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Spectroscopy of extremely cold silver clusters in helium droplets

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Abstract. The first highly resolved electronic spectra of small non-alkali metal clusters embedded in nanoscopic helium droplets ($N \approx 20\,000$) are presented. The helium droplets serve as an extremely cold liquid matrix with a temperature of 0.37 K. Resonant two-photon-ionization is used for size-selective spectroscopy on a silver cluster distribution ($N \leq 10$). Results are reported for Ag_2, Ag_3 and for Ag_8. For the latter, a very narrow absorption spectrum is resolved corresponding to the Ag_8 plasmon resonance. The linewidth of the observed resonance is a factor of two smaller than theoretical zero-temperature predictions for the plasmon line width of closed-shell metal clusters. In contrast, the lifetime of the Ag_8 resonance is estimated to be of the order of nanoseconds, which is inconsistent with the plasmon picture and typical for molecular transitions.

PACS. 36.40.Mr Spectroscopy of clusters – 67.40.Yv Impurities and other defects in ^{4}He

1 Introduction

One of the most important problems in the spectroscopic study of metal clusters is the insufficient control over cluster temperature. The high heat of condensation released in the process of metal atom clustering often limits the accessible temperature range to values close to the evaporation limit. Under these conditions, gas-phase metal clusters carry high internal energies and their optical spectra exhibit broad features with little structure. As a consequence, it is difficult to decide whether the spectral features are intrinsically broad as expected for plasmon resonances or the spectra are broadened by temperature effects. Ellert *et al.* have recently published a gas-phase study on cold sodium clusters which seems to suggest that the latter is the case [1]. Matrix studies do not suffer from a temperature limitation but have other disadvantages. The solid lattice of the matrix alters the symmetry of the embedded clusters and multiple implantation sites lead to inhomogeneous broadening. The interpretation of such spectra can be very complicated.

In this paper it is demonstrated that the use of liquid helium droplets as a spectroscopic matrix has the advantage of providing a very low temperature environment without inhomogeneous broadening. Helium droplets have been shown to be an extremely cold and soft liquid matrix for high resolution spectroscopy of single molecules, small van der Waals clusters [2] and of small alkali clusters [3]. Even in the case of a large molecule such as C_{60}, the spectral line shifts of vibronic transitions were found to be much smaller than in other spectroscopic matrices [4]. From rotationally resolved absorption lines of various chromophore molecules the temperature of small helium droplets was measured to be 0.37 K [5]. High resolution vibronic spectra in the visible provide first evidence that the finite-sized helium clusters are superfluid [2]. The technique used for preparing a beam of nanoscopic helium droplets with embedded metal clusters was recently described and evidence presented that Ag atoms are located in the interior of the droplet [6]. Since then, large clusters of silver, indium and europium with sizes extending up to about $N = 100$ have been assembled inside the droplets and detected using mass spectrometry [7]. In this contribution, the method is described in more detail, and initial results on the electronic spectra of small silver clusters including Ag_8 obtained by resonant two-photon ionization (R2PI) are presented.

2 Experimental method

The helium droplets are produced in a supersonic expansion of cold, pure ^{4}He gas through a 5 μm nozzle, typically at a source temperature and pressure of $T_0 = 10$ K and $P_0 = 20$ bar, respectively. The helium gas condenses under these conditions to droplets with an average size of about 20 000 ^{4}He atoms [8]. The droplet size can be varied by changing the nozzle temperature or pressure. After passing through a skimmer, the helium droplets traverse a silver vapour with typical pressures of $P_{\mathrm{Ag}} \simeq 10^{-4}$ mbar produced in an oven held at a temperature of about 800 °C. Collisions between the helium droplets and the silver atoms lead to successive capture of single silver atoms which subsequently coagulate to a cluster inside the droplets. The condensation energy is rapidly dissipated into the helium droplets, which in turn evaporate several thousand helium atoms within 10^{-8} s and quickly acquire back a temperature close to the initial value below 0.5 K [9]. The droplets thus act as evaporation cryostats for the embedded silver clusters. The size distribution of the embedded metal clusters can be adjusted by varying the droplet size as well as the metal vapour pressure, both of which affect the number of collisions of the droplets with the silver atoms. The metal doped helium droplets are then ionized using either a pulsed electron gun at energies of 70 eV or alternatively a frequency-doubled Nd:YAG pumped dye-laser providing nanosecond pulses in the UV region (pulse duration ≈ 10 ns). The ionization products are mass selected and detected with a reflectron-type time-of-flight mass spectrometer.

