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Theory for the ultrafast structural response of optically excited small clusters: Time dependence of the ionization potential

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Combining an electronic theory with molecular-dynamics simulations we present results for the ultrafast structural changes in small clusters. We determine the time scale for the change from the linear to a triangular structure after the photodetachment process $Ag_3^- \rightarrow Ag_3$. We show that the time-dependent change of the ionization potential reflects in detail the internal degrees of freedom, in particular coherent and incoherent motion, and that it is sensitive to the initial temperature. We compare with experiment and point out the general significance of our results. [S1050-2947(96)50512-3]

The excitation of a cluster by a laser pulse induces time-dependent changes of its electronic and atomic structure. These changes involve bond formation and bond breaking. The understanding of the relaxation mechanisms induced by the excitation is of general interest. In particular, it is of fundamental importance to study how the system approaches equilibrium in order 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 Ag_3^- clusters, which serves as an example for the investigation of the structural relaxation times [1]. The initially negatively charged clusters were neutralized through photodetachment by the pump pulse and after a delay time Δt ionized by the probe pulse in order to be detected. Due to the remarkable differences in the equilibrium geometries of the ground states of Ag_3^-, which is linear [2], and Ag_3, which consists of an obtuse isosceles triangle [3], the ultrashort photodetachment process puts the neutralized trimer in an extreme nonequilibrium situation. As a consequence of that, a structural relaxation process occurs. The experimental signal, consisting of the yield of Ag_3^+, was measured as a function of Δt and the frequency of the probe laser pulse. For a frequency slightly above the ionization potential (V_i) of Ag_3 a sharp rise of the signal is observed at $\Delta t \simeq 750$ fs. After a maximum is reached, there is

a saturation of the signal, which then remains constant for at least 100 ps, which is the longest time delay used in the experiment. New features appear for higher frequencies. Again the signal increases sharply, but after reaching a maximum it decreases to a constant value.

A preliminary interpretation of these results uses the Franck-Condon principle [1]. The first laser pulse creates a neutral linear silver trimer that bends and comes to a turning point near the equilateral equilibrium geometry of the positive ion [3]. After rebounding, the neutral trimer starts pseudorotating through its three equivalent obtuse isosceles equilibrium geometries. This would explain the saturation behavior of the signal. However, this would mean that the pseudorotations have an extremely long mean life, which seems improbable. Furthermore, this model does not explain why the signal changes as a function of the frequency of the laser pulse.

In this paper we perform a theoretical analysis of the physics underlying the ultrafast dynamics of Ag_3 clusters produced by photodetachment. In particular, we analyze the time evolution of the ionization potential and the dependence of the dynamics on the initial temperature of the clusters. We show that the experimental results can be explained using a physical picture which can be generally applied to other ultrashort-time processes. 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 surface (PES) needed for the MD simulations, we start from a Hamiltonian of the form $H = H_{TB} + \frac{1}{2}\Sigma_{i \neq j}\phi(\mathbf{r}_{ij})$, where the tight-binding part H_{TB} is given by

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

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. $\phi(\mathbf{r}_{ij})$ 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 use the functional form proposed in Ref. [4]. 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 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

