Embedded metal cluster in strong laser fields
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Abstract
We discuss microscopic mechanisms of the violent dynamics following strong laser excitation of a metal cluster embedded in a rare gas matrix, taking as test case Na₈@Ar₄³₄. This covers at least two aspects: first, it represents the typical experimental situation of metal clusters handled in raregas matrices or a finite drop of surrounding raregas material, and second, it serves as a generic test case for highly excited chromophores in inert surroundings addressing questions of energy transport and perturbation of the medium. We simulate the process up to 10 ps using a mixed quantum mechanical (for the electrons) and classical (ions and atoms) approach and analyze the emerging dynamics with respect to all basic constituents: cluster electrons, cluster ions, and matrix atoms. We find several stages of relaxation taking place with time scales from a few fs to over a few ps and much slower processes remaining for long after the simulation. A particularly interesting aspect is that the surrounding raregas material stabilizes a highly charged metal cluster which would otherwise explode without delay.

Key words: metal clusters, raregas matrix, strong laser fields, energy transport, Coulomb explosion, pump-probe analysis, time-dependent density-functional theory, polarization potentials
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1. Introduction
Nanotechnology, which was predicted long ago to stimulate an industrial revolution [1], now constitutes a fast developing research field, for example to increase the control of material at nanometer scale [2]. Especially metal clusters have attracted much attention in the past decades [3,4,5,6,7,8]. Among their many interesting characteristics and applications, their optical properties are particularly appealing [3]. These are dominated by the Mie surface plasmon which plays a key role in all dynamical regimes [8]. It provides a strong coupling to photons in a very narrow frequency window which makes clusters an ideal laboratory for laser induced non-linear dynamics [9,10]. The plasmon also serves as a versatile handle for pump and probe experiments [11,12,13,14,15], and it provides the key mechanism in driving the hefty Coulomb explosion of clusters [16,17]. For a recent summary on this great variety of phenomena of the dynamics of free metal clusters, see [18,19]. An even richer variety of phenomena emerges for metal clusters in contact with other materials, either embedded in a matrix or deposited on a surface. There is, e.g., second harmonic generation [20,21,22], dedicated shaping of clusters with intense laser pulses [23,24],

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and many more new phenomena emerging from the combination, for a review see [25]. Thus the proper combination of materials is a key issue in nanotechnology [26]. There are also practical reasons for dealing with such compounds. The substrate simplifies the handling of the clusters such that many interesting experiments can only be done with clusters in contact with a carrier material [27,28,29,30]. Simple compounds are also useful model systems for principle studies. For example, clusters in contact with insulators can serve as a versatile model system for chromophores which can be used as indicators in biological tissues [31,32] or for studies of radiation damage in materials [33,34]. The latter application deals with high energy density related to intriguing questions of energy, momentum and particle transport in materials. It is this aspect which we will address in the present manuscript. We are going here to study from a theoretical perspective the (hindered) Coulomb explosion of a metal cluster embedded in a raregas matrix. That as such is a topic of actual interest in cluster physics, see e.g [10,13,35,36,37]. And it serves as a well manageable test case for the more general issue of strong energy impact on matter and subsequent transport processes which are also of high current interest [38,39,40].

The theoretical description of embedded clusters is a great challenge because of the inevitable complications by the cluster-matrix interface and because of the huge number of atoms in the matrix. This holds even more so for the simulation of their dynamics. The quest for robust and efficient schemes is omnipresent in all areas where one deals with large compounds. The solutions rely usually on a hierarchical modeling combining carefully quantum-mechanical and classical descriptions, see e.g. [41] for bio-molecules or [42,43] for chemical reactions on surfaces. Along these lines, we have developed a hierarchical model for the dynamics of metal clusters in contact with rare gas materials [44,45]. First successful tests of the performance of this approach in the moderately non-linear regime were presented in [46,47].

