Optical absorption of small silver clusters: Ag$_n$, (n=4−22)

M. Harb,[1] F. Rabilloud,[1] D. Simon,[1] A. Rydlo,[2] S. Lecoultre,[2] F. Conus,[2] V. Rodrigues,[2,a)] and C. Félix[2,b)]

[1]*Université Lyon 1, CNRS, LASIM UMR 5579, 43 Boulevard du 11 Novembre 1918, F-69622 Villeurbanne, France*

[2]*Institut de Physique des Nanostructures, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

We present a joint theoretical and experimental investigation of the absorption spectra of silver clusters Ag$_n$ ($4 \leq n \leq 22$). The experimental spectra of clusters isolated in an Ar matrix are compared with the calculated ones in the framework of the time-dependent density functional theory. The analysis of the molecular transitions indicates that the *s*-electrons are responsible for the optical response of small clusters ($n \leq 8$) while the *d*-electrons play a crucial role in the optical excitations for larger *n* values. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3013557]

I. INTRODUCTION

Small metal particles have attracted a lot of attention for many years since their physical and chemical properties vary drastically with size. In particular, several theoretical and experimental studies have been carried out on the structural, electronic, and optical properties of small silver nanoclusters, stimulated by their importance in both basic and applied researches. The electronic complexity of silver clusters lies between that of alkali metals and transition metals. Understanding their electronic properties and optical response remains an interesting challenge due to the close lying *d*-electrons, which quench the oscillator strengths by screening the *s*-electrons and get partially involved in the excitations.

Experimentally, the optical spectra of small silver cationic Ag$_n^+$ (n=9,11,15,21) clusters were first obtained by photofragmentation of mass-selected cluster beams.[1,2] These studies were followed by optical absorption measurements of small silver neutral Ag$_n$ (n=2−39) clusters embedded in rare-gas matrices.[3,4]

Theoretically, *ab initio* optical spectra of small silver neutral Ag$_n$ (n=2−8) clusters as well as small silver cationic Ag$_n^+$ (n=2−4) clusters were calculated in the framework of the linear response equation-of-motion coupled cluster (EOM-CC) method.[5,6] Several time-dependent density functional theory (TDDFT) studies have been performed for Ag$_n$ (n=2−11) clusters, either in the local-density approximation[7–9] or recently with the PW91 functional[10] and the BP86 functional.[11]

While the optical absorption of small silver clusters can only be fully explained by a calculation taking into account the atomic structure of the cluster as well as the contribution of both *s*- and *d*-electrons, such calculations were not available up to now for clusters larger than Ag$_{11}$. The observed spectra for larger clusters were therefore first interpreted very successfully by adopting the point of view that they reflect a collective excitation of the electrons, and that Mie theory in relation to simple models can be used to describe them. This approach is justified by the fact that silver is the most "alkali-like" transition metal and that the classical theory explains successfully the results of optical spectroscopy of alkali clusters in terms of plasmon excitations. It is not our intention to give here a complete development of these ideas (for this see Refs. 2, 3, and 12–14 and references therein), but we remind here the main ideas and the corresponding interpretation of the electronic structure of these objects.

In Mie theory,[15] the interaction of light with a spherical particle embedded in a medium is described in the framework of classical optics, assuming that the particle and the medium are continuous, homogeneous, and characterized by their dielectric function.

The absorption spectra of Na clusters were understood as a collective oscillation of the 3*s* valence electrons and the shift of absorption energies of the very small particles compared to the bigger ones explained by a spillout (extension of the electronic wave functions out of the "classical volume" of the cluster) of these *s*-electrons. The Nilsson–Clemenger model,[16] which allows a deformation of the sphere along the three different particle axes by conserving its volume, reproduced very successfully the main electronic structures.[17–21]

For small Ag clusters, the same approach, using a Drude-type dielectric function (that takes into account only the 5*s*-electrons), leads to three absorption peaks in qualitative agreement with the measurements.[3] To understand the size evolution of the absorption spectra, in particular, the redshift with increasing size as reported by Charlé *et al.*,[12] one has to account for the evolution of the relative contributions of the *s*- and *d*-electrons as a function of size. The effect of interband transitions due to the *d*-electrons is essential to understand the experimental plasmon resonance for large particles (diameter ∼100 Å) (Ref. 12) and in bulk silver. The optical spectra of silver clusters were therefore modeled using a two-shell sphere model.[2,3,14] The internal sphere was described by the bulk dielectric function, which includes

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a)Present address: Instituto de Física "Gleb Wataghin," UNICAMP, C.P. 6165, 13083-970 Campinas SP, Brazil.
b)Electronic mail: christian.felix@epfl.ch.

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the effects of the *d*-electrons, while the external shell, which accounts for the spillout of the 5*s*-electrons, was described by a Drude-type dielectric function.

In this paper, we report a joint experimental and theoretical study of the absorption spectra in UV-visible range for Ag_n ($n=4-22$) clusters. The experimental spectra of mass-selected clusters embedded in an argon matrix are presented for $n=4-14$. Since the crystallinity of the surrounding matrix was shown to influence the absorption spectra of the embedded clusters,[22] all the spectra reported here were recorded in an argon matrix annealed at 28 K. We present new calculations for $n=4-22$ in the framework of TDDFT. Our theoretical results will be compared to the experimental spectra for $n \leq 14$, and to previous works already available for $n > 14$. Together with the computational studies reported in a very recent paper by Baishya *et al.*,[23] the calculations presented here represent the first systematic TDDFT modeling study performed from first principles on relatively large Ag_n clusters.

