Spectroscopy of Size-Selected Neutral Clusters: Femtosecond Evolution of Neutral Silver Trimers

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Negatively charged, mass-selected clusters of silver atoms are caught in a linear quadrupole trap. There their excess electrons are photodetached with a nearly 100 fs pulse of ~400 nm radiation. The neutrals so prepared would remain in the trap for ns or even ms. However, a second ultrashort delayed pulse of radiation, intense enough to induce two-photon ionization of the clusters, is put into the trap, allowing the neutral to carry out internal motion. The positive ions generated are then mass analyzed and collected. The transient ion signal reveals the internal motions of the atoms of the neutral, monodisperse clusters, particularly in cases in which detachment, ionization, or both involve a significant change of geometry.

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A desideratum of experimental cluster science has been a means to study structures, spectra, dynamics, and reactions of neutral clusters of a single, known mass. One method for doing this with relatively small clusters is deflection by collision with He atoms [1]. Here we describe a new approach which we have used to study silver clusters Ag_n ($n = 3$, 5, 7, and 9). The method begins with a beam of mass-filtered, negatively charged clusters, which are subjected to photodetachment and, after a variable but selected temporal delay, photoionized. The positive ions are then mass analyzed and collected. The intensity of the positive ion signal as a function of the delay interval between the fs pulses is a measure of the evolving Franck-Condon factor for photoionization of a neutral prepared by a vertical detachment process from a low-lying vibrational state of the negative ion. In this way, we probe the vibrational motion in the neutral. For convenience, we shall refer to the process as NeNePo, negative to neutral to positive.

Our first studies have been done with clusters of silver atoms because there is considerable information about them from experiment and from theory. We have looked only at the clusters Ag_3, Ag_5, Ag_7, and Ag_9 because their ionization potentials are low enough to ionize them by two-photon absorption with the laser available. However, these are in some respects an ideal series because they provide several different structural relationships among the negative, neutral, and positive species [2,3]. In this Letter, the NeNePo results for the Ag_3 will be presented.

The experiment makes use of a high intensity cluster anion source, an ion trap, a mass analyzing detector for cluster cations, and a laser system which produces pairs of ultrashort laser pulses with an adjustable time delay between the first (pump) and the second (probe) laser pulse. The laser system consists of a titanium-sapphire oscillator (Spectra Physics Tsunami) which is pumped by a 12 W argon ion laser and a Nd:YLF-pumped regenerative amplifier (Quantronix 4800 Ti:sapphire RGA) to produce ultrashort ($\tau < 100$ fs, 500 mJ/pulse) laser pulses at a repetition rate of 1 kHz. The pulses are efficiently (~40%) frequency doubled in a BBO crystal. The second harmonic is split into pump and probe pulses, with the probe pulse delayed with respect to the pump pulse by a computer controlled translation stage.

The clusters are produced in a sputtering ion source, especially designed to yield a high flux of well thermalized cluster ions. Details will be given in a subsequent publication [4]. In brief, silver cluster anions are generated by sputtering silver targets with Xe cations from a cold reflex discharge ion source. In order to maximize the yield of anions, the targets have been lightly covered with Cs metal prior to the sputtering process. The anions are extracted into a large helium-filled quadrupole ion guide, where they are thermalized by a large number of collisions with the background gas ($p_{\mathrm{He}} \sim 10^{-2}$ mbar) [5]. Thereby internal energy is removed from the clusters, and the volume of the ion cloud both in real space and in momentum space is substantially compressed. This matches the emittance of the sputtering ion source to the acceptance of the subsequent quadrupole mass spectrometer. The anions are then transferred to a quadrupole mass filter, where the cluster size of interest is selected. The final cluster intensity ranges from some nanoamperes in the case of the small clusters (e.g., Ag_3^-) to a few hundred picoamperes for the larger clusters like Ag_9^-. The mass-selected cluster ions are then accumulated in a linear quadrupole drift tube, which is operated as an ion trap [6]. Here they are again exposed to a buffer gas of helium ($\sim 10^{-3}$ mbar), which helps to trap the ions and leads to further thermalization. Their residence time as negative

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ions can be minutes. When the photodetachment is carried out, the negative ions typically reside in the trap for about 100 ms. During this time, they undergo more than 1000 collisions with the buffer gas. The ion density in the trap is limited by space charge effects to ~ 107 ions per cm^3, independent of the cluster size.

