

Fluorescence spectroscopy of silver clusters formed in rare gas droplets

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Received 30 November 2000

Abstract. The Pick Up technique allows continuous formation of high density metal cluster beams in the otherwise hardly accessible size range Me_2 to about Me_{50} . With an apparatus based on the use of cryo-condensation pumps, Ar as inert gas for production of the host clusters by adiabatic expansion and silver as metal we demonstrate how the various source parameters influence the composition and mean size of the resulting cluster distributions. The analysis in the gas phase by means fluorescence spectroscopy allows to conclude that an Ar shell encapsulates the metal clusters.

PACS. 36.40.Vz Optical properties of clusters – 39.10.+j Atomic and molecular beam sources and techniques

1 Introduction

Capture of atoms or molecules by weakly interacting host droplets, the so-called pick up technique has been rapidly gaining in popularity since it successfully combines a supersonic free jet with the matrix isolation technique [1]. Usually, a beam of ultra cold helium droplets produced by expansion in a supersonic jet is passed through the low pressure vapour of the substance of interest. The host droplets react to the perturbation by evaporation of some atoms and quickly return to their initial temperature cooling also the stored particle which can be subsequently investigated by means of spectroscopy. In the case of a multiple capture, picked up atoms or molecules might react with each other to form complexes or clusters whereby the weakly bound host always compensates for heating due to the reaction by the same mechanism - evaporation. The composition of the beam after the passage of the pick up chamber, thus, can be adjusted to attack a wide spectrum of scientific questions ranging from isolation and spectroscopic characterization of molecules [2] to metal cluster production. In the latter case, however, residence of the metal atom captured (localized on the surface or dissolved) seems to play the decisive role: From the LIF experiments on Na_n ($n = 1-3$) grown in a helium pick up source it was concluded that the particles were formed on the surface of a He droplet whence they detached easily so that no larger clusters could be grown [3]. On the other hand, the experiments on silver also with the use of a He pick up source clearly show that the silver cluster up to Ag_{13} grow within a droplet [4]. For spectroscopic studies the use of Ar as a host gas is less favorable than

that of He: the stronger guest-host interaction and higher droplet temperature are distinct drawbacks. These are of lesser importance, however, when intensive metal cluster production is to be achieved. In such a case, Ar offers considerable advantage because Ar is much easier to handle than He and the requirements on the host droplet size are less strict. In addition, the wealth of spectroscopic data from Ar matrix isolation studies can serve as guide lines in the understanding of the spectra in Ar droplets. In this work we present results on silver clusters produced in a pick up source with argon droplets. Our set up is a compact, since we employ cryo-pumping - and very intense source for metal cluster production in the size range up to 30 atoms/cluster [5]. The intensity of the metal clusters produced is such that fluorescence spectroscopy can be performed on the clusters in the gas phase - Ag₈ is given as an example.

2 Experimental

For the present experiments a beam of argon clusters was generated by adiabatic expansion through a conical nozzle with throat diameter of 100 μm and opening angle of 25°. A resistively heated crucible with silver mounted below the axis, 7 cm away from the nozzle in the downstream direction, was operated at the temperature range 1000-1100 °C corresponding to a vapour pressure of about 10^{-2} – 10^{-1} mbar. Vacuum conditions in the apparatus are achieved by two axial cryo-pumps mounted along the main axis of the set up with the first pump positioned directly behind the expansion tube and the second one at the exit of the source. At the stagnation pressures of 2-10 bar the pressure in the region between the cryo-pumps, *i.e.* in the

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pick up region is $0.7\text{--}1.5 \times 10^{-3}$ mbar whereas at the exit of apparatus it drops to $1.3\text{--}6 \times 10^{-4}$ mbar, respectively. For mass spectrometric analysis the cluster beam is directed into an axially aligned mass spectrometer. An additional cryo-pump mounted in this device removes Ar gas and lowers the pressure to the 10^{-6} mbar range. The mass spectrometer is a modified version of the type SMIA (Varian-MAT) [6], a singly focusing magnetic device with a high transmission, a mass resolution $M/\Delta M \approx 250$ and a mass range of 12000 amu at the operating acceleration voltage of 2 kV. It is equipped with an electron impact ionization source and a post-acceleration unit to ensure effective detection at high masses [7]. The ion current registered in the present experiments ranges from 10^{-14} to 10^{-12} A which corresponds to a single particle abundancies of $10^5\text{--}10^7$ particles per second. For optical spectroscopy study two quartz windows were mounted vertically at the end of the pick up zone. White light of Xe lamp focused onto the apparatus axis traversed this region just in front of the second cryo-pump. The resulting fluorescence light was analyzed in the spectral range 200-1000 nm through a horizontally mounted quartz window (*i.e.* perpendicularly to the direction of cluster beam and to that of the exciting light) by means of a monochromator connected to a charge coupled device (CCD).