II. EXPERIMENTAL

The experimental setup used to record the absorption spectra has been described in detail elsewhere.[24] In brief, the clusters are formed from a metal target sputtered by a 15 mA Xe^+ ion beam at 25 keV. The cluster cations are guided to a quadrupole mass filter and then to a sample holder at 28 K, where they are deposited together with argon and neutralized to form a seeded rare-gas matrix of neutral species. The deposition energy typically ranges from 20 to 30 eV. The size-selected clusters are accumulated in the matrix for 2.5 h while a 40 μm thick matrix is grown. A capping layer of argon is then grown on top of the matrix to protect it from any contamination and to optimize the optical transmission of the matrix. Optical absorption is performed by injecting white light through the 2 mm length of matrix and by collecting the residual light on the other side with an optical fiber. The elongated optical path allows for a good sensitivity. The collected light is then analyzed by an optical spectrometer coupled to a liquid-nitrogen-cooled charge coupled device. Comparing the intensity of the light passing through a matrix doped with clusters with a reference signal of light passing through a pure argon matrix yields the absorption spectrum of the deposited species. Hereafter we stress some experimental facts that are important for the analysis of the spectra measured in this work.

A. Cluster intensities and stabilities

In a sputter cluster source like the one used here, the cluster intensity decreases nearly exponentially with size, due to the clustering mechanism and the high internal temperature of the produced clusters (see mass spectrum in Fig. 2 of Ref. 24). In addition, even-sized clusters have a low intensity because they are less stable due to the electronic shell closing effects;[19] Ag_4^+, Ag_6^+, and Ag_{10}^+ have particularly low intensities indicating that their stability is particularly low, which in other words means that the barriers for fragmentation are small compared to the close lying odd sized clusters.

Fragmentation during deposition is important for dimers and trimers[25] but is much smaller for bigger clusters such as Ag_8 or Ag_9 since the deposition energy is distributed among more internal degrees of freedom. It is, however, present as evidenced by observation of the fluorescence lines of neutral silver atoms. It is clear that the fragmentation yield depends on the stability of cluster ions and will therefore be more important for less stable clusters ions.

In a deposition of Ag_{10}, for example, clusters have been accumulated in the matrix for 2.5 h with a current of 18 pA, corresponding to a cluster ion flux of 0.6 nA cm^{-2} and cluster densities in the matrix of 8×10^{15} cm^{-3}. Due to these low densities, the absorption spectra of Ag_n, $n=4,6,10,12,14$, had therefore not been measured so far but are now possible due to the increase in sensitivity of our new absorption measurement setup.[24] However, the combination of lower densities in the matrix and higher fragmentation in the deposition process leads to an overall lower reliability of the corresponding experimental spectra.

B. Clusters in matrices

To achieve appreciable sensitivity for absorption spectroscopy, the clusters are accumulated in a condensed rare-gas matrix. Even though condensed rare-gases are the most inert solids one can think of, they do have an effect on the measured optical spectra.[22] Fedrigo *et al.*[26] discussed the role of the matrix dielectric constant on the absorption spectra for different rare gases. Later, Andersen and Bonderup[27] corrected this simple description by considering the local field corrections for light absorption using the Onsager cavity model.

In addition to the purely dielectric effects, different additional effects can play a role and are discussed here. In a crystallized matrix, clusters with differing but well-defined local environments, known as site isomers, may coexist. This has been observed, for example, in Ag_2 and Ag_3.[28–30] Using quantum calculations on sodium clusters embedded in an argon matrix, Gervais *et al.*[31,32] showed the possible coexistence of several site isomers with slightly different transition energies and intensities. In these calculations, the matrix effects are rationalized in two competing effects: the dielectric effect discussed above leading to a redshift and a confinement of the valence electrons of the clusters due to the presence of the rare-gas atoms leading to a blueshift.

As mentioned above, the cluster source produces hot clusters, and therefore isomers with close ground state energies coexist in the molecular beam. The collision process produces a sudden local heating of cluster and matrix, followed by a rapid dissipation of the heat in the matrix,[33,34] which can result in the coexistence of different low energy isomers in the rare-gas matrix.[35] Finally, it has to be noted that the relative stability of different embedded isomers has to account for their insertion energy into the matrix (that can be important in Ref. 31); the possibility exists that the relative stabilities are reversed as compared to the free ones.

III. COMPUTATION

The cluster geometries were optimized in the framework of the DFT implemented in the GAUSSIAN03 package.[36] The exchange and correlation functional of second generation of type generalized gradient approximation called BP86 was used. It includes the exchange functional of Becke[37] and the correlation functional of Perdew.[38] Ag was represented through a LANL2DZ relativistic effective core potential[39] (RECP) and considered as a $[Ag^{19+}]$ core. The associated Gaussian basis set was $(8s6p4d)$ contracted in $[3s3p2d]$. This approach has been validated in the sense that it provided theoretical results in good agreement with the experimental data concerning the ionization potential for small Ag_n clusters $(n \leq 6)$.[40]

In the optimization process of cluster geometries, a number of structures were tested, but in this paper only the lowest-energy stable isomers are reported. The geometry optimization process was initiated from the structures found in the literature.[11,40–48] New structures have also been tested, in particular, for $n > 13$, in which, to our knowledge, very few results are available.[47,48] The structures for a given size n were constructed from those obtained for smaller clusters with an additional Ag atom placed on different sites. All optimizations were carried out without symmetry constraints ($C1$ symmetry group). Harmonic frequency analysis was performed to guarantee that the optimized structures are local minima. Our optimized structures are very similar to those published previously by Yang *et al.*[47] Of course, the explicit treatment of all the electrons in a cluster having a large number of atoms constitutes a demanding computational task and the search for the lowest isomer cannot include a global optimization procedure of the potential energy surface. So we cannot exclude the existence of a cluster more stable than those found in our calculations.