Pump and probe laser beams are imaged into the trap collinear with the ion trajectories and overlap throughout the whole length of the trap. The electrons of the stored cluster anions are detached by the light of the pump laser, and after a certain delay time *Dt*, the newly created neutrals are ionized by the probe laser. This is achieved by nonresonant two-photon ionization rather than by resonant two-photon ionization [7,8]. Direct one-photon ionization experiments, however, are in preparation as well. The cluster cations so produced are extracted from the trap and are mass analyzed and detected with a second quadrupole mass filter equipped with a channeltron ion detector. We thus observe the yield of mass-selected cluster cations produced from mass-selected cluster anions as a function of the delay time between pump and probe pulse at fixed wavelength and fluence of these pulses.

The first experiments were carried out using the silver trimer anion. Mass-selected Ag_3^- ions were produced with an intensity of ~ 2 nA and stored in the ion trap. The detachment was performed at wavelengths of 420, 415, 400, and 390 nm so that one-photon detachment of the anions was possible. The ionization was performed nonresonantly using two photons of the same wavelength. The energy of two photons of 420 nm is only slightly above the ionization potential of the silver trimer, thus allowing a very soft, nondissociative ionization.

Using a wavelength of 415 nm, we find that positive ions are mainly detected when there is a nonzero time delay between pump and probe laser pulses, confirming that sequential processes of detachment and ionization are involved in the creation of the cations. Remarkably, more than 90% of the cluster cations are detected as trimers, showing that with ultrashort laser pulses nonresonant multiphoton ionization with very little dissociation is indeed possible. Nevertheless, small fragment peaks are detectable.

Both results are clearly visible in Fig. 1, showing mass spectra of cluster cations which were produced using a single laser pulse [Fig. 1(a)], or pump and probe lasers at zero [Fig. 1(b)] or finite [Fig. 1(c)] time delay. It is clearly apparent that neither a single laser beam nor pump and probe laser pulses with zero time delay produce silver cluster cations efficiently. The ion signal rather reaches a maximum when the time delay Δt is approximately 650 fs [Fig. 1(c)]. Note that this increase is not observed to the same degree for the fragment peak Ag_2^+. This indicates that the ionization process is less likely to lead to dissociation if there is some time for the relaxation of the neutral cluster (cf. discussion section).

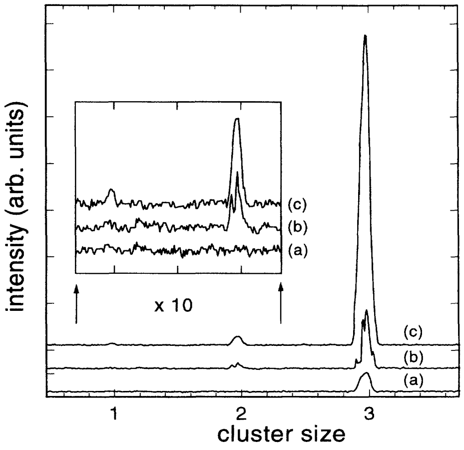

FIG. 1. Mass spectra of cationic silver clusters produced from mass-selected Ag anions using (a) a single laser pulse, (b) two laser pulses with $\Delta t = 0$, and (c) two subsequent laser pulses with $\Delta t = 650$ fs. The structure in (b) is due to interference between pump and probe pulses and demonstrates that the timing assignment $\Delta t = 0$ is correct.