In this paper, we continue the study of the dynamics of embedded metal clusters, considering now a violent laser excitation. The intensity is chosen such that a free cluster would explode immediately while the embedded configuration remains intact for a sufficiently long observation time of several ps. As test case, we consider the dynamics of a Na₈ cluster embedded in Ar₄₃₄, following irradiation by an intense and short (33 fs) laser pulse. We will pay particular attention to the impact of the environment on the dynamics of the metal cluster and analyze the interlaced processes from several points of view: detailed ionic and atomic trajectories, evolution of global shape parameters (radius, quadrupole deformation) with their associated vibrational time scales, and energy transfer providing information on the various relaxation times. Finally, we discuss a possible identification by pump and probe analysis in relation to recent experiments [23].

2. Formal framework

In order to allow for a sufficiently large Ar matrix, we use a hierarchical approach. The many different ingredients make a complete representation rather bulky. In that section, we sketch only briefly the basic constituents of the approach and refer to [44,48] for a detailed layout.

The Na cluster is treated in full microscopic detail using quantum-mechanical single-particle wavefunctions \{\varphi_{n}(\mathbf{r},t), n = 1...N_{Na}\} for the valence electrons. These are coupled non-adiabatically to classical molecular dynamics (MD) for the Na ions which are described by their positions \{\mathbf{R}_{I}, I = 1...N_{Na}\}. The electronic wavefunctions are propagated by time-dependent local-density approximation (TDLDA). The electron-ion interaction in the cluster is described by soft, local pseudo-potentials. This TDLDA-MD has been validated for linear and non-linear dynamics of free metal clusters [8,9].

Two classical degrees-of-freedom are associated with each Ar atom: center-of-mass \{\mathbf{R}_{a}, a = 1...N_{Ar}\}, and electrical dipole moment which is parameterized as \{\mathbf{R}'_{a} = \mathbf{R}_{a} + \mathbf{d}_{a}, a = 1...N_{Ar}\}. Note that the Ar dipole is practically handled by two constituents with opposite charge, positive Ar core (at \mathbf{R}_{a}) and negative Ar valence cloud (at \mathbf{R}'_{a}). With the atomic dipoles, we explicitly treat...
the dynamical polarizability of the atoms through polarization potentials [49]. Smooth, Gaussian charge distributions are used for Ar ionic cores and electron clouds in order to regularize the singular dipole interaction. We associate a Gaussian charge distribution to both constituents having a width of the order of the 3p shell in Ar, similar as was done in [51]. The Coulomb field of the (softened) Ar dipoles provides the polarization potentials which are the dominant agents at long ranges. The Na+ ions of the metal cluster have net charge qNa = +1 and interact with the Ar dipoles predominantly by the monopole moment. The small dipole polarization of the Na+ core is neglected. The cluster electrons do also couple naturally to the Coulomb field generated by the atoms.

The model is fully specified by giving the total energy of the system. It is composed as

$$E_{\text{total}} = E_{\text{Na cluster}} + E_{\text{Ar}} + E_{\text{coupl}} + E_{\text{VdW}}.$$  

The energy of the Na cluster $E_{\text{Na cluster}}$ consists out of TDLDA for the electrons, MD for ions, and a coupling of both by soft, local pseudo-potentials; that standard treatment is well documented at many places, e.g. [8,9]. The Ar system and its coupling to the clusters are described by

$$E_{\text{Ar}} = \sum_a \frac{P_a^2}{2M_{\text{Ar}}} + \sum_a \frac{P_a^2}{2m_{\text{Ar}}}$$

$$+ \frac{1}{2} k_{\text{Ar}} (R_a' - R_a)^2$$

$$+ \sum_{a < a'} \left[ \int d\rho_{\text{Ar},a}(r) V^{(\text{pol})}_{\text{Ar},a}(r) \right.$$  

$$\left. + V^{(\text{core})}_{\text{Ar}}(R_a - R_{a'}) \right] ,$$  

$$E_{\text{coupl}} = \sum_{I,a} \left[ V^{(\text{pol})}_{\text{Ar},a}(R_I) + V^{(\text{pol})}_{\text{Na},a}(R_I - R_a) \right]$$

$$+ \int d\rho_{\text{Red}}(r) \sum_a \left[ V^{(\text{pol})}_{\text{Ar},a}(r) \right.$$  