For the optical part, the calculation of the properties (excitation energies, oscillator strengths, and transition dipole moments) have been carried out in the framework of TDDFT implemented in Q-CHEM 3.0 (Ref. 49) with the time-dependent Kohn–Sham formalism and related techniques by employing LANL2DZ RECPs with the BP86 functional.

Pre- and post-processing operations were performed with the graphical interface GABEDIT.[50]

IV. RESULTS

In this section, we present the experimental and theoretical spectra of silver clusters from Ag_4 to Ag_{14}. Several results had been obtained previously and are confirmed by the present measurements. Others had not been observed, i.e., Ag_4, Ag_6, Ag_{12}, and Ag_{14} because of their low abundance in the beam. Figure 1 compares size by size the experimental absorption spectra of Ag_n, $n=4–14$, embedded in an argon matrix grown at 28 K with calculated spectra obtained by TDDFT calculations. Table I gives the main transitions obtained in the present calculation and in the previous studies when available.

a. Ag_4. The experimental spectrum of Ag_4 shows three well-defined and narrow transitions at 3.07, 4.15, and 4.50 eV. Less intense structures at 3.21 and 4.82 eV are also vis-

ible. Comparison of the experimental spectrum with the excitation one in Fig. 2 obtained by Félix *et al.*[51] in very similar conditions unambiguously confirms the three main transitions as well as the smaller ones mentioned above. This excellent correlation gives an indirect proof of the presence of only one isomer inside the matrix as excitation spectroscopy is isomer specific.[35]

The calculated positions of the absorption peaks for the D_{2h} ground state isomer also show three intense transitions at 3.00, 4.20, and 5.28 eV and smaller ones at 3.61, 3.87, and 4.57 eV. An insight on the overall shape of both spectra shows a relatively good concordance between them. In particular, the peak at 3.07 is well reproduced as well as the peak around 4.15 eV if one takes into account a small redshift of 0.1 eV.

The narrow peak at 4.5 eV is more difficult to assign as only one intense absorption has been calculated in the energy range between 4 and 5 eV. Interestingly, one single peak was measured at ~4.2 eV in Ref. 52 by photodepletion of Ag_4Kr_2 complexes. In order to explain this discrepancy, it might happen that the calculated transition at 5.25 eV is redshifted due to the matrix environment and observed around 4.5 eV. Similar effects have been predicted in the case of Na_4 embedded in argon.[31] Another explanation would be that the transition at 4.5 eV corresponds to a symmetry forbidden transition that is observed when the cluster is embedded due to the interaction with the rare-gas atoms. Calculations show that there are indeed symmetry forbidden transitions around 4.5 eV.

Table I compares the present calculated main transitions to previous calculations in the framework of the TDDFT[8,10] or EOM-CCSD[5,6,35] for Ag_n $(4 \leq n \leq 9)$. For Ag_4, the first transition at about 3.0 eV is found for all the methods used. The second peak is found at about 4.1–4.2 eV except in the TDDFT study by Zhao *et al.* in which a peak is found at 3.72 eV. The previous TDDFT investigations have found, in contrast with the present work, a transition at about 4.4 eV which could be assigned to the experimental peak at 4.50 eV.

b. Ag_5. In the case of the pentamer, two broad transitions at 3.25 and 3.75 eV are observed experimentally. Interestingly, the overall shape of the observed Ag_5 spectrum is not very sensitive to the environment. Previous measurements done in argon at 10 K (Ref. 3) as well as unpublished ones in neon confirm the peak at 3.25 eV as well as the broader one around 3.75 eV.

The calculated spectrum also gives two main peaks at 3.15 and 3.64 eV. Moreover, the theoretical prediction indicates that the transition at 3.64 eV is the sum of two transitions at 3.58 and 3.65 eV. Note that the intensity between the peaks is not observed experimentally and that the blueshift of about +0.1 eV cannot be explained by the dielectric shift caused by the argon environment. Nevertheless the general agreement between theory and experiment is good.

