# Optical properties of pure and core-shell noble-metal nanoclusters from TDDFT: The influence of the atomic structure

H.-Ch. Weissker<sup>1,2</sup> and C. Mottet<sup>1</sup>

<sup>1</sup>CINaM-CNRS, Campus de Luminy, case 913, 13288 Marseille Cedex 9, France\*

<sup>2</sup>European Theoretical Spectroscopy Facility (ETSF)

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Pseudopotential time-dependent density-functional theory (TDDFT) calculations are carried out to investigate the optical absorption spectra of magic-number noble-metal nanoparticles of 13, 38, 55, 140, and 147 atoms. In particular, we study the differences between isomeric structures such as  $Ag_{13}$  in both cubic and icosahedral structures. Differences are well visible up to sizes of about 55 atoms, demonstrating the need for proper treatment of the structural details on the atomic level. For the largest sizes of about 150 atoms, our calculations confirm earlier results of TDDFT using a structureless jellium model. In particular, we recover the surface plasmon resonance for silver nanoclusters. The bimetallic  $Ag_{32}Au_6$  core-shell cluster displays an intense peak corresponding to the surface-plasmon resonance in the Ag cluster, but the spectrum does not lie between the spectra of the pure  $Ag_{38}$ and  $Au_{38}$  clusters. By contrast, a copper core in a  $Ag_{38}Cu_6$  cluster leads to a strong damping of this peak.

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# I. INTRODUCTION

The optical response of noble-metal nanoparticles, in particular for silver, is dominated by a large surface-plasmon resonance (SPR) which corresponds to collective excitations of the *sp* valence electrons. The SPR is well described within the quasistatic approximation of classical Mie theory<sup>1,2</sup> for nanospheres of diameters smaller than about one-tenth of the electromagnetic wave length (diameters smaller than about 30 nm). For sizes smaller than about 10 nm, a proper quantum-mechanical description is needed.<sup>2–6</sup>

Unlike in the simple alkali metals where it is determined solely by the free *s* electrons, the SPR in noble-metal clusters is influenced by the onset of the interband transitions from the *d* band. The interband threshold is higher in Ag (4 eV, i.e., 300 nm) than in Cu and Au (2 eV, i.e., 650 nm). Consequently, the SPR is largely decoupled from the interband transitions in Ag clusters and appears clearly down to very small sizes (fewer than 20 atoms),<sup>7</sup> while the strong coupling with the interband transitions in Cu and Au clusters<sup>8,9</sup> leads to broadening and attenuation of the resonance until it disappears in Cu clusters smaller than 3 nm.<sup>10,11</sup>

In the noble-metal clusters, a blue shift of the surface plasmon frequency is observed with decreasing cluster size,  $^{12-15}$ unlike in alkali clusters, which show a red shift.  $^{16,17}$  This size dependence of the plasmon resonance results from a number of effects; for a detailed discussion, see for instance Refs. 2, 18, and 19. In particular, a spill-out of the *s* electrons beyond the classical particle radius leads to a red shift with respect to the classical description, and a reduced *s*-*d* screening in the surface region in the case of the noble metals leads to a blue shift.  $^{15,20}$ The sum of the two counteracting effects produces the size dependence in the noble-metal clusters because the surface region becomes more important when the size decreases. The blue shift is stronger in gold and copper and weaker in silver due to the larger separation of the *d* electrons from the *s* valence electrons in the latter material.<sup>6</sup>

The size dependence of the SPR energy, as well as the broadening and the damping of the resonance, are well described for sizes between 1.5 and 10 nm within a semiquantal

approach based on a structureless jellium-type model and the time-dependent density-functional theory (TDDFT).<sup>3–6,21–23</sup> In this model, the ionic background is phenomenologically described by a steep-walled homogeneous spherical charge distribution, while the screening by the *d* electrons is phenomenologically represented by a homogeneous dielectric medium corresponding to the interband transitions and a skin layer of ineffective ion polarizability (reduced screening) at the surface of the particle.<sup>6</sup>

The structural details on the atomic level are not taken into account in this approach. Moreover, in the case of bimetallic clusters, it is difficult to include the distribution of the different species. For instance, the model is not able to distinguish the spectra of core-shell structures, as opposed to homogeneous alloys, in comparison with experimental results.<sup>24–28</sup> Nonetheless, it remains unclear if this is a failure of the model to describe the relevant effects or if these effects are too small to allow for a distinction between the structures.

On the lower side of the size range, clusters of a few atoms exhibit spectra marked by single transitions which depend strongly on the precise structure.<sup>2,29–31</sup> Therefore, the connection between structure and optical properties can be used, in this size range, to distinguish different possible geometries by means of a comparison of calculated and measured spectra. This has been done, for instance, for different isomers of small silver clusters Ag<sub>n</sub> (n = 4-22).<sup>32–34</sup>

Thus, the question arises as to how important the structural details are for the spectra of clusters of *intermediate* size where collective excitations like the surface plasmon play an important role while they couple strongly to individual molecular-like transitions for which the structural details are expected to be important. To this end, a method is needed which reflects the quantum-mechanical nature and the structural details.

