Theory for the Nonlinear Ultrafast Dynamics of Small Clusters after Ionization

M. E. Garcia\textsuperscript{1}, D. Reichardt\textsuperscript{2} and K. H. Bennemann\textsuperscript{1}

\textsuperscript{1}Institut für Theoretische Physik der Freien Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.

\textsuperscript{2}Walther-Nernst Institut für Physikalische und Theoretische Chemie, Humboldt Universität zu Berlin, Bunsenstr. 1, 10117 Berlin, Germany

(November 3, 2018)

Abstract

The ultrafast relaxation of small clusters immediately after ionization is studied. For small Hg\textsubscript{n} clusters we determine the fragmentation-time distributions induced by ionization. A dramatic change of the fragmentation behaviour occurs when the temperature before ionization reaches the melting point of the neutral clusters. The ultrafast dynamics depends nonlinearly on initial conditions regarding atomic positions and velocities. The resultant largest Lyapunov exponent increases strongly upon ionization.

36.40.-c, 31.70.Hq, 32.80.Fb

Typeset using REVTeX
A fundamental problem in the physics of small clusters and molecules is the description of the relaxation mechanisms in the sub-picosecond time-domain. The ultrafast dynamics (UD) of a cluster is usually induced with the help of an ultrashort laser pulse which excites or ionizes the cluster, abruptly transferring it to a nonequilibrium state. It is presently still unclear how the excess energy released by this process is transferred to the various modes of the cluster.

Since the recent development of the Femtosecond Spectroscopy [1], which permits a time-resolved monitoring of the atomic motion and fragmentation processes, many different pump-probe experiments have been performed to study the UD of excited and ionized clusters [2–4]. The experimental results are usually interpreted in terms of master-equations, assuming constant decay probabilities. This allows to obtain some information about decay-times due to fragmentation processes. However, many questions still remain open. For instance, not much is known about the time-scales for energy transfer from the electronic to the atomic degrees of freedom. Moreover, one of the most important problems which has not even been addressed so far, is the dependence of the UD on the initial conditions, and, in particular, on the initial temperature and cluster size. A temperature-sensitive ionization-induced short-time dynamics could allow to use the short-time spectroscopy after ionization as a method to determine the temperature of the clusters before ionization. Of particular interest is also whether the fragmentation of clusters is sensitive to phase transitions like the solid-liquid transition and if it reflects the intrinsic nonlinear, chaotic behaviour of clusters [5,6].

The ionization induced changes in the electronic structure are particularly strong in van der Waals systems, like small Hg$_n$ clusters [7,8], which leads to a rapid fragmentation, as it has been observed in recent pump-probe experiments [8].

It is the purpose of this letter to study the dynamics of small Hg$_n$ clusters as prototype for strong response to ionization. Of course, for clusters with other bond character the relaxation time scales are expected to be different. However, the general features of ionization induced fragmentation and underlying mechanisms of van der Waals clusters should be of general validity.
We describe the UD of small Hg\textsubscript{n} clusters immediately after ionization with the help of electronic structure calculations and molecular dynamics (MD) simulations in the Born-Oppenheimer approximation. Usually, for MD simulations of neutral van der Waals clusters, parameterized pair potentials are used [9]. However, this description is no longer valid when these clusters become ionized. The electronic ground state of ionized van der Waals clusters is governed by the interplay between delocalization energy of the positive charge- and polarization energy [7,8]. Thus, in order to account for the time-dependent changes of the charge- and dipole distributions during the relaxation following ionization, the potential energy surface (PES) must be determined self-consistently. Therefore, we use a microscopic electronic theory based on the ionic-core model [7]. We assume that the hole created in the ionization process delocalizes only within a dimer. Hence, after imposing this constraint for the charge distribution, and neglecting charge-dipole fluctuations, the ground-state energy of the ionized cluster is given by

\[
E = \frac{\left(\phi_1 + \phi_2\right)}{2} - \sqrt{t_{ss}^2(r_{12}) + \frac{\left(\phi_1 - \phi_2\right)^2}{4}} \\
+ \varepsilon \sum_{k,k',k \neq k'} \left[ \left(\frac{r_0}{r_{kk'}}\right)^{12} - 2 \left(\frac{r_0}{r_{kk'}}\right)^6 \right] \\
- \frac{1}{2} \alpha \sum_{k \in \{n-2\}} |\mathcal{E}_k^Q + \mathcal{E}_k^P|^2 + E_{dc}(\{\langle P_k \rangle\}, \{\langle Q_l \rangle\}).
\]