Previous calculations by Idrobo *et al.* in the framework of TDLDA (TDDFT within the local-density approximation) have found similarly two dominant peaks at 3.18 and 3.54 eV (Table I). With the EOM-CCSD method, the main peak is blueshifted by about 0.4 eV at 3.55 eV.
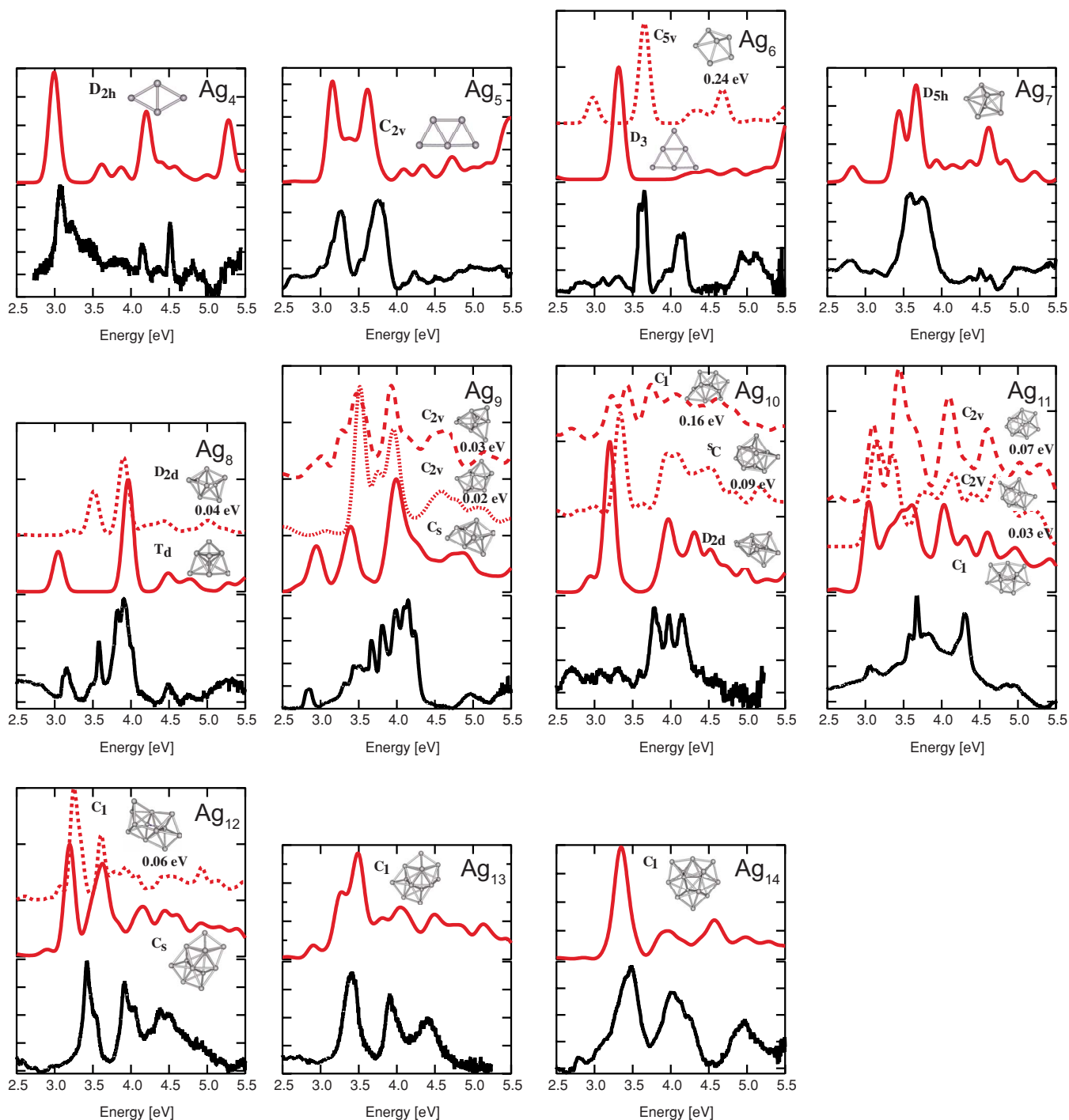
c. Ag_6. The measured spectrum of Ag_6 in argon shows

FIG. 1. (Color online) Absorption spectra of Ag$_n$, $n=4-14$. Comparison between the experimental spectra (black line, bottom of each box) and the calculated ones for the lowest-energy isomers.

two distinct double peaks at 3.63 and 4.15 eV, as well as smaller intensity peaks at 4.92 and 5.10 eV.

This experimental spectrum is not in good agreement with the calculated one for the lowest-energy isomer D_{3h}, which mainly shows one peak at 3.31 eV. Although the presence of the C_{5v} is not really favorable as it lies 0.24 eV higher in energy, the position of the main transition would be in better agreement. Note that the most important transitions calculated at 3.31 and 3.65 eV for both isomers are doubly degenerated and that this degeneracy might be lifted up when this system is embedded inside a matrix. As for Ag$_4$, calcu-

lations show symmetry forbidden transitions around 4.15 eV that could possibly explain the measured peak at this energy.

Similar to the present work, the calculated spectra in the previous studies for the D_{3h} ground state isomer only reproduce the first experimental main peak at 3.63 eV. The EOM-CCSD calculation presents a transition at 3.69 eV while the TDDFT calculations give a peak at about 3.3 eV (Table I).

d. Ag$_7$. Concerning the heptamer, the experimental spectrum gives mainly one broad structure with two maxima at 3.6 and 3.75 eV and smaller transitions at 2.81 and around 4.5 eV. This result is confirmed by measurements at 10 K,

TABLE I. Main intense peaks in calculated absorption spectra (in eV). The symmetry of Ag_9 is C_{2v} in Ref. 35 while it is C_s in the present work.

