

**Isomer-specific spectroscopy of metal clusters trapped in a matrix: Ag<sub>9</sub>**

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Clusters of metal atoms at a fixed size can assume different structural arrangements, known as isomers, which may have nearly the same energy. Therefore, at given experimental conditions distribution of these isomers can be present. While the size selection is a relatively common technique, the isomer selection is not; it is therefore more difficult to obtain information about a single isomer. We report here on isomer-specific spectroscopy of Ag<sub>9</sub> clusters together with *ab initio* calculations allowing to identify the isomer responsible for the measured excitation pattern and fluorescence.

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Recent experiments by fluorescence microscopy of nano-scale silver oxide [1] have demonstrated that strong photo-activated emission can be generated by uv excitation. The individual luminescent species are thought to be silver nano-clusters that are photochemically generated from the oxide. The color of individual emissive sites changes as a function of time, and the authors relate it to the changing charge and size of the Ag clusters. This work, together with further investigations, indicates that silver nanoclusters and, more generally, metal clusters could be useful in optoelectronics as storage devices [1], full quantum logic elements [2], or possibly as lasing media. It is thus important to understand better the emissive properties of supported metal clusters.

In the gas phase, small metal clusters have been investigated using optical spectroscopy techniques such as resonant two-photon ionization (R2PI), laser-induced fluorescence [3,4], and pump-probe techniques. However, as the size increases, fragmentation becomes a dominant process and non-dissociative electronic excitation processes have not been observed for gas-phase metal clusters larger than the trimer, unless very short pulses are used [5]. The optical absorption spectra of larger metal clusters have thus been obtained using photodepletion spectroscopy [6].

The situation is different in a matrix due to the cage effect, which effectively prevents dissociation. This opens the possibility to observe the fluorescence of particles larger than the trimer, if the excited state of the particle has a sufficient lifetime for radiative transition to take place. It was, in particular, recently shown that neutral Ag<sub>4</sub> [7] and Ag<sub>8</sub> [8] clusters embedded in an argon matrix have a strong fluorescence signal.

However, a major difficulty, both in the gas phase and supported cluster experiments, is that in general molecular beams are not formed from a single isomer. This is particularly true for metal clusters, in which the delocalized nature of the valence electrons leads, for a given size, to isomers which may be quasidegenerate with the lowest energy structure [9,10]. This can lead to ambiguities in the assignment of measured features to a given isomer and to enlargement of the peaks. There are, however, exceptions, especially at low temperature [11]. For size-selected clusters deposited in a

rare-gas matrix, it has been shown that conditions can be found to minimize fragmentation [14]. However, it is not clear that the embedded clusters all correspond to the minimum-energy configuration: the different isomers present in the beam and the deposition process itself could lead to the trapping of different isomers.

It is thus important to use isomer-specific experimental techniques, which allow one to extract out of a sample formed of several isomers a signature characteristic of a single isomer. We present in this Rapid Communication the observation of an intense and very narrow fluorescence line for Ag<sub>9</sub> clusters trapped in an argon matrix. The narrowness of the line and the observation of a well-defined vibrational structure are strong indications that this fluorescence is associated with a single isomer. The excitation spectrum, measured by changing the excitation wavelength while recording the fluorescence intensity at the position of the fluorescence line, is thus an indirect measurement of the transition probabilities between the electronic states of this single isomer. We can exclude energy transfer between different clusters due the high dilution ratio of the clusters in the matrix. Indeed, although the absorption spectrum previously measured [14] shows broad features due to the contribution of different isomers, the excitation spectrum that we measure has a well-defined four peaks structure.

Isomer-specific experimental techniques have been applied to molecules and clusters in a beam. For gas-phase organic molecules, e.g., uv-hole-burning spectroscopy coupled with R2PI spectroscopy has been used to differentiate the absorption spectra of different isomers [15,16]. Another promising route is to separate a gas-phase isomeric ion mixture prior to a spectroscopic probe. This has been recently achieved [17] in the case of carbon clusters by coupling photoelectron spectroscopy to ion mobility/mass spectrometry. Excitation spectroscopy by detecting the fluorescence in a narrow band has previously been used to characterize, e.g., small matrix isolated carbon clusters [18], organic molecules [19], or metal dimers [20] placed in different environments or at different sites. This paper reports on isomer-specific spectroscopy measurement of metal clusters in a matrix.