In the case of alkali-metal clusters with a very small number of atoms, quantum calculations using configurationinteraction (CI) techniques have been used to calculate the absorption spectra, for example, for Na<sub>3</sub> through Na<sub>8</sub><sup>35</sup> and Li<sub>4</sub> through Li<sub>8</sub>.<sup>36,37</sup> The calculated transitions are in excellent agreement with the observed spectra and allow one to distinguish different isomers. However, these methods are numerically heavy and therefore restricted to clusters with a small number of electrons.

For larger numbers of electrons, TDDFT calculations using the pseudopotential description of the electron-ion interaction have been carried out for a variety of clusters ranging from a few atoms to several tens of atoms.<sup>30,31,38</sup> Recently, calculations of larger structures containing up to 120 atoms have been carried out by Aikens *et al.* using certain tetrahedral model structures.<sup>29</sup> These calculations demonstrate the transition from molecular spectra to collective plasmon excitations with increasing particle size. Durante *et al.* recently presented TDDFT calculations on charged gold clusters up to 172 atoms.<sup>39</sup>

Complementarily, calculations based on many-body perturbation theory using the Bethe-Salpeter equation (BSE) are likewise able to describe the optical response.<sup>40</sup> In fact, small sodium clusters have been one of the first cases treated using the BSE.<sup>41</sup> However, recent studies have shown that for small silver clusters up to eight atoms, the TDDFT spectra are in better agreement with experimental results than the BSE results.<sup>34</sup>

In the present work, we use pseudopotential TDDFT calculations to determine the degree to which the structural differences between noble-metal isomers of between 13 and 147 atoms and core-shell nanoalloys  $Ag_{32}X_6$  with X = Au and Cu influence their optical response. In particular, we discuss the size of the characteristic differences which could be used in comparison with experiments to infer information on the experimental samples of this type of system.

Unfortunately, most experiments measure the spectra of a collection of nanoparticles presenting a more or less wide size distribution. As the measured spectra present an average over the spectra of many different clusters, tiny differences mostly vanish in the averages over the distribution. Recent advances in single-dot spectroscopy<sup>42</sup> as well as experiments with size-selected clusters promise spectra in which the small differences remain visible. Finally, it must be kept in mind that for many of the experimental studies, the clusters are produced and characterized within a surrounding matrix or covered by molecules as in the case of colloidal clusters, which modifies both the position and the width of the SPR. The spectra of the present work are calculated for clusters in vacuum.

The paper is organized as follows. In Sec. II, we present the structural models, and in Sec. III we give the technical details of the calculations. Results about the energetics of the clusters and TDDFT absorption spectra are presented and discussed for pure and bimetallic clusters in Sec. IV and V, respectively, before conclusions are drawn at the end.

## **II. STRUCTURAL MODELS**

In order to calculate spectra comparable with experiment for clusters of small and intermediate size, a precise structural model is needed that reflects the structure of the nanoparticles in the experimental sample. These structures and their size distribution depend on the experimental conditions during their elaboration. A reasonable first step toward realistic structures is to choose the respective lowest-energy structures, that is, to neglect kinetic effects in their growth. The search for lowestenergy structures of metallic nanoclusters and nanoalloys has been addressed by numerous studies over the past ten years in pure clusters<sup>43–46</sup> and in nanoalloys.<sup>47–50</sup> The use of global optimization techniques<sup>51</sup> with semiempirical potentials facilitates the exploration of the energy landscape in order to select the best symmetries together with the best chemical configuration in the case of nanoalloys. Subsequently, the structures are often locally relaxed using DFT calculations in order to obtain a more realistic electronic structure and reliable energetic estimates of their ground state.

As the size becomes smaller, the number of possible symmetries becomes larger. In the present work, we concentrate on high-symmetry structures with magic size (compact atomic shells) for pure clusters: icosahedra (Ih) and face-centered cubic (fcc) cuboctahedra (cubo) for the 13-, 55-, and 147-atom size and fcc TOh for the 38- and the 140-atom clusters (illustrated in Fig. 1). These structural motives have all been found experimentally, albeit for somewhat larger clusters (see, e.g., Refs. 52–54). Moreover, in particular the fcc  $X_{13}$  and the X<sub>55</sub> and X<sub>147</sub> clusters belong to the family of so-called full-shell clusters that have been investigated in many studies; for a recent review concerning the Au<sub>55</sub> system, see Ref. 55. These clusters are all approximately spherical, which allows us to study the influence of structural differences on the spectra without strong morphological effects. However, unlike some of the structures treated in previous studies, <sup>32,33,56</sup> they are not necessarily the lowest-energy structures. For instance, in the case of the 13-atom clusters, there is a large number of possible symmetries, and the lowest ones are neither icosahedral nor cubic.<sup>44,46</sup> This is also the case, to a lesser extent, in the 55-atom gold cluster for which relativistic effects lead to lower symmetries.45