3 Results and discussion

Production of the rare gas clusters by adiabatic expansion has been thoroughly studied [8]. Reliable scaling laws allow to estimate the average cluster size as a function of stagnation pressure, nozzle temperature and jet geometry [9,10]. At fixed nozzle temperature and nozzle geometry the main parameter governing the cluster growth is reduced to the stagnation pressure at which expansion takes place. The size of the silver cluster, in turn, depends on the initial size of a rare gas droplet and on the number of silver atoms in the capture process, *i.e.* silver vapour pressure. Fig. 1 summarizes the essential features of this dependence: The spectra a) and b) were taken at stagnation pressure of 5 and 10 bar (the corresponding average size of Ar droplets is estimated to 250 and 1000 atoms per droplet, respectively) and at a fixed silver oven temperature. For the spectrum c) the oven temperature had been increased at the stagnation pressure kept constant at 10 bar. The mass spectra were measured at 100 eV electron impact energy, *i.e.* the ionization induced fragmentation is expected to shift the observed distributions to the lower masses. It has been shown by Möller that fragmentation of pure Ar clusters can be neglected for the cluster sizes beyond 100 atoms/cluster [11]. For the mixed clusters one expects a considerable evaporation of rare gas atoms following the ionization event: The localization of the positive charge on the metal cluster and the large energy difference between the ionization energies of the Ar droplet and the metal cluster leads to energy release which might be sufficient to completely remove the rare gas shell. The fragmentation extent of the remaining metal cluster can be determined only experimentally. In

the present work, however, the fact that the spectra do not correspond to the neutral cluster distributions is of minor relevance because we want to discuss the apparent relative changes which are not obscured by the underlying fragmentation. In the spectrum 1a) silver monomers dominate the distribution and no silver cluster bigger than Ag₅ is detected. In the insert which shows the expanded view of the spectrum in the mass range 50-420 amu, in addition to Ag_n ($n = 1, 2, 3$), one finds the following series: Ar_n ($2 \leq n \leq 10$) AgAr_n ($1 \leq n \leq 7$), Ag₂Ar_n ($1 \leq n \leq 4$) and Ar₃Ar_n ($n = 1, 2$). These series are indicative of the process by which metal clusters grow within a rare gas droplet and of the fact that the droplet must not be completely removed by the ionization. Increasing the stagnation pressure to 10 bar at the constant oven temperature results in the spectrum b): In the distribution with intensity detectable up to Ag₁₅ a silver monomer has lost its dominating character as the distribution maximum has moved to Ag₅. A pronounced odd-even intensity alternation - well known from the previous mass spectrometric studies of silver clusters [12,13] - points at the fragmentation of metal clusters. It is less pronounced towards the bigger clusters indicating that some stabilization by the surrounding droplet occurs. In addition to silver clusters and the mixed series one observes throughout the whole mass range a distinct background of Ar_n lines. These are absent from the spectrum c) which was measured at the same stagnation pressure but a higher silver vapour pressure. There are essentially only silver clusters to be seen with the distribution maximum centered at Ag₉. Doubly charged clusters are also detected at the "half masses" up to Ag₂₁, their abrupt disappearance at the higher n coincides with the end of the distribution of the singly charged ions. Although in this spectrum the enhanced stability of the odd ions indicates fragmentation of the metal cluster after the ionization event neither mixed clusters nor Ar_n series could be observed under these experimental conditions. Hence, we conclude that the growth of the present distribution was accompanied by substantial evaporation of the host droplets prior to ionization. The dependence of silver cluster size on the silver vapour pressure presented here is in excellent agreement with the results obtained on the silver distributions in He droplets [4].