In Fig. 2, we display the yield of Ag_3^+ as a function of the delay time Δt for various wavelengths of the detachment and ionization laser. At $\Delta t = 0$, pump and probe laser pulses exchange their roles. The traces are not symmetrical, as the respective fluences of pump and probe pulse are different. At long wavelengths [Figs. 2(c) and 2(d)], the ion yield rises from almost zero to a maximum around $\Delta t = 750$ fs and then decays to a constant value at longer time delays. There it stays constant for more than 100 ps, the longest time delay used in our experiment. This phenomenon is progressively washed out if we use light of shorter wavelength. In the case of 390 nm [Fig. 2(a)] the ionization efficiency is almost independent of the delay time Δt. The time required to reach the maximum grows with increasing wavelength from 500 fs [Fig. 2(a)] to about 800 fs [Fig. 2(d)], consistent with the notion that the extra energy goes at least in part into the bending vibration. The yields of the charged cluster fragments Ag_2^+ and Ag^+ exhibit the same delay time dependence as the trimer cation. We therefore conclude that the fragments were formed from Ag_3^+ after the multiphoton ionization. The dependence of the cation yield on the power of the pump and probe laser pulses shows that the detachment process depends linearly, but the ionization process quadratically, on the respective light intensity. This is in good agreement with the creation process of the cations as indicated above.

Theoretical predictions indicate that the most stable geometry of the trimer is linear as a negative ion, obtuse isosceles as a neutral, and equilateral as a positive ion. The pentamer is expected to have a planar trapezoidal negative ion (with point group symmetry C_{2v}), a trigo-

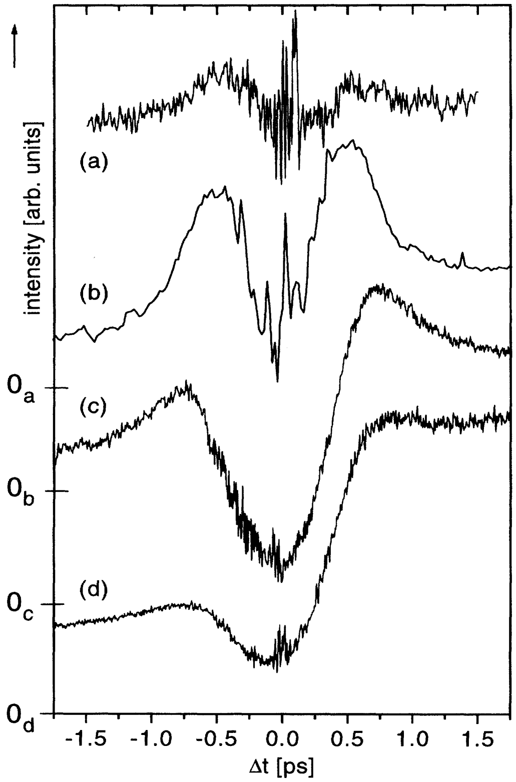

FIG. 2. NeNePo spectra of the silver trimer taken with wavelengths of (a) $\lambda = 390$ nm, (b) $\lambda = 400$ nm, (c) $\lambda = 415$ nm, (d) $\lambda = 420$ nm. Note that each curve, (a) through (d), has its own axis of zero signal, and that the time-independent background increases steadily with decreasing wavelength. The fine structure around $\Delta t = 0$ is, as in Fig. 1, due to interference of pump and probe pulses.

nal bipyramidal positive ion, and a neutral with nearly degenerate minima at both of these structures. The heptamer is expected to have pentagonal bipyramidal global minima for all three charge states, Ag_9, a transbicapped pentagonal bipyramid, for its negative ion, and, for neutral and cation, an assembly of six tetrahedra with shared faces and C_{2v} symmetry [2,3]. Insofar as the detachment and ionization processes can be treated as vertical Franck-Condon processes, these can be expected to give rise to several situations.