In the case of nanoalloys, we consider different core-shell structures of  $Ag_{32}X_6$  with X = Au and Cu, in which the six gold or copper atoms form the core while the 32 silver atoms enclose them and form the surface of the structure. These structures have been obtained by a global optimization method using a semiempirical tight-binding potential in the second-moment approximation<sup>57</sup> with the parameters given in Ref. 47. We compare the TOh, the decahedral (Dh), and the polyicosahedral (plh) symmetries, the stability of which depends on the cluster composition. The plh structure is one of the particularly stable core-shell nanoalloys proposed by Rossi *et al.*<sup>47</sup> in the presence of a large lattice mismatch between the two elements, which is the case for the Ag-Cu<sup>58</sup> system but not for Ag-Au.<sup>59</sup> The structures are illustrated in Fig. 1.

### **III. TECHNICAL DETAILS**

The structures presented in the previous section have been locally relaxed by means the VASP code<sup>60–62</sup> using density-functional theory in the PW91 generalized-gradient approximation (GGA) and with the projector-augmented wave method (PAW).<sup>62</sup>

The resulting geometries are then used for TDDFT calculations by means of the real-space code OCTOPUS.<sup>63,64</sup> Following a ground-state calculation, spectra are calculated using the time-evolution formalism and a GGA exchangecorrelation potential. Norm-conserving Troullier-Martins



FIG. 1. (Color online) Structures of the noble metal clusters: Ih (a), cubo (b) and TOh (c) with two different views and of different isomers of the  $Ag_{32}X_6$  nanoalloys with X = Au or Cu in yellow: TOh (d), Dh (e) and pIh (f).

pseudopotentials have been used which include the *d* electrons in the valence, that is, with 11 valence electrons for each atom. The spacing of the real-space grid was set to 0.25 Å, the radius of the spheres making up the calculation domain to 4.5 Å. All spectra are averaged over all directions, except for the spectra in the inset of Fig. 5 where the anisotropy of the  $Ag_{32}Au_6$  Dh structure is shown.

In order to obtain precise total energies, the structures have been re-relaxed using VASP,<sup>60–62</sup> again using density-functional theory in the PW91 GGA and the PAW method.<sup>62</sup> The cutoff energy was set to 500 eV, and a Fermi smearing of 0.002 eV was used. In order to obtain reliable energies for the clusters of lower stability, the symmetry was imposed to be kept during the relaxation.

# **IV. RESULTS: ENERGETICS**

The total energies are presented in Table I for the directly comparable isomers of the pure clusters of 13 and 55 atoms, as well as for the  $Ag_{32}Au_6$  and  $Ag_{32}Cu_6$  nanoalloys in the pIh, Dh, and TOh symmetries.

We see clearly in Table I that there is an inversion of the structural stability between the Ih and the cubo structure

TABLE I. Relative total energies of the different isomers comparing structures of fivefold symmetry (Ih, pIh, or Dh) to fcc clusters (cubo or TOh).  $\Delta E = E_{\text{Ih}} - E_{\text{cubo}} < 0$  means that the Ih structure is more stable than the cubo one and so forth. The stable structures are highlighted in boldface.

Cluster	Structure	(eV/at.)
Cu <sub>13</sub>	Ih - cubo	0.01
Ag <sub>13</sub>	Ih - cubo	0.05
Au <sub>13</sub>	Ih - cubo	0.12
Cu <sub>55</sub>	<b>Ih</b> - cubo	-0.06
Ag <sub>55</sub>	<b>Ih</b> - cubo	-0.04
Au <sub>55</sub>	Ih - cubo	-0.02
Ag <sub>32</sub> Au <sub>6</sub>	pIh - <b>Toh</b>	0.04
$Ag_{32}Au_6$	Dh - Toh	0.01
Ag <sub>32</sub> Cu <sub>6</sub>	<b>pIh</b> - TOh	-0.03
$Ag_{32}Cu_6$	Dh - TOh	-0.01

for the sizes of 13 and 55 atoms, with the 13-atom cluster being fcc whereas the 55-atom cluster prefers the Ih symmetry for all the metals. Moreover, there is a tendency along the noble metal series to increase the gap in energy between the two structures: the difference is weak for Cu and Ag and higher for Au. This tendency is in general agreement with the so-called bond-order/bond-length correlation of the many-body character of the metallic bond. Many structural features are related to the parameter governing the attractive interaction dependence with distance, which increases from Cu to Au along the noble-metal series. In particular, the vacancy formation energy in Ih clusters<sup>65</sup> but also the crossover size from Ih to Dh or TOh clusters are governed by this parameter and also the surface energy (bond order), leading to an easier stabilization of fivefold symmetry clusters in Cu than in Au<sup>66</sup> for which amorphous structures are even better stabilized. This has been confirmed by ab initio calculations for the 55-atom gold cluster<sup>45</sup> where less symmetrical structures have been found as ground states due to relativistic effects, in agreement with many-body semiempirical potentials<sup>67</sup> which are fitted on experimental bulk properties, including intrinsically the relativistic effects.

