Excited-State Relaxation of Ag$_8$ Clusters Embedded in Helium Droplets

Paul Radcliffe, Andreas Przystawik, Thomas Diederich, Tilo Döppner,
Josef Tiggesbäumker, and Karl-Heinz Meiwes-Broer

Fachbereich Physik, Universität Rostock, 18051 Rostock, Germany

Neutral silver clusters Ag$_N$ are grown in ultracold helium nanodroplets. By exploiting a strong absorption resonance recently found for Ag$_8$, first photoelectron spectra of this *neutral* species are recorded. Variation of the laser photon energy reveals that direct vertical two-photon ionization is hindered by rapid relaxation into the lower edge of a long-living excited state manifold. The analysis of the dynamics gives a precise value of (6.89 ± 0.09) eV for the vertical ionization potential of Ag$_8$. The influence of the helium matrix on photoemission is discussed.

Electronic confinement is known to induce the specific properties of semiconductor quantum dots. The confining potential gives rise to a series of discrete, atomiclike energy levels for the conduction band electron and valence band hole states. *Metallic* quantum dots should also exhibit such effects. However, due to the higher effective electron mass, the system now needs to be in the 1 nm size range. This dimension encompasses the field of cluster physics. In recent decades the optical and electronic properties of metal clusters have been the subject of intense study [1,2]. Likewise, superfluid helium in its droplet form has inspired a whole body of experimental and theoretical work. For a recent review see Ref. [3]. Helium droplets provide a weakly interacting matrix for spectroscopy; however, it is well known that a strong interplay between charged species and the helium medium exists. Therefore, the influence of the matrix on the ionization process of clusters is of particular interest. Understanding the dynamical processes of molecules and clusters in helium droplets cannot be understated. For instance, the femtosecond charging dynamics of lead aggregates were found to proceed *faster* when embedded in helium droplets [4]. In this contribution we would like to highlight the excitation dynamics of the unique silver cumulate, Ag$_8$, encapsulated in a droplet, which has unexpected properties. As the smallest cluster with a closed electronic shell, it is known to possess an optically accessible long-living excited state [5,6]. Here we make use of photoelectron spectroscopy to help further characterize the ionization via this intermediate state of neutral Ag$_8$.

Photodetachment spectroscopy has been widely used to investigate free, negatively charged metal clusters in beams, proving the existence of well-defined excited states and energy gaps, which are not present in the corresponding bulk [7–12]. Thomas *et al.* [13] found that the electronic structures of small magnesium cluster anions possess a pronounced *s-p* band gap, which closes directly at 18 atoms, marking the onset of metallic binding. Performing similar experiments on free *neutrals* is hindered by the inability to make an intense mass-separated

cluster beam. In addition, the energy required to remove an electron from a neutral species is far greater than that of an anion. Size information can be obtained by correlating each photoelectron with the simultaneously produced cation. However, such a method might be compromised by possible fragmentation. Our experiment takes advantage of an excited state (E^*) in Ag$_8$, in order to achieve size selectivity. In other words, E^* serves as a transient stepping-stone, allowing resonant two-photon ionization (R2PI) of solely this cluster. Photoelectron spectroscopy (PES) and resonant ionization are combined to investigate the electronic excitation and relaxation dynamics of neutral Ag$_8$. So far, neither the nanosecond relaxation in metal clusters of this size nor the photoejection process in a doped helium droplet have been studied; here we will pursue these challenges.