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

Here the $|k\rangle$'s are the eigenstates of H_{TB}. The parameters of H are determined in the following way. The on-site energies were obtained from atomic data [8]. We fit the parameters $V_{\alpha\beta}$ and the potential $\phi(\mathbf{r}_{ij})$ 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 $V_{\alpha\beta}$ to fulfill Harrison's relations [9]. The best fit was obtained by the following parameters: $V_{sp} = 0.954$ eV, $r_c = 4.33$ Å, $n_c = 2$, $m = 5.965$, and $A = 0.605$ eV, where r_c and n_c refer to the cutoff radius and exponent, whereas m and A stand for the exponent and strength of the repulsive potential $\phi(\mathbf{r}_{ij})$ [4]. Using these parameters we have calculated the vibrational frequencies of the dimers, which compare reasonably well with the experimental values [10] and quantum-chemical calculations [2,3]. Then, we determined the equilibrium geometries of the ground states of the silver trimers Ag_3^{-}, Ag_3, and Ag_3^{+} which again yielded excellent agreement with the all-valence-electron calculations of Refs. [2] and [3]. We have also determined a linear equilibrium geometry for the excited state $^2\Sigma_g^+$ of Ag_3, which can be reached by photodetachment of Ag_3^{-} [6]. However, in our calculations this state lies 1.2 eV higher than the ground state (in relatively good agreement with photodetachment experiments [6]) and therefore cannot be excited by the laser
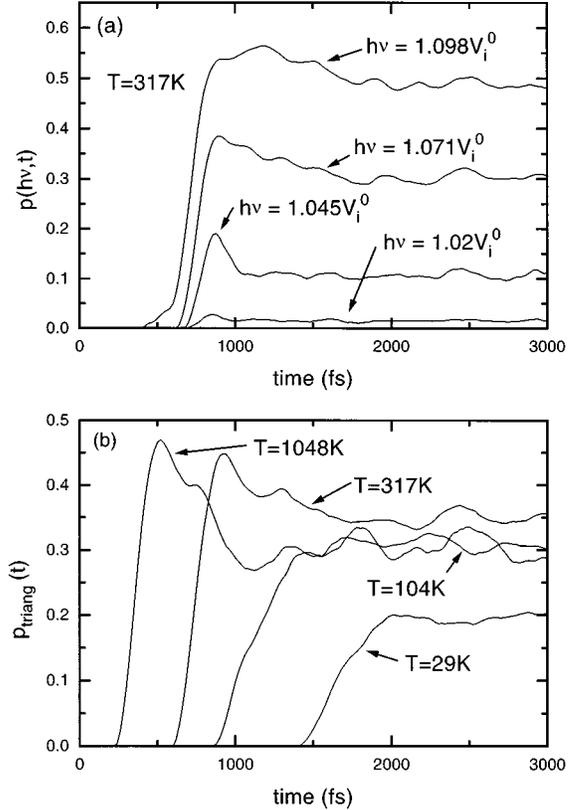

FIG. 1. (a) Time dependence of the fraction of clusters $p(h\nu,t)$ with $V_i(t)$ smaller than $h\nu$. The sharp increase and the overall time dependence of $p(h\nu,t)$ for increasing $h\nu$ should be compared with the experimental results of Ref. [1]. The initial temperature was $T = 317$ K. (b) Time dependence of the fraction of clusters $p_{triang}(t)$ having triangular structures for different initial temperatures.

frequencies used in Ref. [1]. Therefore we consider in the following only the dynamics of the ground state of Ag_3. Note, our hopping parameters are comparable to those of silver bulk [7]. This gives another justification for the neglect of Coulomb interactions.

The MD simulations are performed applying the Verlet algorithm in its velocity form. We used a time step of $\Delta t = 0.05$ fs. This ensures an energy conservation up to 10^{-6} eV after 10^5 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 characterized by the ensemble temperature T, defined as the time average of the kinetic energy for a long trajectory ($\sim 10^6$ time steps) [11].

