Time dependent energy absorption of atomic clusters from an intense laser pulse

Christian Siedschlag and Jan M. Rost

Max-Planck-Institute for the Physics of Complex Systems, Nöthnitzer Str. 38, D-01187 Dresden, Germany

(November 2000)

For the energy absorption of atomic clusters as a function of the laser pulse duration we find a similar behavior as it has been observed for metallic clusters [Köller et al., Phys. Rev. Lett. 82, 3783 (1999)]. In both situations there exists an optimum radius \( R_o \) of the cluster for energy absorption. In the metallic case the existence of \( R_o \) has been interpreted as a consequence of the collective oscillation of a delocalized electron cloud in resonance with the laser frequency. Here, we give evidence that in the atomic cluster the origin of \( R_o \) is very different. Based on field assisted tunneling it can be related to the phenomenon of enhanced ionization as it occurs in small molecules. The dependence of \( R_o \) on the laser frequency turns out to be the key quantity to distinguish the processes.

PACS numbers: 36.40 -c, 33.80 Rv, 36.40 Gk

Exposed to an intense laser pulse a cluster absorbs a considerable amount of energy which is released subsequently through fragmentation into fast electrons \([1]\), multicharged ions \([2]\) and radiation in the x-ray regime \([3]\). These effects depend on the size of the cluster, i.e., the number of constituent atoms and the pulse duration, somewhat less on the kind of atoms and the wavelength of the light.

In a recent experiment Köller et al. measured the intensity dependent energy absorption of a cluster consisting of some ten platinum atoms as a function of laser pulse duration \([4]\). This has been done by keeping the energy content (fluence) of the laser pulse constant and varying the pulse duration as well as the peak intensity accordingly.

Interestingly, the absorbed energy decreases with increasing laser intensity, after having reached a maximum. We have found the same behavior in calculations for atomic clusters containing a similar number of atoms. However, as we will see below, the mechanism responsible for the phenomenon is quite different from the one described in \([4]\) for the metallic clusters.

We will show that a sensitive indicator for the underlying mechanism is the existence of an optimal mean internuclear distance \( R_o \) for energy absorption which changes with the laser frequency \( \omega \) for a cluster of delocalized electrons (a metal cluster) while it is independent of \( \omega \) in the case of an atomic cluster. In both cases the existence of \( R_o \) is also the origin of the peculiarity that the energy absorption can decrease with increasing peak intensity of the laser, as mentioned above.

In order to discriminate between different mechanisms we had to choose an approach which is capable of handling, at least in principle, both situations: atomic clusters with localized electrons and delocalized electrons as they are typical for metallic behavior. Furthermore, the numerical treatment had to be fast enough to follow an appreciable number of particles (ions and electrons). Clearly, this cannot be done fully quantum mechanically, for the time being. Our approach is a combination of the ones described in \([4]\) \([5]\), i.e., essentially based on classical equations of motion for all ionized charged particles under full mutual Coulomb interactions. As in \([6]\) we have used Coulomb soft-core potentials

\[
V_c(r) = (r^2 + a^2)^{-1/2}.
\]

We will see later, that the choice of \( a \) allows us to describe an atomic cluster with localized electrons \((a_a \sim 1 \text{ a.u.)}\) or to simulate a metallic cluster with delocalized electrons \((a_m \gg a_a)\).

The initial ionization of an electron bound to an atom or ion is described with an analytically known rate \([5]\), dependent on the instant (static) electric field at the position of the atom/ion to be ionized. The field is created by all surrounding charges (ions and electrons) and the laser. In contrast to \([6]\) we do not include additional electron impact ionization. Its effect is small (see \([3]\)), moreover, its implementation based on empirical cross sections, such as the Lotz formula, bears the danger that the contribution of electrons to ionization is counted twice: through field ionization and through additional impact ionization.

The actual computation goes as follows: After a relaxation to an equilibrium under Lennard-Jones potentials the atomic configuration is exposed to the laser pulse. We compute a probability for ionization for each atom (later ion) from the rate in an time interval \( \Delta t \). Is it larger than a generated random number \( 0 \leq s \leq 1 \), the atom is considered as 'ionized' \([3]\) and turns into an ion, and a new electron is created outside the instant potential barrier with zero kinetic energy. The ionization rate for the ion is adjusted to the corresponding higher
binding energy and the procedure is repeated, of course, simultaneously for all atoms/ions. Newton’s equations are solved for the time evolution of all charged particles interacting through mutual Coulomb soft-core potentials Eq. (1) with \( a^2 = 2 \text{a.u.} \).