Here, the first two terms refer to the energy of the ionic dimer, where \(t_{ss}\) is the interatomic ss hopping element and \(\phi_l\) is the potential of the induced dipole distribution at the site \(l\) of the dimer core. The third term describes the van der Waals energy and the core-core repulsions in the whole cluster, being \(\varepsilon\) and \(r_0\) the cohesive energy and the bond-length of Hg\textsubscript{2}, respectively. The fourth term refers to the energy of the neutral subcluster. \(\alpha\) is the atomic polarizability, whereas \(\mathcal{E}_k^Q\) and \(\mathcal{E}_k^P\) are the charge- and dipole fields on the neutral atom \(k\). Finally, \(E_{dc}\) stands for the double-counting energy arising from the decoupling procedure used [8].

The expectation values of the charge- (\(\langle Q_l \rangle\)) and dipole distributions (\(\langle P_k \rangle\)) are coupled through the nonlinear relations \(\langle P_k \rangle = \alpha (\mathcal{E}_k^Q + \mathcal{E}_k^P)\) and \(\langle Q_l \rangle = |e| \sum_\sigma \langle n_{ls\sigma}^h \rangle\) (where \(\sum_\sigma \langle n_{ls\sigma}^h \rangle\)
is the number of holes at atom \( l \) \(^8\). The PES for the motion of the atoms is thus defined by the function \( E(\mathbf{r}_1, \ldots, \mathbf{r}_n) \). Consequently, the \( \mu \) component of the force acting on a given atom \( i \) is given by \( F_i^\mu = -\partial E / \partial \mathbf{r}_i^\mu \). Note, that the energy \( E(\mathbf{r}_1, \ldots, \mathbf{r}_n) \) cannot be described as a sum of pair potentials.

Assuming that the width of the ionizing laser pulse is negligible compared to the time scale of the nuclear motion, the main physics of the dynamics described by this theory can be visualized as follows. Through the ionization process, the Lennard-Jones PES of the neutral cluster is modified by two rather strong attractive terms, hole delocalization- and charge-dipole energy, and one mainly repulsive but weaker term, the dipole-dipole interaction energy. The binding energy of the ionized cluster is much larger than that of the neutral cluster, and equilibrium interatomic distances are considerably smaller. Thus, immediately after the vertical ionization, a relaxation process follows, for which the anharmonic part of the PES plays an important role. The excess energy \( \delta E \) comes from the charge-dipole interactions and from the delocalization energy of the hole. The latter contribution is the largest, and therefore for increasing times there will be a net transfer of kinetic energy from the dimer to the neutral rest of the cluster.

Using this theory we determine the fragmentation behaviour and its dependence on initial temperature for \( \text{Hg}_n \) with \( 3 \leq n \leq 13 \). For the parameters \( \varepsilon \) and \( r_0 \) we use experimental values \[^{10}\]\(^\text{a}\), whereas \( \alpha \) is obtained from atomic data \[^{11}\]\(^\text{b}\). For the distance dependence of the hopping element \( ss \) we use the functional form proposed in Ref. \[^{12}\]\(^\text{c}\). To integrate the equations of motion we use the Verlet algorithm in velocity form, and calculate the forces through the above described self-consistent procedure for each time step \( \Delta t \) (\( \Delta t = 7 \cdot 10^{-16} \text{s} \)). As a starting point, we determine the atomic structure of the neutral clusters by simulated annealing. Then, by using standard numerical procedures \[^4\]\(^\text{d}\) we generate, for each size, a distribution of clusters at a given temperature \( T \), where \( T \) is defined as the time-average of the kinetic energy over a long MD run (\( \sim 10^6 \) time-steps). This ensemble of clusters is ionized, i.e., the PES is switched from the neutral to the ionized electronic state. The dimer core is assumed to be formed by the pair of atoms closest to each other.
We obtain ionization induced fragmentation for all clusters sizes under consideration. The neutral fragments are mainly monomers, but dimer, and even trimer emission can also occur. In order to have a rough estimation of the fragmentation times, we perform first calculations at zero initial temperature and highly symmetric initial structures. Results show for very small clusters \((3 \lesssim n \lesssim 6)\) a fast emission of the first fragment, which results from a rapid energy transfer into particular modes of the cluster ("cold" fragmentation). The corresponding fragmentation time \(\tau_F\), i.e., the time at which the first fragment leaves the original cluster, is rather independent of the cluster size, and smaller than 10ps. In contrast, for \(n = 13\), \(\tau_F\) is larger than 30ps, and there are no longer privileged modes to which the excess energy is transferred. As a consequence, some thermalization takes place before evaporation of atoms. Our results for \(\tau_F\) for the different sizes at \(T = 0\) are in relative good agreement with those determined from pump-probe experiments \[^{3}\]. However, in order to simulate real experimental conditions, clusters must be given a nonzero initial temperature. For this purpose we study the fragmentation behaviour on a distribution of approximately 1000 clusters for each initial temperature. Thus, we obtain a distribution of fragmentation-times \(N(\tau_F)\), defined by the number of clusters whose first fragmentation occurs at \(\tau_F\).