We have shown that a suitable choice of the host droplet size and of the silver flux allows to grow silver particles which would still reside in the droplets, thus producing the so called doped nanomatrices. The nanomatrices can be subjected to optical spectroscopy *in situ*. The comparison of the spectra with those obtained from the conventional matrix isolation spectroscopy might unambiguously answer the question of the metal cluster location, *i.e.* within *vs.* surface location. The fluorescence spectra were measured while irradiating the exit of the pick up zone with white light. An argon cluster beam of an average cluster size of ~ 1000 atoms per cluster is estimated for the conditions of the adiabatic expansion that were maintained throughout the measurement. The silver flux was tuned to produce a cluster distribution corresponding approximately to the mass spectrum of Fig. 1b).

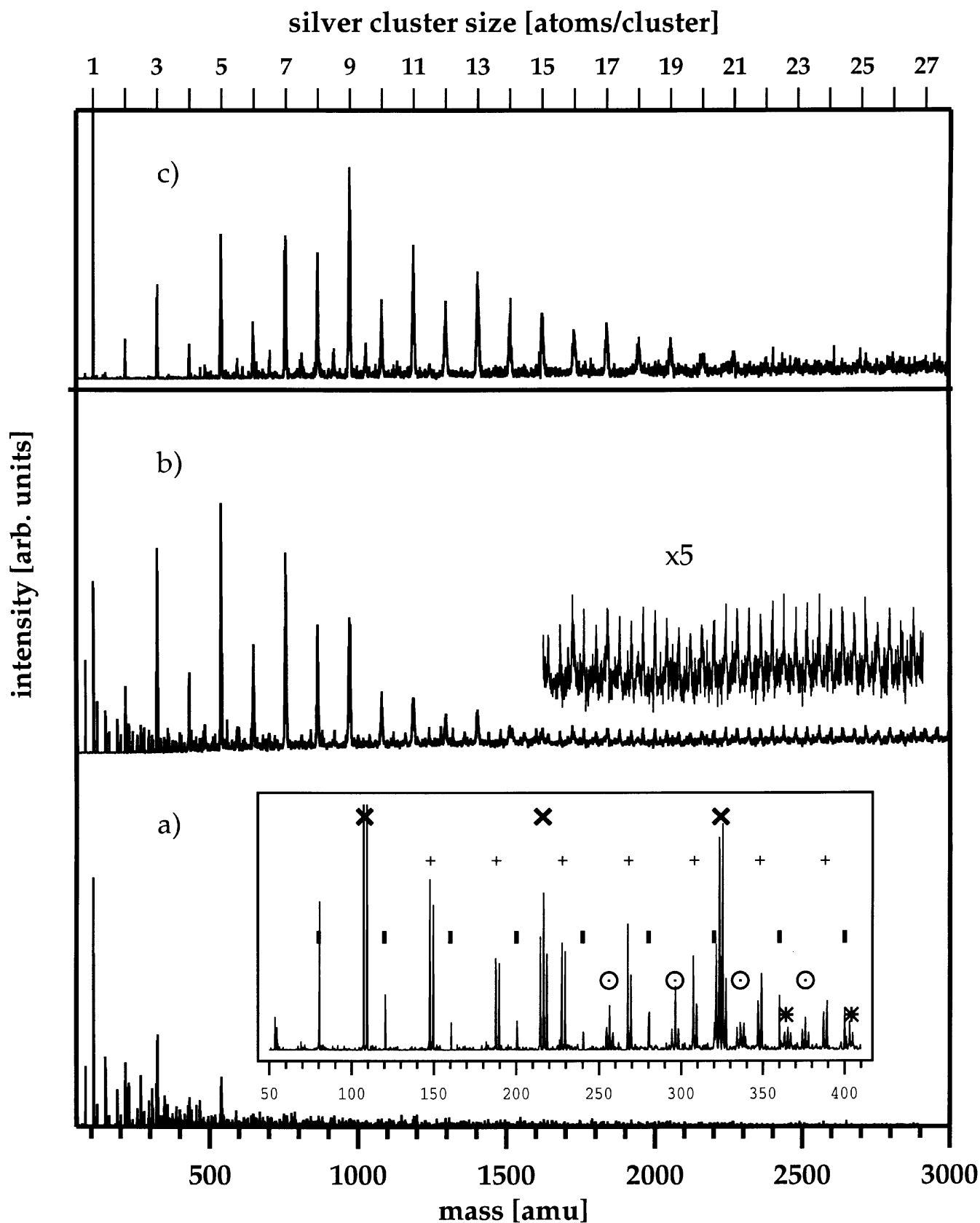


Fig. 1. Mass spectra of the particles emerging from the pick up source as a function of stagnation pressure and silver vapour pressure: a) 5 bar, $\sim 10^{-1}$ mbar; b) 10 bar, $\sim 10^{-1}$ mbar; c) 10 bar, $\sim 2 \times 10^{-1}$ mbar. The insert of (a) shows the series: (x) Ag_n ; (l) Ar_n ; (+) AgAr_n ; (o) Ag_2Ar_n ; (*) Ag_3Ar_n .

