Multiple Excitation and Lifetime of the Sodium Cluster Plasmon Resonance

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The large collective resonance of the spherical cluster Na_{93}^+ has been studied using a femtosecond laser, which directly excites the resonance. Photofragment size and charge distributions have been measured. A large intensity of doubly and triply charged fragments has been observed, which is absent when applying nanosecond laser pulses of the same wavelength and pulse energy. The efficient ionization processes can be understood as autoionization of the multiply excited collective resonance. A simple rate model gives an estimate of about 10 fs for the lifetime of the resonance. [S0031-9007(97)05248-4]

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Alkali clusters have a very strong collective, plasmonlike resonance in the visible part of the optical spectrum, which can classically be described as a collective oscillation of a homogeneous electron gas against a background of positively charged ions. Although this resonance has been intensively studied in recent years [1–3], some fundamental questions still remain unsolved. Among them are two which are addressed here: (1) What is the lifetime of the resonance and (2) is a double (or multiple) excitation of the plasmon possible, as in the kindred nuclear physics case?

The nuclear physics analogue of the collective oscillation is the giant dipole resonance, the classical picture of which is that of a proton liquid oscillating against a neutron liquid [2]. A few years ago it was discovered that a doubly excited state of this giant resonance exists [4]. An interesting question therefore is: Does such a doubly excited collective state also exist in clusters, and how can it be excited? As will be shown below, this type of excitation exists indeed, and can be excited by a sequential absorption of two photons from an ultrashort laser pulse.

It has to be emphasized that the experiment presented here is very different from recent experiments, where the nonresonant interaction of very intense, ultrashort laser pulses with clusters has been studied [5]. In these experiments, where laser fluences 5–8 orders of magnitude higher than employed here have been used, the clusters are so highly excited that copious amounts of x rays and high energy electrons are emitted. Such nonlinear effects are absent at the power levels used in this experiment.

There are other studies where comparably weak femtosecond laser pulses have been employed to study cluster excitation and ionization. In most cases these were multiphoton ionization studies of neutral clusters: mass distributions of charged products are monitored while ionizing non-mass selected clusters with femtosecond laser pulses [6,7].

Here we want to present a study of large sodium clusters, where the clusters are mass selected before and after the laser interaction. As will be seen below, this double mass selection is indispensable for the problems studied here. The only earlier experiment using this scheme with femtosecond laser excitation studied small silver clusters [8].

The experimental setup (see Fig. 1) is similar to that described earlier [9–11]. Cluster ions with a temperature of ~105 K are produced in a gas aggregation source [11], and mass selected in a first time-of-flight mass spectrometer (TOF1). The intensity is typically 10–50 clusters of Na_{93}^+ per pulse. The clusters are photoexcited, and the resulting photoproducts are mass separated in TOF2 and detected. Two different laser systems can be used. Either an excimer pumped dye laser with a typical pulse length of 10 ns is used, or a femtosecond titanium-sapphire laser system can be employed, which has today's standard configuration. Briefly, the second laser consists of an Ar^+ laser pumping a Ti:sapphire oscillator employing Kerr-lens mode locking [6,7]. Its 80 fs pulses are stretched by a factor of 2000, amplified by a regenerative amplifier, and recompressed. The intensity at 800 nm is typically 1 mJ per pulse with a repetition rate of 30 Hz. Frequency resolved optical gating gives a pulse length of 75 to 110 fs with no visible chirp [12]. After frequency doubling the pulse length is 100–150 fs. The intensity at $\hbar\omega = 3.1$ eV is typically 0.3 mJ which corresponds to 2×10^{14} photons per pulse.

The diameter of the laser beam has to be matched to that of the cluster beam in the interaction region, which

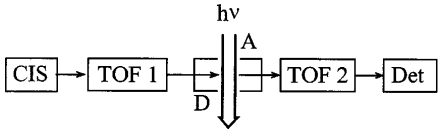

FIG. 1. Schematic of the experiment. Clusters from a temperature controlled cluster ion source (CIS) are mass selected by the first time-of-flight mass spectrometer (TOF1). They are irradiated by a photon pulse, whose length is either 10 ns or 100–150 fs. Charged fragments are separated by the second time-of-flight mass spectrometer (TOF2). Both TOFs are of the reflectron type, having mass resolutions of 1500 and 800, respectively. The clusters are decelerated (D) before, and accelerated (A) after, the laser interaction, in order to overcome the limited acceptance window of TOF2. Det represents the detector.