The two different ionization methods both yield mass spectra displaying pronounced peaks of bare metal cluster ions. This suggests that the metal cluster ions are formed with sufficient internal energy to shake off any attached helium atoms. In the case of electron impact ionization, this process can be explained with a model proposed by Scheidemann *et al.* for embedded molecules in small helium droplets [10]. The impacting electron first ionizes a helium atom in the droplet rather than the embedded metal cluster. The created positive charge diffuses inside the droplet via resonant transfer with jumps on a timescale of 10^{-12} s and will therefore, with some probability, eventually be localized at the metal cluster. The much lower ionization energy of the metal cluster then leads to the release of about 10 to 20 eV of excess energy which is expected to be at first deposited into the metal cluster ion. This internal energy leads to a breakup of the helium droplet and the evaporation of any attached helium atom. A major problem with electron impact ionization is the extensive fragmentation of the metal clusters due to the large amount of energy released to the cluster in the charge transfer process. In the two-photon ionization used here, the embedded metal cluster is first promoted to an electronically excited state and then ionized by a second photon. Under these circumstances, the excess internal energy is reduced to values of only several eV, and mass spectra recorded with photoionization may even exhibit a number of cluster ions with attached helium atoms. Since the metal clusters are not size selected before excitation, the observed cluster ions are either a direct result of resonant ionization or they are fragments of larger cluster ions. To ensure low fragmentation, the laser power must therefore be chosen low enough, so that fragmentation of the cluster ions in multi-photon processes is reduced to a minimum.

