Attosecond Resolved Charging of Ions in a Rare-Gas Cluster

Ionuţ Georgescu, Ulf Saalmann, and Jan M. Rost

Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, 01187 Dresden, Germany

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A scheme to probe dissipative multielectron motion in time is introduced. In this context attosecond probing enables one to obtain information which is lost at later times and cannot be retrieved by conventional methods in the energy domain due to the incoherent nature of the dynamics. As a specific example we will trace the transient charging of ions in a rare-gas cluster during a strong femtosecond vacuum-ultraviolet pulse by means of delayed attosecond pulses.

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One of the most prominent applications of attosecond pulses is to perform microscopic time measurements of electron motion. Since the photon flux of currently available attosecond sources is too low for a microscopic clock involving start and stop pulses, novel pump-probe schemes have been developed. In recent experiments [1–3] the system is pumped by an attosecond extreme-ultraviolet (XUV) pulse and probed by a few-cycle infrared (IR) pulse. In one case [1,2], referred to as attosecond *streaking*, the final electron momenta $\vec{p}_{\text{final}} = \vec{p}_{\text{excited}} + \vec{\mathcal{A}}(\tau)$, in which the excitation time τ is encoded by the instantaneous vector potential $\vec{\mathcal{A}}(t)$ of the IR pulse, are measured. In the other case [3], the ion yield $P_{\text{final}} = \int_{\tau}^{\infty} dt' P(t')$ is recorded, whereby the *nonlinear* dependence of the tunnel ionization P on the instantaneous electric field $\vec{\mathcal{E}}(t)$ of the IR pulse allows one to determine the initial time τ with subfemtosecond resolution.

Since the new attosecond technique leads into unexplored territory, the first experiments have addressed relatively simple coherent dynamics: one-electron [1], two-electron [2], and in the third case a seemingly simple almost separable case of multielectron [3] motion. One may argue that, at least regarding the pump-probe experiments, the time-resolved quantities could in principle also be retrieved from an experiment which exhausts the full parameter space in electron energy. This is the case since the electron distribution of interest (directly after the attosecond pulse) remains essentially coherent until it can be measured (time-resolved or, more conventionally, energy-resolved). Time- and energy-resolved measurements are to a large extent Fourier related in this context.

Here, we would like to draw attention to another possibly fruitful use of attosecond pulses in the context of complex systems, exemplified with rare-gas clusters. The difference to the simpler electron dynamics as discussed above lies in the fact that due to dissipation and other many-particle interaction effects one can by the very nature of the process not recover time-resolved information from the (energy-resolved) traditional observables. Hence, time-resolved information from ultrashort pulses will provide so far unobtainable insight into the dynamics of those larger, dissipative systems. Clearly, because of these dissipation processes, like multiple electron-electron and (laser-driven) electron-ion collisions, such information is dominantly incoherent.

To be specific, we will propose a pump-probe scenario which is inverse to the one mentioned above: We expose a small rare-gas cluster to a femtosecond vacuum-ultraviolet (VUV) laser pulse and probe the time-dependent excitation and ionization dynamics in the cluster, i.e., its charging, by time-delayed attosecond XUV pulses. The latter simply kick out electrons, still bound to an ion in the cluster at that time, and provide in this way information on the (transient) charging status of the cluster ions, as will be detailed below and is schematically shown in Fig. 1.

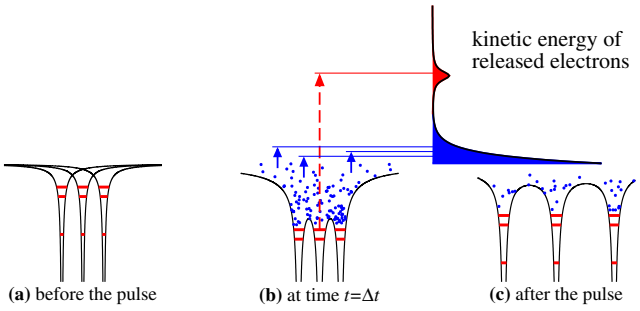

FIG. 1 (color online). Scheme for the slow-pump fast-probe time-resolved measurement of the transient charging in a multi-ion and multielectron system. Before the pulse (a) the electrons are localized in atomic orbitals (thick horizontal lines) and the cluster is held together by van der Waals forces. The initial ionization will lead to a cluster potential (b), allowing for further excitation of bound electrons into the cluster; these "quasifree" electrons (dots) are eventually ionized with low kinetic energies (arrows). The attosecond XUV pulse pushes electrons from the upper bound states, directly into the continuum by one-photon absorption (long dashed arrow). The measured energy of these electrons traces their instantaneous binding energy and thus the transient charge state of the ion and the overall charge of the cluster as a function of the time delay Δt between both pulses. Finally, after the pulse, the charged cluster fragments (c).