	EOM-CCSD[a]	TDLDA[b]	TDDFT[c]	Present work
$Ag_4[D_{2h}]$	3.21	3.01	3.03	3.00
	4.29	4.11	3.72	4.20
		4.44	4.49	5.28
$Ag_5[C_{2v}]$	3.55	3.18		3.15
	3.81	3.54		3.58
	4.25			3.64
$Ag_6[D_{3h}]$	3.69	3.24	3.39	3.31
$Ag_7[D_{5h}]$	3.89	3.52		3.43
		3.63		3.66
		4.46		4.62
		4.58		
$Ag_8[T_d]$	3.27	3.02	3.06	3.04
	4.16	3.82	4.10	3.96
$Ag_9[C_{2v}, C_s]$	3.92			2.91
	4.14			2.98
				3.36
				3.44
				3.87
				3.96

[a]References 5, 6, and 35.
[b]Reference 8.
[c]Reference 10.

although the 3.75 eV peak appears only as a shoulder.

The agreement with the theoretical spectrum is very convincing. If one accepts the fact that the main transitions are slightly blueshifted by ~0.1 eV, all structures are well generated and can be assigned to the three-dimensional D_{5h} isomer. This new calculation supports that the two peaks at 3.6 and 3.75 eV are an intrinsic property of the cluster itself.

The present calculations are in line with the calculations of Idrobo *et al.*, which found two main peaks at 3.52 and 3.63 eV (Table I). With EOM-CCSD method, only one peak is found at 3.89 eV.

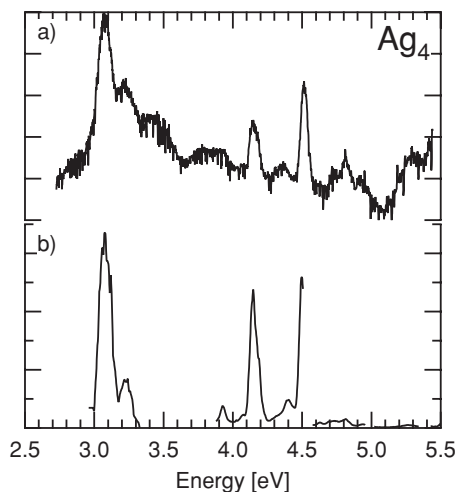*e. Ag_8.* Ag_8 in argon at 28 K has a well-defined spectrum with narrow peaks at 3.15, 3.57, 3.82, 3.90, and 4.50 eV. This

FIG. 2. Experimental spectra in an argon matrix at 28 K: (a) absorption spectrum of Ag_4; (b) excitation spectrum of Ag_4 obtained by Félix *et al.* (Ref. 51).
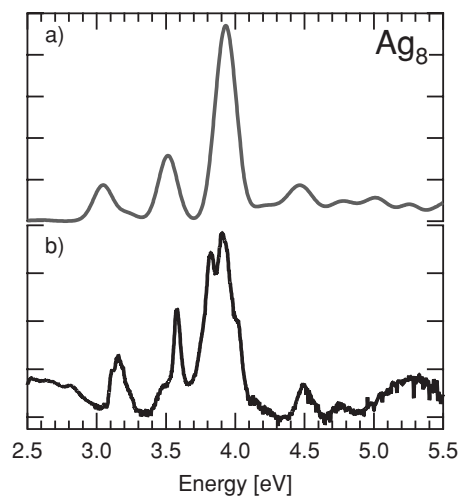

FIG. 3. Comparison between the experimental spectra and the calculated ones for Ag_8: (a) superposition of both calculated isomers with adjusted weight; (b) experimental spectrum obtained in argon.

spectrum is in excellent agreement with the one previously obtained at 10 K by Fedrigo *et al.*,[3] if we take into account a general broadening of the peaks, and with measurements in neon,[53] if we include a blueshift by ~0.1 eV.

This insensitivity to the matrix environment has to be related to the great stability of the octamer that has eight *s*-electrons forming a complete electronic shell.

The present calculations indicate that the highly symmetric T_d structure corresponds to the global minimum whereas the D_{2d} structure is a local minimum differing only by 0.04 eV. Neither spectrum of the calculated structures can account for the measured absorption spectrum. However, comparing (see Fig. 3) the experimental absorption spectra of Ag_8 with the sum of the calculated spectra for both isomers, there is little doubt that the two lowest-energy isomers are present inside the matrix. The transitions at 3.15, 3.90, and 4.50 eV are attributed to the T_d isomer whose calculated values for the corresponding peaks are 3.04, 3.96, and around 4.4 eV, whereas the narrow peaks at 3.57 and 3.82 eV correspond to the peaks of the D_{2d} isomer at 3.51 and 3.89 eV.

From Table I, one can note that two main transitions are found for the ground state isomer of T_d symmetry for all the methods used. The first one is at 3 eV while the second is at 4 eV.

f. Ag_9. The experimental spectrum of Ag_9 in argon at 28 K presented in Fig. 1 is composed of two well separated peaks at 2.84 and 4.95 eV and a broader structure composed of distinct and narrow peaks between 3.3 and 4.25 eV. We repeated this measurement of Ag_9 in argon several times and we found that all the peaks are clearly reproducible, except the one at 4.95 eV.

Ag_9 is an interesting system since several calculations indicate that different structures have minimum energies in an energy range as close as 0.05 eV.[41,43] We reproduce the absorption spectra for the three minimum energy structures obtained in this calculations. Clearly none of these absorption spectra can account for the measured spectrum; how-

ever, their sum could confirm, as was supposed previously,[35] that the observed spectrum is the sum of several isomers present inside the matrix.

g. Ag_{10}. A silver cluster composed of ten atoms is the most difficult system to produce as it can be seen on the mass spectrum.[24,54] Although the signal to noise ratio of the experimental spectrum is low, it shows three distinct narrow lines at 3.79, 3.98, and 4.15 eV.