In the following we will discuss the energy transfer to a Ne\(_{16}\) cluster from a laser pulse with \( \sin^2 \)-envelope and an optical frequency of \( \omega = 0.055 \text{ a.u.} \). If we record the energy gain after the pulse as a function of pulse duration \( T \), we obtain Fig. 1. Since for constant fluence under a variation of \( T \), the peak intensity behaves as \( I \propto 1/T \), one recognizes the increasing energy absorption for decreasing intensity. Only for very short pulses (high intensities) the trend is reversed indicating that in this regime the pure atomic response dominates cooperate cluster effects. An analogous behavior of the energy absorption, including the rise for very short pulses, is found in calculations for excitation of an Na\(_9\) cluster [11], and in the experiment on platinum clusters (exemplified by the dependence of the charge states for ejected ions as a function of the pulse duration, see Fig. 2 in [4]).

\[ R(t) = \left( \sum_{i} R_i^2 / N \right)^{1/2}, \]

FIG. 1. Absorbed energy as a function of laser pulse duration \( T \) for constant fluence such that a peak intensity of \( 10^{13} \text{W/cm}^2 \) is reached with a pulse of 20 cycles (\( \omega = 0.055 \text{ a.u.} \)). Note that an atomic time unit is 0.0242 fs. The line is to guide the eye.

The authors of [4] provided an appealing interpretation in terms of a plasma model for the delocalized electron density of the platinum cluster: The eigenfrequency \( \Omega \) of the electron cloud depends on its density, which, in turn, is a function of the cluster radius, i.e. \( \Omega = \Omega(R(t)) \). When the cluster expands due to the net positive charge after initial ionization, the electron density decreases and so does the plasma frequency \( \Omega \) which will eventually match the laser frequency \( \omega \). Then, energy absorption becomes resonant and is greatly enhanced. The maximum in the absorption as a function of pulse duration is now essentially a matching problem: The best condition is a coincidence of the peak intensity with the time when \( \Omega(R(t)) = \omega \). If the laser pulse is too short, the resonance condition is reached when the pulse is already over. On the other hand, if the pulse is too long, the cluster has expanded beyond \( R_o \) when the peak intensity is reached.

We define as a characteristic length scale for the cluster

\[ R(t) = \left( \sum_{i} R_i^2 / N \right)^{1/2}, \]

the mean over all individual internuclear distances \( R_i \). Equivalently, we will speak of the cluster radius which is directly proportional to \( R \) for a fixed number of atoms in the cluster [2]. Typically, \( R(t) \) increases adiabatically slowly compared to the electronic and optical time scales. This allows us to gain more insight into the dynamics by considering the energy absorption of the cluster for different but fixed mean internuclear separations \( R \). Figure 3 demonstrates that the energy absorption for fixed \( R \) peaks at a critical \( R_o \) independent of the laser frequency.

This is a key observation which has several consequences: Firstly, the existence of \( R_o \) for an atomic cluster explains the shape of the energy absorption in Fig. 1 with a maximum due to the monotonic increase of \( R \) as a function of time. Large energy absorption occurs for a pulse duration \( T \) such that peak intensity is reached at \( T/2 \), when the cluster has the optimal seize \( R(T/2) \approx R_o \). Secondly, the mechanism which leads to the existence of \( R_o \) must be different from the one proposed for a metal cluster in [4], since a resonant absorption with \( \Omega(R_o) = \omega \) points to optimal cluster radii \( R_o \) which change with the frequency \( \omega \). Rather, the mechanism we have identified for these relatively small atomic clusters is akin to a behavior in small molecules which has been described under the name enhanced ionization [13] or CREI (charge resonant enhanced ionization) [4]. In short, the idea is that in a diatomic molecule the electron, localized on one atom most of the time due to the oscillatory light field, can easier tunnel through the barrier formed by the attractive Coulomb potential and the electric field since this barrier is lowered by the additional electric field generated by the neighboring (positively charged) nucleus.

An optimal internuclear distance \( R_o \) for this field assisted tunneling exists since in the united atom limit \( R = 0 \) there is only one well (and deeper binding) while in the separated atom limit \( R \to \infty \) the additional field simply goes to zero. The signature of this mechanism is the existence of \( R_o \) and its independence of the laser frequency \( \omega \), precisely as seen in Fig. 2. Hence, the mechanism of field assisted tunneling is indeed also operative for our cluster where many surrounding charged ions form a strong field for the specific atom or ion to be ionized in the cluster.

