

LETTER TO THE EDITOR

Analysis of the ultrafast dynamics of the silver trimer upon photodetachment

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Abstract. We study the ultrafast dynamics of Ag_3 clusters immediately after the photodetachment of Ag_3^- by performing molecular dynamics simulations based on a microscopic electronic theory. We determine the time scale for the change from the linear (initial situation) to a triangular structure (potential minimum) of the ground state of Ag_3 . Our results are in good agreement with experiment. We show how the time dependence of the internal degrees of freedom is reflected in the ‘pump and probe’ signal. Furthermore, we discuss the application of our results to magnetic systems and chemical reactions.

In the last few years the femtosecond spectroscopy of the atomic motion in molecules and clusters has become a major research field. The understanding of the relaxation mechanisms induced by the excitation of the cluster with an ultrashort laser pulse and the interplay of electronic and atomic structure is of fundamental importance to determine how the time scales of the relaxation processes can be controlled by varying the experimental conditions.

Recently, a ‘pump and probe’ experiment has been performed on mass selected silver clusters, which serves as a prototype for the investigation of the structural relaxation times [1]. Ag_3^- clusters were neutralized through photodetachment by a pump laser pulse. Due to the remarkable differences in the equilibrium geometries of Ag_3^- (linear [2]), and Ag_3 (obtuse isosceles triangle [3]), the ultrashort (vertical) photodetachment process generates an extreme nonequilibrium situation for the neutral trimers. As a consequence, a structural relaxation process occurs. The neutral clusters were ionized after a time delay Δt by the probe pulse in order to be detected. Thus, the yield of Ag_3^+ was measured as a function of the delay time Δt and the frequency of the laser pulses. For a frequency slightly above the ionization potential of Ag_3 only a very small signal $S(\Delta t)$ is observed up to $\Delta t \sim 750$ fs. Then, a sharp increase of $S(\Delta t)$ occurs. After a maximum is reached, $S(\Delta t)$ saturates and remains constant for at least 100 ps, which is the longest time delay used in the experiment. New features appear for higher frequencies. Again, $S(\Delta t)$ increases sharply, reaches a maximum and then decreases to a constant value.

In this paper we present a theoretical analysis of the physics underlying the ultrafast dynamics of Ag_3 clusters produced by photodetachment and we show that the experimental results can be explained using a general physical picture. In our calculations, we combine molecular dynamics (MD) simulations in the Born–Oppenheimer approximation with a microscopic theory to describe the time-dependent electronic structure of the clusters.

In order to determine the potential energy surfaces of Ag_3 and Ag_3^- needed for the MD simulations, we start from a Hamiltonian of the form $H = H_{TB} + \frac{1}{2} \sum_{i \neq j} \phi(r_{ij})$, where the tight binding part H_{TB} is given by

$$H_{TB} = \sum_{i,\alpha,\sigma} \varepsilon_{i\alpha} c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma} + \sum_{\substack{i \neq j, \sigma \\ \alpha, \beta}} V_{i\alpha j\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma}. \quad (1)$$

Here, the operator $c_{i\alpha\sigma}^\dagger$ ($c_{i\alpha\sigma}$) creates (annihilates) an electron with spin σ at the site i and orbital α ($\alpha = 5s, 5p_x, 5p_y, 5p_z$). $\varepsilon_{i\alpha}$ stands for the on-site energy, and $V_{i\alpha j\beta}$ for the hopping matrix elements. For simplicity, and since the 5s electrons are expected to be rather delocalized, we neglect the intra-atomic Coulomb matrix elements. $\phi(r_{ij})$ refers to the repulsive potential between the atomic cores i and j . For the distance dependence of the hopping elements and the repulsive potential we write, following Goodwin *et al* [4],

$$V_{i\alpha j\beta}(r_{ij}) = V_{\alpha\beta}^0 \left(\frac{r_0}{r_{ij}} \right)^n \exp \left[n \left(- \left(\frac{r_{ij}}{r_c} \right)^{n_c} + \left(\frac{r_0}{r_c} \right)^{n_c} \right) \right]$$