Ag_{10} has also several isomers in a narrow energy range. The absorption spectra of the three lowest-energy structures are given in Fig. 1. Apparently, contrary to the case of Ag_9, none of the calculated spectrum or the sum of them can reproduce the experimental spectrum which does not show any transition between 3 and 3.5 eV.

However, the Ag_{10} spectrum has a similar overall shape as the Ag_9 spectrum, and, in particular, all three peaks are present in the Ag_9 spectrum at the same positions. A possible explanation is thus that one observes, in fact, Ag_9. This would be in agreement with the low stability of Ag_{10}^+ and a small energy barrier for fragmentation into Ag_9^+ and Ag atoms.

h. Ag_{11}. The experimental spectrum of Ag_{11} in argon shows an important number of narrow transitions between ~3.0 and 5.0 eV. The position of the main transitions at 3.06, 3.67, and 4.31 eV are well reproduced in neon.[53] However, measurements at 10 K by Fedrigo *et al.*[55] show much broader transitions and very different relative intensities, which indicates that this system is sensitive to the environment contrary to Ag_9, for example.[22]

Ag_{11} clusters have already been studied in detail by Idrobo *et al.*[9] They concluded in their calculations that the experimental spectra cannot be attributed to one specific isomer but that the lowest-energy isomer exhibits the best overall agreement with our experimental spectrum.

The present calculated spectra for the three lowest-energy isomers are shown. Contrary to Ag_{10}, the calculated transitions are in an energy range similar to the measured ones. But here again, none of the calculated spectra is in complete agreement with the measurements. The experimental spectrum is therefore certainly due to a superposition of different contributions. Excitation spectroscopy on this system could be an efficient way to attribute the different transitions to specific isomers.

i. Ag_{12}. The experimental spectrum of Ag_{12} shows two main peaks at 3.42 and 3.91 eV and a less intense one at 4.38 eV. All three peaks have a shoulder at slightly higher energy.

Both spectra obtained for the two lowest-energy isomers given by the calculation have very similar shapes with two main peaks at similar energies and broader and less intense transitions at higher energy.

This supposes that our spectrum could be the sum of both isomers, although the experimental spectrum is blueshifted indicating that the confinement effect is more important than the dielectric effect.

Note that there is a remarkable similitude between Ag_{12}, Ag_{13}, and Ag_{14} spectra that are mainly formed of three broad structures between 3.3 and 5 eV that are energetically almost equidistant and decreasing in intensity.

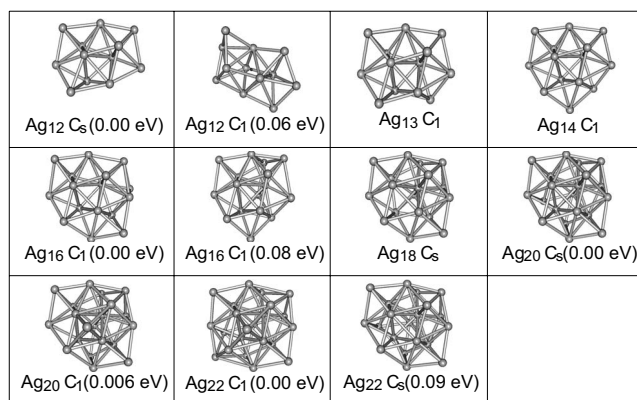*j.* Ag_{13}. In the case of Ag_{13}, the measurement obtained in

FIG. 4. Lowest-energy isomers for Ag_n ($n=12-22$) clusters. Relative energies are given together with spatial symmetries.

argon consists of three well-defined peaks at 3.40, 3.90, and 4.40 eV. It is in excellent agreement with unpublished results in neon if we take into account a small blueshift of ~0.1 eV due to the matrix.

The calculated spectrum of the lowest-energy isomer has an overall similar shape, with broad transitions around the measured ones.

k. Ag_{14}. Silver clusters containing 14 atoms have a similar spectrum to those of Ag_{12} and Ag_{13} with three broad structures at 3.48, 4.00, and 4.96 eV.

The agreement with the calculated spectrum is obvious and the positions of the different peaks are well reproduced if one takes into account a small blueshift.

V. SPECTRAL EVOLUTION FROM Ag_{12} TO Ag_{22} AND DISCUSSION

Let us now discuss the absorption spectra for larger Ag_n ($n=12-22$) clusters for which our theoretical results are compared to existing experimental data. To our knowledge, the present study is the first one on these relatively large clusters in the framework of the TDDFT. We discuss the evolution of the spectra with cluster size and try to characterize the main transitions. Finally, we compare our results to previous ones obtained in the framework of the Mie theory.

Figure 4 gives the lowest-energy structures for each size. The most stable isomers undergo a transition from double-layered structures for $n=12-16$ to quasispherical and compact arrangements for $n \geq 18$. For Ag_{18} and Ag_{20} clusters, the core is formed by a 13-atom icosahedron, while for Ag_{22} it is formed by a 19-atom double icosahedron, with the additional atoms capping the faces.