The experiment on Ag$_8$ is performed in superfluid helium nanodroplets, which are generated in a supersonic nozzle source cooled by a liquid helium cryostat to 9–16 K [14]. The droplet size depends on the nozzle temperature and can be varied over several orders of magnitude. Scheidemann *et al.* [15] and Goyal *et al.* [16] were the first to demonstrate the implanting of molecules and atoms in the droplet. In our case the beam passes through a heated oven filled with silver, where the droplets are loaded with atoms from the metal vapor. By varying the nozzle temperature, the size distribution of the metal core can be influenced, and silver clusters with up to 150 atoms aggregate inside the droplet; see Fig. 1. Excess energy from particle formation evaporates about 1800 helium atoms per 1 eV binding energy. This mechanism effectively cools the metal clusters down to 370 mK [17]. The ultracold and clean droplets transport the clusters into the ionization regions of a magnetic bottle type photoelectron spectrometer and a high resolution time-of-flight mass spectrometer. Here the cluster beam interacts with nanosecond light pulses from tunable laser systems. In order to help with the classification of the measured electron signals, corresponding mass spectra are recorded.
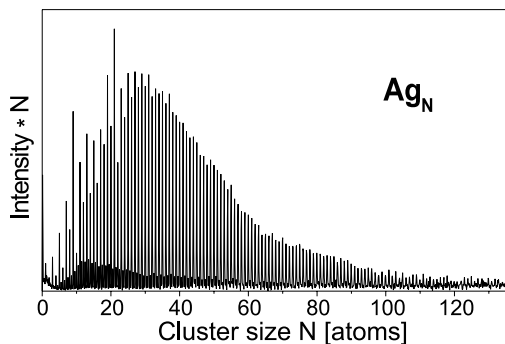
FIG. 1. Mass spectrum of silver clusters embedded in helium droplets ionized by electron impact.

Tuning the laser system to 312 nm (3.97 eV), the ionization of Ag_8 is strongly enhanced by absorption via E^*. Federmann et al. [5] as well as Diederich et al. [6] investigated this optical transition with R2PI, which was found to have a width (FWHM) of 56 meV. We assign to the upper and lower energy bounds of this band the terms E_U and E_L, respectively. E^* corresponds to an optical excitation associated with a Td symmetry, which is the structural minimum of Ag_8 [18]. At this photon energy, the dominant contribution in the mass spectrum is from Ag_8 and Ag_2. In order to be able to distinguish between photoelectron signals originating from the octamer and the dimer, we control the cluster size distribution in the beam via the droplet size, as shown in Fig. 2. At 9.5 K nozzle temperature, the main contribution in the R2PI intensity is due to resonant ionization of Ag_8, while at 12 K the signal is dominated by Ag_2. Figure 3 shows the correlative photoelectron spectra to Fig. 2. Two main structures are present, which have different temperature dependencies. By comparing these spectra with the associated mass spectra, the double peak at a binding energy
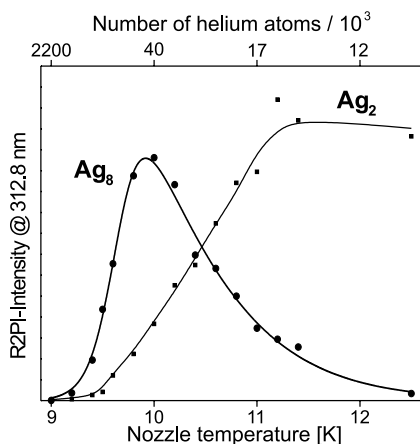

FIG. 2. Silver clusters embedded in helium droplets are exposed to laser light with a wavelength of 312.8 nm (3.96 eV). The resulting R2PI signals of Ag_2 and Ag_8, the dominant species in the mass spectrum [6], are recorded as a function of the nozzle temperature (and thus the mean droplet size) to identify the photoelectron signals.

of 6.4–6.8 eV and the single peak at 7.3 eV coincide with the dimer signal [21]. We concentrate now on the PES intensity in the shaded region, which can be assigned to emission from Ag_8. From the onset of the Ag_8 signal, an estimated value of 6.9 eV for the ionization potential (IP) can be readily obtained, assuming a direct two-photon ionization.

To further investigate the nature of E^*, and especially its dynamics, electron spectra are recorded at different photon energies. Scanning over the full width of E^* (3.92–4.05 eV), by tuning the wavelength of the laser, a shift of the photoelectron spectra is observed. A plot of the threshold kinetic energies against excitation energy (see Fig. 4) shows a linear dependence as expected. However, the fitted slope hints to only a *one* photon process. Therefore the assumption made above of a direct two-photon transition is questionable. Instead, the analysis doubtlessly shows that the second step always proceeds from the same level, irrespective of the energy of the first photon. This evaluation clearly proves the *relaxation* of the laser-excited level to the lower edge of the manifold, E_L; see Fig. 5.