Having established the origin of the peculiar behavior of energy absorption in an atomic cluster as a function of laser pulse duration, we may subject our modelling of cluster dynamics to an ultimate test by comparing exact quantum results for the simplest system \( \text{H}_2^+ \) to predictions from our approach. This is done in one dimension
FIG. 2. Energy absorption from an intense laser pulse ($T = 55$ fs) in different situations: (a) for Ne$_{16}$ as a function of fixed mean interatomic distance $R$ at two different laser frequencies, $\omega = 0.055$ a.u. (solid), $\omega = 0.11$ a.u. (dashed) and with peak intensity $I = 10^{15}$ W/cm$^2$, (b) as in (a) but for the 16 atom metallic cluster model as a function of the initial mean ion distance $R_e$ and for $I = 3.51 \times 10^{14}$ W/cm$^2$, see text, (c) for $H^+_2$ as a function of fixed internuclear distance with the one dimensional quantum result (solid) and the present tunneling approach (dashed) at a peak intensity of $I = 5.6 \times 10^{13}$ W/cm$^2$.

(Where the internuclear axis is aligned along the electric field of the laser) in Fig. 2c. Although we model the bound electron being attached to one proton and calculate its tunneling rate subject to the laser field and the field generated by the second proton, the actual ionization probability is in surprisingly good agreement with the exact quantum result, particularly compared to a purely classical over barrier model whose ionization yield is too small to be visible in Fig. 2c. Note that $R_o$ for the cluster (Fig. 2a) is even roughly equal to $R_o$ in $H^+_2$ (Fig. 2c).

Designed for an interaction of several ions with many electrons and an intense laser pulse the fairly accurate description of $H^+_2$ is an unexpected confirmation of the modelling. However, it raises also the question if the mechanism we have identified for energy absorption in clusters being akin to that for molecules in intense laser fields is merely a consequence of the modelling which seems to be ideally suited to describe tunneling related phenomena.

To doublecheck that our result is independent of the modelling and also, to clarify further the different mechanism which seems to be responsible for the (similar) energy absorption and existence of a critical mean distance $R_o$ in metal clusters we have simulated with our approach the behavior of delocalized electrons as they occur in a metal cluster. This has been achieved by artificially softening the potential Eq. (1) with $\alpha^2 = 30$ a.u. As a consequence the cluster ions at equilibrium distance of each form one structureless well for the "collective" binding of the electrons. Comparing the excitation spectrum of the electrons, one sees for the original situation of atomic clusters with localized electrons a single peak which corresponds to the local excitation (Fig. 3a) while for the delocalized electrons with $\alpha^2 = 30$ one sees two peaks (Fig. 3b), the lower and wider one corresponds to the softened local excitation of the local binding, the higher peak is the new feature of collective excitation which is believed to be responsible for the mechanism of resonant energy absorption as described above. If this is true, we would expect in our model for delocalized electrons a dependence of the optimal cluster radius for energy absorption on the laser frequency. This is indeed the case, as one can see in Fig. 2b. As expected for a decreasing electron density with growing cluster radius, and corresponding decreasing eigenfrequency $\Omega$ of the electron cloud, we find that $R_o$ is smaller for the higher laser frequency.

This confirms the existence of a different mechanism which leads to a critical cluster radius in a situation of delocalized electrons, in accordance with what has been found by very different modelling of the valence electrons in sodium clusters [15,16]. It also demonstrates that our

FIG. 3. Excitation spectrum for the electrons in the cluster, (a) localized electrons in Ne$_{16}$, (b) delocalized electrons in the metallic cluster model.
formulation of intense field dynamics of clusters is capable of describing both, atomic clusters with localized electrons and, at least qualitatively, the situation of delocalized electrons as they occur in metal clusters. Hence, the result reassures that the mechanism of field enhanced ionization by surrounding charged particles is not an artifact of the theoretical description.