$$\left. + W_{\text{el Ar}}(r - R_a) \right] ,$$  

$$V^{(\text{pol})}_{\text{Ar},a}(r) = e^2 q_{\text{Ar}} \left[ \frac{\text{erf}(|r - R_a|/\sigma_{\text{Ar}})}{|r - R_a|} \right. \right.$$

$$\left. \left. - \frac{2}{1 + e^{\alpha_{\text{Na}}/R}} \left( \frac{C_{\text{Na},6}}{R^6} + \frac{C_{\text{Na},8}}{R^8} \right) \right] ,$$  

$$V^{(\text{core})}_{\text{Ar},a}(r) = e^{\beta_{\text{Na}} R}$$

$$\frac{2}{1 + e^{\alpha_{\text{Na}}/R}} \left( \frac{C_{\text{Na},6}}{R^6} + \frac{C_{\text{Na},8}}{R^8} \right) ,$$  

$$E_{\text{VdW}} = \frac{e^2}{2} \sum_a \left[ \frac{1}{N_{\text{el}}} \left( \int \frac{d\rho_{\text{Red}}(r)}{|r - R_a|} \right)^2 \right.$$  

$$\left. - \frac{2}{1 + e^{\alpha_{\text{Na}}/R}} \left( \frac{C_{\text{Na},6}}{R^6} + \frac{C_{\text{Na},8}}{R^8} \right) \right] ,$$  

$$\text{erf}(r) = \frac{2}{\sqrt{\pi}} \int_0^r dx e^{-x^2} .$$  

The calibration of the various contributions is taken from independent sources, except perhaps for a final fine tuning to the NaAr dimer modifying only the term $W_{\text{el Ar}}$ of Eq.(4). The parameters are summarized in table 1. The third column of the table indicates the source for the parameters. In the following, we report briefly the motivations for the choices.

Most important are the polarization potentials defined in Eq.(3). They are described by the model of a valence electron cloud oscillating against the raregas core ion. Its parameters are: $q_{\text{Ar}}$, the effective charge of valence cloud, $m_{\text{Ar}} = q_{\text{Ar}} m_{\text{el}}$ the effective mass of valence cloud, $k_{\text{Ar}}$ the restoring force for dipoles, and $\sigma_{\text{Ar}}$ the width of the core and valence clouds. The $q_{\text{Ar}}$ and $k_{\text{Ar}}$ are adjusted to reproduce the dynamical polarizability $\alpha_D(\omega)$ of the Ar atom at low frequencies, i.e. we choose to reproduce the static limit $\alpha_D(\omega = 0)$ and the second derivative of $\alpha''_D(\omega' = 0)$. The width $\sigma_{\text{Ar}}$ is determined consistently such that the restoring force from the folded Coulomb force (for small displacements) reproduces the spring constant $k_{\text{Ar}}$.

The short range repulsion is provided by the various core potentials. For the Ar-Ar core interaction,
Eq. (5), we employ a Lennard-Jones type potential with parameters such that binding properties of bulk Ar are reproduced. The Na-Ar core potential, Eq. (6), is chosen according to [50]. Note that the Na-Ar potential from [50] does contain also a long range part $\alpha_{Ar}$ which accounts for the dipole polarization-potential. We describe that long range part explicitely and have to omit it here. We thus choose the form as given in $V'_{ArNa}$.

The pseudo-potential $W_{elAr}$, Eq. (4), for the electron-Ar core repulsion has been modeled according to the proposal of [51]. Its parameters determine sensitively the binding properties of Na to the Ar atoms. We use them as a means for a final fine-tuning of the model. The benchmark for adjustment is provided by the Na-Ar dimer. The dimer binding energy, bond length, excitation energy) are taken from [60] and [61]. The adjustment shows some freedom in the choice of $A_{el}$. We exploit that to produce the softest reasonable core potential.

The Van-der-Waals energy $E_{VdW}$, Eq. (8), is a correlation from the dipole excitation in the Ar atom coupled with a dipole excitation in the cluster. We exploit that $\omega_{Mie}$ is far below the excitations in the Ar atom. This simplifies the term to the variance of the dipole operator in the cluster, using again the regularized dipole operator $f_{r_{d}}$ defined in Eq. (9), corresponding to the smoothened Ar charge distributions. The full dipole variance is simplified in terms of the local variance.