We will use a 100 fs VUV pump pulse with a frequency of 20 eV similar to the one applied at FLASH (Free-electron LASer in Hamburg) in 2002 [4]. The interpretation of the experimental results is still somewhat controversial [5–8], and a future attosecond resolved observation of the charging of the cluster could discriminate between the different theoretical scenarios which predict quite different degrees of the transient charging of the cluster.

In our specific example we want to trace the ionization stage of the cluster ions through the kinetic-energy spectra of the photoelectrons from the attosecond pulse. Three possible problems come immediately to mind. They all have to do with the unique relation of the time-of-flight spectra of the electrons to the time-dependent charging of the target: (i) The attosecond pulse will act perturbatively on the electrons bound to the ions, but one needs to make sure that the least bound electron is kicked out and therefore identifies uniquely the present charge state of the ion. (ii) The attopulse photoelectron should not lose its energy, characteristic of the bound state it came from, through inelastic collisions while leaving the cluster. (iii) One needs to distinguish between ''normal'' ionized electrons and photoelectrons originating from the attosecond probe pulse. In order to address these issues and to see if the idea of slow-pump fast-probe is feasible, a realistic calculation is necessary. We base our calculation on previous experience in modeling cluster dynamics [5,7,9,10] and briefly describe the present approach below. The attosecond probe pulse acts perturbatively (via photoionization rates) onto individual ions in their respective charge state. The photoionization rates for the argon atom in the XUV region are easily accessible [11] since $3s$ and $3p$ electrons from the outer shell can be ionized by single-photon absorption. Electrons in other states are not affected by the attosecond XUV pulse. Core-shell electrons ($1s$, $2s$, $2p$), on one hand, would require multiphoton processes which are negligible at the XUV intensity applied. Quasifree or plasma electrons, on the other hand, have due to their delocalization in the cluster volume much lower cross sections for ionization. Altogether, the well defined coupling of the $n = 3$ shell electrons to the attosecond pulse solves problem (i), although in the case of argon, indeed, $3s$ and $3p$ electrons are ionized, as we will see. Problem (ii) is solved by minimizing the probability of collisions for the photoelectron using a small Ar_{13} cluster and a high frequency for the attosecond pulse creating fast photoelectrons. We mention in passing that in order to access larger clusters one would need even higher XUV photon energies. High photon energies also solve problem (iii) since the quasifree electrons form a well characterized electron plasma whose Maxwellian distribution yields electrons in the continuum with energies of only a few eV [12], which should be very small compared to the energies of the photoelectrons.

For clusters exposed to a VUV laser pulse we have developed a hybrid quantum-classical approach to simulate the time-dependent dynamics of the cluster ions and electrons [7]. Bound electrons are not explicitly treated, but can be ionized with probabilities according to their quantum ionization rates. Special attention has been paid to adopt the photoionization rates to the cluster environment, where electrons screen the ions and neighboring ions lower the threshold for ionization into the cluster. Once an electron is ionized into the cluster, it becomes quasifree and is propagated together with all other charged particles (ions and electrons) classically under the full Coulomb interaction and the dipole coupled electric field

$$\vec{\mathcal{E}}(t) = \vec{e}_z \sqrt{I_{\mathrm{vuv}}/I_0} \cos^2\left(\frac{\pi t}{2.75 T_{\mathrm{vuv}}}\right) \sin(\omega_{\mathrm{vuv}} t) \qquad (1)$$

of the VUV pulse which has a peak intensity of $I_{\mathrm{vuv}} = 7 \times 10^{13}$ W/cm^2 at $\hbar\omega_{\mathrm{vuv}} = 20$ eV photon energy and $T_{\mathrm{vuv}} = 100$ fs pulse length (FWHM for the intensity). The intensity $I_{\mathrm{xuv}} = 1.4 \times 10^{15}$ W/cm^2 of the attosecond pulse (photon energy $\hbar\omega_{\mathrm{xuv}} = 150$ eV, duration $T_{\mathrm{xuv}} = 500$ as) is chosen such that on average 0.5 electrons/cluster are photoionized by the attopulse to ensure that the atto-electrons do not perturb the charging dynamics of the cluster. Apart from the time delay Δt, the attopulse is also given by Eq. (1) with the corresponding parameters. Because of the short duration it has a significant bandwidth of $\Delta\omega \approx 4.5$ eV (FWHM). Therefore, electrons excited by the attosecond pulse have a finite spread in their kinetic energies taken into account by folding the spectra (see below) with the Fourier transform of the attosecond pulse.