To summarize, we have found that the energy absorption in small atomic clusters depends strongly on the laser pulse duration, similarly as in metallic clusters and large \((N \approx 10^6)\) atomic clusters. However, the mechanism is very different. While in metallic clusters \([12]\) a similar plasmon resonance mechanism prominently involving delocalized electrons has been advocated to explain the observations, we find that in small atomic clusters field assisted tunneling is responsible. By making use of the adiabaticity of the ionic motion compared to the electronic motion we could show that a critical cluster radius exists for maximum energy absorption which is \textit{independent} of the laser frequency \(\omega\). This behavior is akin to the one known from diatomic molecules as "enhanced ionization" \([13,14]\) and can be attributed to the same physical effect of field assisted tunneling. As a sideffect, we have shown that our approach also describes the ionization of the smallest molecule, \(H_2^+\), in a strong laser pulse rather well.

Furthermore, we have simulated the behavior of delocalized electrons within the same theoretical approach. Thereby, we could confirm that for delocalized electrons enhanced energy absorption can be attributed to a plasmon type resonance. It occurs when the eigenfrequency of the delocalized electron density and the laser frequency agree, as suggested by Köller et al to interpret their experiment \([15]\). However, we could only clearly identify this type of resonance behavior if exclusively the valence electrons are involved in the ionization dynamics, i.e., if the laser intensity is sufficiently weak (in our case \(3.51 \times 10^{12} \text{ W/cm}^2\)). Once electrons from the ionic cores are ionized, the local character of the electron binding starts to dominate. Moreover, field ionization triggered by surrounding charges takes over the ionization caused by the collective electron cloud and the laser field. Since in the experiment \([15]\) the peak intensity of the laser was rather large (more than \(10^{15} \text{ W/cm}^2\)) and highly charged ions have been detected (which probably were even higher charged through the initial ionization before recombination took place), it is possible that the actual mechanism for the energy absorption pattern as a function of pulse duration is closer to that of field assisted tunneling as in atomic clusters than to the plasmon resonance enhanced ionization of metallic valence electrons. As we have shown, the two mechanisms differ by their dependence on the laser frequency. Hence, it would be desirable to repeat the experiment of \([15]\) at a higher laser frequency, the best choice being an \(\omega\) high enough that the resonance condition cannot be fullfilled. If the energy absorption pattern still shows a pronounced maximum, one could exclude the plasmon induced absorption mechanism and rather would have to conclude that the field assisted tunneling scenario is a universal mechanism for intense laser field ionization in molecules and clusters of moderate seize.

It is a pleasure to thank K.H. Meiwes-de Broer, P. Corkum, R. Schmidt, and P.-G. Reinhard for fruitful discussions. We also acknowledge O. Frank's input at the initial stages of this work which has been supported by the DFG through the Gerhard Hess-program.

[1] Y. L. Shao et al, Phys. Rev. Lett. 77, 3(1996).
[2] T. Ditmire et al, Nature (London) 386, 54 (1997).
[3] A. Mc Pherson et al, Nature (London) 370, 631 (1994).
[4] L. Köller, M. Schumacher, J. Köhn, S. Teuber, J. Tiggesbäumker, and K. H. Meiwes-Broer, Phys. Rev. Lett. 82, 3783 (1999).
[5] L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon, New York, 1965)
[6] C. Rose-Petruck et al, Phys. Rev. A 55, 1182 (1977).
[7] T. Ditmire, Phys. Rev. A 57, R4094 (1998).
[8] I. Last and J. Jortner, Phys. Rev. A 62, 013201 (2000).
[9] K. Ishikawa, and T. Blenski, Phys. Rev. A 62, 063204 (2000).
[10] In a simple model of dense spheres of atoms, the acutal cluster radius \(R\) is directly proportional to \(R\) with \(R = N^{1/3} R/2\), see, e.g., Kreibig and Vollmer, Optical properties of Metal Clusters (Springer, 1995).
[11] private communication, R. Schmidt, see also U. Saalmann and R. Schmidt, Phys. Rev. Lett. 80, 3213 (1998).
[12] 'Ionization' means here that the electron is no longer bound to its mother atom, however, it may be still bound to the entire cluster. See also the distinction of 'outer' and 'inner' ionization in \([15]\).
[13] T. Seidemann, M. Yu. Ivanov, and P. B. Corkum, Phys. Rev. Lett. 75, 2819 (1995).
[14] T. Zuo and A. D. Bandrauk, Phys. Rev. A 52, R2511 (1995).
[15] P. G. Reinhard et al, Physics Reports 337, 493-579 (2000)
[16] E. Suraud and P. G. Reinhard, Phys. Rev. Lett. 85, 2296 (2000)
[17] J. Zweiback, T. Ditmire, and M. D. Perry, Phys. Rev. A 59, R3166 (1999).