The optical absorption spectrum of the three most stable isomers of the Ag$_{11}$ system was calculated using the time-dependent density functional theory, with the generalized gradient approximation for the exchange and correlation potential, and a relativistic pseudopotential parametrization for the modelling of the ion–electron interaction. The computational scheme is based on a real space code, where the photoabsorption spectrum is calculated by using the formalism developed by Casida. The significantly different spectra of the three isomers permit the identification of the ground-state configuration predominantly present in the laboratory beams in base to a comparison between the calculated photoabsorption spectrum of the most stable configuration of Ag$_{11}$ and the measured spectra of medium-size silver clusters trapped in noble gas Ar and Ne matrices at different temperatures. This assignment is confirmed by the fact that this isomer has the lowest calculated energy.

I. INTRODUCTION

The study of transition and noble metal clusters has focused considerable attention along the last years due to the different properties detected respect to their corresponding bulk-phases. Additionally, these cluster properties have demonstrated to be strongly dependent on the cluster size. On the other hand, noble metal clusters, and silver clusters in particular, present important applications from the scientific and technological point of view in interesting researching fields such as catalysis [12–15, 16, 17, 18, 19, 20, 21, 22, 23]. The structural and electronic properties of silver clusters [11] have recently been studied, however unlike the optical properties [11, 12, 13, 14, 15, 16] have been widely studied, however no full agreement with experimental measurements, in order to improve the description of previous theoretical studies by reducing the numerical uncertainty; (b) since significant differences have been found among the spectra of the different isomers of Ag$_{11}$ (see Fig. 1), to propose the comparison of experimental and TDDFT absorption spectra as a powerful tool to elucidate between the different isomeric forms of small clusters; and (c) finally, to predict Ag$_{11}$ photoabsorption spectrum for energies higher than 5.5 eV, a range of energies which has not been considered in previous experimental or theoretical studies for this system (our calculations extend the range of excitation energies up to 8 eV).

II. METHOD

Prior to the calculation of the photoabsorption spectra, the lowest energy geometrical structure of each isomer was determined by using the Density Functional Theory [31]. The ion–electron interaction is modelled by replacing the ionic cores (1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^2$4p$^6$10d$^{10}$5s$^1$ Krypton–like core) by pseudopotentials within the relativistic scheme of Hartwigsen and
coworkers [32], previously validated for several metal elements in pure and organometallic clusters [24, 25, 33]. This pseudopotential is built in such a way that is separable by construction, is highly accurate, and has an analytical form that can be specified by a small number of parameters. For exchange and correlation effects we have used the generalized gradient approximation (GGA) [34].

As initial geometries for the structural optimization of the Ag_{11} isomers were considered the three most stable structures previously obtained by Fernández et al. [12]. Starting from those geometries we performed structural relaxations by making use of the Broyden algorithm [35] with a convergence criterion of 10^{-2} eV/Å in the net forces on every atom. The structural relaxations, performed with the ABINIT package [36], did not produce significant variations with respect to the original structures. In order to test the influence of using a well-tailed exchange-correlation potential in the structural properties we have additionally checked the simple GGA by comparison with a functional with improved asymptotic behavior: the van Leeuwen–Baerends (LB94) GGA functional [37], which led to practically identical optimized structures.

The geometries obtained, which are then used in the calculations of the photoabsorption spectra, are shown in Fig. 1.

Once the ground-state structures of the different isomers were established, we performed the calculation of the excitation spectra. For this purpose, we have used the TDDFT formalism [26, 27, 28], implemented in the real space code octopus [29]. The theoretical foundations underlying the TDDFT calculations, as well as the computational scheme, have been presented elsewhere [29, 38, 39, 40], and here we only summarize the main points. The photoabsorption spectrum is calculated by using the formalism developed by Casida [29, 30]. Application of this technique to obtain the oscillator strengths requires a previous calculation of the ground state electronic structure, that is, the occupied electronic states, and also the unoccupied states. The whole set of occupied states, joint to twenty extra unoccupied states for each spin channel, were necessary to reach convergence of the excitation spectra for an energy range up to 8 eV. After that, each excitation peak is broadened by a Lorentzian profile to give the photoabsorption cross section

$$
\sigma_{abs}(\epsilon) = \sum_{\epsilon_i} \frac{A^2}{(\epsilon - \epsilon_i)^2 + A^2},
$$

where $\epsilon$ is the energy, $\epsilon_i$ are the discrete excitation energies obtained by the Casida method, and the value of the parameter $A$ determines the full width at half maximum.

