Supporting Text

Methodology of Simulations

We performed molecular dynamics simulations of inner ionization, nanoplasma response, outer ionization, and Coulomb explosion (CE) of coupled cluster–laser systems. We followed the simulation procedure for high-energy electron dynamics and for nuclear (ion) dynamics developed by Last and Jortner (1, 2). Briefly, the laser electric field F_ℓ was taken as

$$F_\ell = F_{\ell 0}(t)\cos(2\pi\nu t + \varphi_0), \qquad \textbf{[1]}$$

being characterized by a Gaussian-shaped envelope function of the pulse

$$F_\ell(t) = F_M \exp[-2.773(t/\tau)^2], \qquad \textbf{[2]}$$

with the frequency $\nu = 0.35$ fs^{-1} (photon energy of 1.44 eV), phase $\varphi_0 = 0$, and temporal width $\tau = 25$ fs (FWHM of the intensity profile of 18 fs). The electric field maximum F_M is related to the peak intensity I (in Wcm^{-2}) by

$$|eF_M| = 2.745 \times 10^{-7}(I_M)^{1/2}\ \text{eVÅ}^{-1}. \qquad \textbf{[3]}$$

The laser field, Eqs. **1** and **2**, is defined in the temporal range $t > -\infty$, and the peak of the laser pulse is attained at $t = 0$. An initially truncated Gaussian pulse was used in the simulations, with the initial laser field $F_\ell = F_s$ being located at the finite (negative) time $t = t_s$. The initial time t_s for the onset of the simulations was taken as $F_s = (F^{th} + F^{CO})/2$, where F^{th} corresponds to the field-induced one-electron barrier suppression ionization (BSI) of each molecule, while F^{CO} corresponds to the field induced one-electron BSI of all of the atoms (1). Typical values of t_s are given below. At $I_M = 10^{17}$ Wcm^{-2}, $t_s = -24.6$

fs for $(D_2)_n$ and $(HT)_n$, $t_s = -22.7$ fs for $(CD_4)_n$ and $t_s = -27.4$ fs for $(DI)_n$. At $I_M = 10^{18}$ Wcm^{-2}, $t_s = -29.4$ fs for $(D_2)_n$ and $(HT)_n$, $t_s = 27.2$ fs for $(CD_4)_n$ and $t_s = -31.7$ fs for $(DI)_n$. At $I_M = 10^{19}$ Wcm^{-2}, $t_s = -33.5$ fs for $(D_2)_n$ and $(HT)_n$, $t_s = -30.2$ fs for $(CD_4)_n$ and $t_s = -35.6$ fs for $(DI)_n$. The cluster inner ionization was described in terms of the BSI mechanism, which is driven by a composite field consisting of the laser field and the inner field that acts on BSI for each constituent, with the electrons being ionized directly over the barrier (neglecting tunneling effects). When the conditions for BSI of an ion in the composite field are satisfied, the inner ionization event is initiated by locating the removed electron at x_b, which corresponds to the BSI barrier distance. Multielectron ionization is then realized in a sequential way, with one electron being removed at each inner ionization time step of 20 attoseconds (as). The choice of this (arbitrary) ultrashort time step rests on the assumption that in the ultrahigh intensity domain used herein ($I \geq 10^{17}$ Wcm^{-2}) electron tunneling effects on the BSI are negligible. An additional contribution to the inner ionization originates from electron impact ionization (3). The molecular dynamics simulations of the energetic electrons and the ions were performed by classical molecular dynamics, using the five-value Nordsieck predictor–corrector algorithm, with a propagation time step of 1 as for electrons and 20 as for nuclei. These simulations incorporated electron–electron, electron–ion, ion–ion, and electron/ion–laser interactions (1, 2). High-energy electron dynamics included relativistic effects and were subjected to magnetic effects for electron–laser interactions (1). The effects of electron recollision (4, 5), which are of considerable importance for smaller clusters [e.g., C_{60} (5)] and lower intensities ($I_M \leq 10^{15}$ Wcm^{-2}), were included in our treatment of impact ionization. However, these effects are not important for the large clusters at very high laser fields ($I_M \lesssim 10^{17}$ Wcm^{-2}) studied herein. The simulation results provide a complete picture of electron-nuclear dynamics, including hydrodynamic effects.

The validity conditions for the applicability of classical molecular dynamics to the nanoplasma electrons rest on the conditions for the localization of the wavepacket (6) and for the distinguishability of identical particles (7). The wavepacket localization condition (6) implies that the de Broglie wavelength $\lambda_{DB} = h(2m\in)^{-1/2}$ is considerably smaller than the interelectron separation $r_0 = R_0/n^{1/3} \cong 2.2$–$5$ Å (Table 1), where R_0 is the initial

deuterium cluster radius and n is the number of electrons. For $\in$ = 1 keV, λ_{DB} = 0.36 Å. The distinguishability condition for identical particles, which implies the neglect of quantum permutation symmetry constraints, is valid provided that (7) $f = \exp[-(r_0/\lambda_{DB})^2] << 1$. For $\in$ = 1 keV, f is negligibly small ($f \sim 10^{-32}$), so this condition is satisfied over the entire relevant electron energy domain.

Nonuniform CE of $(DI)_n$ Heteroclusters. Electron and nuclear dynamics in $(DI)_{2171}$ heteroclusters, coupled to a Gaussian laser field with peak intensity $I_M = 10^{18}$ Wcm^{-2} (Fig. 7), manifest the following facets of electron and nuclear dynamics: (*i*) the formation and response of the nanoplasma (snapshots *b* and *c* in Fig. 7), (*ii*) the onset of CE before the complete depletion of the nanoplasma (snapshots *b* and *c* in Fig. 7), (*iii*) the completion of the outer ionization (snapshot *d* in Fig. 7), and (*iv*) the subsequent highly nonuniform CE (snapshots *e* and *f* in Fig. 7), which results in the formation of exterior spherical nanoshells of the light D^+ ions.

Energetics and Dynamics of CE of Deuterium Containing Molecular Clusters. The cluster size dependence of the energetics of CE (Fig. 3) were analyzed by the scaling laws for the D^+ ions (see text) $E_M = Zn^{2/3}$ and $E_{av} = \kappa E_M$. The Z parameters evaluated from the simulation data (Fig. 3) are assembled in Table 1. In Table 1 we also present the predictions of the electrostatic models for the following cases:

1. Uniform CE of homonuclear $(D_2)_n$ clusters;
2. Uniform CE of $(CD_4)_n$ [a scheme that is only approximate, as at $I = 10^{18}$ the CE of $(C^{4+}(D^+)_4)_n$ is η_{DC} = 1.5].
3. Nonuniform CE of the $(DI)_n$ and $(CD_3I)_n$ ECLHHs.

The Z data presented in Table 1 exhibit good agreement within 10% between EML and simulation results for $(D_2)_n$ and $(CD_4)_n$. For the $(DI)_n$ and $(CD_3I)_n$ ECLHHs the EML overestimates the Z values by ≈30%, because of the limitations of this model, which does not account for the concurrent expansion of the interior $(I^{q+})_n$ subcluster.

In Table 1 we also present the dynamic data for the time dependence of $\langle R \rangle / \langle R \rangle_0$. The slopes a of the linear time dependence $\langle R \rangle / \langle R \rangle_0 = a(t - t_{onset})$ are compared in the text with the predictions of the electrostatic model, in excellent agreement for $(D_2)_n$ and with a 20% agreement for $(DI)_n$.

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