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is about 3 mm and cannot be reduced without severe intensity loss. Thus, in contrast to most experiments with ultrashort pulses, the laser beam is *not* focused, but has a FWHM of 2.5 mm in the interaction zone. This first study was performed on Na_{93}^{+}, which has a closed electronic shell of 92 electrons and is thus spherically symmetric in the nearly free electron (or jellium) model [2]. Its one-photon absorption cross section has been measured earlier to be about 60 Å^2 at $\hbar\omega = 3.1$ eV [10].

A typical photofragment distribution is shown in Fig. 2. A large intensity of doubly and triply charged clusters is observed. This is in stark contrast to the observations for nanosecond laser pulses, where no ionization occurs at this wavelength, even if the laser intensity is high enough to totally fragment the cluster [3,13]. The size distributions of the singly and multiply charged fragments show an enhanced intensity every three to four atoms. This is due to the fact that the binding energy of one atom is about 0.9 eV [3], so that for one absorbed photon of $\hbar\omega = 3.1$ eV on average 3.4 atoms are ejected. This structure is visible only for clusters of a well defined temperature. Its observation is very helpful, as it enables the determination of the exact number of photons absorbed, which, in a different experiment, has allowed us to determine the specific heat of size-selected sodium clusters [14].

Spectra like the one shown in Fig. 2 have been measured for a broad range of laser intensities. Two results can be obtained immediately for Na_{93}^{+}: (1) Unlike the case of excitation by nanosecond laser pulses, no singly charged fragments smaller than about Na_{73}^{+} are observed. As explained above, about six photons of $\hbar\omega = 3.1$ eV are necessary to eject 20 atoms. Additionally two photons are needed before a 93 atom sodium cluster at 105 K

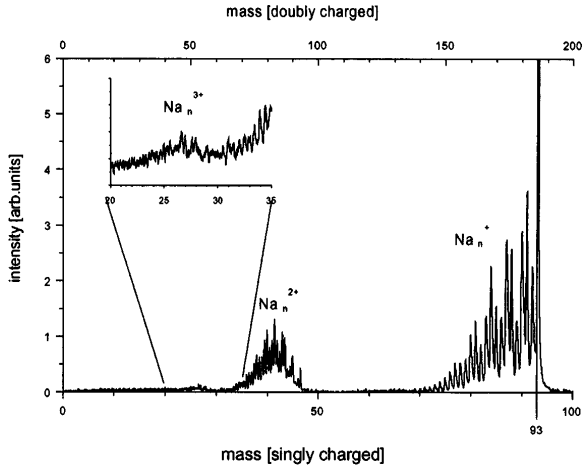

FIG. 2. Photofragmentation mass spectrum of Na_{93}^{+} produced by a 140 fs pulse. The smallest singly charged fragments observed have lost around 20 atoms. A large intensity of doubly and some triply charged fragments is seen. There is a different mass scale for singly and doubly charged fragments. Note that for a 10 ns pulse length one observes only singly charged fragments.

starts evaporating atoms on the time scale of this experiment (10^{-5} s). It thus follows directly that if more than eight photons are absorbed by the cluster, ionization takes place with near 100% probability. This observation allows an estimate of the lifetime of the resonance as discussed below. (2) For higher laser intensities the doubly charged fragments are ionized again, and triply charged clusters are produced. At even higher power levels, fourfold charged clusters might be produced, but these are unstable due to Coulomb repulsion [13]. However, in the case of larger clusters this is possible; for the ionization of Na_{345}^{+} we detected up to fivefold ionized products [15]. This efficient production of high charge states reveals that the photoionization of the excited clusters has a cross section similar to the very large cross section of the first excitation step; this can be explained only by a multiple excitation of the collective resonance, followed by autoionization.

In order to further evaluate the measured laser power dependence of the fragment distribution, we have used a simple rate model. It is an extension of a rate model which was successfully used earlier for the sequential photoexcitation with a nanosecond laser [16]. The assumptions of this latter model are (1) the cluster absorbs photons with rate $p = \sigma\phi$, where ϕ is the laser intensity, and σ is the photoabsorption cross section which is assumed to be independent of the cluster size. (2) The electronic energy relaxes with rate r into the vibrational degrees of freedom, which finally leads to the ejection of atoms. This model is generalized here (see Fig. 3). The main assumption is that not only one collective excited state exists, but a ladder of equally spaced excited states. If the lifetime of the collective resonance is comparable to the mean time between two photon absorptions, one has the possibility of climbing up this ladder to multiply excited states. Technically, the main ingredients of the rate model are (1) the cluster absorbs photons with rate $p = \sigma\phi$ not only independent of cluster size, but also independent of charge state and excitation. (2) Excited states below the threshold for electron emission relax with rate nr into vibrations (n being the state quantum number as given in Fig. 3). (3) Above the threshold, electron ejection occurs immediately.