In Fig. 1(a) we show the time dependence of the fraction of Ag_3 clusters $p(h\nu,t)$ with ionization potentials $V_i(t) \leq h\nu$. We scale $h\nu$ with V_i^0, which is the minimal ionization potential of Ag_3 in the equilateral equilibrium geometry of Ag_3^{+}. The quantity $p(h\nu,t)$ can be interpreted as the time-dependent probability for ionization with a laser pulse of frequency $h\nu$ (i.e., half of this energy, if the ionization is achieved in a two-photon process as in Ref. [1]). $p(h\nu,t)$ is proportional to the signal detected in the experiment. Note, slightly above the ionization threshold ($h\nu = 1.02 V_i^0$), clus-
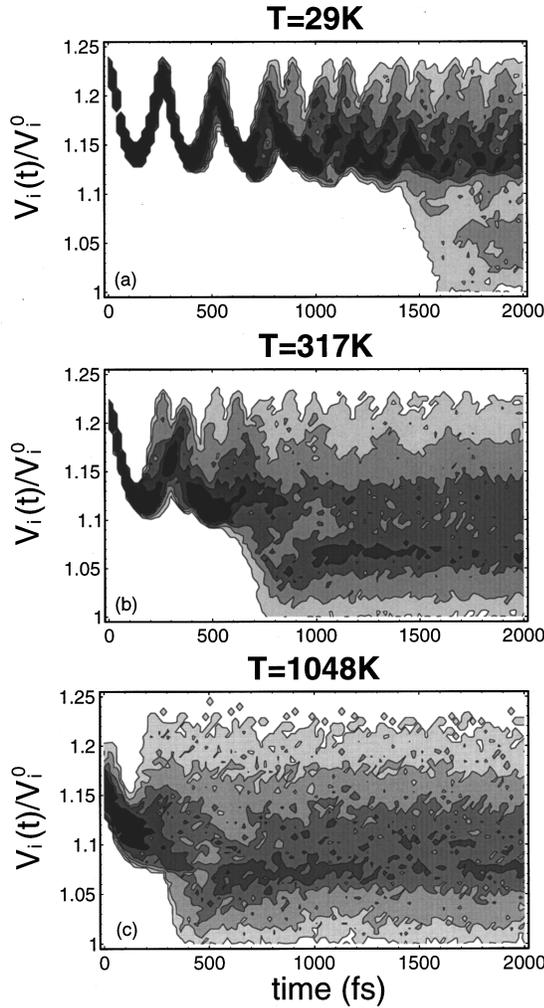
FIG. 2. Distribution of photodetached clusters as a function of time and V_i at different temperatures. Black regions indicate large number of clusters, whereas no clusters are present in the white parts. Note the progressive destruction of the coherent motion after photodetachment for increasing initial temperatures.

FIG. 3. (a) Average distribution of neutral silver clusters over values of V_i for 2 ps$\leq\Delta t\leq$20 ps after photodetachment. (b) Calculated $p(h\nu,t)$ for a large value of $h\nu$. Note that also the internal vibration of the chain before and during bending can be detected. (c) Spectral analysis of the pseudorotations. Note that the lifetime is smaller than one pseudorotation period.

ters can be ionized only after a delay time $t_0(h\nu)\simeq750$ fs, at which $p(h\nu,t)$ begins to increase. $p(h\nu,t)$ displays the features observed in the experiment, namely, first a sharp increase, then a maximum, and finally a decrease to a smaller value, which remains constant. There is, however, a narrow range of frequencies $h\nu$, where the enhancement of the signal after the sharp increase is largest. For higher laser frequencies the maximum becomes broadened and the enhancement factor is smaller.

These results can be understood physically as follows. Upon photodetachment of a binding electron vibrational excitations occur, in particular, those of the central atom along the chain direction. Due to the shape of the PES the motion of the central atom dominates the ultrashort-time response over 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 case of uniform energy distribution, also a regular vibrational mode such as pseudorotations.