In Fig. 1 (a) we show the normalized fragmentation-time distribution (FTD), \(W(\tau_F)\), calculated for Hg\(_3\) clusters with an initial temperature of \(T = 40K\). Note that one can interpret the function \(W(t)\) as the probability of fragmentation as a function of time. It becomes clear, that for \(T \neq 0\) one cannot distinguish anymore between cold and thermal fragmentation as a function of the cluster size. For all sizes studied, both forms of fragmentation are present. The FTD of Fig. 1 (a) exhibits two general features common to all calculated distributions (s. also Fig. 1(c)). It has a certain width (usually larger than 10ps), and its weight at short times is small. It is important to remark that the calculated decay-probability \(W(t)\) is not constant, as is usually assumed. In contrast to what one would expect, the width of \(W(t)\) does not decrease for decreasing temperature. Since lower temperature implies smaller displacements of the atoms around their equilibrium positions,
this is a clear indication of a nonlinear dependence of $\tau_F$ on the initial conditions. For the
sake of illustrating this effect, we determine the FTD for Hg$_3$ clusters at an extremely low
temperature, for which the atomic displacements are of the order of $10^{-6}$Å [13].

In Fig 1 (b) the resulting FTD is shown. The salient feature is a still large width,
the presence of a gap and several sharp peaks. This strange form is another indication of
the intrinsic nonlinear behaviour of the fragmentation dynamics. Small clusters are chaotic
systems [5,6]. This means that the trajectories in phase space are very sensitive to the initial
conditions. Since the fragmentation times strongly depend on the trajectories of the ionized
clusters on the PES, it is clear that they should exhibit nonlinear behaviour. The trajectories
corresponding to the various peaks of $W(t)$ in Fig 1 (b) could be somehow interpreted as
"attractors", since the resulting fragmentation times occur starting from many different
initial configurations. We obtain this chaotic behaviour after fragmentation for all cluster
sizes studied ($n > 2$). A very small change of the initial conditions leads to completely
different trajectories which involve different processes (e.g., cold- or thermal- or even no
fragmentation). Note that in our simulations energy is conserved up to $10^{-4}$eV for $10^5$ time
steps after ionization.

Of course, at very low temperatures quantum effects must dominate and will tend to
smear out the nonlinear features. But at low temperatures above the zero point motion,
where the mean displacements of the atoms are still very small ($\sim 0.05$Å) the chaotic
behaviour might play a role in the fragmentation dynamics.

In the inset of Fig. 1(b) we show the time evolution of the total polarization of one
of the clusters which contributes to the first peak. Notice that, even in the case of fastest
fragmentation, the neutral atom needs a few oscillations against the charged dimer in order to
gather the kinetic energy necessary to escape. This arises from the fact that the frequencies
of this mode and the inner vibrational mode of the dimer core are different (as is reflected
in the time-dependence of the polarization) and consequently an efficient energy transfer is
prevented. At high temperatures, however, there is a nonzero probability for fragmentation
within the first oscillation period [s. Fig. 1(a)]. When the neutral atom leaves the cluster,
its induced dipole moment starts to decrease with time and goes to zero as the distance to
the ionic dimer becomes large.

We have already pointed out that all our calculated distribution functions $W(t)$ exhibit
a very small weight at short times. This means that the probability for fragmentation is
small at times shorter than the characteristic times for excess-energy transfer. If one writes
a master equation for the decay of the original cluster, one obtains for the time-dependent
number of clusters with the original size $n$

$$N_n(t) = N_n(0) e^{-\int_0^t dt' W(t')} ,$$

and $d^2 N_n/dt^2 |_{t=0} < 0$ in agreement with what is observed in pump probe experiments, and in contrast with what one would obtain by assuming a constant $W$.