The classical MD for Na ions, Ar atoms and Ar dipoles is treated in full three dimensions. However, the quantum mechanical treatment of the Na cluster involves two approximations. The Kohn-Sham equations for the electron cloud involves axially averaged potentials and the self-interaction correction (SIC) to TDLDA is treated at the level of average-density SIC (ADSID) [62,63]. Both approximations enhance somewhat the barriers for fragmentation of the cluster. The axial approximation and ADSIC are needed to allow the large scale calculations performed here. The SIC, on the other hand, is compulsory for an appropriate description of ionization which is the leading process in the initial stage of laser excitation. These two approximations mean that we provide rather a qualitative picture. The effects shown are certainly relevant. The thresholds concerning charge state and laser field strength are probably not too precise. However we also dispose of a full three-dimensional treatment for the valence electrons which, moreover, can handle various levels of SIC and even exact exchange. We used that for occasional counterchecks and we never found significant deviations from the approximate treatment.

Finally, a few words are in order about the possible range of validity for that hierarchical model. The structure of the coupled systems is well described by construction, see the predecessor in [51] and the extensive testing in [44]. The same holds for optical response (see [45,64]). However, one has to remain aware that the model has limitations with respect to allowed frequencies and amplitudes. The dynamical response of the Ar atoms is tuned to frequencies safely below the Ar resonance peak, i.e. safely below 1 Ry. This is well fulfilled in all our calculations because the leading frequency is the

\[
V^{pol}_{Ar,el} = \frac{\alpha_{Ar} m_{el} \omega_{Mie}^2}{c^2}, \quad k_{Ar} = \frac{e^2 q_{Ar}^2}{\alpha_{Ar}}, \quad m_{Ar} = \frac{q_{Ar} m_{el}}{\alpha_{Ar}}
\]

\[
\sigma_{RG} = \left( \frac{\alpha_{Ar} 4 \pi}{3(2\pi)^{3/2}} \right)^{1/3}
\]

\[
W_{elAr} = \beta_{el} = 0.47, \quad A_{el} = 1.6941 /a_0, \quad r_{el} = 2.2 a_0 \quad \text{fit to NaAr}
\]

| Parameters | Value |
|------------|-------|
| $A_{el}$   | 1.367 * 10^{-3} Ry |
| $R_{Ar}$   | 6.501 a_0 |
| $A_{Na}$   | 334.85 |
| $C_{Na,6}$ | 52.5 a_0^6 |
| $C_{Na,8}$ | 1383 a_0^8 |
| $A_{Na}$   | 1.815 a_0 |
| $\beta_{Na}$ | 1.7624 a_0^{-1} |
| $\alpha_{Na}$ | 1.815 a_0 |
| $\omega_0$ | 1.755 Ry |

Table 1

Parameters for the various model potentials.
cluster’s Mie plasmon at around 0.2 Ry. The amplitudes of the dipole oscillations in Ar should stay below the threshold where free electrons are released from the Ar atom into the matrix. We have checked that process by fully quantum mechanical calculations of laser excitation on Ar atoms and we find a critical field strength of order of 0.1 Ry/\(a_0\). We protocol during our calculation the actual field strength at each Ar site and thus check that we do not exceed that limit in our simulations.

3. The test case

We focus here on a Na\(_8\) cluster embedded in a large Ar cluster with 434 atoms. This should serve as a finite model of an Ar matrix, although aspects of finite mixed clusters will also be addressed briefly. From a more general perspective, we encounter here a typical example of a chromophore inside an inert environment. The case is particularly interesting because the mix of simple materials allows to concentrate on the basic effects of a chromophore without the need to bother about the elaborate technical details of more complex materials, as e.g. large organic molecules. We consider the case of low initial temperatures, safely below the Ar melting point of 84 K, where spatial fluctuations of the atoms and ions can be safely neglected.

