Ag$_8$ Fluorescence in Argon

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The fluorescence of Ag$_8$ in an argon matrix and in argon droplets is reported. This is the first unambiguous assignment of the fluorescence of a metal cluster larger than the tetramer, indicating that the excited state lifetime is longer than previously thought. It is discussed as a possible result of a matrix cage effect. The excitation spectrum is compared with two-photon-ionization measurements of Ag$_8$ in helium droplets and to known absorption data. The agreement is excellent. We propose that the excited states relax rapidly through vibrational coupling to a long-lived state, from which the fluorescence occurs.

Optical spectroscopy has proven to be a powerful tool for understanding the electronic structure of atoms and molecules. Over the past decade these techniques have also been applied very successfully to metal clusters. Small metal clusters have been investigated in free beam experiments, using techniques such as resonant two-photon-ionization (R2PI) spectroscopy [1,2], laser-induced fluorescence [3], and pump-probe [4,5] techniques. Fragmentation becomes, however, more important as the cluster size increases and nondissociative electronic excitation processes have not been observed for free metal clusters larger than trimers [6]. Photodepletion spectroscopy was therefore used to measure optical absorption spectra of free metal clusters larger than three atoms [7–9].

Also the fluorescence lines of free metal clusters are expected to be observed only for very small clusters. Wöste and co-workers have shown that, in the case of K$_3$, the fragmentation of optically excited clusters occurs within a few hundred femtoseconds [10]. This is much shorter than the characteristic time scale necessary for a dipole transition and therefore no fluorescence can be observed in this case.

Alternatively, optical absorption measurements of matrix isolated and mass-selected silver clusters have been performed for sizes up to $n = 39$ [11]. No signal decrease has been observed over time, so it is clear that the matrix is effectively preventing the clusters from dissociating. This so-called *cage effect* is well known for molecules in a gas atmosphere or in a liquid. In the case of I_2, for example, it has been shown that a single rare gas atom adsorbed on the molecule hinders the photofragmentation and allows the fluorescence [12].

This opens the possibility of observing fluorescence for small metallic clusters if the excited state of the particle has a sufficient lifetime for a radiative transition to take place. However, with increasing size the competition between the different possible relaxation processes (vibrations, fluorescence, fragmentation) increases and, due to their shorter

characteristic time, the radiationless relaxation processes are expected to quench the fluorescence [13–15].

In the case of silver, fluorescence of Ag$_3$ and, more recently, Ag$_4$ has been unequivocally determined. A number of hitherto unidentified emission bands have been observed in the studies of non-mass-selected silver clusters in argon matrices which were ascribed to Ag$_n$, $n > 4$ [16]. Moreover, the chemiluminescence found in the agglomeration of silver clusters in noble gas matrices and noble gas droplets also indicates that fluorescence is not limited to cluster sizes below 4 [17].

In this Letter we report the fluorescence of Ag$_8$ isolated in argon and its excitation spectrum. This is the first unambiguous assignment of a fluorescence for a metallic cluster larger than $n = 4$. Our results are compared to optical absorption [11] and recent two-photon ionization experiments in helium droplets [18].

Three alternative methods have been applied to measure the fluorescence of Ag$_8$ in argon. In the first one, the clusters are mass selected to have size specific information, and in the other two methods the clusters have a statistical mass distribution but a higher intensity. A very short description of the different methods and their critical parameters are given in the next paragraphs; the reader is referred to other papers for a more detailed description of the different experimental setups.

The production and mass selection of positively charged silver clusters have been described in detail elsewhere [19,20]. Silver ions are sputtered from a silver target and mass selected. The positively charged clusters are co-deposited with Ar (and simultaneously neutralized) to form a neutral seeded matrix. The deposition energy is $E_{Dep} = 30$ eV (where fragmentation has shown to be low) with a typical current for Ag$_8^+$ of 0.4 nA. Clusters are deposited with an Ar:cluster ratio of $\sim 2 \times 10^4$ and a final cluster surface density of $\sim 5 \times 10^{14}$ cm^{-2}. Matrix samples are studied *in situ* using excitation and fluorescence spectroscopy. For the excitation we use a frequency doubled optical

parametric oscillator (OPO) pumped by a Nd:YAG laser (pulse length ~10 ns).