We have performed the calculations of the photoabsorption spectra with the GGA, using the Perdew-Burke-Ernzerhof parameterization [41] of electronic correlation. The corresponding occupied and unoccupied single–particle states are used in the Casida method with the adiabatic LDA exchange–correlation kernel. Although not entirely consistent, this is a common practice because the use of a better kernel does not significantly affect the results as long as the single–particle orbitals have been calculated with a suitable static $v_{xc}(r)$ potential [25]. This computational framework has been used successfully in the calculation of the optical spectra of atoms and clusters [24, 25, 33, 42, 43, 44, 45, 46, 47, 48, 49]. In the case of free atoms, the energies for one-particle low-energy excitations agree with experiment to within 5-10 per cent [45]. For clusters of s–p metals, the errors in the position of the absorption peaks are usually in the 0.1-0.2 eV range [45, 46, 47], and the results are also very reasonable for carbon and BN clusters [48, 49], and transition metal, organometallic, and molecular and van der Waals clusters [24, 25, 33, 42], even in the high-energy range.

This formalism, used in combination with both adiabatic local density (ALDA) and GGA approximations for the XC effects, has provided successful results, establishing this technique for the calculation of excitations in this kind of nanoscale systems as an effective tool in the characterization of a great number of cluster properties and behaviors, such as the elucidation of ground-state structures, the characterization of dimeric growths in molecular clusters, and the theoretical justification of collective electronic behaviors [24, 25, 33, 42].

### III. Results and Discussion

Fig. 1 shows the calculated equilibrium structures of the three lowest-energy isomers of the Ag_{11} system, starting from the geometries obtained by Fernández et al. [12]. The results do not reveal significant variations respect the original structures; where, during the relaxation process, all the atoms in the clusters are free to move. The obtained G-S configuration is based in a seven-atom pentagonal bypiramid, as predicted in previous references [13, 18, 22]. The ordering of the most stable isomers presented here do not fully agree with these previous studies, but is in complete agreement with the accurate structural analysis given by Fernández et al. (for a...
FIG. 2: Calculated photoabsorption cross sections (in arbitrary units) for the three most stable isomers of Ag$_{11}$ (see Fig. 1) for energies up to 8 eV. All the absorption strengths are shown in the same scale, and superposed to the photoabsorption profiles vertical dashed lines have been included for a better visualization of the different regions of the spectra.

Energy (eV)
Absorption Cross Section (arb. units)

More detailed description about the structures see Ref. [12]). However, this factor can be due to the small differences in the total energy detected between the different, almost energy-degenerated, isomers shown in the recent literature (in the range of meV). In the present study the gap in the total energy between the G-S structure and the two most stable isomers is 0.08 and 0.15 eV for ISO1 and ISO2 structures, respectively. Nevertheless, and according to the previous theoretical studies, the ground-state of this kind of systems has demonstrated to be highly sensitive to the common DFT numerical implementations.

Figure 2 shows the photoabsorption cross sections for the three most stable isomers of Ag$_{11}$ up to 8 eV as obtained by TDDFT under the Casida formalism. The finite width of the absorption peaks in an experiment – linked to the accessible resolution – is mostly determined by the temperature. In our calculations, on the other hand, the width of the peaks is an artifact and may be reduced or enlarged by modifying the $A$ parameter. We have broadened the peaks in the way shown in the figure (with $A=0.05$ eV), so as to simulate the approximate resolution yielded by most of the experiments of photoabsorption and photodissociative spectroscopy [24].

All three spectra are rich in features in the whole energy region up to 8 eV from the beginning of the absorption. Three regions can be clearly distinguished in all the spectra (separated by dashed lines superposed to each profile in the picture). A region of no absorption at all covers the energy range up to 2 eV (common to all isomers), a region of strong absorption is observed at energies between 2 and 6 eV, and another region of weaker absorption at energies larger than 6 eV, with an absorption strength dependent on the isomer in particular.