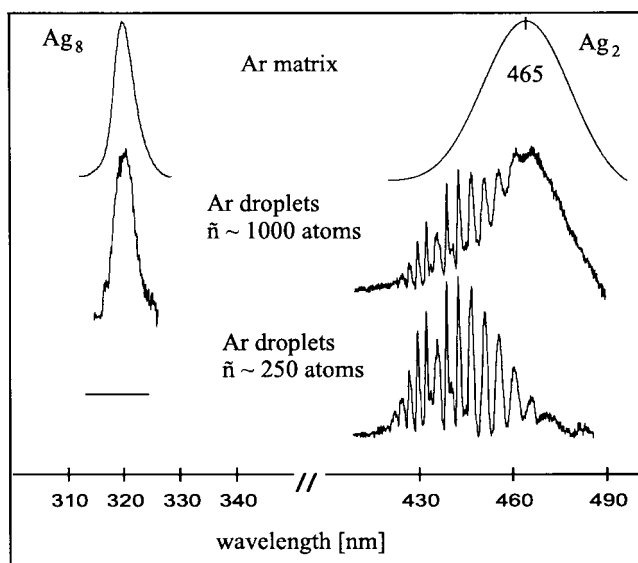


Fig. 2. Comparison of the emission spectra of Ag_8 (left part) and Ag_2 (right part) measured in Ar matrix (top) and Ar droplets. Note that wavelength axes have different scaling to reflect the natural width of the respective peaks.

The resulting emission spectrum contains contributions of the various clusters present in the distribution. To perform the full analysis one would require not only the knowledge of every peak position but also the weight of the individual contributions *i.e.* their oscillation strength and the abundance of the corresponding cluster. However, in a number of cases, the peaks are well separated so that they could be positively identified and compared to the corresponding fluorescence spectra in an argon matrix. One of such cases is the emission line of the Ag_8 - a cluster with outstanding properties: It is so stable that in the mass spectra above its abundance breaks the odd-even pattern; Ag_8 was the only larger cluster in He droplets for which a R2PI spectrum could be recorded which fact the authors attributed to its anomalously long lived excited state [14]. In Fig. 2 emission bands of Ag_8 and Ag_2 are compared with those observed in the previous studies of silver clusters isolated in Ar matrices. The fluorescence band of dimer at ~ 460 nm (Ar droplets, middle portion of Fig. 2) consists of two contributions: A-X progression with origin at 435 nm partly overlaps with the broad band centered at 465 nm. This broad band is one of the well known emission bands of silver dimer isolated in argon matrix (upper part of Fig. 2) [15]. Similarly, in the left side of Fig. 2 a narrow fluorescence band at 320 nm measured in Ar droplets is compared to the one found in an Ar matrix. The latter was recently unequivocally ascribed to Ag_8 in Ar matrix [16]. The full coincidence of the emission line of Ag_8 isolated in an argon matrix and in argon clusters indicates that the

Ar cluster shell is sufficiently large to emulate an argon matrix surrounding which encapsulates the silver cluster. A reduction of the host droplets size to about 250 atoms per droplet leads to disappearance of the fluorescence at 320 nm (Ag_8) and to the redistribution of the individual components of the band at 460 nm (Ag_2): Intensity of the A-X transition of free dimers grows at the expense of that of solvated ones. The disappearance of Ag_8 emission from the spectrum reflects the fact that at the given host cluster size Ag_8 has little chances to be built which is in agreement with the mass spectrum (Fig. 1, bottom) taken at similar conditions.

4 Conclusion

We have shown that with our experimental set up we can produce pure silver cluster distributions as well as Ar droplets doped with silver clusters. Comparison of fluorescence spectra in Ar droplets with those obtained *via* matrix isolation spectroscopy allows us to conclude that silver cluster resides within an Ar droplet.

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