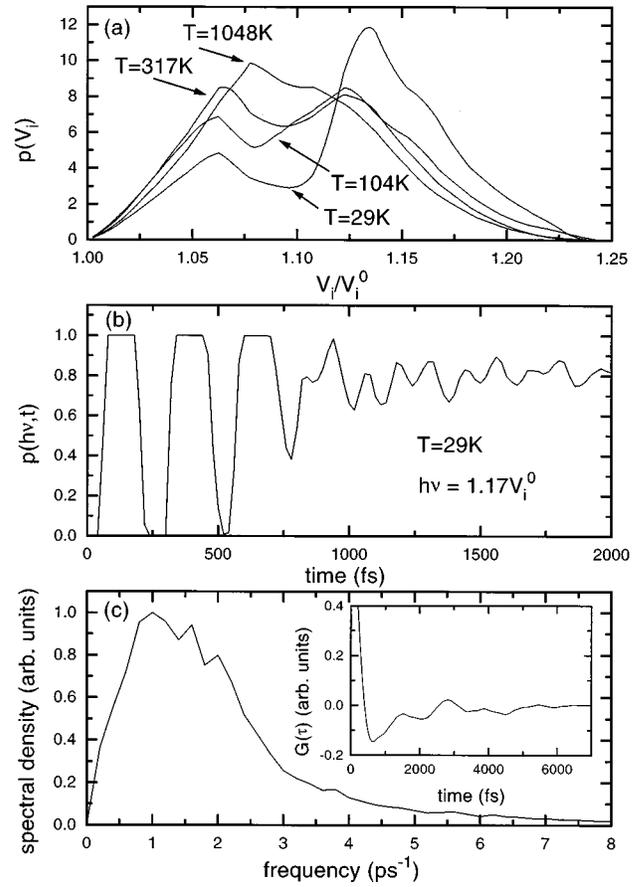In order to demonstrate the temperature dependence of the

bond-formation and bond-breaking processes, we present in Fig. 1(b) results for the time-dependent probability $p_{triang}(t)$ of finding triangular clusters for different initial temperatures. $p_{triang}(t)$ is defined as the fraction of clusters having all angles between 45° and 90°. Comparison of the behavior of $p_{triang}(t)$ for $T=317$ K with the curves of Fig. 1(a) clearly shows that only these particular cluster geometries contribute to the signal observed in the experiment [1]. Note that the onset of the abrupt increase of $p_{triang}(t)$ shows a strong temperature dependence. For increasing initial temperature the clusters bend faster. Notice also the remarkable fact that at low temperature the maximum in $p_{triang}(t)$ disappears.

Figure 2 shows contour plots for the time development of the distribution of ionization potentials of neutral silver trimers after photodetachment at $t=0$. The most prominent feature of these pictures is the coherent oscillation of V_i of all clusters, which continues for about 700 fs in the case of clusters starting at $T=29$ K and which is destroyed much more quickly at the higher temperatures. These coherent oscillations of V_i are due to the internal vibrations of the linear chain before and during bending. High values of V_i correspond to a rather symmetric geometry, while the lower values stand for the turning points of the oscillation. The second

feature to be noted is the areas in the plot with values of V_i below approximately $1.07V_i^0$, which become populated only after time delays of 1500, 700, and 300 fs, respectively, and which represent those clusters that have bent to form geometries close to the equilibrium geometry of Ag_3. For $T = 1048$ K we observed fragmentation of 31% of the trimers (after 20 ps), and in Fig. 2(c) we show only the distribution corresponding to the nonfragmented clusters.

With the help of Fig. 2 it is also possible to explain the maximum of V_i 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 V_i in the same way as for the unbent trimers. This effect accounts for the dark areas in Figs. 2(b) and 2(c) for $V_i(t)/V_i^0$ below 1.07 approximately and is quantified by integration over energies in the calculation of $p(h\nu,t)$ [Fig. 1(a)]. Since the clusters responsible for this effect have gained an average energy of 900 K while descending the PES towards the equilibrium structure of Ag_3, their coherent motion is quickly destroyed and this explains why no further maxima occur. This is supported by the fact that the cluster ensembles starting out with temperatures of 29 and 104 K do not show this maximum. Here, the coherent motion has already disappeared before the clusters bend toward the equilibrium geometry of Ag_3.

Figure 2 reveals that for longer times ($t > 2000$ fs) the clusters approach a time-independent distribution over the values of V_i or, equivalently, over the Ag_3 geometries. These asymptotic distributions are plotted in Fig. 3(a).