In general, our calculated FTD show only a week temperature dependence. The same
holds for the corresponding average fragmentation times $\langle \tau_F \rangle$. But as soon as the tem-
perature before ionization crosses the solid-like to liquid-like transition temperature of
the neutral clusters $W(t)$ undergoes strong changes. This indicates a correlation be-
tween the energy transfer mechanisms after ionization and the thermodynamical state of
the cluster before ionization. In Fig. 2 (a), (b) and (c) we show the temperature de-
pendence of of the root-mean-square (rms) bond-length fluctuation $\delta$, defined as usual as

$$\delta = (n(n-1)/2)^{-1} \sum_{i<j} \sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2 / \langle r_{ij} \rangle} ,$$

where $\langle ... \rangle$ means time-average over a long

trajectory ($10^6$ time steps), which gives an idea of the degree of mobility of the atoms. For
bulk material, as a function of the temperature, $\delta$ shows typically a sharp increase at the
solid-liquid transition, consistent with the Lindemann-criterion. This behaviour has been
used as a numerical tool to determine the melting-temperature of small clusters. From
Figs. 2 (a), (b) and (c) the temperature dependence of $\delta$ is shown for $n = 3, 4$ and 13. For
$n = 3$ and 13, $\delta$ clearly shows a jump. The smoother increase of $\delta$ for $n = 4$ is related to the
interplay (isomerization) between the tetrahedral and the planar rombic structure, which
occurs at a temperature lower than the actual melting point and gives rise to larger values
of $\delta$, smearing out the sharp increase at $T_M$. Now, the important result of our calculations
becomes obvious by noting that the inverse of the average fragmentation times $\langle \tau_F \rangle$ shows exactly the same temperature dependence as $\delta$. This occurs even for $n = 4$, reflecting a strong sensitivity of $\langle \tau_F \rangle$ to the melting dynamics. This result can be interpreted as follows. The distribution of the excess energy $\delta E$ among the different degrees of freedom leads (except for the unlike cases of cold fragmentation) to an homogeneous weakening of the bonds. Only those atoms in a liquid-like environment have a larger probability to evaporate. If the neutral cluster is already liquid, fragmentation can occur faster, since $\delta E$ can be fully used for evaporation. Note that the above argument is independent of the bond character of the clusters considered. However, it is essential that a vertical ionization puts the cluster in a non-equilibrium situation. For an adiabatic ionization the above picture does not necessarily hold, because the melting temperature of the ionized cluster could be much larger than that of neutral one. Obviously, if $\delta E$ is smaller than the latent heat of the cluster, fragmentation may only occur above the melting point. We believe that this effect can also be observed in metallic and covalent clusters, as long as the conditions discussed above are fulfilled.

The remarkable correlation between $\langle \tau_F \rangle$ and $\delta$ could allow to determine the solid-like to liquid-like transition of small clusters by pump&probe experiments. From the experimental signal $N_n(t)$ one can first obtain $W(t)$ by using Eq. (2), and then calculate $\langle \tau_F \rangle = \int_0^\infty dt \, t \, W(t)$.

In order to demonstrate the importance of chaos in the short-time dynamics and to quantify the influence of ionization in the chaotic behaviour of clusters, we determine the corresponding local Lyapunov exponents [3] before and after ionization process. The largest Lyapunov exponent is a measure for the average divergence of two initially nearby trajectories in the phase space, and is given by