The neutral trimer is presumably generated in a linear and therefore highly vibrationally excited configuration, at a saddle, from which it bends slowly at first and then faster, comes through the geometry of the obtuse isosceles minimum, and then decelerates until it approaches equilateral geometry, where its overlap with the positive ion is greatest. The pentamer negative ion has high overlap with one of the two lowest minima of the neutral, so its photodetachment has a favorable Franck-Condon factor, but the cross section for photoionization to a low-lying region of the potential surface of the positive ion becomes large only if the cluster isomerizes to its trigonal bipyramidal structure. The barrier for this isomerization is not yet known but may be evaluated theoretically in the near future. The heptamer should be relatively easy to photodetach and ionize without much change of geometry, and the 9-mer should have a vertical detachment energy of ~0.4–0.5 eV above the adiabatic detachment energy of approximately 1.93 eV, with the difference available for the vibrational excitation associated with the relatively small change in geometry from the capped rhomboidal prism of the negative ion to the C_{2v}-symmetry structure of the neutral and positive clusters.

In principle, whichever vibrations are excited in any of these photodetachment processes may reveal themselves as recurrent peaks in the time-dependent photoionization probability and be identified by frequency from the Fourier transform of the time-dependent, mass-analyzed photoion current [9]. If such signals can be found, they will constitute vibrational spectra of size-selected neutral clusters prepared in well-defined initial states [10].

In fact, the results obtained with the silver trimers have not shown the multiply periodic behavior of a simple vibrational spectrum measured in the time domain. Rather, some of the results reveal less of the vibrational spectra but more of the dynamics of the internal rearrangements of these species, as shown by the time-dependent currents of positive ions in Fig. 2. Our working interpretation—but in no way a demonstration of the physical process—of the behavior of the trimer is this: initially, the neutral is produced in a linear configuration from the vertical, Franck-Condon detachment process. The Franck-Condon overlap factor of the linear neutral with the equilateral positive ion is so low that virtually no positive ions are generated. However, the neutral bends, passes through the obtuse equilibrium geometry of the neutral, and approaches the equilateral equilibrium geometry of the positive ion. During this time the positive ion signal grows and reaches a maximum when the system reaches its classical turning point near the equilateral triangular geometry. Then the system rebounds and the signal decreases. However, the vibrational excitation is high enough that the modes mix, and, after the rebound, the still-neutral trimers are left with enough energy to pseudorotate through their three equivalent obtuse-triangular equilibrium structures, going around the trough of their "Mexican hat" potential energy surface [11]. In so doing, they remain at a roughly constant distance from the equilateral geometry so that the Franck-Condon factor also remains nearly constant, and therefore so does the positive ion signal. The signal at short times is more pronounced at relatively short wavelengths of the ionization laser because there the ionization probability is strongly dependent on the vertical ionization potential in the momentary configuration of the neutral.

There might seem to be a possible inconsistency between our observation of Ag_2^+ and the energies reported in Ref. [2]. If the energy of the dissociation $Ag_3^+ \rightarrow Ag_2^+ + Ag$ is about 2.9 eV and the ionization potential of Ag_3 is approximately 5.7 eV, as this reference gives, then dissociative ionization could occur only from vibrationally excited molecules. Of course the neutrals produced by photodetachment are expected to be quite excited vibrationally since they should be nearly linear, but the energy deficit of 2.66 eV seems too large to make this explanation plausible. Simultaneous three-photon absorption has an energy deficit of >2 eV and no significant reservoir of vibrational energy since the negative ions are relatively cool. Hence we must assume that the fragment ions of Figs. 1(a) and 1(b) are due to four-proton absorption.

NeNePo is a quite general scheme for investigating the time evolution of a coherent nonequilibrium state in neutral clusters. Further investigations will be carried out using different cluster systems and different ionization pathways. NeNePo might also be used to investigate reactive compounds (i.e., cluster ligand systems) where a chemical reaction or molecular rearrangement starts after the neutralization. The associated dynamics could eventually be deduced by detecting and energy analyzing the photoelectrons of the probe process as a function of Δt.

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