The small Na cluster at low temperature has a very clean excitation spectrum with rather narrow excitation peaks in the plasmon range around 2.5 eV [8]. Correlation effects beyond TDLDA remain negligible for the global observables considered here. Spectral fragmentation from coupling to energetically close electron-hole states (Landau fragmentation) is negligible for that system size because the Mie surface plasmon resides in a gap of such states [53]. Broadening from higher correlations is also small [54], again due to the spectral gap for that magic electron number. Thermal broadening in the initial state is negligible at the presently studied low temperatures [52]. Larger electronic temperatures develop in the course of the dynamics and they call, in principle, for a description beyond pure mean field. Electron-electron collisions could be included by switching to a semi-classical Vlasov-Uehling-Uhlenbeck description of the electron cloud [48,65]. But long-time semi-classical propagation is still extremely hard to stabilize and, as we will see in section 4.3, electrons are thermally almost decoupled from ions. Thus we can neglect that effect for time scales explored in the present study. The surrounding Ar cluster has to be sufficiently large to absorb the energy from the highly excited chromophore without breakup and to avoid specific size or surface effects. We have checked matrix sizes from 30 to 1048 Ar atoms for the dynamical regime intended here and found qualitatively similar behaviors from 164 Ar atoms on. To be on the safe side, the present results have been obtained for a model matrix of 434 Ar atoms. The setup was generated by cutting a closed pack of 447 Ar atoms out of a crystal, removing further 13 atoms from the center, placing the Na\(_8\) in the cavity, and finally re-optimizing the whole configuration by Monte-Carlo simulated annealing techniques. The Na\(_8\) cluster with a radius of 7 \(a_0\) (r.m.s.-radius of 5.5 \(a_0\)) then resides in a cavity of about 10 \(a_0\) radius. The outermost Ar shell has a radius of 31 \(a_0\). This provides a substantial coverage of the embedded Na\(_8\). The spatial structure is still very close to the configuration before re-optimization [45]. The Na\(_8\) consists out of two rings of four ions each and the rings have a relative rotation of 45° to minimize the Coulomb repulsion between the ions. The global shape is axially symmetric, only slightly oblate deformed. The surrounding Ar maintains basically its original crystal structure with some small rearrangement for the innermost shells.

The dynamics in the linear regime was studied in [45]. A first case of moderate laser excitations was discussed in [46]. Here we aim at a more violent, still non-destructive, process. To that end, we irradiate the Na\(_8\)@Ar\(_{434}\) system with a laser of frequency 1.9 eV, intensity \(2.4 \times 10^{12}\) W/cm\(^2\), and a \(\cos^2\) pulse envelope with total pulse length of 100 fs (FWHM = 33 fs). The laser is polarized along the symmetry axis of the system, henceforth called z axis. The rather short and intense laser excitation produces very quickly a net ionization stage 3\(^+\) and deposits a large amount of energy in the system. We then continue to propagate the system up to about 10 ps in order to cover the relevant
time scales.

4. Results and discussion

4.1. Detailed view at the propagation of ions and atoms

The initial reaction of the system is dominated by the large dipole response of the electrons. For the short pulses used here, the strong electrical field with subsequently large dipole amplitude leads to a direct emission of 3 electrons which escape instantaneously (i.e., within 3-10 fs). The thus produced large Coulomb pressure leads to a rearrangement of the whole system (Na ions and Ar atoms) at ionic/atomic time scale as is demonstrated in figure 1 showing the time evolution of Na ions and Ar atoms in detail. It exhibits different interesting time scales. The first time scale (after the electronic one, of order of a few fs) is observed in the reaction of the Na ions. They perform a Coulomb explosion whose first signs can be seen at about 50 fs. That proceeds almost identical to the similar case of a free Na\(_8\) cluster lifted to charge 3\(^+\). But the “explosion” is abruptly stopped at about 200 fs when the ions hit the repulsive core of the first shell of Ar. The ionic motion turns to damped oscillations around a (r.m.s.) radius of about 7 \(a_0\).