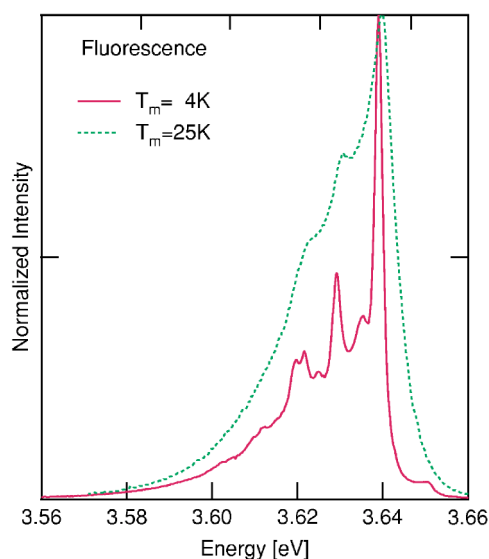


FIG. 1. Fluorescence spectra of  $\text{Ag}_9$  at 25 and 4 K (laser excitation 4.03 eV). Cooling the sample down unravels the details of vibrational progressions of the ground state of  $\text{Ag}_9$ . Notice that the width of a single peak is only 2.4 meV FWHM.

It remains to identify the isomer responsible for the measured fluorescence and excitation spectra. We present in this communication theoretical results of the absorption spectra carried out for different  $\text{Ag}_9$  structures, as well as a study of the geometric relaxation in the excited state of the lowest energy isomer. On that basis we make a tentative assignment of the isomer and the transition responsible for the measured fluorescence.

The experimental setup has been described in more details elsewhere [7]. Briefly, silver clusters cation are produced by sputtering, and then size selected and codeposited with neutral argon atoms to form a seeded matrix. A frequency doubled optical parametric oscillator (OPO) pumped by a Nd:YAG laser is used for excitation. The fluorescence light is analyzed spectrally and detected by a liquid-nitrogen-cooled charge-coupled device (CCD) camera.

Figure 1 shows the fluorescence spectrum of  $\text{Ag}_9$  embedded in an argon matrix at two different temperatures. Cooling the matrix down to 4 K reveals vibrational fine structures in the fluorescence signal. Given the low temperature at which the measurements are made, we attribute these modes to the vibrational structure of the ground state [21].

Figure 2 presents the absorption spectrum [14], the fluorescence spectrum (measured at 25 K), and the corresponding excitation spectrum of  $\text{Ag}_9$  in an argon matrix.

The excitation spectrum has a dominant peak, that we can experimentally approach only from the high-energy side. In the last measurement point (at 3.69 eV) shown in Fig. 2, we could still distinctly separate spectrally the fluorescence and the excitation light. The dominant excitation peak is very close to the fluorescence peak and therefore supports involvement of the same electronic state. The corresponding Stokes shift is estimated to be smaller than 0.04 eV. In addition, there are three distinct and narrow peaks of lower intensities centered at 4.02, 4.20, and 4.34 eV.

The absorption signal has broader features and does not match the excitation spectrum, although it lies in the same

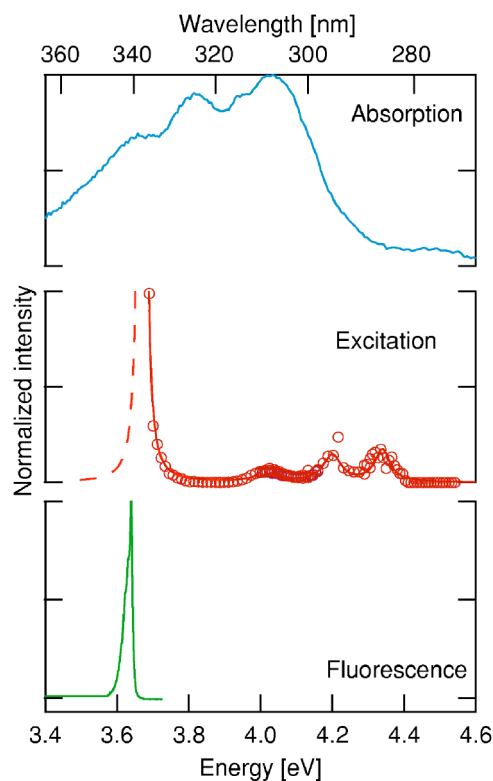


FIG. 2. Absorption [14], excitation, and fluorescence spectra of  $\text{Ag}_9$  in an argon matrix. The continuous and dotted line in the excitation spectrum is a multi-Lorentzian fit to the data.

