Surface plasma resonance in small rare gas clusters by mixing IR and VUV laser pulses

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The ionization dynamics of a Xenon cluster with 40 atoms is analyzed under a pump probe scenario of laser pulses where an infrared laser pulse of 50 fs length follows with a well defined time delay a VUV pulse of the same length and peak intensity. The mechanism of resonant energy absorption due to the coincidence of the IR laser frequency with the frequency of collective motion of quasi free electrons in the cluster is mapped out by varying the time delay between the pulses.

In recent years, much work has been devoted to the ionization mechanisms of clusters in few-cycle, intense laser fields (i.e. pulse lengths of the order of 100 fs and intensities \( I = 10^{13} \ldots 10^{19} \text{W/cm}^2 \)): from the case of plasmon excitation when exposing metal clusters to relatively weak fields \( \text{[1]} \) over *enhanced ionization* akin of molecular ionization for small rare gas clusters in intense fields \( \text{[2]} \) to collective excitation of a plasma resonance in clusters of intermediate \( \text{[3]} \) to large sizes \( \text{[4]} \), ultimately leading to ionic charge states of 40+ and higher \( \text{[5]} \), thus potentially providing a new source for the generation of x-rays, energetic ions or electrons and, via nuclear fusion, even neutrons \( \text{[6]} \). A new parameter regime for laser-cluster interaction has been proven to become accessible with the first experiment using VUV-FEL light of 98nm wavelength for the ionization of rare gas clusters \( \text{[7]} \), soon followed by the first proposals for an explanation of the unexpectedly high charge states seen in this experiment \( \text{[8]} \text{[9]} \text{[10]} \).

While XUV-cluster interaction is still the subject of an ongoing debate, there seems to be a more or less common understanding regarding the qualitative picture of IR laser-cluster interaction: during the rising part of the laser pulse, a few electrons are ionized \( \text{[11]} \) leaving the cluster with a net positive charge which leads to an expansion typically on the same time scale as the duration of the laser pulse. Hence, effects which depend on the internuclear distances can be resolved by varying the pulse length \( \text{[12]} \) and/or applying pump-probe techniques \( \text{[12]} \text{[13]} \). The resolution of an optimum time delay \( \Delta t \) and the contrast of the signal in a pump-probe experiment increases if \( \Delta t \gg T \), the length of each pulse. Since \( \Delta t \approx t_c \), the critical expansion time of the cluster at which maximum absorption energy from the cluster pulse is possible, long times \( t_c \) are desirable which implies large clusters consisting of heavy atoms (slower Coulomb explosion). Also, the large number of quasi-free electrons temporarily trapped in the cluster, lead to a good contrast for the optimized versus non-optimized signal \( \text{[13]} \).

The critical time \( t_c \) originates from a critical radius \( R_c = R(t_c) \) of the cluster, usually larger than the equilibrium radius \( R_0 \), where energy absorption is most efficient. For larger clusters (resonant mechanism) this radius is determined by the surface plasma frequency approximately given by

\[
\Omega_t = \sqrt{\frac{N_t Z_t}{R_t^3}} = \frac{\omega_{pl}}{\sqrt{3}},
\]

where \( N_t \) is the number of atoms/ions in the cluster, \( Z_t \) is their average charge, \( R_t \) is the cluster radius and \( \omega_{pl} \) the bulk plasma frequency. The indices \( t \) indicate a slow dependence on time (at this point we want to emphasize that, at least as long as the cluster is neutral, the surface plasma resonance is mathematically completely equivalent to the surface plasmon resonance and can be derived along the same pathway. Nevertheless, we prefer to call it a plasma resonance since there is in principle a physical difference between a metal cluster being excited perturbatively and a rare gas cluster turned into a nanoplasma by a nonperturbative laser field). If \( \Omega_t \approx \omega \), the laser frequency, then the cloud of electrons which are trapped inside the cluster behaves like a (damped) harmonic oscillator driven to resonance \( \text{[14]} \), leading to efficient energy absorption and ionization.