Concerning the nanoalloys in Table I, the fcc TOh Ag<sub>32</sub>Au<sub>6</sub> structure is favored over the fivefold symmetries because Ag and Au have almost identical lattice constants, unlike the Ag-Cu system with 12% mismatch. Consequently, Ag<sub>32</sub>Cu<sub>6</sub> TOh is no longer stable, to the benefit of the pIh structure and, to a lesser extent, of the Dh one. This tendency has been demonstrated in a previous work, where a family of pIh core-shell structures with a particularly high electronic and thermodynamic stability has been found theoretically.<sup>47</sup> The origin of the high stability was clearly attributed to the lattice misfit between the core atoms and those in the outer shell. Because the pIh is more strained than the Dh cluster, the effect of the lattice misfit on the energy is stronger in the pIh than in the Dh structure, which inverts the relative energies between the two systems. Dh and TOh nanoalloys present in both cases a weak difference of energy so that the two isomers are potentially observable in experiments.



FIG. 2. (Color online) Size dependence of the absorption spectra for the pure fcc noble-metal clusters Ag, Au, and Cu. In all the figures, the spectra are normalized by the number of atoms for comparability. The spectra are averaged over the three Cartesian axes for the clusters which do not have an isotropic response.

### V. RESULTS: TDDFT OPTICAL ABSORPTION SPECTRA

# A. Size effect on the spectra of pure nanoclusters: Ag, Au, and Cu

In order to characterize the size effect on the optical response independently of structural effects, we compare the spectra of silver, gold, and copper nanoclusters of various sizes from 13 to 140 atoms with the same fcc structure. We treat two morphologies: the cubo shape (13 and 55 atoms) and the TOh shape (38 and 140 atoms). The results are displayed in Fig. 2. We note the fact that our clusters of 140 atoms, although "large" for the *ab initio* calculations, are at the lower end of the validity range of the calculations using the structureless jellium model of Lermé *et al.* discussed in the introduction.<sup>6</sup>

In other words, we expect to recover for our *largest* clusters the general results for the *smallest* clusters treated by that model.

As expected, the absorption in the silver clusters is the strongest among the three materials. This is coherent with the fact that surface-plasmon resonances in silver nanoparticles have been demonstrated down to very small sizes.<sup>7</sup> However, for the smaller clusters, there is no single well-defined surfaceplasmon resonance but rather a main peak with secondary structures next to it. The appearance of individual structures in the spectrum as the size decreases reflects the molecular character of the small clusters displaying distinctly the molecularlike transitions as calculated for very small clusters<sup>30,31,38</sup> and observed experimentally.<sup>7,33,68</sup> It is also a direct consequence of the structure of the clusters, taken into account in our calculation, unlike in the structureless jellium model. This remains true for the larger sizes, until for the biggest,  $Ag_{140}$ , the picture of one resonance with a defined energy seems to be recovered. This interpretation of the broadened peak at about 3.1 eV is based on comparison with previous work, in particular that of Lermé *et al.*<sup>5,6</sup> The transition from molecular spectra to collective plasmon excitations with increasing size agrees with the findings of Aikens et al.<sup>29</sup> In the light of this comparison, the contributions beyond 3.5 eV appear to be due to interband transitions from the *d* electrons.

The global tendencies concerning the damping and the broadening of the SPR peak with varying cluster size are comparable with previous studies.<sup>6</sup> The blue shift that has been found in experiments and calculations<sup>6,12–15</sup> is clearly seen in our results for Ag, even though it is hard to quantify due to the multiple structures in the spectra.

For Au and, even more, Cu, the plasmon resonance is absent for the size of 140 atoms, which is consistent with the results of the structureless jellium model.<sup>6</sup> For clusters between 1.5 and 7 nm, our 140-atom cluster being at the lower end of this size range, the latter calculations describe the increasing broadening and, eventually, the disappearance of the surface-plasmon resonance with decreasing particle size by the interaction with the *d* electrons, which in both gold and copper lie much closer to the Fermi energy than in silver. In view of this explanation, the structures found in our spectra for the smaller Au and Cu clusters are attributed to molecular-like transitions rather than to a collective surface plasmon.

In order to highlight the differences among the three metals, we present the absorption spectra of the pure noble-metal clusters in Fig. 3, comparing in each of the panels the three metals in identical structures. The absorption in the Ag clusters is generally stronger than in the Au and the Cu clusters, in particular for the largest sizes where the surface plasmon in Ag is clearly established while it is broadened out in the other two metals. For the smallest sizes ( $X_{13}$ ), it is interesting to note that the absorptions due to individual molecular-like transitions in Au and Cu are roughly of the same strength as the absorption in the Ag clusters. However, they quickly lose their importance with increasing size until, for our largest clusters, they are not visible at all.