Figure 5 presents the calculated and experimental spectra in argon[3] in the 2.5–5.5 eV range. Note that for Ag_{20} and Ag_{22}, the spectra were only calculated in the 2.5–4.6 eV range. The experimental spectra are characterized by the emergence of a dominant and relatively broad peak between 3.2 and 3.8 eV, accompanied by one or two absorption peaks at higher energies but smaller intensities (Fig. 5). This common feature is coupled to a blueshift of the main peak with increasing cluster size. The calculated spectra reproduce well the experimental ones. For example, for Ag_{18}, our present calculations give a main peak at 3.6 eV followed by a shoul-
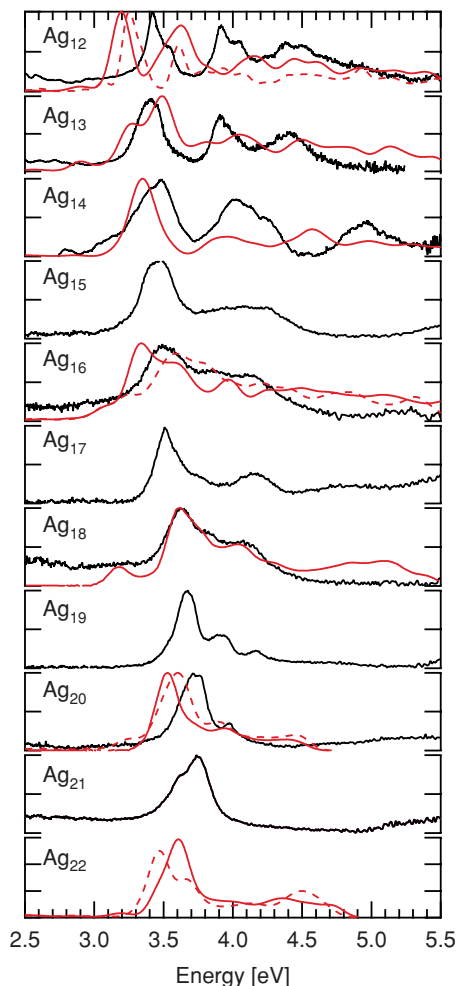
FIG. 5. (Color online) Experimental and TDDFT calculated absorption spectra for an Ag_n in argon, $n=12–22$. The experimental spectra (continuous black line) are taken from this work ($n=12–14$) and from Ref. 3 ($n=15–21$). The calculated spectra (this work) are given in continuous red line for the lowest-energy structure; the interrupted red line corresponds to the closest isomer (0.06 eV for Ag_{12}, 0.08 eV for Ag_{16}, and 0.09 eV for Ag_{22}).

der at higher energies, in very good agreement with the experimental spectrum. The calculated peak at 3.2 eV is, however, not observed. For Ag_{20}, two isomers are found to be degenerated within 6 meV. The calculated spectra for the two isomers reproduce well the shape of the experimental one; in particular, the spectrum of the second isomer presents a dominant peak at 3.64 eV in good agreement with the experimental peak at 3.7 eV. The spectrum obtained for the first isomer is redshifted with respect to the experiment by about 0.2 eV with a main peak at 3.53 eV. The second peak found in the experiment at about 4.0 eV with a smaller intensity is also well reproduced by both calculated spectra. With increasing cluster size, the absorption spectra become more regular with only one main intense peak without dispersion of the oscillator strengths over other states, in agreement with the fact that the structure becomes more spherical.

For metallic systems, a systematic analysis of the excitations in a molecular approach like our present TDDFT calculations is very complicated, in particular, for large clusters for which the excited states are in a quasi-continuum. Each peak involves several molecular excitations with equivalent

weights; an analysis based on the orbitals is therefore not relevant. Following this, we have chosen to characterize the excitations by the electron density difference between the excited and the ground states for the main peaks (see Fig. 6). Light colored regions correspond to depletion of the electron density during the transition, while blue (or dark) regions correspond to an increase of the electron density. It appears clearly that the transitions are due to the excitations from inner orbitals, with a shape associated to s or d contributions, to outer region with an $s+p$ character. The densities of d-type orbitals are located on silver atoms while the densities of s and p types are distributed on wide areas involving several atoms. The accumulation of the electrons is found to be done rather outside the cluster. This is confirmed by the fact that a decrease in the density isovalue leads to large outer regions. The contribution of the d-electrons is weak for small clusters as we can see for Ag_8 in Fig. 6, but increases with cluster size, and becomes dominant for $n=20$ and 22. This results in good agreement with recent works by Idrobo et al.,[8,9] who showed that the optical spectra are associated mainly with s-electrons for smaller Ag_n ($n \leq 8$) clusters, while the d-electrons play a crucial role in the optical excitations of Ag_{11}. This can be understood since for small clusters the d and s states are well separated by a significant gap, but this gap decreases with increasing cluster size leading to a mixing of d and s orbitals for $n > 10$.

Fedrigo et al.[3] successfully discussed their experimental results using the two sphere model discussed in Sec. I. In the present work, the clusters are described in the language of quantum chemistry where the excitations are seen as transitions between distinct molecular states and so cannot be directly compared to the description of the excitations in the classical Mie theory. However, the accumulation of electron charges is located at the surface of the cluster (especially for $n \geq 16$) in a rather similar way to the surface plasmons in the Mie theory. Our present calculations, which take explicitly into account the effects of the d-electrons and the geometrical structure of the clusters, also show the importance of the interband transitions $d \rightarrow sp$.