$$\phi(r_{ij}) = \phi^0 \left(\frac{r_0}{r_{ij}} \right)^m \exp \left[m \left(- \left(\frac{r_{ij}}{r_c} \right)^{n_c} + \left(\frac{r_0}{r_c} \right)^{n_c} \right) \right]$$

where r_{ij} is the distance between atoms i and j , r_0 is the equilibrium nearest-neighbour distance for the lattice, $V_{\alpha\beta}^0$ are the hopping coefficients, n is the hopping exponent, ϕ^0 is the pair potential coefficient, m is the pair potential exponent and n_c is the cut-off exponent. With this distance dependence we are able to account properly for the bond breaking and bond formation processes.

By diagonalizing H_{TB} , (taking into account the angular dependence of the hopping elements [5]), and summing over the occupied states, we calculate as a function of the atomic coordinates the attractive parts of the electronic ground-state energies E_{attr}^- and E_{attr}^0 of Ag_3^- and Ag_3^0 , respectively. Then, by adding the repulsive part of H we obtain the potential energy surface (PES), which we need to perform the MD simulations. In order to determine the forces acting on the atoms we make use of the Hellman–Feynman theorem. Thus, the α -component of the force acting on atom i $F_{i\alpha} = -\partial E / \partial r_{i\alpha}$ is given by

$$F_{i\alpha} = - \sum_{\substack{k \\ \text{occ}}} \left\langle k \left| \frac{\partial H_{TB}}{\partial r_{i\alpha}} \right| k \right\rangle - \frac{1}{2} \sum_{i \neq j} \frac{\partial \phi(r_{ij})}{\partial r_{i\alpha}}. \quad (2)$$

Here the $|k\rangle$ are the eigenstates of H_{TB} . The on-site energies $\varepsilon_s, \varepsilon_p$ were obtained from atomic data [7]. We fit the parameters $V_{\alpha\beta}^0$ and the potential ϕ^0 in order to reproduce the equilibrium bond lengths of the Silver dimers Ag_2^- , Ag_2 and Ag_2^+ obtained by effective core potential–configuration interaction calculations [2, 3]. We assumed the hopping elements $V_{\alpha\beta}^0$ to fulfil Harrison’s relations [8]. The best fit was obtained by the following parameters: $V_{sp}^0 = 0.954$ eV, $r_c = 4.33$ Å, $n_c = 2$, $m = 5.965$ and $\phi^0 = 0.605$ eV. Using these parameters we calculated the vibrational frequencies of the dimers, which compare reasonably well with the experimental values [9] and quantum-chemical calculations [2, 3]. We then determined the equilibrium geometries of the silver trimers Ag_3^- , Ag_3 and Ag_3^+ which again yielded excellent agreement with the all-valence electron calculations of [2] and [3]. The fact that our hopping parameters are comparable to those of silver bulk [6] gives another justification for the neglect of Coulomb interactions.

We performed MD simulations by use of the Verlet algorithm in its velocity form. We used a time step of $\Delta t = 0.05$ fs. Energy is conserved up to 10^{-6} eV after 10^6 time steps. The equilibrium structures were obtained by performing simulated annealing. Starting with the equilibrium geometry of Ag_3^- , we generate an ensemble of approximately 1000

clusters corresponding to a given temperature, defined as the time average of the kinetic energy for a long trajectory ($\sim 10^6$ time steps) [10]. This is the initial temperature for the photodetachment process.