#### B. Structure effect on the absorption spectra

We now compare the absorption spectra of clusters of equal size but different structures. This enables a direct comparison



FIG. 3. (Color online) Absorption spectra of pure Ag, Au, and Cu nanoclusters for different sizes and structures.

without any interference of the size effect. The comparison is meaningful, for it considers the influence of the structural differences for clusters that are all roughly spherical. The results are shown in Fig. 4.

Differences appear, in particular, in the lower part of the spectra of the smaller clusters. The spectra of the  $X_{13}$  clusters show marked differences between the two structures. In particular for the Cu<sub>13</sub> clusters, a clear difference of 0.3 eV of the position of the peaks at about 3 eV is visible.

In general, the differences are smaller for the larger  $X_{55}$  clusters. For Au and Cu, as there is little clear structure in the spectra at all, it is practically excluded that the differences could be visible in a comparison with experiment. By contrast,



FIG. 4. (Color online) Absorption spectra of pure Ag, Au, and Cu nanoclusters of different structures (fcc cuboctahedron and icosahedron) at equal sizes.

the strong difference in the resonance of the  $Ag_{55}$  should be discernible in an experiment.

Finally, we note that even for the largest Ag clusters, the spectra of which can be seen in Fig. 3, the position of the surface-plasmon resonance differs by almost 0.1 eV between the icosahedral Ag<sub>147</sub> and the TOh Ag<sub>140</sub>. This difference cannot be explained by the slightly different numbers of atoms, because it is larger and runs counter to the weak size dependence of the surface-plasmon resonance.<sup>6</sup>

These results show that it is important to take into account the structural details on the atomic level in the size range we treated.

### C. Ag<sub>38</sub>Au<sub>6</sub> and Ag<sub>38</sub>Cu<sub>6</sub> nanoalloys

The spectrum of the  $Ag_{38}Au_6$  TOh core-shell structure is shown in Fig. 5 along with the two equivalent pure TOh clusters of its two constituents,  $Ag_{38}$  and  $Au_{38}$ . The TOh core-shell structure exhibits a strong resonance that resembles that of the pure Ag cluster but is red-shifted by about 0.3 eV with respect to the latter. Moreover, it is surprising that the spectrum of the TOh core-shell structure is not intermediate between the spectra of the two pure clusters. The general experimental findings for larger bimetallic Ag-Au clusters indicate a rather smooth transition between Ag and Au.<sup>24,25,27,28,69</sup> On the other hand, by comparison with the calculated optical absorption spectrum of a  $Ag_3Au_{10}$  cluster by Chen *et al.*,<sup>56</sup> the red shift is only partially comparable as they obtained two main absorption peaks situated on both sides of the main peak of the  $Ag_{13}$  cluster.

The spectrum of the Dh  $Ag_{38}Au_6$  cluster has likewise been calculated, since the energy difference between the Dh and the TOh structures is weak (cf. Table I) so that both might be observed in experiment. The Dh and the pIh clusters do not have an approximately spherical structure, unlike all the other clusters treated in the present work. The spectra therefore are strongly anisotropic. In the main panel of Fig. 5, the averaged spectrum is shown. In the inset, we show the spectrum for light



FIG. 5. (Color online) Absorption spectra of the  $Ag_{32}Au_6$  coreshell clusters compared to the pure clusters of the same size of its two constituents,  $Ag_{38}$  and  $Au_{38}$ . The inset shows the anisotropy of the spectra of the Dh cluster, for polarization along and perpendicular to the fivefold rotation axis (cf. Fig. 1).



FIG. 6. (Color online) Absorption spectra of the pure  $Ag_{38}$  and  $Au_{38}$ , as well as of the  $Ag_{32}Au_6$  and  $Ag_{32}Cu_6$  core-shell clusters, all with TOh symmetry.

polarized perpendicular to the fivefold axis, compared to that for polarization parallel to this axis.

When comparing the decahedral and the TOh core-shell structures, it is interesting to note that for the Dh cluster, the SPR is strongly broadened compared to the fcc cluster. The strong difference should be visible in a comparison with experimental spectra even if the different orientations cannot be distinguished.

These results lead us to wonder how much the SPR is influenced by the nature of the core. For a given size (38 atoms in our case), there are essentially two different effects: the nature of the core and the structure (TOh, Dh, and pIh). To investigate the relative importance of the two effects, we consider a second core-shell nanoalloy,  $Ag_{32}Cu_6$ . The copper in the core stabilizes the pIh structure compared to the pure clusters due to the lattice mismatch between the two elements.