In atoms, one also observes two stages, although on longer time scales. The first phase is a spreading of the perturbation (caused by the stopping of Na ions) into the various Ar shells. This is especially visible along the z axis which allows to read off the propagation speed of this perturbation as 20-30 \(a_0/\text{ps}\). We have estimated the sound velocity in the corresponding large pure Ar cluster (Ar\(_{447}\)) by computing its vibrational spectrum. The radial compression mode corresponds to the sound mode in bulk material. Its frequency is \(\omega_{\text{vib}} = 1.8\) meV. The momentum of the radial wave is \(q = \pi/R\) where \(R = 30\) \(a_0\) is the cluster radius. The sound velocity is then estimated as \(v_{\text{sound}} = \omega_{\text{vib}}/q \approx 30\) \(a_0/\text{ps}\) which is very close to the propagation speed as observed in the figure. This suggests an interpretation as a sound wave sent by the initial bounce of the Na ions.

Once transferred to a given Ar shell the perturbation generates oscillations combined with some diffusion which after about 1.5 ps has spread over all shells. The perturbations affect even the outermost shell which thus acquires some oscillations. That is an effect of finite size of the “matrix”. The oscillation amplitude shrinks with increasing system size and grows towards smaller matrices. For example, it was found to be smaller for the larger test case with 1048 Ar atoms and the last Ar atoms are even kicked away for matrices at and below 164 Ar atoms. The reason is twofold: smaller system provide, first, less Ar shells to absorb energy, and second, less dipole binding as whole. This question will be discussed more systematically in a larger forthcoming paper.

The relaxation of matrix oscillations is much slower than that of Na ions and beyond the time scale computed here. These long time scales for full relaxation and evaporation of Ar atoms are well known from experiments of dimer molecules embedded in Ar clusters, see e.g. [55].

We finally comment briefly on the finite net charge of our test system. It emerges because the electrons propagate almost unhindered through the surrounding Ar cluster and eventually escape to infinity. In a macroscopically large matrix, the electrons would be stuck somewhere within the range of their mean free path, drift very slowly back towards the now attractive cluster well, and eventually recombine there. We have simulated that by using reflecting boundary conditions rather than absorbing ones and we find recombination times of the order of several 10 ps. Furthermore the ionic/atomic rearrangements following the irradiation turn out to be qualitatively very similar whatever the boundary conditions. Thus the present scenario should provide a pertinent picture for several ps, the time window studied here.

4.2. Time evolution of global shapes

Figure 2 visualizes the ionic/atomic dynamics in terms of simple global observables. The middle panel shows the ionic r.m.s. radius which provides an even clearer picture of the ionic dynamics de-
Fig. 1. Time evolution of the atomic (full lines) and ionic (dotted lines) $z$-coordinates (lower panel) and radial distances $r = \sqrt{x^2 + y^2 + z^2}$ (upper panel) for $Na_8Ar_{434}$ excited with a laser of frequency $\omega = 1.9$ eV, intensity $2.4 \times 10^{12}$ W/cm$^2$, and a cos$^2$ pulse profile with FWHM = 33 fs. The laser was polarized along the $z$ axis which is also the symmetry axis of the system.

scribed above. Let us first concentrate on the lower two panels showing the global radial oscillations (breathing). The electronic radius expands during the short excitation phase. However, as soon as the laser is switched off after 100 fs, the electronic radius quickly relaxes towards the ionic one, as can be seen in the lower panel of figure 2. Indeed the strong monopole Coulomb forces ties electronic and ionic radius always closely together. The radial oscillations of the cluster have the typical cycle of about 250 fs, well known from free Na clusters [56] and re-established for embedded ones [46]. The most interesting aspect is here the clearly visible relaxation of the cluster oscillations at a time scale of about 4 ps. It seems that a slow energy transfer from the ionic cluster vibrations into the raregas environment takes place. This will be inspected further in section 4.3. The breathing oscillation of the Ar environment (i.e. of the atomic radii) proceeds at a cycle of about 3 ps (see middle panel of figure 2), corresponding to a volume frequency of about 1.4 meV. This is within fac-
Fig. 2. Time evolution of global shape observables of atoms (solid lines), ions (dotted lines), and electrons (fine dashed lines). Lowest panel: r.m.s. radii of cluster constituents, ions and electrons. Middle panel: r.m.s. radius of Ar atoms. Upper panel: Quadrupole moments of ions and atoms.