energy range. It is clear that for a given isomer the excitation spectrum does not have to be identical to the absorption one. Its features depend not only on the transition probabilities to the excited states, but also on the details of the relaxation mechanisms to the fluorescence state. However, the position of the different peaks should be the same, which is clearly not the case. Therefore, we assume that the absorption spectrum results from the superposition of the spectral features of different isomers.

In order to clarify the experimental findings we performed *ab initio* calculations to determine the geometric structures of the low-energy isomers, and the corresponding optical absorption spectra. In our previous work on optical properties of silver clusters [22] it has been shown that an 11-electron relativistic effective core potential (11e-RECP) with (6s5p5d) AO basis set for silver allows one to accurately determine transition energies and oscillator strengths in the range up to 5 eV [22,23]. Structures of the isomeric forms of  $\text{Ag}_9$  cluster have been fully optimized in the framework of the density functional (DFT) method, with S-VWN and Becke-Perdew parametrization (BP86) [24] using gradient-based optimization methods. Notice, that for smaller size clusters geometry optimization using DFT and more accurate coupled cluster (CCSD) method gave very similar results. Therefore, we employed DFT techniques to determine the ground-state structural properties of  $\text{Ag}_9$ , which is computationally less demanding.

For calculation of optical spectra, unrestricted formulation of the random-phase approximation (RPA) has been em-

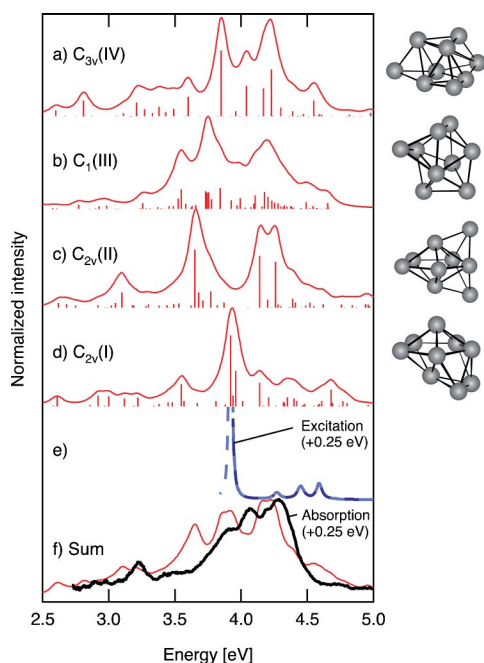


FIG. 3. (a)–(d) Intensity of the optically allowed transitions and simulated absorption spectra of different isomers (artificially broadened by a Lorentzian function of 0.1 eV). (e) Measured excitation spectrum shifted by 0.25 eV to account for the matrix shift [25]. (f) Measured absorption spectrum of  $\text{Ag}_9$  shifted by 0.25 eV, compared to the sum of the different spectra with the following weights:  $C_{2v}$  (I) 26%,  $C_{2v}$  (II) 37%,  $C_{3v}$  (IV) 37%.

ployed. This method gives reliable transition energies and oscillator strengths for electronic states dominated by singly excited configurations, which is usually the case for optically allowed transitions with large intensities. We have verified this by comparing RPA results and equation of motion coupled cluster (EOM-CCSD) calculations in our previous work [22]. In order to study the fluorescence of  $\text{Ag}_9$ , geometry optimization in the excited state has been performed by using numerically calculated gradients combined with the conjugated gradient method.