Comparing first all the TOh structures in Fig. 6, we find that the Cu core in the nanoalloy has a much stronger effect on the absorption spectra than the Au core. In particular, the SPR of the  $Ag_{32}Cu_6$  TOh is very strongly damped and broadened compared to that of the TOh  $Ag_{32}Au_6$  cluster. Moreover, it is slightly red shifted. These results show that the nature of the inner atoms (Au or Cu) can change the absorption spectra completely. The strong damping corresponds to the stronger damping of the SPR in pure Cu than in pure Au clusters.<sup>6</sup>

On the other hand, in order to consider the structural effects, we compare in Fig. 7 the (stable) plh structure to the TOh one for  $Ag_{32}Cu_6$  along with the pure  $Ag_{38}$  and  $Cu_{38}$  TOh clusters. Like the Dh, the plh is not approximately spherical. We show the averaged spectra. The difference between the plh and the TOh spectra is relatively small, in particular smaller than between the Dh and TOh structures for the  $Ag_{32}Au_6$  system. In this case, it does not appear likely that the two different core-shell structures (plh and TOh) could be distinguishable in experiments, except for the strong difference in intensity around 4 eV. At any rate, the difference introduced by the core as compared to the spectrum of the pure  $Ag_{38}$  is far stronger than the difference between the TOh and the plh structures.



FIG. 7. (Color online) Absorption spectra of the two  $Ag_{32}Cu_6$  core-shell clusters of both cubic and icosahedral symmetry, compared to the pure cubic clusters of the same size of its two constituents, namely,  $Ag_{38}$  and  $Cu_{38}$ .

### VI. CONCLUSIONS

We have carried out pseudopotential TDDFT calculations of the absorption spectra of noble-metal clusters of small and intermediate size with the aim to study the sensitivity of the optical response to the atomic and chemical structure of the nanoparticles. In agreement with the literature, we see the transition from molecular-like spectra to spectra dominated by the surface-plasmon resonance for the silver clusters. At about 150 atoms, the surface-plasmon resonance is clearly visible for Ag, while it is absent for Au and Cu, in agreement with the literature showing increasing damping with decreasing size, due to the smaller energetic separation of the d electrons from the Fermi energy than in Ag. We demonstrate that the spectra of isomeric high-symmetry structures exhibit clear differences, despite the overall approximately spherical shape of the clusters. Our results therefore give an estimate of the size range in which it is important to take into account the structural details on the atomic scale and an estimate of the differences that could be used to distinguish different structures based on comparison with experimental results.

Moreover, we calculated the spectra of different bimetallic core-shell structures. The surface-plasmon resonance of the Ag<sub>32</sub>Au<sub>6</sub> TOh core-shell cluster with the gold atoms in the core is red shifted with respect to that of the pure  $Ag_{38}$ . In particular, the spectrum is not intermediate between the spectra of the pure Ag and the pure Au clusters, an effect that, to our knowledge, has not been observed before. The SPR is strongly broadened in the Dh structure, which has a slightly larger total energy than the TOh cluster. This influence of the geometry is very strong and should easily be detectable in comparison with experimental spectra. Exchanging the core with Cu atoms in the TOh cluster leads to a strong damping of the surface-plasmon resonance, which corresponds to the strong damping of the SPR in pure Cu clusters. In conclusion, both the structure of the cluster and the nature of the core can strongly influence the spectra of core-shell nanoalloys.