The most important prerequisite for this mechanism is a significant amount of trapped (quasi-free) electrons before \( R_c \) is reached, which can be achieved in two ways: either the laser field strength is small enough to leave enough electrons inside the cluster before \( R = R_c \); this possibility is limited, however, by the fact that the inner ionization process will eventually not start if the field strength is too small, so that no quasi-free electrons will be created in the first place. For metal clusters, this problem does obviously not occur; on the other hand, one has to ionize the cluster to a certain degree in order to start the expansion process, and the range of intensities and pulse lengths which can start the Coulomb explosion while at the same time keeping the valence electron cloud intact is quite small \( \text{[14]} \). On the other hand, the force
that keeps the electrons inside the cluster is generated by the space charge of the ions. Hence, going to larger clusters while leaving the average ion charge constant, will make it more and more difficult for electrons to leave the cluster, so that the number of trapped electrons will increase with the cluster size. This is the reason why the resonance absorption is much clearer seen with IR pulses for large clusters (compare [12] with [13]).

To summarize, resonant absorption in intense IR fields occurs (i) for metal clusters in weak fields ($I \lesssim 10^{13} \text{W/cm}^2$); the size of the clusters then only plays a role in so far as it will change the expansion speed, which has to be accounted for by changing the pulse lengths accordingly; or (ii) for clusters with $N \gtrsim 10^2$ and intensities of $I \lesssim 10^{14} \text{W/cm}^2$, where a substantial fraction of the quasi-free electrons which are created by the laser is kept inside the cluster, so that a collective oscillation can develop.

In the case of small rare gas clusters in strong IR fields, none of the above scenarios applies. Rather, ionization is dominated by charge enhanced ionization, known already from diatomic molecules, where the shape of the interatomic barrier leads to an optimal distance between the cluster nuclei which results in an efficient interplay between inner and outer ionization [2]: the neighboring charges must be close enough to start an ionization avalanche [3] once the first electrons are created; on the other hand, they must not be too close in order to decrease the space charge which prevents the electrons from escaping the cluster. Obviously, the whole process relies on the ionization of the first electrons relatively early in the pulse; once the field strength drops significantly below the field strength $F_{th}$ required to field-ionize a single cluster atom ($F_{th} = E_0^2/4$, where $E_0$ is the first atomic ionization energy), the avalanche will not be started and the cluster will survive the radiation relatively undamaged. For Xe clusters, for example, $F_{th} = 0.0493 \text{ a.u.}$, which corresponds to an intensity of $I_{th} = 8.53 \times 10^{13} \text{W/cm}^2$.

As has been shown in the Hamburg experiment, the threshold for an ionization avalanche is considerably lower when using VUV instead of IR light. With intensities of the order of $10^{12} \text{ W/cm}^2$ and a photon energy of 12.7 eV, complete breakup of Xe clusters and unexpectedly high ionic charges have been observed [8]. These findings can be explained [10] by using standard atomic photoabsorption rates but taking into account the effective (inner) ionization threshold which is lowered by the surrounding charges in a cluster (see Fig. 1). Due to this mechanism and due to the fact that the quiver amplitude is two orders of magnitude smaller than for IR radiation, a VUV pulse is much more efficient in creating quasi-free electrons than an IR pulse of the same peak intensity.

This opens up an elegant way to study the dynamics of collectively excited electrons and hence the resonance absorption mechanism in a small cluster by combining a VUV pump pulse with a time delayed IR probe pulse: The VUV pulse generates a large number of quasi-free electrons. At the same time the cluster gets only moderately charged and a slow expansion sets in mainly driven by the hydrodynamic pressure of the quasi-free electrons. Hence, one can observe with a time delayed probe pulse very cleanly the optimum condition for energy absorption by the quasi-free electrons as a function of cluster size starting at a size as small as $N = 40$ as we will demonstrate with the following pump-probe scenario: a Xe$_{40}$ cluster is first irradiated by a 50 fs VUV pulse ($\omega = 12.7$ eV, $I = 7.9 \times 10^{12} \text{ W/cm}^2$) Then, after a variable time delay $\Delta t$, we apply a second pulse of the same length and intensity, but now with a wavelength of 780 nm. The simulation has been done using the quasiclassical model introduced in [2].