In the ground state of  $\text{Ag}_9$ , four isomers close in energy have been obtained. The lowest energy structure (isomer I) with  $C_{2v}$  symmetry assumes a pentagonal bipyramid structure with two atoms capping two neighboring faces of one pyramid, as shown on Fig. 3. The second isomer is 0.104 eV higher in energy and has also a pentagonal bipyramid with two atoms capping two neighboring faces belonging to the different pyramids. The third isomer has a  $C_1$  structure which can be obtained by capping one face of the  $D_{2d}$  structure in  $\text{Ag}_8$  and is 0.235 eV higher in energy than isomer I. The fourth isomer has trigonal structure with  $C_{3v}$  symmetry (a section from the fcc lattice) and lies 0.535 eV higher in energy. These results are in agreement with recent calculations of  $\text{Ag}_9$  [26], which predict that four isomers have energies comprised within a 0.05 eV range, and more isomers are still close in energy.

The intensities of the optically allowed transitions for isomers I–IV are reported in Fig. 3, as well as the corresponding absorption spectra. They exhibit very distinct spectral features and allow for the interpretation of the measured absorp-

tion spectra. In particular, the absorption spectrum of isomer I shows one dominant transition at 3.92 eV corresponding to the measured dominant band in the excitation spectrum shifted by 0.25 eV to account for the influence of the argon matrix [14]. Lower intensity transitions are distributed in the blue and red region with respect to the dominant transition. In the blue region the calculated intense transition at 4.14 eV, few close lying transitions at  $\sim 4.35$  eV, and the one located at 4.68 eV could correspond to the weaker features measured in the excitation spectrum. While the position of the most dominant peak is very well reproduced in the framework of the RPA method, the positions of the secondary peaks are less accurate. This is due to the fact that the RPA method cannot describe accurately those transitions in which doubly excited configurations have significant contributions. The calculated spectra for other isomers do not match the most intense transition, which confirms the conclusion that isomer I is responsible for the measured fluorescence and excitation spectra.

In order to determine the position of the fluorescence band, a geometry optimization of the excited state with the largest oscillator strength, corresponding to the vertical transition at 3.92 eV of isomer I has been carried out. We find that the transition from the ground state to the  $16^2B_1$  excited state is responsible for the observed fluorescence, and that the ground state and the excited state with dominant intensity have related structures with the same symmetry. The calculated lowering of energy with respect to the vertical transitions is equal to 0.19 eV, which is quantitatively larger than the experimental finding of 0.04 eV. This difference lies within the accuracy of the method used.

We compare in Fig. 3(f) the measured absorption spectrum to a weighted sum of the absorption spectra of isomers I, II, and IV. This confirms the assumptions that a sample of  $\text{Ag}_9$  clusters deposited in an argon matrix is composed of several isomers.

In addition, since the ground and excited states structures have the same symmetry, the structural relaxation in the ground state after the fluorescent deexcitation of the first excited states should take place along totally symmetric normal modes in the ground state. Harmonic vibrational frequencies for the ground-state structure of  $\text{Ag}_9$  have been calculated. Altogether, seven totally symmetric vibrational modes have been obtained with frequencies of 50.7, 61.3, 79.9, 92.1, 101.3, 142.3, and 159.2  $\text{cm}^{-1}$ . The low-lying vibrational modes with 50.7 and 79.3  $\text{cm}^{-1}$  frequencies are in perfect agreement with experimentally observed progressions in the fluorescence spectrum.

We have shown in this communication that size-selected  $\text{Ag}_9$  clusters deposited in a rare-gas matrix take different isomeric structures and that great caution must be taken in interpreting absorption spectra of metal clusters. This work is a clear demonstration that a small metal cluster like  $\text{Ag}_9$  is still a molecule and that a plasmon approach is incorrect. The coexistence of different isomers is in agreement with *ab initio* calculations [26] which predict that several  $\text{Ag}_9$  isomers are close in energy. This points out the importance of isomer specific experimental techniques when the size of clusters increases. They allow to identify the structural properties of an isomer by comparing well-resolved spectra with *ab initio*

calculations. The method that we have used can be applied to neutral and not only to charged clusters.

One surprising result of this work is that only one  $\text{Ag}_9$  isomer fluoresces in the wavelength range of 285 to 800 nm of our measurements. This may have important conse-

quences for the understanding of emissive properties of photoactivated Ag clusters.

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