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- \*The CINaM is associated to the Universities of Aix-Marseille II and III.
- <sup>1</sup>G. Mie, Ann. Phys. **25**, 377 (1908).
- <sup>2</sup>U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer-Verlag, Berlin, 1995).
- <sup>3</sup>W. Ekardt, Phys. Rev. B **31**, 6360 (1985).
- <sup>4</sup>W. Ekardt and Z. Penzar, Phys. Rev. B **43**, 1322 (1991).
- <sup>5</sup>J. Lermé, B. Palpant, B. Prével, M. Pellarin, M. Treilleux, J. L. Vialle, A. Perez, and M. Broyer, Phys. Rev. Lett. **80**, 5105 (1998).
- <sup>6</sup>E. Cottancin, G. Celep, J. Lermé, M. Pellarin, J. Huntzinger, J. Vialle, and M. Broyer, Theor. Chem. Acc. **116**, 514 (2006).
- <sup>7</sup>S. Fedrigo, W. Harbich, and J. Buttet, Phys. Rev. B **47**, 10706 (1993).
- <sup>8</sup>M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. Shafigullin, I. Vezmar, and R. L. Whetten, J. Phys. Chem. B **101**, 3706 (1997).
- <sup>9</sup>B. Palpant, B. Prével, J. Lermé, E. Cottancin, M. Pellarin, M. Treilleux, A. Perez, J. L. Vialle, and M. Broyer, Phys. Rev. B **57**, 1963 (1998).
- <sup>10</sup>I. Lisiecki and M. P. Pileni, J. Phys. Chem. **99**, 5077 (1995).
- <sup>11</sup>I. Lisiecki, F. Billoudet, and M. P. Pileni, J. Phys. Chem. **100**, 4160 (1996).
- <sup>12</sup>U. Kreibig and L. Genzel, Surf. Sci. **156**, 678 (1985).
- <sup>13</sup>Y. Borensztein, P. De Andrès, R. Monreal, T. Lopez-Rios, and F. Flores, Phys. Rev. B **33**, 2828 (1986).
- <sup>14</sup>W. Harbich, S. Fedrigo, and J. Buttet, Chem. Phys. Lett. **195**, 613 (1992).
- <sup>15</sup>J. Tiggesbäumker, L. Köller, K.-H. Meiwes-Broer, and A. Liebsch, Phys. Rev. A 48, R1749 (1993).
- <sup>16</sup>W. A. de Heer, K. Selby, V. Kresin, J. Masui, M. Vollmer, A. Chatelain, and W. D. Knight, Phys. Rev. Lett. **59**, 1805 (1987).
- <sup>17</sup>C. Bréchignac, P. Cahuzac, F. Carlier, and J. Leygnier, Chem. Phys. Lett. **164**, 433 (1989).
- <sup>18</sup>W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
- <sup>19</sup>M. Brack, Rev. Mod. Phys. **65**, 677 (1993).
- <sup>20</sup>A. Liebsch, Phys. Rev. B 48, 11317 (1993).
- <sup>21</sup>A. Rubio and L. Serra, Phys. Rev. B 48, 18222 (1993).
- <sup>22</sup>J. Lermé, B. Palpant, B. Prével, E. Cottancin, M. Pellarin, M. Treilleux, J. L. Vialle, A. Perez, and M. Broyer, Eur. Phys. J. D 4, 95 (1998).
- <sup>23</sup>J. Lermé, B. Palpant, E. Cottancin, M. Pellarin, B. Prével, J. L. Vialle, and M. Broyer, Phys. Rev. B 60, 16151 (1999).
- <sup>24</sup>E. Cottancin, J. Lermé, M. Gaudry, M. Pellarin, J.-L. Vialle, M. Broyer, B. Prével, M. Treilleux, and P. Mélinon, Phys. Rev. B 62, 5179 (2000).
- <sup>25</sup>B. Prével, J. Lermé, M. Gaudry, E. Cottancin, M. Pellarin, M. Treilleux, P. Mélinon, A. Perez, J. L. Vialle, and M. Broyer, Scr. Mater. 44, 1235 (2001).

- <sup>26</sup>M. Gaudry, J. Lermé, E. Cottancin, M. Pellarin, J. L. Vialle, M. Broyer, B. Prével, M. Treilleux, and P. Mélinon, Phys. Rev. B 64, 085407 (2001).
- <sup>27</sup>M. Gaudry *et al.*, Phys. Rev. B **67**, 155409 (2003).
- <sup>28</sup>M. Broyer, E. Cottancin, J. Lerme, M. Pellarin, N. Del Fatti, F. Vallee, J. Burgin, C. Guillon, and P. Langot, Faraday Discuss. **138**, 137 (2008).
- <sup>29</sup>C. M. Aikens, S. Li, and G. C. Schatz, J. Phys. Chem. C **112**, 11272 (2008).
- <sup>30</sup>M. Harb, F. Rabilloud, and D. Simon, Chem. Phys. Lett. **449**, 38 (2007).
- <sup>31</sup>G. Zhao, Y. Lei, and Z. Zeng, Chem. Phys. **327**, 261 (2006).
- <sup>32</sup>J. C. Idrobo, S. Öğüt, K. Nemeth, J. Jellinek, and R. Ferrando, Phys. Rev. B **75**, 233411 (2007).
- <sup>33</sup>M. Harb, F. Rabilloud, D. Simon, A. Rydlo, S. Lecoultre, F. Conus, V. Rodrigues, and C. Felix, J. Chem. Phys. **129**, 194108 (2008).
- <sup>34</sup>M. L. Tiago, J. C. Idrobo, S. Öğüt, J. Jellinek, and J. R. Chelikowsky, Phys. Rev. B **79**, 155419 (2009).
- <sup>35</sup>V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, J. Chem. Phys. 93, 3802 (1990).
- <sup>36</sup>P. Dugourd, J. Blanc, V. Bonacic-Koutecky, M. Broyer, J. Chevaleyre, J. Koutecky, J. Pittner, J. P. Wolf, and L. Wöste, Phys. Rev. Lett. **67**, 2638 (1991).
- <sup>37</sup>J. Blanc, V. Bonacic-Koutecky, M. Broyer, J. Chevaleyre, P. Dugourd, J. Koutecky, C. Scheuch, J. P. Wolf, and L. Wöste, J. Chem. Phys. **96**, 1793 (1992).
- <sup>38</sup>J. C. Idrobo, S. Öğüt, and J. Jellinek, Phys. Rev. B 72, 085445 (2005).
- <sup>39</sup>N. Durante, A. Fortunelli, M. Broyer, and M. Stener, J. Phys. Chem. C **115**, 6277 (2011).
- <sup>40</sup>G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002), and references therein.
- <sup>41</sup>G. Onida, L. Reining, R. W. Godby, R. Del Sole, and W. Andreoni, Phys. Rev. Lett. **75**, 818 (1995).
- <sup>42</sup>H. Baida *et al.*, Nano Lett. **9**, 3463 (2009).
- <sup>43</sup>K. Michaelian, N. Rendón, and I. L. Garzón, Phys. Rev. B **60**, 2000 (1999).
- <sup>44</sup>E. Aprà, R. Ferrando, and A. Fortunelli, Phys. Rev. B **73**, 205414 (2006).
- <sup>45</sup>H. Hakkinen and M. Moseler, Comput. Mater. Sci. 35, 332 (2006).
- <sup>46</sup>L.-L. Wang and D. D. Johnson, Phys. Rev. B **75**, 235405 (2007).
- <sup>47</sup>G. Rossi, A. Rapallo, C. Mottet, A. Fortunelli, F. Baletto, and R. Ferrando, Phys. Rev. Lett. **93**, 105503 (2004).
- <sup>48</sup>R. Ferrando, A. Fortunelli, and G. Rossi, Phys. Rev. B **72**, 085449 (2005).
- <sup>49</sup>R. Ferrando, J. Jellinek, and R. L. Johnston, Chem. Rev. **108**, 845 (2008).
- <sup>50</sup>D. Bochicchio and R. Ferrando, Nano Lett. **10**, 4211 (2010).