To determine the position of E_L below the IP, we extrapolate the measured kinetic energy thresholds in the expression $E_{kin} = h\nu - E_L$, which yields $E_L = 2.95$ eV. With knowledge of the position of E_L above the ground state, we can obtain the exact value for the IP, which is achieved by recording a data set at the low energy flank of
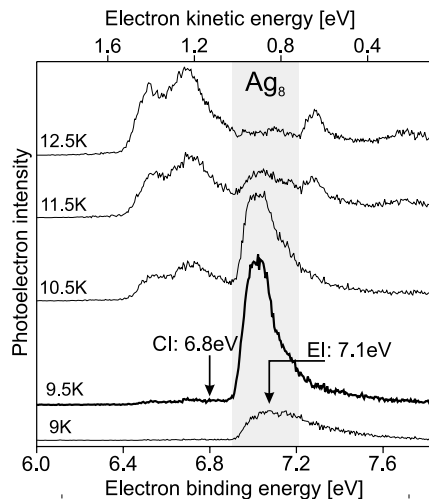

FIG. 3. Photoelectron spectra of neutral silver clusters in He droplets taken at various nozzle temperatures between 9.0 and 12.5 K, corresponding to mean droplet diameters between 60 and 5 nm, respectively. Laser pulses of 312.8 nm ($2h\nu = 7.93$ eV) are used for resonant two-photon ionization. According to the R2PI result shown in Fig. 2, the peak in the shaded region can uniquely be assigned to Ag_8. From the threshold kinetic energy of 1.03 eV, an IP of 6.90 eV is deduced. For comparison, the results of quantum chemical calculations (CI: 6.8 eV) [19] and electron impact ionization measurements (EI: 7.1 eV) [20] for the vertical ionization potential are marked by arrows.
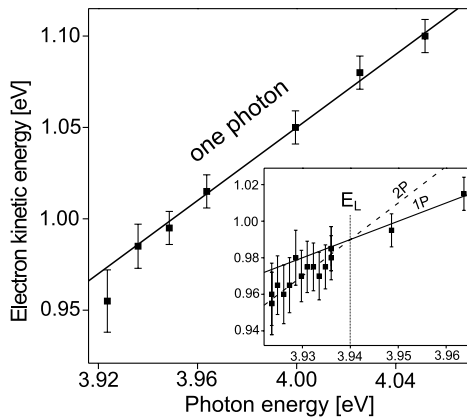
FIG. 4. Measured electron kinetic energies at the ionization threshold plotted against the photon energy shows an almost exact one-to-one correspondence, indicating only a single photon process. From the slope E_L can be determined to be 2.95 eV below the IP. Inset: At the low energy side of E^*, evidence for the transition to a direct two-photon ionization (2P, dashed line) is observed.

E^*. The result is shown in more detail in the inset of Fig. 4. Although the quality of the data is reduced by the weaker optical response of Ag_8 and the presence of the Ag_2 signal, the overall trend indicates that a transition from slope one (one-photon ionization) to slope two (two-photon ionization) occurs at an energy of 3.94 eV. Assigning this point to E_L, we arrive at IP = (6.89 ± 0.09) eV. We note that Felix *et al.* observed fluorescence of Ag_8 in argon with an onset around $h\nu = 3.94$ eV [24]. The agreement gives us confidence that the same system and its unique electronic structure is probed in both experiments. With this information we can construct a complete picture of the resonant ionization of Ag_8, as depicted in Fig. 5.

To date, no measurement has determined the IP of Ag_8 with a single photon. The ionization threshold was out with the photon energies used by Alameddin *et al.* [25]. LaiHing *et al.* [26] set the IP to be between 6.0 and 6.4 eV, though they remark that the signal was very weak. However, the value obtained in our experiment agrees well with *ab initio* quantum chemical calculations (6.8 eV) [19] and electron impact ionization measurements (7.1 eV) [20] for free Ag_8. Despite this excellent agreement, it should be noted that in our case the IP might be affected by the helium environment. The dominant short range interaction between an electron in liquid helium is strongly repulsive, forming a *bubble* around the impurity, which could be as large as 3.4 nm [27]. About 1 eV is needed to create such a cavity. The formation time was measured recently to be around 150 ps [28]. In helium droplets, however, one can imagine that the probability of creating a bubble becomes vanishingly small. Indeed, assuming a typical electron velocity in the order of 0.1–1 μm/ps, an electron will have left the droplet after several tens of femtoseconds. Furthermore, the diameter of the droplet is comparable with that of the bubble in
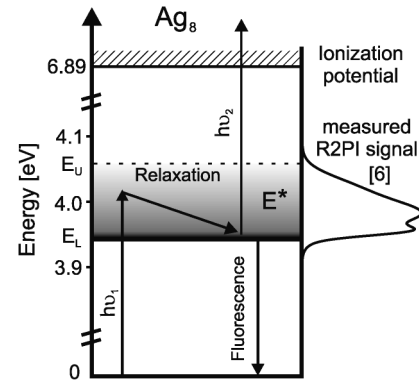

