j}\nabla_k\phi(r_{ij}), \quad (7)$$

where $\nabla_k \equiv \partial/\partial\mathbf{r}_k$ and $|m\rangle$ is the eigenvector of H corresponding to eigenvalue ϵ_m. It has been shown [22,23] that Eq. (7) produces the correct dynamics without further terms involving derivatives of the occupation numbers $n(\epsilon_m,t)$. It is important to keep in mind that we are actually using a generalization of the adiabatic principle when we consider the 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 of $E_0 = 3.5$ eV/atom from a $\tau = 80$ fs laser pulse. As in all the results for laser excited C_{60} molecules presented here the cluster was equilibrated at a temperature of $T = 300$ K before the action of the 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 sub-picosecond dynamics of the main fragment four more monomers are emitted. Carbon atoms that

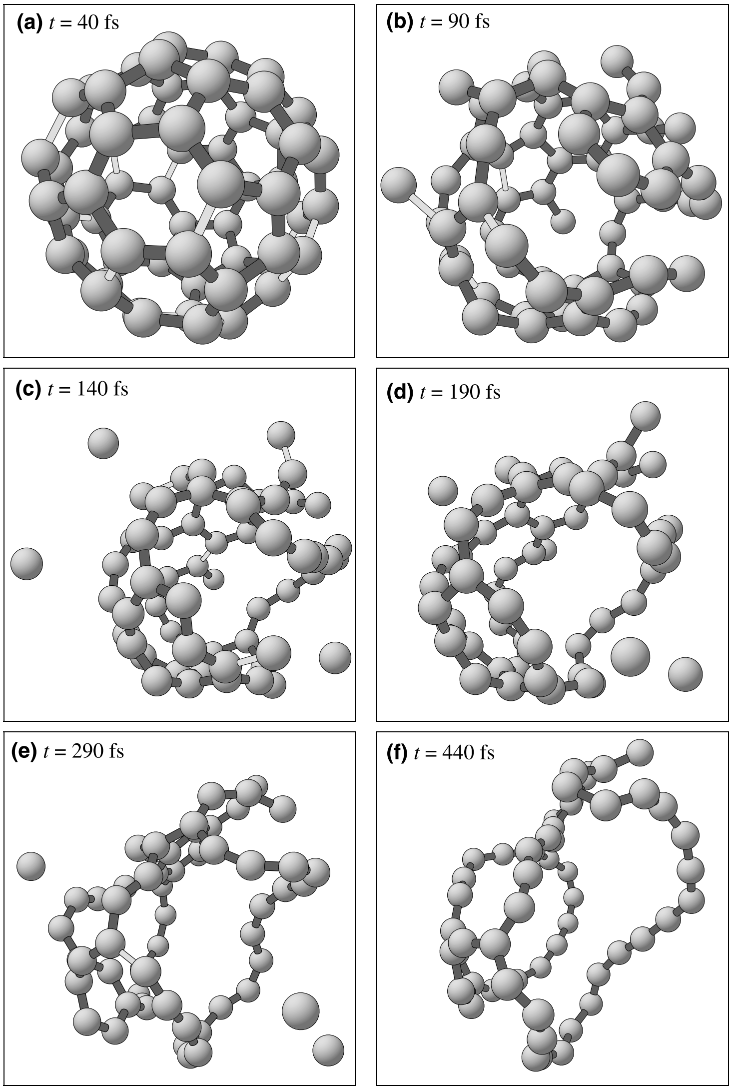

Fig. 1. Nonthermal fragmentation of a C_{60} in response to a $\tau = 80$ fs laser pulse. An energy of $E_0 = 3.5$ eV/atom was absorbed. While the cluster is still intact at the time $t = 40$ fs (measured with respect to the pulse maximum), at $t = 90$ fs the cage structure has already been partially destroyed. In (c) we see three monomers being ejected from the cluster. A coil of linear carbon chains remains at $t = 440$ fs after the emission of a total of six carbon monomers.

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 [24]. 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 concentrate on excitations below the continuum. While in the experiments both kinds of mechanisms are present, multiple ionization is expected to lead to Coulomb explosion of the cluster which is a process qualitatively different from that analyzed in this Letter and therefore out of the scope of the present study.