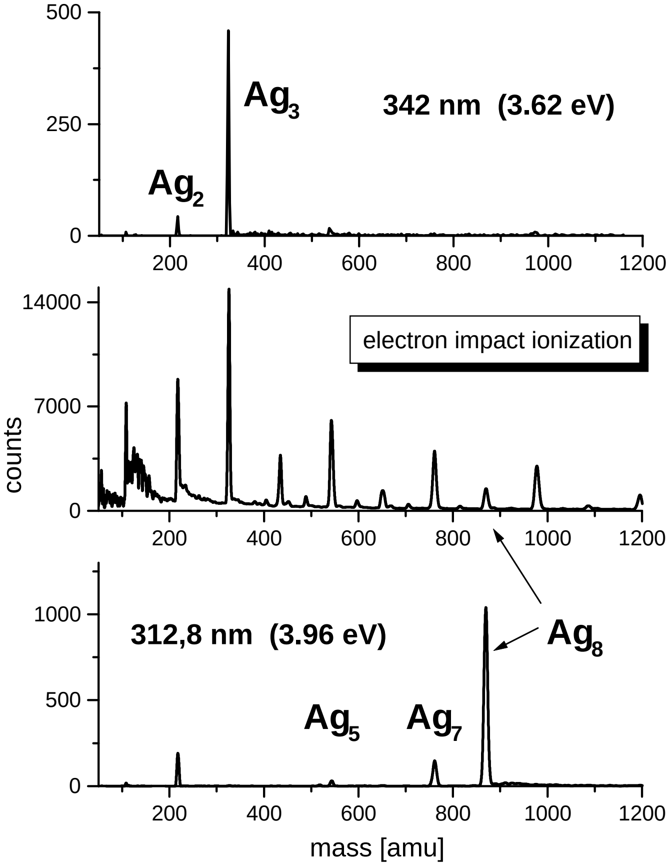

Fig. 1. Mass spectra of silver clusters embedded in helium droplets. The comparison between electron impact ionization (centre) and resonant laser ionization (top & bottom) shows the high size selectivity of photoabsorption. All spectra were recorded in a sequence probing the same cluster beam ($T_0 = 9.5\,\mathrm{K}$, $p_0 = 20$ bar, laser fluence $F \approx 2.4\,\mathrm{mJ/cm^2}$ (top) and $F \approx 0.6\,\mathrm{mJ/cm^2}$ (bottom)).

3 Results and discussion

Figure 1 shows a comparison of the mass spectra of silver clusters obtained by laser ionization at two different wavelengths with a mass spectrum obtained with electron impact ionization of the same neutral cluster distribution. The electron impact spectrum confirms the presence of the expected broad silver cluster distribution ranging from $N = 1$ to $N \geq 11$. The abundances show the odd-even oscillations well-known from mass spectra of silver cluster ions which reflect the stability of the different ion species [11]. Thus the odd-even pattern provides direct evidence for a considerable degree of fragmentation. At suitably low laser fluences ($F = 0.4$–$2\,\mathrm{mJ/cm^2}$ per pulse) the laser ionization mass spectra are much simpler. As shown in Fig. 1, a single ion peak on the trimer channel is observed at 342 nm. Tuning to shorter wavelengths, the trimer signal vanishes, while a strong Ag_8^+-signal becomes visible at 312 nm. The Ag_8^+ is accompanied by a progression of additional weak ion signals indicating the occurrence of Ag_7^+ and Ag_5^+. The observed increase in their intensities with increasing laser power is evidence for the photofragmentation of excited Ag_8^+ cluster ions. This agrees with the fragmentation channels of Ag cluster ions determined by Krückeberg *et al.*, who have reported a predominant dimer evaporation for small excited odd-numbered cluster ions, as well as monomer ejection for even numbered species [12]. The dimer signal visible at both wavelengths in Fig. 1 may result partly from fragmentation of larger clusters and partly from a direct ionization. Thus, Fig. 1 demonstrates that resonant photoionization is able to select specific sizes out of a broad distribution of helium-embedded silver clusters. This opens up the possibility to perform size-selective spectroscopy on extremely cold silver clusters.

The present experiments focus on small silver clusters with sizes below $N = 10$, which can be prepared with relatively high densities in the beam. The R2PI signal of a silver cluster distribution was measured in the spectral range from 300 nm to 375 nm, which corresponds to a photon energy range from 3.3 eV to 4.15 eV. The count rates for the resonantly ionized monomer, dimer, trimer and octamer ions in this wavelenth region are high enough that the integration times are only several minutes per data point. The most interesting observation is the very narrow resonance for the Ag_8 cluster around $h\nu = 4\,eV$ with an overall width of only 56 meV (FWHM). Figure 2 shows the signal on the Ag_8^+ channel as a function of photon energy. A striking feature is the complete absence of background noise: the count rate goes to zero on both sides of the resonance over the whole energy range examined. This confirms that the Ag_8^+ ions are indeed produced by a resonant process. Influences of the ionization threshold on the spectrum at these photon energies can be safely excluded. According to ionization threshold measurements, the Ag_8 cluster has an IP of 7.1 eV [13], while calculations predict a vertical IP of 6.8 eV [14]. Both values are well below the 8.0 eV of energy available with two photons in our measurement.