We have calculated the dynamics of an Ar_{13} cluster (smallest magic number, icosahedral structure) exposed to the laser pulses specified above. Figure 2 presents a series of electron spectra with different delays Δt between the maxima of the femtopulse and the attopulse. One can clearly follow the charging of the cluster with increasing delay of the attopulse. For a time delay $\Delta t = -137$ fs of the attopulse, the atomic ionization spectrum is obtained; see uppermost curve and additional graphs (a) and (b) to the right in Fig. 2, with the main peak from the $3p$ orbitals and a smaller peak from the $3s$ orbitals. The $3p$ peak (at $E_{\mathrm{kin}} \sim 133$ eV) is higher mainly because of the larger multiplicity of the p shell with six electrons. The location of the peaks differ by about 15 eV corresponding to the difference of the binding energies of $3s$ and $3p$ electrons. Note that the peaks are slightly redshifted with respect to the expected line from an isolated atom (dashed lines in Fig. 2). This is due to the positive background charge of the cluster against which the electrons must find their way to the continuum. Consequently, the redshift becomes larger as the peak of the attosecond pulse moves closer to that of the VUV pulse (i.e., as Δt increases to smaller negative values), when the cluster charge increases. However, apart from the growing redshift and a slight broadening, the shape of the spectrum remains the same until a delay of $\Delta t = -105$ fs: There, for the first time, a signal at higher

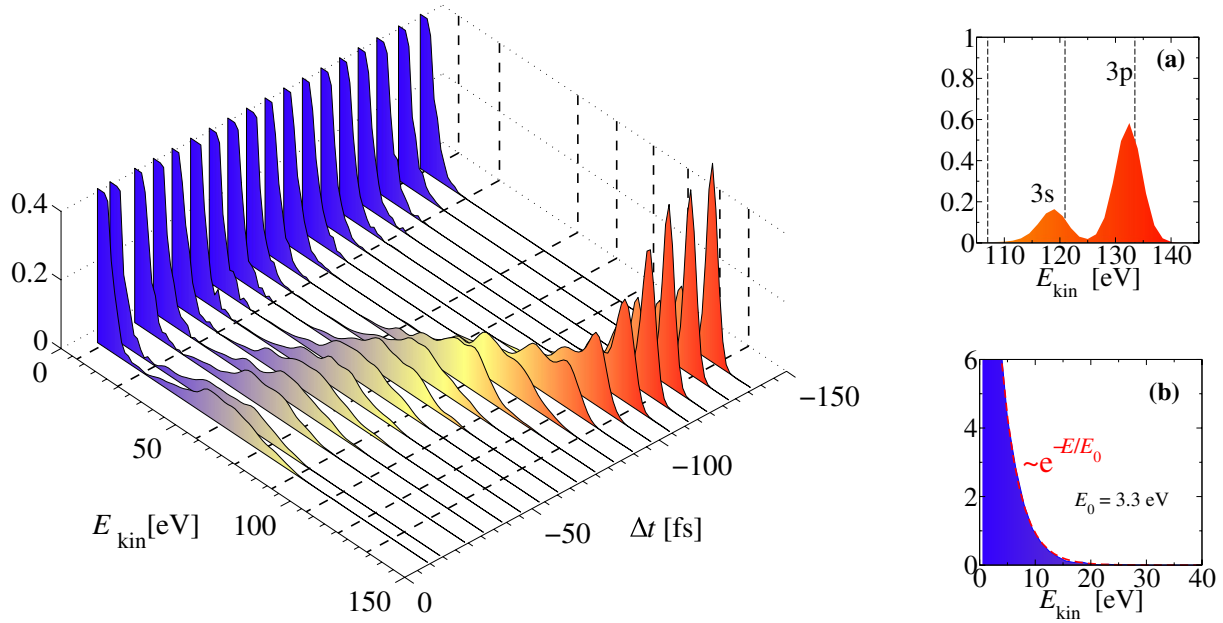

FIG. 2 (color online). Series of kinetic-energy spectra of the released electrons for several time delays Δt between XUV pump and VUV probe pulse. The dashed lines indicate the excess energy $\hbar\omega_{xuv} - E_{ip}(Ar^{q+})$ over the ionization potential E_{ip} of an isolated q-fold charged argon atom ($q = 0 \ldots 7$ from right to left). They allow for the identification of the transient charge q of the mother ion. The low-energy part of the spectrum is independent of Δt. It is formed by quasifree electrons, evaporated from the electron plasma which is typically generated by the VUV excitation [12]. Right column: Details of the spectrum for a delay of $\Delta t = -137$ fs, i.e., the XUV probe precedes the VUV pump pulse, for high (a) and low (b) kinetic energies. The latter is fitted by an exponential curve.