VI. CONCLUSION

We have presented a joint theoretical and experimental investigation of the absorption spectra of Ag_n ($4 \leq n \leq 22$) clusters. New experimental spectra of clusters embedded in an argon matrix have been obtained, particularly for even n values for which the abundance in the beam is very low. Calculated spectra in the framework of TDDFT are also presented for $n=4–22$ and compared with both previous and new experimental results. The present theoretical study is the first one using a quantum chemistry approach investigating the optical properties of silver clusters larger than $n=11$. The most stable isomers obtained in a DFT approach undergo a structural transition from double-layered structures for $n=12–16$ to quasispherical and compact arrangements for $n \geq 18$.

For small n values, the spectra are characterized by a strong optical response in the 3.0–5.0 eV range with several narrow or broad peaks, while for $n \geq 12$ they are character-
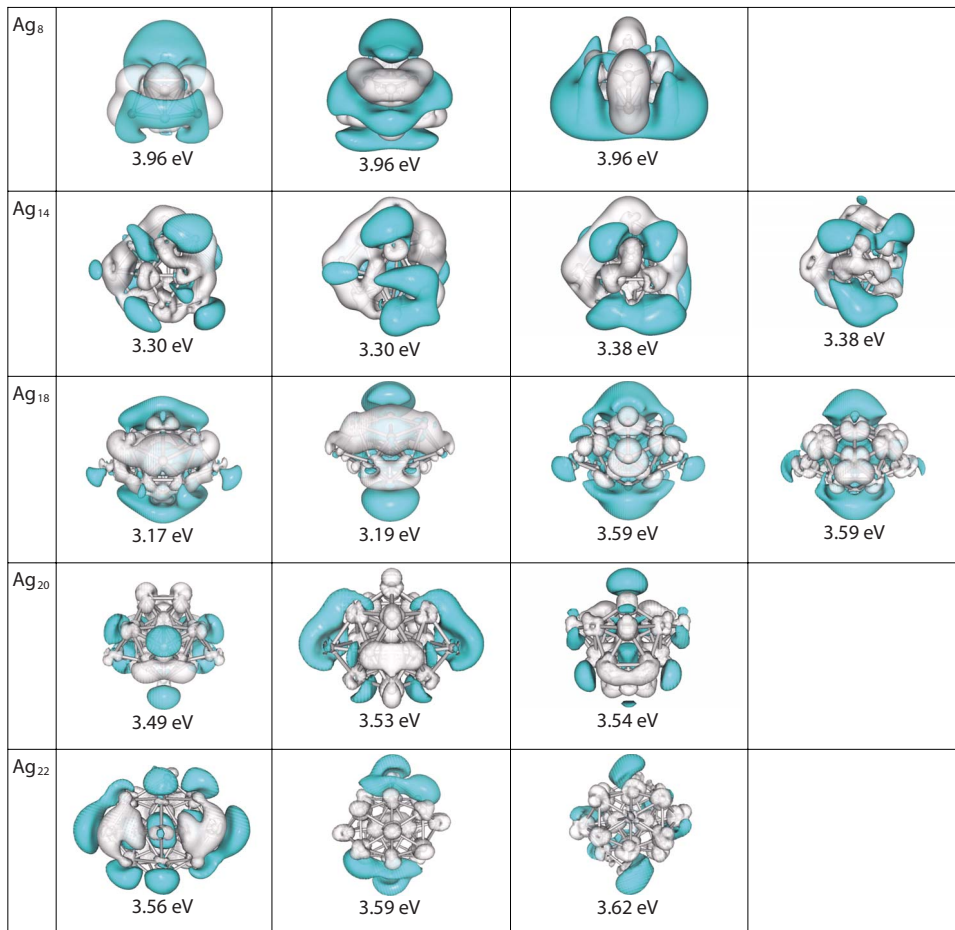
Ag$_8$			
3.96 eV	3.96 eV	3.96 eV	
Ag$_{14}$			
3.30 eV	3.30 eV	3.38 eV	3.38 eV
Ag$_{18}$			
3.17 eV	3.19 eV	3.59 eV	3.59 eV
Ag$_{20}$			
3.49 eV	3.53 eV	3.54 eV	
Ag$_{22}$			
3.56 eV	3.59 eV	3.62 eV	

FIG. 6. (Color online) Electron density difference between the excited and the ground states for the main peaks in the cases of Ag$_8$, Ag$_{14}$, Ag$_{18}$, Ag$_{20}$, and Ag$_{22}$ clusters (isovalue of 0.0002 a.u.). Light regions correspond to the depletion of the electron density during the transition while blue (or dark) regions correspond to the accumulation. The transitions are due to the excitations from inner orbitals located on silver atoms to orbitals distributed on wide areas involving several atoms.

ized by the emergence of a dominant and relatively broad peak between 3.2 and 3.8 eV, accompanied by one or two absorption peaks at higher energies but smaller intensities.

Globally, the calculated spectra for the lowest-energy isomer compare well with the experimental ones, except for some sizes for which the spectrum is nevertheless well reproduced either by summing contributions from several low-lying isomers close in energy or by considering that symmetry forbidden transitions in gas phase could be observed when the cluster is embedded in the matrix.

From our analysis, the transitions are due to the excitations from inner s or d orbitals located on silver atoms to outer orbitals with an $s+p$ character distributed on wide areas involving several atoms. The optical spectra are associated mainly with s-electrons for smaller Ag$_n$ ($n \leq 8$), but the contribution of the d-electrons increases with the cluster size and plays a crucial role for $n=20$ and 22.

ACKNOWLEDGMENTS

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