The small line width as well as the presence of a distinct shoulder on the high energy side of the resonance are perhaps the most interesting features of the Ag_8 absorption. The shoulder is present in all of the spectra recorded for different laser powers and helium droplet sizes. Increased laser power causes saturation which leads to a broader peak while the asymmetric shape remains unchanged. This suggests that at least two closely neighboring transitions contribute to the observed absorption profile. The spectrum in Fig. 2 can be very well fitted with two Gaussians, one narrow peak centered at 3.96 eV, ($\gamma = 18$ meV FWHM) and a broader one at 3.99 eV, ($\gamma = 46$ meV FWHM). Previously, the Ag_8 absorption was observed by Harbich *et al.* in rare gas matrix deposition experiments. Using a neon matrix at 5 K, they found a 180 meV wide (FWHM), substructured absorption peak with a maximum at 3.91 eV [15], which is red-shifted by about 50 meV compared to the maximum of our spectrum. By using photofragmentation, Tiggesbäumker *et al.* observed a broad, featureless resonance of hot gas-phase Ag_9^+ ions centered around 4.02 eV with a line width about 10 times larger than the total linewidth in our spectrum, which is explained by the much higher cluster temperature of about 2000 K leading to thermal line broadening [16].

Because of the extremely low temperatures, the individual quantum states have to be considered in order to explain the spectrum. Quantum mechanical descriptions of small metal clusters are available based either on the jellium model or on more sophisticated *ab initio* quantum chemical calculations. In the jellium picture, a low temperature prediction for the linewidth of cluster transitions with collective character has been made by Penzar *et al.*, who found zero-point fluctuations of the cluster shape to be the dominant mechanism leading to a finite plasmon line width in the limit $T \to 0$ [17]. They predict a width of $\delta E \approx 150$ meV FWHM for a Na_{10} resonance at 2.97 eV. Pacheco *et al.* have more accurately calculated the plasmon line width for jellium metal clusters in the low temperature limit, taking into account the coupling between a dipole plasmon mode and a complete set of possible quadrupole deformations of the cluster shape [18]. For Na_8 they predict a relative width of the resonance of $\Delta E/E = 0.03$, as well as an asymmetric line shape with a tail to the high energy side and gaussian behaviour in the wings. Within a factor of 2, this agrees well with the present measurement of Ag_8, which even has a smaller width of $\Delta E/E = 0.014$.

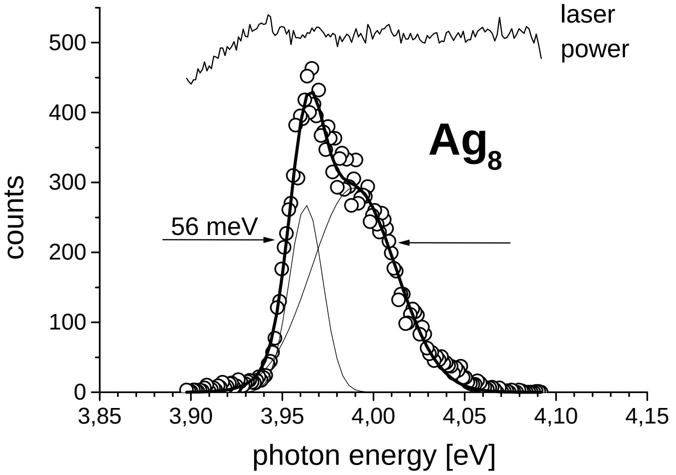

Fig. 2. R2PI spectrum of Ag_8 in helium clusters ($T_0 = 10\,K$, $P_0 = 20\,bar$, $F \approx 0.6\,mJ/cm^2$). A normalisation is not necessary because the laser fluence is very constant as indicated above. The asymmetry of the peak requires a fit with two Gaussians suggesting that more than one transition is involved.