charges (lower kinetic energy) becomes visible which intensifies for later probe pulse, i.e., less negative time delays from $\Delta t = -98$ fs to $\Delta t = -75$ fs. One notes that after $\Delta t = -70$ fs the attosecond pulse induced photoelectron distribution remains roughly the same in shape but moves still to lower kinetic energies for later probe pulses. This indicates that the internal charging of the cluster has come to an end, but plasma electrons slowly evaporate, leaving a higher and higher background charge which makes it more difficult for the photoelectrons to escape. Note, that the low-energy part ($E_{kin} < 20$ eV) of the electrons from the plasma (blue wings in Fig. 2) is not influenced by the XUV pulse. In fact, it can be fitted by an exponential curve with a decay constant of about 3.3 eV. This value corresponds to the temperature of the electron plasma around the time when the VUV pulse is at its maximum ($t = 0$).

Since for the high-energy part the kinetic energy is given by $E_{kin} = \hbar\omega_{xuv} - E_{ip}(Ar^{q+})$, the latter being the ionization potential of a q-fold charged argon ion, one can measure the average charge from the center of mass of the obtained energy distribution. The measured (probed) charge leads the real one (Fig. 3). They agree within their standard deviations (thin vertical lines in Fig. 3) which are mainly due to different charge states in the cluster; the finite bandwidth of the attosecond pulse is of minor importance (<10% of the error bars). The measured charge is systematically larger due to the overall charge of the cluster and the excited states of the ions, whose $3s$ and $3p$ orbitals are stronger bound than in the corresponding ground state. One may think that a slower probe than with attosecond pulses may be sufficient for the charging dynamics. However, the simulation (without attopulse) suggests that the interesting charging happens within some

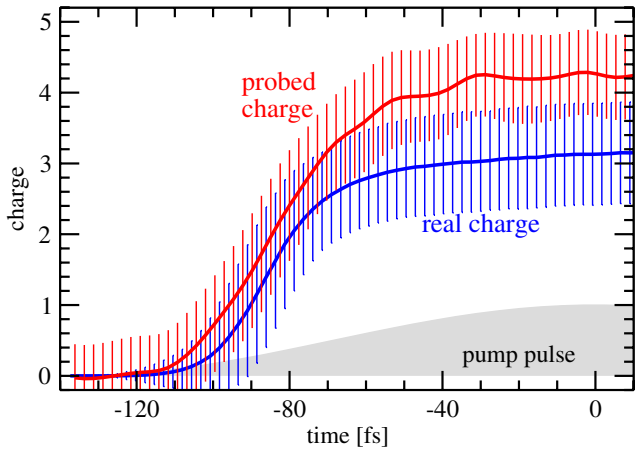

FIG. 3 (color online). Charging of the Ar_{13} cluster as a function of time for a VUV pulse (gray-shaded area) with a photon frequency of 20 eV, an intensity of 7×10^{13} W/cm^2, a pulse length of 100 fs and the peak at $t = 0$. The final real ionic charge (thick line: average; thin lines: standard deviation) is reached early in the pulse during the time interval from -100 fs to -60 fs. Attosecond XUV probing nicely reproduces the charging (probed charge) by converting the kinetic-energy spectra (Fig. 2) for the respective time delay Δt.

10 fs; see Fig. 3. Hence, probe pulses of at least subfemtosecond length are convenient. Moreover, the probe pulse must have considerably higher photon energy to generate photoelectrons, clearly separated in energy from the cluster electrons, see problem (iii).

The direct access to the transient charge of ions in the cluster may help to discriminate between different theoretical interpretations. The one applied here [7] is connected with transient ion charges that are considerably *larger* than the measured ones. Other approaches [8] attribute the heating to enhanced inverse bremsstrahlung at *weakly* charged ions. We emphasize that measuring the final charge distributions would not give the same information; because of further evaporation of electrons and recombination during the cluster expansion, the final charges can differ considerably from those observed during the pulse.

To summarize, we have proposed a scheme to probe the transient charging of a rare-gas cluster during exposure to a strong VUV pulse with attosecond pulses. This specific example conveys the general idea for a so far not suggested use of attosecond pulses: Initiate a relatively slow excitation process in an extended system through a femtosecond laser pulse, and probe the nonstationary, most likely dissipative relaxation dynamics by time-delayed attosecond pulses. This type of experiment should be possible in the future, either with two synchronized light sources or with higher harmonics and the fundamental of a VUV light source.

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