FIG. 5. Schematic diagram of the ionization dynamics of Ag_8. After excitation to the unoccupied band E^* roughly 4.0 eV above the ground state, the cluster quickly relaxes to the lower edge E_L. In a R2PI experiment, ionization occurs from this long-living level. Thus, via excitation into E^*, an occupation inversion between E_L and the ground state could be reached, a requirement for laser operation. Indeed, Ag_8 fluorescence measurements in argon matrix [24] show a radiative decay in this spectral region.

liquid helium; hence it is highly probable that it can be destroyed with a fraction of the 1 eV formation energy. This fraction should reflect the droplet size distribution (log-normal), leading to an asymmetric broadening of the signal. Evidence for such a broadening can be seen in the recorded spectra in Fig. 3, which is especially prominent with the largest droplet size at 9 K. An alternative explanation is that the peak shape reflects the population density of the final ionic density of states. In spite of this uncertainty, we can conclude that the photoelectron threshold of Ag_8 in a helium droplet closely corresponds to the ionization potential of the free Ag_8, although the shape of the peak may be affected by the helium environment. In a recent experiment carried out by the group of Neumark, the electron emission from pure helium droplets, photoionized by synchrotron radiation, is dominated by very low energy (~ 1 meV) electrons. These were attributed to the autoionization of vibrationally excited He_n^* Rydberg states [29]. In our case the helium matrix itself is completely transparent to the excitation wavelengths used; hence we would not expect to create such tardy electrons.

As discussed above, from the dependence of the spectrum on the photon energy, it can be inferred that the final ionization step always occurs from the lower edge of E^*. That requires a fast relaxation process before the second photon is absorbed, shown pictorially in Fig. 5. The strong rise of the signal in the threshold region (see Fig. 3) for each spectrum recorded, shows evidence that the excited state E^*, which is populated by the first photon, relaxes within much less than a nanosecond to E_L. Otherwise, the photoelectron threshold would be blurred out. There are two plausible relaxation channels in the Ag_8 *plus* helium droplet system. First, intracluster relaxation could lead to a slight heating of the system, which would immediately

result in the evaporation of helium atoms. When exciting close to E_U, the excess energy of about 80 meV has to be dissipated among the available degrees of freedom. The time scale for such a redistribution of initially nonthermal modes into lower frequency modes can be as small as 100 fs, e.g., in dye molecules [30]. Second, direct transfer of energy into the surrounding helium might contribute as well. For atoms the interaction with the surrounding helium is known to influence their electronic transitions [31,32]. Because of the higher spatial extension of the electron wave function in the excited state, a broad band of bubble oscillations (*ripplon* states) is produced. The bubble relaxes within picoseconds to its equilibrium size. Rotationally resolved spectra of tetracene and pentacene embedded in helium droplets show a lifetime broadening due to vibrational relaxation in the range of 1 ps [33]. The existence of this effect in small clusters is also conceivable. Electron-phonon interaction might contribute as well, which is the main relaxation channel in semiconductor quantum dots. However, this conduit probably plays only a minor role here.

A novel point to note for possible future applications is the potential for population inversion within Ag_8. From the ionization dynamics scheme presented in Fig. 5, a three level system can be imagined, with excitation and subsequent relaxation within E^*, which could be suitable for light amplification.

In conclusion, first photoelectron spectra of neutral, mass-selected Ag_8 in ultracold helium droplets have been measured. The observed ionization threshold is in excellent agreement with previous calculations and experiments, and strongly suggests that the threshold is not significantly altered by the helium surroundings. The measurements carried out with different laser wavelengths show that after the optical transition, the excitation rapidly decays to the lower edge E_L of the excited state E^*, 2.95 eV below the ionization threshold of 6.89 eV. Possible excess energy will be dissipated into the helium droplet. For an investigation of further details of the relaxation process, pump-probe experiments in the fs- and ps-time scale would be helpful.

[1] *Metal Clusters*, edited by W. Ekardt, Wiley Series in Theoretical Chemistry (Wiley & Sons Ltd., Chichester, 1999).