To our knowledge, no experimental or theoretical study has been carried out for Ag$_{11}$ in a range of excitation energies up to 8 eV. In the region between 2 and 6 eV, the absorption strength is more pronounced, the spectra are dominated by a sharper profile whose position rather varies between the different clusters, and formed by pronounced peaks at 3.6, 4.2 and 4.6 eV. For the ISO1 and ISO2 isomers an additional peak at 5.2 eV is found, not present for the G-S structure. Although this wide absorption region is always located between 2 and 6 eV, and despite of other previous TDDFT theoretical photoabsorption studies in metallic clusters [33], it cannot be inter-
The low energy response of these isomers up to 5.5 eV can be compared with the experimental results of the Refs. [20], [21], and [23] for the measured spectra of medium-size silver clusters trapped in noble gas matrices at several temperatures. Figure 3 shows the experimental absorption cross sections of Ag_{11} in a Ne matrix at 6 K, and Ar matrices at 10 and 28 K (lower panels), and the TDDFT spectrum for the obtained Ag_{11} G-S structure (upper panel). The estimated uncertainties of the relative cross sections in this kind of experiments use to be around 10% (the uncertainties in the absolute cross sections are even larger). The experimental absorption cross sections show a clear three peaks structure, where the relative strength of the peaks depend strongly on the temperature and the matrix surrounding the trapped cluster, but not their excitation energies. The peaks arise at 3.2, 3.7 and 4.4 eV, with a region of no absorption up to 5.5 eV. The TDDFT spectrum, for the G-S isomer, shows a similar three peaks profile located at 3.6, 4.2 and 4.6 eV. As we can appreciate in Fig. 3 there exist a very good agreement between the calculated and the experimental peak positions if we just allow for a constant shift of around 0.2-0.4 eV. This shift to the red of the experimental spectra can be justified by the additional effect of the noble gas matrices to the photoabsorption response, which has been quantified by Fedrigo et al. [20], and Sieber et al. [50] in 0.2-0.25 eV. However, most of authors coincide in that value of the shift may not be appropriate because additional contributions could arise, such as compression effects of the cluster by the matrix, or matrix-induced polarization of the cluster charge density [18]. On the other hand, previous authors suggest that the deviation in the experimental photoabsorption spectra of the small silver clusters showing several isolated peaks, instead of only one pronounced excitation detected in large-sized clusters [19, 20], is due to the presence of several isomers in the experimental beams [18, 21].

However, the present study reveal theoretical spectra for three different Ag_{11} isomers where such isolated peaks are found. From these results, we can conclude that the presence of these distinct peaks in experimental spectra is not only due to the existence of several isomeric forms in the experimental samples since it seems to be an intrinsic optical property of this kind of aggregates. Other discrepancy sources in the spectrum may be due to additional factors: (i) the error introduced in the calculation by the necessarily approximated exchange and correlation potential, (ii) the expectable influence of the silver clusters coupling to the surrounding noble metal matrices, and (iii) the possible presence in the experimental sample of a mixture of various isomers, coinciding with other authors.

The calculated spectrum for this isomer provides the best matching with experiment, and this confirms the assignment of the ground state structure as predicted even by the total energies. We then conclude that the calculated spectrum of the most stable isomer obtained provides a very accurate description of the experimental cross section and permits to conjecture with a high confidence that the isomer present most abundantly in the Ag_{11} cluster beams has that structure. This is reasonable, since this is indeed the calculated lowest energy isomer.

IV. SUMMARY AND CONCLUSIONS

We have performed calculations of the optical absorption cross sections of three structural isomers of Ag_{11}. For that purpose we have first employed DFT to optimize the geometries of those isomers. For each of those structures TDDFT has been used to calculate the photoabsorption spectrum. In
the calculations, we used the generalized gradient approx-
imation for the exchange and correlation potential, relativistic
norm-conserving pseudopotentials, and the Casida formalism
to calculate the excitation spectrum. This approach yields
spectra for the different isomers that are significantly dif-
terent. The spectrum corresponding to the most stable structure
obtained matches well the experimental results, and we con-
clude that this is the isomer predominantly present in the lab-
oratory cluster beams; confirmation comes from the fact that
this is the isomer with the lowest calculated energy. The effi-
ciency of DFT and TDDFT for the calculation of both ground
state and spectroscopic features of molecules and clusters per-
cise geometrical atomic arrangement of the probed systems.

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