In the second method, a cluster distribution with a high content of Ag_n, $n > 3$, is produced by means of the high temperature matrix preparation (HTMP) technique which has been described elsewhere [17]. Briefly, a gas aggregation cluster source is operated under such conditions that cluster formation is suppressed, i.e., only atoms and a minor amount of dimers, together with the matrix gas, reach the matrix target maintained at a temperature of 42 K. The flux of deposition amounts to 1.8×10^{19} atoms s^{-1} cm^{-2} of Ar and 6×10^{14} atoms s^{-1} cm^{-2} of Ag.

In the third method, we prepare silver clusters by letting a beam of argon clusters traverse a silver vapor zone, i.e., by the so-called pickup method [21]. Argon clusters capture silver atoms, which aggregate within the argon clusters. A silver cluster distribution of the desired average size can be produced by tuning the initial size of argon clusters and the silver density. Our experimental setup allows optical measurements at any point along the cluster beam path. Silver cluster distributions thus prepared are analyzed by optical spectroscopy. For excitation we use the light of a 450 W Xe-lamp dispersed by a double monochromator. The emitted light is analyzed by means of a monochromator coupled to a charge-coupled device detector.

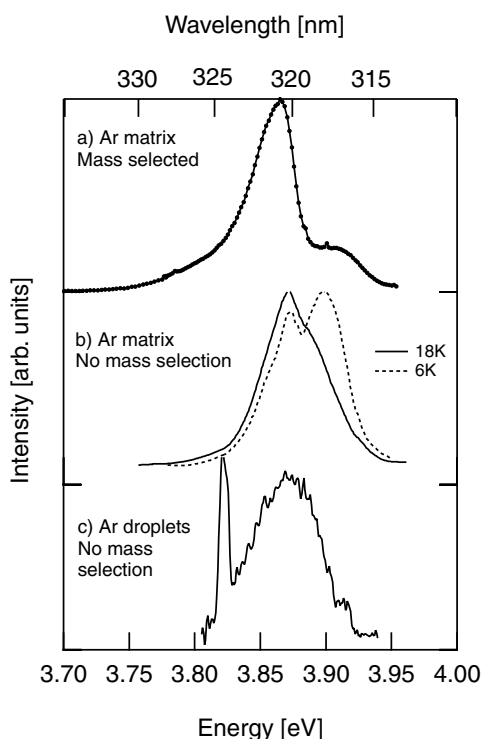Figure 1(a) shows the fluorescence spectrum of monodispersed Ag_8 for an excitation energy of 3.98 eV.

We observe two fluorescence peaks: a principal peak at 3.87 eV and a second peak at 3.90 eV. The asymmetry of the principal peak indicates an additional peak at ~3.85 eV, which despite higher instrumental resolution could not be resolved. For this excitation energy, we have not observed other sharp fluorescence peaks in the rest of the visible spectrum.

The fluorescence at 3.87 eV is new and cannot be assigned to the previously assigned fluorescence peaks of Ag_1 (3.80, 3.36, 2.92, and 2.71 eV) [22], Ag_2 (4.46, 4.34, 4.16, and 2.59 eV) [23], Ag_3 (3.32, 2.04, and 1.76 eV) [24], and Ag_4 (2.71 eV) [20].

During the deposition process, Ag_8 could fragment into smaller sized clusters, actually optical absorption experiments on Ag_8 have shown that the principal dissociation channel is $Ag_8 \rightarrow Ag_7 + Ag_1$ [11]. The comparison between the absorption spectrum of Ag_8 and its excitation and fluorescence spectra (see Fig. 2) allows us to confidently assign this fluorescence to Ag_8.