The corresponding rate equations have been solved [15]. The results are Poisson distributions for the intensity $I(k, j)$ of the cluster in charge state j, after having absorbed k photons from a laser beam of pulse length τ.

$$I(k, j) = A(k, j, r, \tau)\,(\sigma\phi\tau)^k \exp(-\sigma\phi\tau)/k! \quad (1)$$

The factor $A(k, j, r, \tau)$ gives the branching ratio between the different charge states. These equations have been fitted to the photofragment intensities which were measured as a function of the laser intensity ϕ. Good agreement is obtained, as shown in Fig. 4. The great value of this analysis is that, in principle, it yields three important parameters: the number of photons (k) necessary to produce

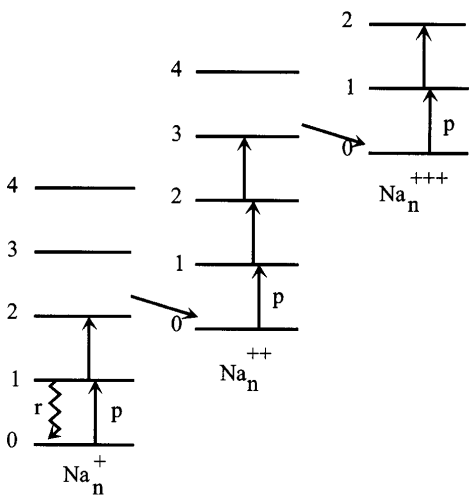

FIG. 3. Graphical representation of the rate models described in the text. The electronically excited $n = 1$ state of the mass selected (and therefore charged) cluster Na_n^+ is populated with rate p. The $n = 2$ state is populated if the next photon is absorbed before the electronic energy is relaxed into vibrational energy (which happens with rate r). The $n = 2$ state of Na_{93}^+ can decay by electron emission to the $n = 0$ state of Na_{93}^{++}. Here the same ladder climbing continues, only now three photons are necessary to produce a triply charged cluster. Every excited state can of course relax, which is drawn only once for the $n = 1$ state of the initially prepared cluster.

a certain cluster size, the average absorption cross section (σ) of the excitation process, and the lifetime of the excitation ($1/r$). The parameter k follows also from the fragment size (as discussed above), and can thus be used to check the validity of the fit.

The rate model used is as simple as possible, in order to obtain the relevant physics with a minimum number of free parameters. The assumptions involved will now be discussed. (1) Rate models loose their validity if the laser pulse length τ is of the order of the physical time scales involved, and have to be replaced for shorter τ by the optical Bloch equations [17]. These have been solved numerically for the present model [15]. Significant deviations from the rate model results are found for $\tau \leq 50$ fs, which is a factor of 2–3 shorter than our pulse length. (2) The electron emission is assumed to be very fast, but not fast enough to significantly influence the absorption cross section. The fact that the electron loss is a very fast process indeed has been demonstrated earlier in a study of Na_{91}^- (which has 92 valence electrons as well) [18]. (3) The photoabsorption cross section σ is assumed to be independent (within a factor of 2) of the charge state, the temperature, and the excitation of the cluster. The first two of these points are in agreement with recent measurements [19,20]. The last point, σ being independent of the degree of electronic excitation, can be understood if the plasmon resonance is regarded as the excitation of a damped harmonic oscillator. This analogy is explained below.

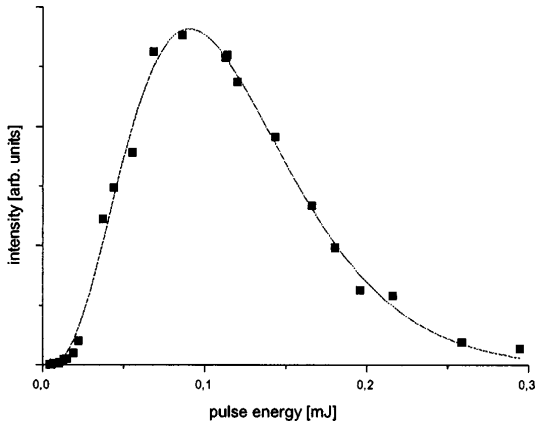

FIG. 4. The intensity of Na_{87}^+ as a function of laser flux is well approximated by a Poissonian. The exponent of Eq. (1) gives the mean number of photons absorbed ($n = 3.3 \pm 0.2$ here). This is in good agreement with the value calculated from the known values of the atom binding energies and the cluster's heat capacity.