In Fig. 3(b) we have plotted the quantity $p(h\nu,t)$ as in Fig. 1(a), but for an initial temperature of $T = 29$ K and for a higher energy $h\nu = 1.17V_i^0$ A new feature appears which consists of sharp oscillations of the probability between 0 and 1 within the time range $0 \leq t \leq 700$ fs. These oscillations result from the dominant vibrational mode of the trimers for the first 700 fs approximately. This interesting effect was not observed in the experiment [1], because the laser energies used were not high enough. In order to demonstrate that the excited state $^2\Sigma_g^+$ does not contribute to the signal observed in the experiment of Ref. [1], we have performed MD simulations on the corresponding PES and confirmed its one-dimensional dynamics. Its signal $p(h\nu,t)$ consists of oscilla-

tions with no sharp increase such as that observed in Ref. [1]. However, it is important to point out that this structureless signal could interfere with the bending or stretching dynamics of the ground state if the state $^2\Sigma_g^+$ were excited by the pump pulse.

The last important point to be investigated is the role of pseudorotations. In order to study these vibrational excitations we determine the autocorrelation function

$$G(\tau) = \frac{\Sigma_k q_x(t_k)q_x(t_k + \tau)}{\Sigma_k q_x(t_k)q_x(t_k)}, \tag{3}$$

where q_x is one of the normal coordinates of the triangular Ag_3 molecule [12]. If the pseudorotations had a long lifetime, $G(\tau)$ would show an oscillatory behavior. However, as shown in the inset of Fig. 3(c), the correlations are strongly damped. This becomes clear by analyzing the Fourier transform of $G(\tau)$. The lifetime of the pseudorotations, determined from the width of the peak at half maximum, is only slightly lower than the duration of one cycle. This shows that pseudorotations do not play an important role in the dynamics of the trimers. The high kinetic energy of the atoms seems to prevent the occurrence of a regular mode such as pseudorotations. The saturation of the signal is rather a statistical effect induced by the temperature.

In summary, by employing an electronic theory and MD simulations we have analyzed the femtosecond dynamics of Ag_3 upon photodetachment. Our results show that an uncomplicated theory that can easily be extended to deal with larger systems is able to account for all experimental observations. Most importantly, we find that the time scales for bond formation and breaking are affected by temperature. Our results might also be of general interest regarding laser control of chemical reactions. Figure 3(a) suggests that temperature can be used to design special distributions for the ionization potentials or for the cluster geometries present in the initial ensemble. Figure 3(b) immediately suggests new experiments with a probe laser pulse energy of $h\nu = 1.17V_i^0$. Thus a direct measurement of the dominant vibration of the trimers seems possible.

[1] S. Wolf, G. Sommerer, S. Rutz, E. Schreiber, T. Leisner, L. Wöste, and R. S. Berry, Phys. Rev. Lett. **74**, 4177 (1995)

[2] V. Bonacic-Koutecky, L. Cespiva, P. Fantucci, and J. Koutecky, J. Chem. Phys. **98**, 7981 (1993).

[3] V. Bonacic-Koutecky, L. Cespiva, P. Fantucci, J. Pittner, and J. Koutecky, J. Chem. Phys. **100**, 490 (1994).

[4] L. Goodwin, A. J. Skinner, and D. G. Pettifor, Europhys. Lett. **9**, 701 (1989).

[5] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[6] G. Ganteför, M. Gausa, K. H. Meiwes-Broer, and H. O. Lutz, J. Chem. Soc. Faraday Trans. **86**, 2483 (1990).

[7] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum Press, New York, 1986).

[8] C. Moore, in *Atomic Energy Levels*, edited by C. C. Keiths, Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, DC, 1958), Vol. III.

[9] W. A. Harrison, Phys. Rev. B **24**, 5835 (1981).

[10] J. Ho, K. M. Erwin, and W. C. Lineberger, J. Chem. Phys. **93**, 6987 (1990).

[11] See, for example, T. L. Beck, J. Jellinek, and R. S. Berry, J. Chem. Phys. **87,** 545 (1987).

[12] J. L. Martins, R. Carr, and J. Buttet, J. Chem. Phys. **78**, 5647 (1983).