### H.-CH. WEISSKER AND C. MOTTET

- <sup>51</sup>D. J. Wales and J. P. K. Doye, J. Phys. Chem. A **101**, 5111 (1997).
- <sup>52</sup>C.-M. Wu, C.-Y. Li, Y.-T. Kuo, C.-W. Wang, S.-Y. Wu, and W.-H. Li, J. Nanopart. Res. **12**, 177 (2010).
- <sup>53</sup>M. Tsuji, D. Yamaguchi, M. Matsunaga, and M. J. Alam, Cryst. Growth Des. **10**, 5129 (2010).
- <sup>54</sup>J. Zeng, Y. Zheng, M. Rycenga, J. Tao, Z.-Y. Li, Q. Zhang, Y. Zhu, and Y. Xia, J. Am. Chem. Soc. **132**, 8552 (2010).
- <sup>55</sup>G. Schmid, Chem. Soc. Rev. **37**, 1909 (2008).
- <sup>56</sup>F. Y. Chen and R. L. Johnston, Appl. Phys. Lett. **90**, 153123 (2007).
- <sup>57</sup>V. Rosato, M. Guillopé, and B. Legrand, Philos. Mag. A **59**, 321 (1989).
- <sup>58</sup>A. Rapallo, G. Rossi, R. Ferrando, A. Fortunelli, B. C. Curley, L. D. Lloyd, G. M. Tarbuck, and R. L. Johnston, J. Chem. Phys. **122**, 194308 (2005).
- <sup>59</sup>G. Rossi, R. Ferrando, A. Rapallo, A. Fortunelli, B. C. Curley, L. D. Lloyd, and R. L. Johnston, J. Chem. Phys. **122**, 194309 (2005).

- <sup>60</sup>G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- <sup>61</sup>G. Kresse and J. Furthmüller, Comput. Mat. Sci. **6**, 15 (1996).
- <sup>62</sup>G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- <sup>63</sup>M. A. L. Marques, A. Castro, G. F. Bertsch, and A. Rubio, Comput. Phys. Commun. **151**, 60 (2003).
- <sup>64</sup>A. Castro, M. A. L. Marques, H. Appel, M. Oliveira, C. Rozzi, X. Andrade, F. Lorenzen, E. K. U. Gross, and A. Rubio, Phys. Status Solidi B 243, 2465 (2006).
- <sup>65</sup>C. Mottet, G. Treglia, and B. Legrand, Surf. Sci. 383, L719 (1997).
- <sup>66</sup>F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, and C. Mottet, J. Chem. Phys. **116**, 3856 (2002).
- <sup>67</sup>J. M. Soler, M. R. Beltrán, K. Michaelian, I. L. Garzón, P. Ordejón, D. Sánchez-Portal, and E. Artacho, Phys. Rev. B 61, 5771 (2000).
- <sup>68</sup>F. Conus, V. Rodrigues, S. Lecoultre, A. Rydlo, and C. Felix, J. Chem. Phys. **125**, 024511 (2006).
- <sup>69</sup>I. Russier-Antoine, G. Bachelier, V. Sablonière, J. Duboisset, E. Benichou, C. Jonin, F. Bertorelle, and P. F. Brevet, Phys. Rev. B 78, 035436 (2008).

### PHYSICAL REVIEW B 84, 165443 (2011)