In Figs. 1(b) and 1(c) the fluorescence spectra of Ag_8 produced by, respectively, methods 2 and 3 are presented: The spectra 1(b) (solid and dashed curves) were obtained while using monochromatic light at 3.98 eV for excitation and a sample which contained a cluster distribution prepared by means of HTMP at 35 K and subsequently cooled to 18 and 6 K, respectively. Figure 1(c) is due to the white light excitation of particles present in Ar droplets. The
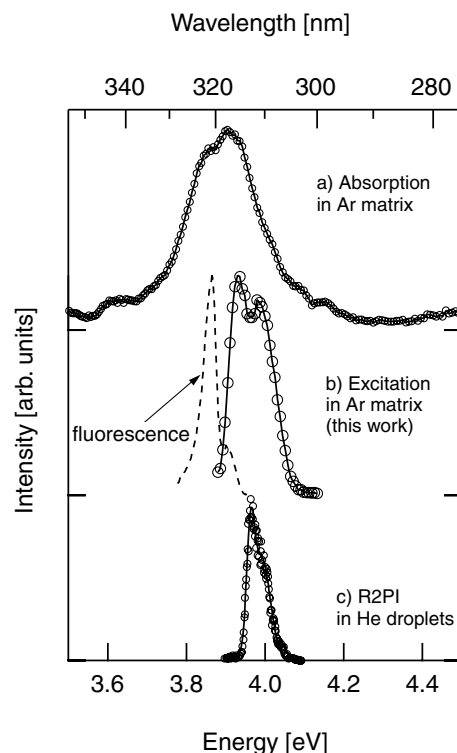

FIG. 1. Fluorescence spectra of Ag_8 in argon. (a) Ar matrix: mass selected Ag_8, excited with an OPO at 3.98 eV; matrix temperature equal to $T_m = 25$ K. (b) Ar matrix: no mass selection, excited with monochromatic Xe light at 3.98 eV; $T_m = 6$ or 18 K. (c) Ar droplets: no mass selection, excited with undispersed Xe light.

FIG. 2. Comparison between (a) absorption spectrum of size-selected Ag_8 in an Ar matrix [11] and (b) excitation spectrum of Ag_8 (recorded at 3.87 eV and excited with monochromatic Xe light); the dashed line shows the fluorescence spectrum from Fig. 1(a). (c) Resonant two-photon-ionization spectroscopy on Ag_8 clusters in He droplets [18].

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broader band at 3.87 eV belongs to Ag_8, whereas the sharp feature at 3.82 eV is assigned to Ag_1. Notice that the two peaks resolved at 6 K in Fig. 1(b) correspond within a few meV to the two peaks measured on the mass selected clusters in Fig. 1(a), and are consistent with the asymmetry of the fluorescence spectrum taken at 18 K. It appears that, depending on temperature and on the preparation technique, the relative amplitude of the peaks at 3.87 and 3.90 eV changes. It is well known from the rare gas matrix studies that host molecules react sensitively to the structure of the surrounding media. Specific embedding sites characteristic for different matrix temperatures have been found for Ag [22], Ag_2 [23], Ag_3 [25], and Ag_5 [26] in Ar matrices. The same phenomenon is probably responsible for the peak position shift in the spectra under discussion.

The excitation spectrum measured by changing the excitation wavelength while recording the fluorescence intensity at maximum is an *indirect* measurement of transition probabilities between the electronic states of the particle. In Fig. 2 it is compared to optical absorption measurements of Ag_8 in a matrix and resonant R2PI experiments on Ag_8 in helium droplets [18].

The agreement between the excitation spectrum in Ar [Fig. 2(b)] and the R2PI data [Fig. 2(c)] in He is remarkable; there is no doubt that we measure the same excited states. We attribute the difference in peak width to the width of our excitation source and to matrix effects. The slight difference in the peak position (~ 0.03 eV) is probably also due to matrix effects.

The absorption [Fig. 2(a)] and the excitation [Fig. 2(b)] spectra are also compared in Fig. 2. Although there is general agreement between both spectra, notice that Ag_8 clusters in an argon matrix also absorb at energies lower than that of the fluorescence line [27].

The optical properties of silver clusters have been interpreted in a solid state physics picture, assuming a collective oscillation of the valence electrons against a background of positively charged ions. Several experiments [28,29] have shown that, due to electron-electron and electron surface scattering, the lifetime of the plasmon oscillation is very short, of the order of 10 to 100 fs for particles of some nm in diameter. For small clusters, quantum chemical approaches have been used and were shown to be very accurate (see [30] and references therein). Ellert *et al.* [31] have shown that the temperature and not only the size was a key parameter. While at high temperature a simple jellium model described adequately the optical response of intermediate sized sodium clusters, at low temperature a molecular quantum calculation was required to describe it. This was explained by the fact that at low temperature the atoms have fixed positions, while at higher temperature the calculated signal has to be weighted and averaged over thermally accessible geometries.