The observation of a sharp R2PI resonance for such a large metal cluster as Ag_8 is surprising in itself. It has been common experience with REMPI on gas-phase metal clusters, that with nanosecond laser pulses sharp spectral features are only obtained for the molecule-like dimers and trimers [19], whose excited states have lifetimes on a nanosecond time scale. The shorter lifetimes of the excited states of larger clusters have been invoked to explain the failure of REMPI spectroscopy on species beyond the trimer. Baumert *et al.* only succeeded in observing the Na_8 resonance with R2PI by using femtosecond laser pulses, confirming with additional pump-and-probe experiments the rapid decay of the Na_8 excited state within about 1 ps [20]. In this context, it is interesting to point out that no evidence was found for resonant ionization of species between Ag_8 and Ag_3, even though, according to the argon matrix studies of Fedrigo *et al.*, both Ag_5 and Ag_7 should have distinct absorption maxima in this wavelength region [21]. For Ag_2 and Ag_3 in helium droplets, resonances were found as expected. Their R2PI spectra are shown in Fig. 3 and display rather broad structures but also some narrow lines and will be interpreted in detail in a forthcoming publication.

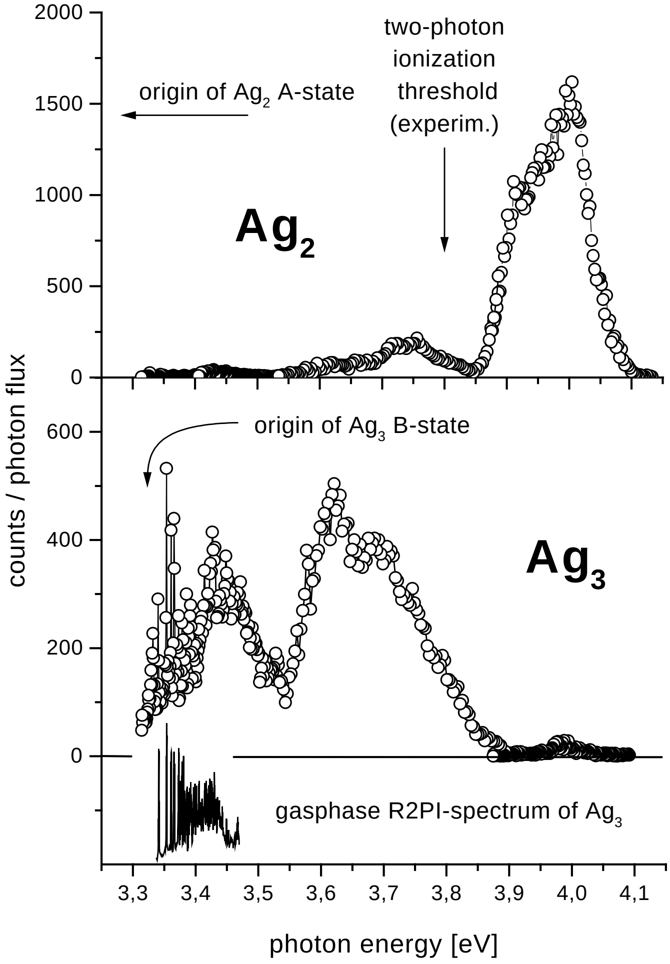

Fig. 3. R2PI spectra of Ag_2 and Ag_3 in helium droplets. The position of the Ag_2 absorption corresponds energetically to high-lying vibrational levels of the excited A-state of a free silver dimer [22]. The dimer ionization threshold at 7.6 eV [13] allows R2PI only for photon energies higher than 3.8 eV. The dimer signal at lower energies documents the photofragmentation of trimers. In the low-energetic part of the trimer absorption, distinct peaks are observed matching R2PI gas-phase data [19, 23]. A R2PI spectrum recorded by Wallimann *et al.* using a seeded beam [23] is also shown for comparison.

To explain the observation of the Ag_8 resonance, we propose that it has an anomalously long lifetime on a nanosecond time scale, while Ag_5 and Ag_7 have much shorter lifetimes and are therefore not detectable with our experimental setup. In view of the small spectral shifts so far observed in the droplets [2], matrix interactions very likely cannot explain the absence of the smaller clusters in the present spectra. The long lifetime of the Ag_8 excitation is in contradiction to the plasmon picture and suggests that molecular transitions are involved.

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