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 $E_d = 2.1$ eV/atom and thus the isomerization process takes place on a fairly long time scale of a few hundred femtosecond. 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

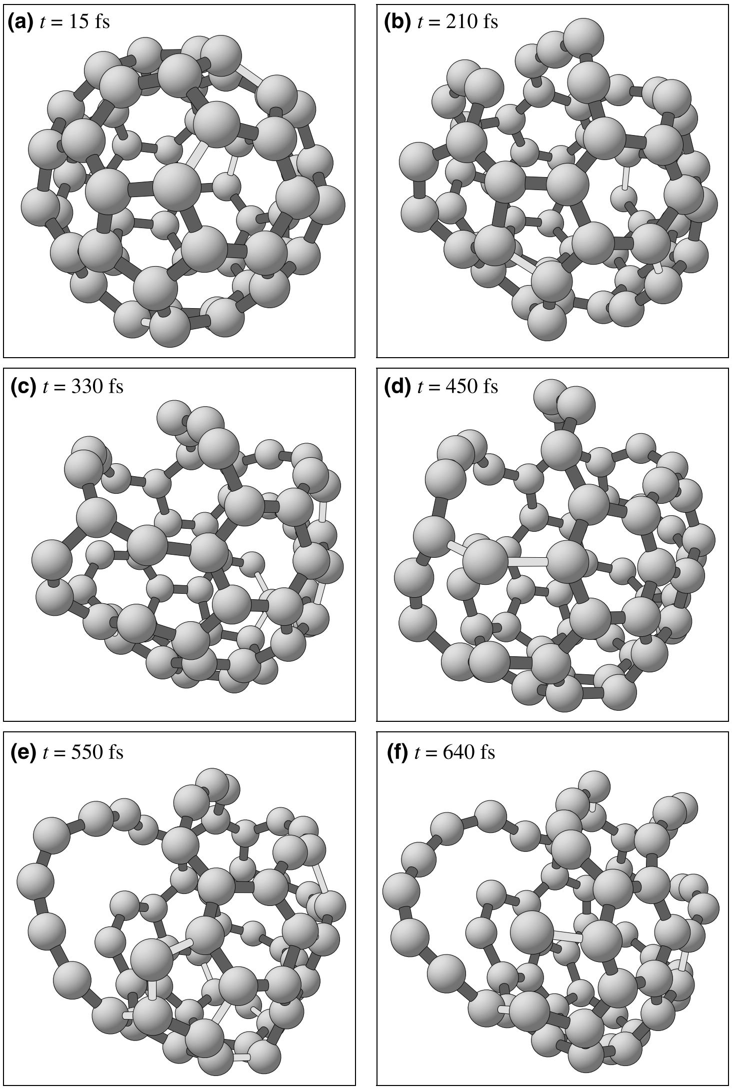

Fig. 2. Nonthermal isomerization of a C_{60} in response to a $\tau = 5$ fs laser pulse. An energy of $E_0 = 2.3$ eV/atom was absorbed. Numerous bonds are broken already at the time $t = 210$ fs after the pulse. The damage develops into a long carbon chain attached on both sides to the remains of the C_{60} cage structure.

certain thermalization of the atomic degrees of freedom starts to occur at $t_d \approx 3$ ps after the pulse maximum. Therefore we define the threshold for nonthermal fragmentation as the maximal absorbed energy for which no fragmentation occurs for $t \leqslant t_d$. 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 $\tau = 5$ to $\tau = 300$ fs duration the threshold is around $E_d = 2.1$ eV/atom. We expect that after redistribution of the energy deposited in the cluster, thermal fragmentation may take place later even for energies below the threshold E_d.

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 [25,26]. These quantities, which are instructive for the characterization of the vibrational excitation and structural changes in C_{60}, are defined by

$$\sigma_i(t) = \sum_j |\mathbf{r}_i(t) - \mathbf{r}_j(t)|, \tag{8}$$

where $\mathbf{r}_i(t)$ 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, σ_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. 4a. The amplitudes of the oscillations of the single atomic equivalence indices σ_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 periodic oscillations as most of the σ_i of the molecule. In the right-hand side of Fig. 4a, the emission of a carbon dimer C_2 can be seen, corresponding to the two approximately parallel σ_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%.