We have determined, as a function of time and frequency ν , the fraction of Ag_3 clusters $p(h\nu, t)$ with ionization potentials $\text{IP}(t) \leq h\nu$. This quantity can be interpreted as the time-dependent probability for ionization resulting from a laser pulse of frequency $h\nu$ (or half of this energy, if the ionization is achieved in a two photon process as in [1]) and should be proportional to the signal $S(\Delta t)$ detected in the experiment. In figure 1 we show $p(h\nu, t)$ for different values of $h\nu$, scaled with IP_0 , which is the ionization threshold (ionization potential of Ag_3 in the equilateral equilibrium geometry of Ag_3^+). Note that, slightly above IP_0 , clusters can be ionized only after a delay of $t_0(h\nu) \simeq 750$ fs, where $p(h\nu, t)$ increases sharply. For longer times $p(h\nu, t)$ remains constant. For increasing energy the delay time $t_0(h\nu)$ decreases, and the signal displays the features observed in the experiment, namely, first a sharp increase, a maximum and then a decrease to a smaller value, which remains constant. For higher laser frequencies the maximum becomes broadened and smaller relative to the long-time value of $p(h\nu, t)$.

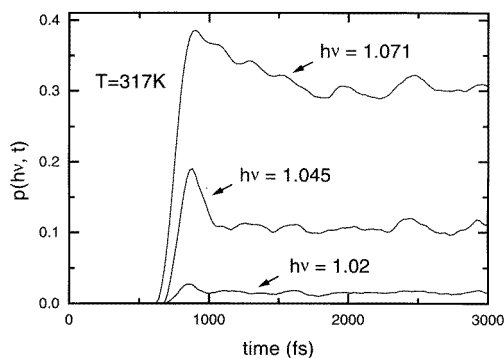


Figure 1. Ionization probability $p(h\nu, t)$ for different values of $h\nu$, scaled by the ionization threshold IP_0 . The initial temperature was $T = 317$ K. The overall time and frequency dependence compares well with the experimental results of [1]. The most striking experimental facts, namely a sharp increase of the signal and a saturation for longer times, are reproduced by our calculations.

The physical picture underlying these results is the following. Upon photodetachment of a binding electron, vibrational excitations occur; in particular, those of the central atom along the chain direction. This motion dominates during the first few hundred femtoseconds. Then, the slower thermally activated bending motion comes into play and yields triangular bonded Ag_3 . The resultant bond formation is exothermic. The excess energy can in turn cause bond breaking or in the case of uniform energy distribution also a regular vibrational mode like pseudorotations. We have also found that only triangular clusters, whose angles lie between 45° and 90° , contribute to the signal observed in the experiment [1].

The maximum of the ionization potential can be explained as a result of the coherent vibrational motion of the clusters. While a large fraction of the clusters bend collectively, they still continue their vibrational motion, which results in a pronounced minimum of the ionization potential in the same way as for the unbent trimers. However these trimers have gained an average energy of 900 K while descending the potential energy surface toward the equilibrium structure of Ag_3 and this explains why their coherent motion is quickly destroyed and why there are no further maxima.