[2] *Clusters of Atoms and Molecules I + II*, edited by H. Haberland, Springer Series in Chemical Physics (Springer, Berlin, 1994).

[3] Special issue on He-droplets [J. Chem. Phys. **115**, 10 065 (2001)].

[4] T. Döppner *et al.*, Eur. Phys. J. D **24**, 157 (2003).

[5] F. Federmann, K. Hoffmann, N. Quaas, and J. P. Toennies, Eur. Phys. J. D **9**, 11 (1999).

[6] Th. Diederich, J. Tiggesbäumker, and K.-H. Meiwes-Broer, J. Chem. Phys. **116**, 3263 (2002).

[7] D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. **86**, 1715 (1987).

[8] K. J. Taylor, C. L. Pettiette-Hall, O. Cheshnovsky, and R. E. Smalley, J. Chem. Phys. **96**, 3319 (1992).

[9] K. H. Meiwes-Broer, Appl. Phys. A **55**, 430 (1992).

[10] H. Handschuh *et al.*, J. Chem. Phys. **102**, 6406 (1995).

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

[12] J. Li, X. Li, H.-J. Zhai, and L.-S. Wang, Science **299**, 864 (2003).

[13] O. C. Thomas, W. Zheng, S. Xu, and K. H. Bowen, Phys. Rev. Lett. **89**, 213403 (2002).

[14] A. Bartelt *et al.*, Phys. Rev. Lett. **77**, 3525 (1996).

[15] A. Scheidemann, B. Schilling, and J. P. Toennies, J. Phys. Chem. **97**, 2128 (1993).

[16] S. Goyal, D. L. Schutt, and G. Scoles, Phys. Rev. Lett. **69**, 933 (1992).

[17] M. Hartmann, R. E. Miller, J. P. Toennies, and A. Vilesov, Phys. Rev. Lett. **75**, 1566 (1995).

[18] V. Bonačić-Koutecký, V. Veyret, and R. Mitric, J. Chem. Phys. **115**, 10 450 (2001).

[19] V. Bonačić-Koutecký, L. Češpiva, P. Fantucci, and J. Koutecký, J. Chem. Phys. **98**, 7981 (1993).

[20] C. Jackschath, I. Rabin, and W. Schulze, Z. Phys. D **22**, 517 (1992).

[21] The IP of the dimer is known to be 7.66 eV [22], indicating that a more complex mechanism than direct two-photon ionization takes place. An explanation might be that the Ag_2^+ signal originates from a three photon process, starting with the excitation of Ag_3 to a dissociative state. The subsequent fragmentation would produce Ag_2 in an excited state, from which photoemission proceeds via direct two-photon ionization. Such a process is known to take place in alkali trimers [23].

[22] V. Beutel, G. L. Bhale, M. Kuhn, and W. Demtröder, Chem. Phys. Lett. **185**, 313 (1991).

[23] A. Ruff, S. Rutz, E. Schreiber, and L. Wöste, Z. Phys. D **37**, 175 (1996).

[24] C. Félix *et al.*, Phys. Rev. Lett. **86**, 2992 (2001).

[25] G. Alameddin, J. Hunter, D. Cameron, and M. M. Kappes, Chem. Phys. Lett. **192**, 122 (1992).

[26] K. LaiHing, P. Y. Cheng, and M. A. Duncan, Z. Phys. D **13**, 161 (1989).

[27] M. Rosenblit and J. Jortner, Phys. Rev. Lett. **75**, 4079 (1995).

[28] A. V. Benderskii, J. Eloranta, R. Zadoyan, and V. A. Apkarian, J. Chem. Phys. **117**, 1201 (2002).

[29] D. S. Peterka *et al.*, Phys. Rev. Lett. **91**, 043401 (2003).

[30] M. L. Horng, J. A. Gardecki, A. Papazyan, and M. Maroncelli, J. Phys. Chem. **99**, 17 311 (1995).

[31] J. Z. Jakubek, Q. Hui, and M. Takami, Phys. Rev. Lett. **79**, 629 (1997).

[32] J. Reho *et al.*, J. Chem. Phys. **112**, 8409 (2000).

[33] M. Hartmann, A. Lindinger, J. P. Toennies, and A. F. Vilesov, J. Phys. Chem. A **105**, 6369 (2001).