In a molecular picture the lifetime of an excited all-electron state depends, as already mentioned, on the interplay between the fragmentation behavior of the excited cluster, the coupling to the vibrational levels of the cluster,

and possible fluorescence. In a matrix, due to the cage effect, fragmentation of the cluster is severely hindered, and coupling to the surrounding matrix can effectively lower the temperature of the cluster and contribute to the relaxation. In this picture, light emission, i.e., fluorescence, results from an electric dipole transition, which happens in a characteristic time scale of 100 ps to 10 ns. In order to emit a photon the excited state of the particle must have a sufficient lifetime.

In their R2PI experiment, Federmann *et al.* [18] used nanosecond pulses. This indicates that the lifetime of the electronic excited states of Ag_8 in a helium droplet is of the order of nanoseconds, larger than that of a plasmon excitation. They have thus suggested that molecular transitions rather than plasmon excitations were involved.

The present observation of a fluorescence line with a narrow width is in complete agreement with these conclusions [32]. It also suggests that in the Federmann *et al.* experiment, after the initial pulse, the observed excited states quickly decay toward the fluorescence state that we measure, from which the electron is then excited to an ionized state.

An alternative explanation is to assume that both excitation and fluorescence probe the same electronic excited state. Because of different positions of the energy minimum of the ground and excited states in the multidimensional configuration space, the excitation and the fluorescence energies are different. This is well known for molecules [33] and it would explain why the excitation and the R2PI signals do not increase near the energy of the fluorescence. The same picture gives at the same time an alternative comprehension of the temperature dependence of the fluorescence. The population of the vibrational levels changes with the temperature while the intensity of the transition is governed by the Franck-Condon factors.

There is unfortunately no reliable calculation of the excited states of an Ag_8 cluster, similar to that known for Ag_4, where the agreement between theory and experiment was excellent. The ground state geometries of Ag_n clusters have been calculated [34], and the two lower energy structures of Ag_8 (T_d and D_{2d} symmetry) are the same as those of Na_8, for which a complete analysis of the excited state has been published and compared with the measurements of Baumert *et al.* [35]. It is clear from the analysis done for Na_8 that the oscillator strength of different excited states varies much from one state to the other, some transitions being forbidden for symmetry reasons. The radiative lifetime consequently varies from some ns to hundreds of ns. In order to pinpoint the state responsible for the fluorescence we observe, a detailed calculation for Ag_8 should be done. The general picture seems, however, clear.

After excitation to the different higher energy all-electron states of Ag_8, fast relaxation processes take place, which lead to the state from which fluorescence occurs. If the excited states are close in energy, vibrational deexcitation channels in the Ag_8 molecule are open. The energy is then transferred to the matrix via phonon coupling. These

are rapid processes, with a time constant of the order of a few ps [36,37]. Once the fluorescence state is reached, the vibrational deexcitation channels are much less effective, allowing the fluorescence channel to be competitive. Such a picture is supported by the fact that the fluorescence state is near the low energy end of the absorption spectrum.

In bulk metals the nonradiative decay can proceed down to the ground state, making luminescence improbable. From this point of view the observation of a fluorescence is typical of clusters. It remains to be seen if it can be observed for larger clusters than Ag_8, and if the high symmetry of Ag_8 plays a crucial role. Notice in this respect that Federmann et al. have not observed resonant ionization species between Ag_3 and Ag_8, contrary to our previous measurements of a fluorescence signal in Ag_4 embedded in an argon matrix.

In conclusion, a sharp fluorescence peak for Ag_8 in argon has been observed. An excitation spectrum is recorded, and found to be in excellent agreement with two-photon-ionization experiments of this same cluster in helium droplets. This is definite proof that this cluster has molecular transitions, i.e., electric dipole transitions. Optically excited states relax vibrationally to a long-lived state, from which the fluorescence can occur.

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