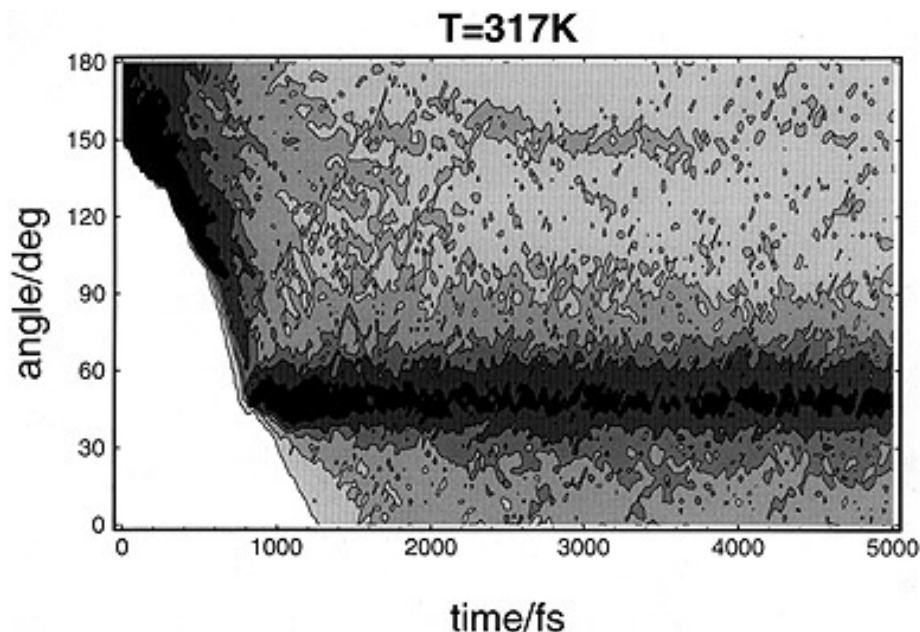


Figure 2. Time-dependent distribution of the (initially) large angle of the silver trimer for the whole cluster ensemble. Black areas correspond to the highest density of clusters, while in white areas no clusters are present.

In figure 2 we show the time development of the (initially) large angle of the silver trimer for the whole cluster ensemble. The distribution of the clusters over different angles is indicated by grey scales. Black areas correspond to the highest density of clusters, while in white areas no clusters are present. In the initial cluster ensemble with a temperature of 317 K, the large angle is in the range of 150° to 180° . Only after a time delay of about 800 fs are clusters with geometries close to the equilibrium structure of Ag_3 present in the ensemble. Two effects contribute to this delay. The first one is that, owing to the nonzero ensemble temperature, the clusters start their bending motion with certain initial velocities, which are only slowly augmented by the energy gained when descending the potential energy surface, because its slope is only small as long as the large angle is in the range of 180° to 120° . The second one is the already mentioned oscillation of the central atom along the chain direction (and of course smaller compensatory oscillations of the other two atoms). Because the slope of the PES in this dimension for the more or less linear molecule is far greater than the slope for the bending motion, the latter only becomes activated by the initial temperature of the clusters. A prominent feature in figure 2 is the large black area roughly in the time interval [800 fs, 1800 fs]. This corresponds to the maxima of $p(h\nu, t)$ in figure 1 and to the maxima seen in the experiment of [1]. Physically this effect can be understood as resulting from the coherent movement of the clusters in the ensemble. Starting with the photodetachment at $t = 0$, a significant part of the clusters oscillates and bends collectively, producing a number of clusters close to the equilibrium geometry of Ag_3 that cannot be reached again at greater times, because the temperature of the ensemble quickly destroys all coherence. Here the fact that the clusters gain an average 900 K by descending the PES toward the equilibrium geometry of Ag_3 plays an important role. The loss of coherence is apparent in figure 2 if we consider that the distribution of

the clusters over different structures approaches a time-independent shape which is already clearly visible in the time interval [3500 fs, 5000 fs] and which remains stable over 19 more picoseconds, i.e. as far as we have calculated the cluster trajectories.

In summary, by employing an electronic theory and molecular dynamics we have analysed the time dependence of the ionization probability of Ag_3 for different frequencies at $T = 317$ K. For low frequencies $P(h\nu, t)$ remains more or less constant, while for higher values of $h\nu$ there is an initial enhancement of the ionization probability. This behaviour is in agreement with experiment. In our calculations we considered only the dynamics of the electronic ground state of Ag_3 . Note that the excited state $^2\Sigma_g^+$ can also be reached by photodetachment of Ag_3^- . However, it lies 1.4 eV higher than the ground state and therefore cannot be excited by the laser frequencies used in [1]. Our results might also be of general interest regarding laser control of chemical reactions. Figure 1 shows that a characteristic time of ~ 800 fs elapses before the third bond in the neutral silver trimer is formed. It would be conceivable to use ultrashort laser pulses in other systems to trigger bond formation or bond breaking on subpicosecond time scales. Interesting effects might be observed in magnetic materials like Ni_3 or Fe_3 . Here, a laser-induced change of the geometry would result in a time-dependent change of the magnetic moments and magnetic anisotropy.

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