$$\lambda = \lim_{N \to \infty} \frac{1}{N} \log | J(\{r\}_n, \{p\}_n) |,$$

where $J(\{r\}_n, \{p\}_n)$ is the Jacobian matrix for the map from configuration at time $t$ to the configuration at time $t + \Delta t$ in the Verlet algorithm [3]. We obtain positive values of $\lambda$ (i.e., chaotic behaviour) for all cluster sizes studied. In Fig 3 we show the temperature
dependence of the (averaged) largest Lyapunov exponent for Hg₄ clusters before \((\lambda^0)\) and after \((\lambda^+)\) ionization. At a given initial temperature, the calculated \(\lambda^+\) are more than one order of magnitude larger than \(\lambda^0\). This clearly indicates that degree of nonlinearity is enhanced by the ionization process. Due to the large energy \(\delta E\) pumped into the atomic degrees of freedom, the cluster can explore a larger part of the PES, which lead to an increase of the nonlinear behaviour. Since \(\delta E\) is of the order of \(10^4 K\) it is also clear that \(\lambda^+\) is almost independent of the initial temperature. This explains why the width of the FTD does not go to zero for \(T \to 0\) [s. Fig. 1(b)]. In contrast, \(\lambda^0\) exhibits an appreciable increase exactly within the temperature range where the solid-liquid transition occurs. This interesting behaviour of \(\lambda^0\) (which has been also observed for Arₙ clusters (3)) reflects the fact that in the liquid phase the motion is more chaotic than in the solid phase.

This work has been supported by the Deutsche Forschungsgemeinschaft through the SFB 337.
REFERENCES

[1] M. Dantus, M. J. Rosker and A. Zewail, J. Chem. Phys. 87, 2395 (1987).

[2] J. Manz and L. Wöste (eds.), Femtosecond Chemistry, Verlag Chemie, Heidelberg, 1995.

[3] T. Baumert, R. Thalweiser, V. Weiss, E. Wiedemann and G. Gerber, Proc. of the Royal Netherlands Academy Colloquium on Femtosecond Reaction Dynamics, edited by Douwe A. Wiersma, 42, 29 (1994).

[4] S. Wolf, G. Sommerer, S. Rutz, E. Schreiber, T. Leisner, L. Wöste and R. S. Berry, Phys. Rev. Lett. 74, 177 (1995).

[5] R.J. Hinde, R.S. Berry and D.J. Wales, J. Chem. Phys. 96, 1376 (1992); C. Amitrano and R.S.Berry, Phys. Rev. Lett. 68, 729 (1992).

[6] S.K. Nayak, R. Ramaswamy and Ch. Chakravarty, Phys. Rev. E51, 3376 (1995).

[7] H. Haberland, Surf. Sci. 156, 305 (1985).

[8] M.E. Garcia, G.M. Pastor and K.H. Bennemann, Phys. Rev. B 48, 8388 (1993).

[9] See for example T.L. Beck, J. Jellinek and R. S. Berry, J. Chem. Phys. 87, 545 (1987).

[10] R. D. van Zee, S. C. Blankespoor and T. S. Zwier, J. Chem. Phys. 88, 4650 (1988).

[11] Handbook of Chemistry and Physics, 66th Edition (CRC, Boca Raton, Florida,1985).

[12] L. Goodwin, A. J. Skinner and D. G. Pettifor, Europhys. Lett. 9, 701 (1989).

[13] Note that this corresponds to a kinetic energy smaller than that of the zero point motion of Hg$_3$ clusters and cannot be used to compare with experiment.
FIGURES

FIG. 1. Calculated ionization induced fragmentation-time distributions $W(t)$ for a) Hg$_3$ clusters at initially $T = 40K$, b) Hg$_3$ clusters at initially $T = 0.05K$, and (c) Hg$_6$ clusters with $T = 40K$. Note that the curves have been normalized so that $W(t)$ also represents the probability of fragmentation at a time $t$. Inset of Figure (b): time behaviour of the polarization of a cluster which fragmentates at $t = \tau_1$.

FIG. 2. Temperature dependence of the inverse average fragmentation times $\langle \tau_F \rangle^{-1}$ of the ionized clusters (up triangles, left axis) and rms bond-length fluctuations (open circles, right axis) $\delta$ before ionization for a) Hg$_3$, b) Hg$_4$ and c) Hg$_{13}$ clusters. Note that the increase in $\langle \tau_F \rangle^{-1}$ characterizes the melting temperature, and could be used for experimental determination of the solid-liquid transition.

FIG. 3. Calculated temperature dependence of the largest local Lyapunov exponent $\lambda(T)$ for Hg$_4$ clusters before ($\lambda^0(T)$) and after ($\lambda^+(T)$) ionization. Note that the ionization process enhances the chaotic behaviour of the clusters, by more than one order of magnitude. The increase of $\lambda^0(T)$ for increasing $T$ reflects the solid-liquid transition.
(a) $n = 3$
$T = 40$ K

(b) $n = 3$
$T = 0.05$ K

(c) $n = 6$
$T = 40$ K
Largest Lyapunov Exponent

Temperature (K)

after ionization

before ionization

n = 4

x 10