In order to illustrate the dramatic qualitative differences between thermal and nonthermal fragmentation we show in Fig. 4b 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. 2). Beginning at the peak of the very short laser pulse at $t = 0$ fs, the cluster expands strongly. However, this nearly coherent motion is quickly resolved into an incoherent oscillation of the σ_i. Then, σ_i lines with large values emerge at $t = 120$ fs and they do not oscillate. This

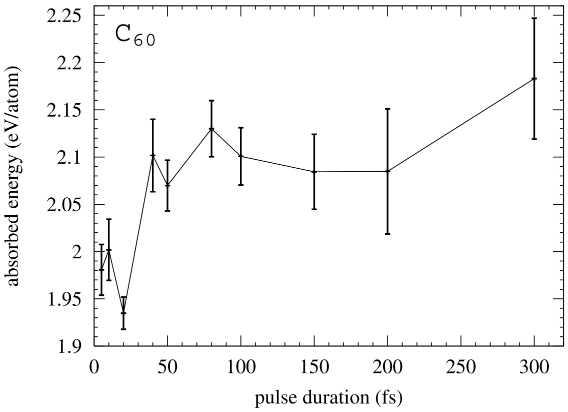

Fig. 3. Nonthermal fragmentation threshold for C_{60} clusters as a function of laser pulse duration. In the range from $\tau = 5$ to $\tau = 300$ fs, no clear dependence of the threshold on pulse duration is observed. A damage threshold of $E_d = 2.1 \pm 0.2$ eV can be attributed to the entire range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