The upper panel complements the analysis by the quadrupole moments of the Na cluster (ions) and of the Ar atoms. The quadrupole oscillations of both subsystems are again at their very own time scale which a very long cycle time, about 7 ps, for quadrupole motion of the Ar atoms. The Na cluster shows, moreover, a global trend to finally oblate shapes. Note that a similar effect, the build-up of persistent quadrupole deformations following laser irradiation, has been observed for Ag clusters embedded in glass [23]. Glass is a much harder material than Ar but we may speculate that the strong laser pulse provides also an intense heating, and thus melting, of the immediate neighborhood of the embedded cluster. For then the mechanisms of deformation may be similar.
4.3. Energetic aspects

The lower left panel of figure 3 shows the kinetic energies of ions and atoms. The Na ions gather energy very quickly from the starting Coulomb explosion. At around 200 fs, the quickly acquired energy is transferred abruptly to the atoms, leaving only one fifth of kinetic energy for the first phase of ionic oscillations. From then on, both kinetic energies proceed for a while at nearly constant values with some residual oscillations. At around 2 ps, a slow transition seems to take place where the ionic energy flows towards the atomic subsystem. The situation stabilizes after 3 ps to a thermal share of energies where practically all kinetic energy resides in the atoms and only a tiny fraction remains for the ions. However, the notion of “thermal share” does not imply a full equilibrium even at final simulation time of 9.5 ps. We know from figure 2 that there are very slow and long lasting atomic vibrations. We should call the present situation more correctly a local (or instantaneous) equilibrium.

The global atomic breathing oscillations carry still a large amount of energy. To quantify that aspect we have computed the collective energy. The fine dashed line in the lower left panel shows the remaining “internal” kinetic energy of the atoms. And indeed, almost two thirds of the energy reside still in the collective breathing yet awaiting final thermalization at a time scale far beyond 10 ps. Nonetheless, it is interesting to have a look at the distribution of kinetic energies. This is shown in the upper left panel of figure 3. It is the distribution of the total kinetic energies and it is compared with the thermal distribution at a temperature of 20 K, equivalent to the full kinetic energy at the late
times in the plot. Both distributions compare fairly well in view of the fact that full equilibrium has not yet been reached (thus allowing for somewhat larger fluctuations).

The right panel sketches the main energy share in the reaction. The system acquires as much as 23 eV energy from the laser pulse. The by far largest portion, namely 83%, is carried away very quickly by the emitted electrons. Two thirds from what remains flow into ionic and atomic motion. We have learned from the lower left panel that this energy arises from the stopped Coulomb explosion, and is shared in two steps between ions and atoms: initially, the ions acquire a large potential energy from sudden charging, this is converted through “Coulomb explosion” instantaneously to a large kinetic energy, which then is transferred quickly to the atoms when the “explosion” is abruptly stopped. A somewhat slower second phase of energy transfer follows after 2 ps which is related to rearrangement and some exchange with still available potential energy. One third of the remaining energy, i.e. about 1 eV, remains with the electrons as internal kinetic energy (this is the excess kinetic energy beyond the unavoidable quantum mechanical minimum, see [9]). That is very little in view of the fact that it has been the cluster’s electron cloud which served as doorway to absorb all energy from the laser field. It is, however, a great deal in terms of temperature. The electronic temperature corresponds to 1500 K whereas the ionic/atomic temperature has yet come up to only 18 K. That makes it clear that the process resides still in a transient stage where the electronic and the ionic/atomic subsystems have reached a local equilibrium amongst themselves. Full equilibration and subsequent evaporative cooling will follow at a much longer time scale, far beyond the capabilities of the very detailed description through a TDLDA-MD approach.

There remains the question which energetic aspects are generic for metal clusters in a rare gas environment and which are specific to the particular mixed system studied here. The generic aspects are related to what happens with the cluster and its immediate rare gas vicinity. This concerns the energy absorption from the laser which proceeds predominantly through the metal cluster’s electrons, the stopping of the Coulomb explosion and associated fast energy transfer to the atoms, the relaxation time scales in these early phases of a few ps, and the energy balance in absolute numbers. The particular property which depends on the matrix size is most of all the atomic temperature. We find that the same absolute amount of energy is transferred from the laser to the Na$_{8}$ cluster, independent of matrix size. The energy loss through ionization is also the same. Thus the final atomic temperature will then be inversely proportional to the matrix size.