The charge spectra after the interaction of the cluster...
In principle there are two ways to check numerically evidence for this hypothesis. On the one hand, if it is very short it will not produce a significant number of quasi-free electron which means unique, since one has to define a cluster “volume” which itself is time dependent (through the increase of the cluster radius) and so are the charge of the ions and the number of electrons. The resonance condition can be determined more reliably by calculating the phase difference between the oscillation of the electronic center of mass (ECM) and the driving laser field $F(t) = F_t \cos \omega t$ [4]: if one assumes a collective oscillation with a damping constant $\gamma$, the time-dependent dipole amplitude for the ECM reads

$$X(t) = A_t \cos(\omega - \phi_t)$$

with

$$A_t = F_t / \sqrt{\left(\Omega_t^2 - \omega^2\right)^2 + (2\Gamma_t \omega)^2}$$

$$\phi_t = \arctan\left(2\Gamma_t \omega / (\Omega_t^2 - \omega^2)\right).$$

For $\phi_t = \pi/2$ the system is at resonance and the laser cycle averaged energy absorption

$$\langle dE/dt \rangle = \frac{1}{T} \int_0^T \frac{dX}{dt} F(t) \, dt \propto \sin \phi_t$$

is at its maximum. Note, however, that the amplitude $X_t$ does not necessarily increase considerably at resonance due to strong damping (see Eq. (3)). Hence, we take the condition $\phi_t = \pi/2$ as the definition for the plasmon resonance and calculate $\phi_t$ from the phase lag between the driving field $F(t)$ and the dipole oscillation $dX_t/dt$ by extracting the maximum of the time correlation $c(\delta t)$ between the two signals, where

$$c(\delta t) = \int_{t_1}^{t_2} F(t) X(t + \delta t) \, dt$$

(note that $\delta t \neq \Delta t$!). We chose the limits of integration in Eq. (6) to be 10 IR cycles before and after the maximum of the probe laser; the radial evolution $R_t$ of the cluster is sufficiently slow so that the phase lag only changes by a small amount during that time. The outcome of this calculation is shown in Fig. 4. Indeed the phase lag is equal to $\pi/2$ for $\Delta t \approx 3800$ a.u.. This proves that the maxima in Fig. 3 are due to a resonance of the collective electron oscillation with the driving laser field.

Hence, the VUV pump combined with a IR probe pulse can map out the internal collective cluster dynamics very clearly and may be the only possibility to resolve this dynamics for small clusters. The reason is simply that the VUV pulse produces a large number of quasi-free electrons which can participate in collective electron motion. On the other hand the VUV pulse itself does not couple to this collective motion. Hence, only the probe pulse probes literally the collective electron dynamics. Using two IR pulses for pump and probe make this distinction difficult: The pump pulse must be very short in order not to “probe” itself the collective electron dynamics. On the other hand, it is very short it will not produce a significant number of quasi-free electron which

![Diagram](image_url)
FIG. 4: Phase lag between the center-of-mass oscillation of the electron cloud and the driving laser field as a function of time delay between the VUV and the IR pulse.

could move collectively since they are produced most efficiently through resonant coupling. In the next phase of the VUV-FEL at Hamburg, a pump-probe facility as “used” in this theoretical investigation will be available for experiments. Furthermore a similar experiment, but much simpler than the one at DESY as far as the experimental set is concerned, is planned in Saclay [15]; it is planned to use an 800 nm femtosecond laser, together with its 9th harmonic (delivering photons with \( E \approx 14 \) eV) as the IR and VUV pulse, respectively; the intensities will be a bit lower than the ones considered here, but this should only result in a quantitative difference. The present paper shows that indeed, interesting and unique experiments can be done with such a time-delayed combination of pulses.

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[16] For rare gas clusters, the concepts of inner and outer ionization, the first being the ionization of an electron out of an atomic orbital into the cluster environment, the latter the process of an electron leaving the cluster as a whole, have proven to be very useful. If one is dealing with the valence electrons of a metal cluster, the inner ionization step is skipped, since these electrons can already move freely throughout the cluster. From the second shell onwards, metal clusters should not behave different from rare gas clusters.