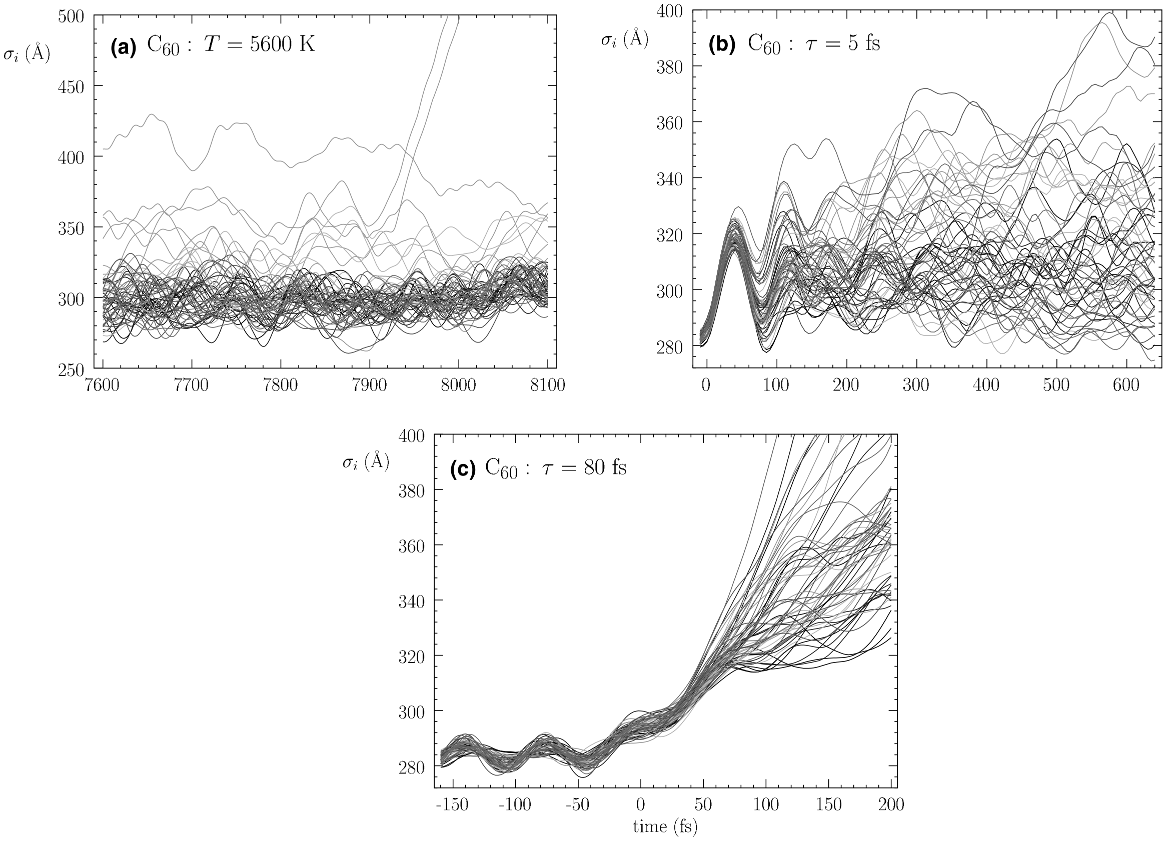

Fig. 4. Atomic equivalence indices $\sigma_i(t)$ for C_{60} clusters. (a) Thermal fragmentation at a temperature $T = 5600$ K. The abscissa indicates the absolute time of the trajectory after heating. At $t = 6.8$ ps the first irreparable damage has developed and can be seen here as the single atomic 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. 2. Immediately after the laser pulse maximum at the time $t = 0$ the cluster expands strongly. At $t = 50$ fs the nearly 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 σ_i evolution corresponds to the cluster in Fig. 1. 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.

indicates damage of the closed cage structure. The range of σ_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. 2.

Fig. 4c shows the time development of atomic equivalence indices $\sigma_i(t)$ during the fragmentation of C_{60} (see Fig. 1). Before the action of the laser pulse of $\tau = 80$ fs duration, the cluster exhibits a breathing mode. 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 σ_i lines stays relatively close to each other corresponds to the fact that a very open linear chain structure has formed in Fig. 1.

In Fig. 5 we show the atomic temperature of C_{60} as a function of time after absorption of $E_0 = 2.3$ and $E_0 = 3.5$ eV/atom from laser pulses of $\tau = 5$

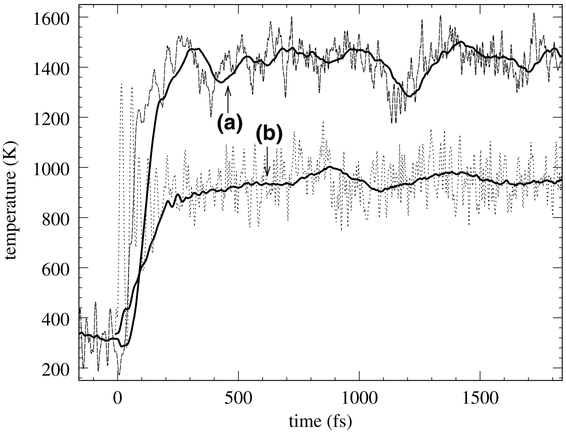

Fig. 5. Atomic temperatures of C_{60} clusters after laser excitation (solid lines). The clusters have absorbed energies of (a) $E_0 = 3.5$ and (b) $E_0 = 2.3$ eV/atom from $\tau = 80$ and $\tau = 5$ fs laser pulses, respectively, and correspond to the same trajectories as Figs. 1 and 2. The dotted lines refer to the instantaneous kinetic energies which have been averaged over intervals of 100 fs for the determination of the shown temperatures. The moderate temperatures that are obtained during the first 2 ps demonstrate that the fragmentation shown in Figs. 1 and 2 is indeed a nonthermal effect.

and $\tau = 80$ fs duration. Only a small fraction of the energy absorbed from the laser pulses is transferred to the atomic motion during the first 2 ps, and the atomic temperatures rise to $T = 900$ and $T = 1400$ K, respectively. Such low temperatures would never lead to dramatic structural changes in thermal equilibrium. Thus, the structural changes shown in Figs. 1 and 2 are mainly due to the strong influence of the electronically excited state on the atomic motion.

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 results with existing experimental evidence based on detection of ionic fragments is difficult. However, experimental fragment mass spectra [9–12] 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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