4.4. Possible pathways to experimental analysis

The question remains how one could analyze the key pattern of the embedded cluster dynamics experimentally. The most interesting effect is the hindered explosion of the imprisoned Na cluster and its subsequent shape oscillations in the Ar cavity. Such shape oscillations and eventual relaxation to deformed shape have been produced and observed experimentally for Ag clusters embedded in glass [23] or deposited on a substrate [58]. The (time-dependent) cluster deformation is verified by probe pulses measuring the actual optical response of the metal cluster, exploiting the pronounced features of the Mie plasmon resonance. Indeed, the plasmon couples strongly to light at very specific frequencies and these plasmon frequencies are uniquely related to the cluster shape. For free clusters, we have discussed a rather simple pump-and-probe setup which allows to map in a unique fashion the evolution of radial shape [12], of quadrupole deformations [59] and of elongation in a fission process [14,15]. We have computed that for the case considered here. To this end, we take the instantaneous configuration at a given time and compute the optical response in all three spatial directions. These expensive calculations have been performed in full 3D TDLDA (which allows to properly access the directions perpendicular to the laser polarization axis) on a representative time of extremal deformations. The other points are interpolated by well benchmarked plasmon calculations for a smaller subsystem. Results are shown in figure 4. The radial oscillations (middle panel of figure 2) re-
late to the oscillations of the average peak position which are particularly well visible here in the early phase up to about 1.5 ps. The then evolving oblate deformation leads to a splitting of the resonance peak where the shorter extension along $z$ is associated to a blue shift of the mode and the larger extension in orthogonal direction to a red shift. The $x$ and $y$ modes are nearly degenerate due to near axial symmetry of the total system. Pump and probe analysis of the time-dependent plasmon peaks thus provides worthwhile information about the shapes of the embedded cluster, which can be measured by probe pulse as explained in [12,59,14,15]. Note here that the experimental results obtained for Ag clusters in glass [23] are in qualitative agreement with our findings. Our model thus provides a microscopic interpretation, the first one, to the best of our knowledge, of these experimental investigations.

5. Conclusion

In this paper, we have analyzed the dynamics of a Na cluster embedded in an Ar matrix following irradiation by an intense laser pulse. We have used a hierarchical model with a detailed quantum-mechanical treatment of the electron cloud in the Na cluster and a classical description of the Na ions and surrounding Ar atoms whereby we include the Ar dipole moments to account for the dynamical polarizabilities. As test case, we have considered Na$_8$@Ar$_{134}$ which provides several interesting aspects: It is a prototype of a chromophore in an else-wise inert material, it serves as model for a cluster embedded in a raregas matrix, and we do also find interesting features which are specific for a finite mixed cluster. For the excitation mechanism, we consider irradiation by a short 33 fs laser pulse with intensity of about $10^{12}$ W/cm$^2$. The laser couples almost exclusively to the clusters electron cloud and deposits about 23 eV energy in the system. This leads to immediate ionization of Na$_8$ to a 3$^+$ charge state. The subsequent Coulomb explosion of the Na$_8$ is abruptly stopped by the Ar atoms, turning the motion into steady shape oscillations of the cluster while the absorbed momentum spreads in a radial sound wave propagating through the atoms and triggers global radial oscillations thereof. A second phase around 2-3 ps transfers most of the remaining ionic energy to the atoms and cools the ions to almost atomic temperature. The relaxation process can be nicely seen in oscillations of cluster radius and deformation. Both these observables are accessible to experimental observation by an especially designed pump-and-probe setup.

A further interesting feature is that the Ar surroundings do not only stop the Coulomb explosion. They even stabilize the high charge state at a time scale which is sufficiently long for an observation of ionic and atomic motion. This is probably a particular feature of finite mixed clusters. The surrounding Ar system should be large enough to deliver stabilization through induced dipole attraction, but small enough such that the cluster electrons which are directly emitted due to the laser excitation can travel nearly unhindered through the Ar shells and finally escape to whole system. The degree of charge stabilization in dependence of system size and the mean free path of electrons through ordered raregas shells is a task for future studies.

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