The classical oscillation of a rigid electron gas against a spherical and homogeneously charged ion background is harmonic unless very high excitation energies are employed. This can be seen by calculating the classical electrostatic energy as a function of the relative displacement of ions and electrons, and fitting the minimum of the resulting potential with a harmonic potential [15]. The frequency of this harmonic oscillator turns out to be the Mie frequency $\omega(Mie) = \omega_P/\sqrt{3}$, where ω_P is the bulk plasmon frequency [1–3]. Save for the spill-out correction [1–3], $\omega(Mie)$ agrees with the experimentally determined peak position of the plasmon resonances, for clusters containing more than 40 sodium atoms [10].

In the experiment, we might reach up to the third or fourth state of this harmonic oscillator. For these energies, the deviation of the calculated electrostatic potential from the harmonic potential is negligible, so that, in a classical approximation at least, the collective resonance represents a perfect harmonic oscillator. As the oscillator strength of a harmonic oscillator and its damping are expected to increase linearly with the quantum number n [17], a constant level-to-level σ results, in agreement with assumption three above.

Within this harmonic oscillator model, the $0 \rightarrow 1$ excitation corresponds to the well known Mie resonance [1–3]. But also the existence of the higher excited states, which have never been observed before, now seems obvious. There is one theoretical result to support this prediction: in a calculation of a Na_9^+, in a strong light field, harmonic excitations up to the fourth level were found [21]. In this respect, the clusters differ from the nuclear case, where it was only possible to excite the doubly excited state. Apparently the long range Coulomb force provides for a much more harmonic potential [22].

It remains to determine the lifetime δt of the resonance. A rough estimate can be obtained from the following

argument: singly charged fragments can be obtained only if the electronic excitation decays before the next photon is absorbed. This gives $\delta t \approx \tau/N^+_{\max}$, where $\tau = 120-150$ fs is the pulse length of the laser, and $N^+_{\max} = 8$ is the maximum number of photons which can be absorbed without ionization occurring. This gives $\delta t = 15-20$ fs. A better value is obtained from the rate equations introduced above, which yields $\delta t = 10 \pm 3$ fs. But also this value can still only be seen as an estimate, of course, due to the simplifications incorporated into the rate model. Experiments and theoretical studies are in progress to improve the accuracy of this determination [15]. These small values for δt, which correspond to only a few periods of the optical cycle of 1.32 fs, are similar to very recent results of lifetime measurements of the collective excitations of gold, silver, copper, and sodium clusters on isolator surfaces, where values of about 10 fs and lower were obtained [23].

This Letter has touched upon several theoretical questions, whose answers are either scarce or unknown: (1) How good is the harmonic approximation? (Probably not bad, in view of Ref. [21] and the results presented here.) (2) What is the dominant decay mechanism giving the short lifetime? (We conjecture that it will be the finite particle analogue of the bulk interband transition.) (3) What is the electron ejection mechanism? Is a $2 \rightarrow 0$ transition possible, with one electron getting all the energy? Or does one have a $2 \rightarrow 1 \rightarrow 0$ cascade, where two excited electrons are produced, followed by autoionization? Theoretical clarification of these points is highly desirable.

It is also possible to reach the higher excitation states of a cluster without using ultrashort laser pulses. They can be excited in the collision of a cluster with highly charged ions [24]. It would be very interesting to compare the results of both experiments.

In summary, an experiment has been described, where the collective resonance of the mass selected cluster Na^+_{93} is excited by laser pulses with pulse lengths of 10 ns and about 100 fs, respectively. In the first case, the lifetime of the collective resonance is much shorter than the mean time between two photoabsorptions. Thus no higher electronic excitation can build up in the cluster, and consequently no electron ejection happens, as observed on many occasions earlier [1,3,13]. For the 100–150 fs pulse, conversely, δt is comparable to, or even longer than, the mean time between two photoabsorptions. Higher electronic excitations are then possible. The large cross sections observed for the higher excitations (e.g., for $1 \rightarrow 2$ in Fig. 3) have been explained by mapping the classical oscillation of the nearly free electron gas onto a harmonic oscillator. Its $0 \rightarrow 1$ transition corresponds to the often studied plasmonlike resonance, which is so prominent in sodium clusters. The lifetime of the plasmon resonance is estimated to be about 10 fs.

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