Determination of the lowest energy structure of Ag$_8$ from first-principles calculations

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The ground-state electronic and structural properties, and the electronic excitations of the lowest energy isomers of the Ag$_8$ cluster are calculated using density functional theory (DFT) and time-dependent DFT (TDDFT) in real time and real space scheme, respectively. The optical spectra provided by TDDFT predict that the D$_{2d}$ dodecahedron isomer is the structural minimum of Ag$_8$ cluster. Indeed, it is borne out by the experimental findings.

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In latter years, a new field has emerged from the understanding, control and manipulation of objects at nanoscale level (nano-objects). It is commonly known as nanoscience. This field involves physics, chemistry and even engineering, and addresses a huge number of important issues starting from basic science and ending in a large variety of technological applications [1]. Among the nano-objects, the small clusters or nanoclusters play a very important role, since they are the bricks of nanoscience. Therefore, the study of small clusters deserves a special attention. In this respect, the steps to follow for a complete description of a cluster can be summarized in the following three questions: what is the lowest energy structure?, what is the effect of increasing or decreasing the temperature on the structural properties of a cluster? and the last step deals with the kinetic effects in the formation of the nanocluster. Here, we are only concerned about the first question for the silver octamer, leaving the other two questions open for future investigations.

From the theoretical point of view, first-principles methods give an enormous advantage for understanding, projecting and inventing new materials that is reflected in the huge number of articles published in the field of materials science. Likewise, density functional theory (DFT) has emerged as a new and promising tool for ab initio electronic structure calculations and gives valuable information about the geometry of nanoscale systems [2] but unfortunately it not always predict the correct structure of the cluster under consideration. In this regard, the silver octamer belongs to the group of the controversial systems for which the lowest energy structure is unresolved by DFT.

Recently, P. Radcliffe et al. [3] have proposed Ag$_8$ clusters embedded in helium droplets as a suitable system for light amplification based on an optically accessible long-living excited state (E*) and thereby, from the theoretical point of view, the determination of the structure becomes a key point as the first step for identifying and controlling the levels that populate E*. Up to now, it has not been possible to make a reliable theoretical prediction of the most stable structure of Ag$_8$. A review of the literature reveals that there are two competing geometries in eight-atom clusters of s-electron elements, having T$_d$ and D$_{2d}$ symmetry. In fact, different levels of theories favor different geometries: DFT in its local density approximation (LDA) [4], multireference configuration interaction approach [5], and the many-body perturbation theory-based calculations [6] give the D$_{2d}$ geometrical shape as the lowest energy structure of Ag$_8$ whereas the equation-of-motion coupled cluster method [7], time-dependent DFT only at LDA level [8] and molecular-dynamics simulations [9] predict a T$_d$ structure as the structural minimum. It was reported in Refs. [8,9] that the D$_{2d}$ geometry is favored energetically over T$_d$ symmetry when explicit correlation treatments for 5s electrons are included, but since the calculated energy difference between T$_d$ and D$_{2d}$ isomers is very small, the predicted theoretical ordering is uncertain. One way of solving this vexing problem comes from the hand of the time-dependent density functional theory (TDDFT) [10] that is a generalization of traditional ground stationary state DFT to treat the dynamic response of the charge density to a time-dependent perturbation. TDDFT is a powerful methodology towards the calculation of the optical spectra, and thereby gives access to excited-state information.

In this brief report, we have calculated the optical response of the T$_d$ and D$_{2d}$ geometries and they were compared both with each other and the experimental findings. The atomic positions were fully optimized with an all-electron DFT implementation at the generalized gradient approximation (GGA) level, representing an improvement over other TDDFT studies in small silver clusters [11]. This work relies on the combination of the traditional DFT and its generalization to excited states, as a promising tool for elucidating structures that DFT by its own is unable to predict. Here, we demonstrate that the D$_{2d}$ structure is the structural minimum of Ag$_8$ and the calculated spectra allow us to estimate the interaction of Ag$_8$ with the surrounding helium or argon matrix presented in experimental observations.

With the aim of elucidating the lowest energy structure of Ag$_8$ cluster, we have performed density functional
theory-based calculations consisting of a linear combination of Gaussian-type orbitals-Kohn-Sham-density-functional methodology (LCGTO-KSDFM) to obtain the structural and electronic ground-state properties \(\text{[12]}\), and a TDDFT implementation to compute the electronic excitations \(\text{[13]}\). For the former, all-electron calculations were carried out with DEMON-KS3P5 \(\text{[12]}\) at GGA level to take the exchange-correlation (XC) effects into account \(\text{[14]}\). An orbital basis set of contraction pattern \((633321/53211*/531+)^{\text{[14]}}\) was used in conjunction with the corresponding (5,5,5,5) auxiliary basis set for describing the s-, p- and d-orbitals \(\text{[15]}\). The grid for numerical evaluation of the XC terms had 128 radial shells of points and each shell had 26 angular points. Spurious one-center contributions to the XC forces, typically found in systems with metal-metal bonds when using a nonlocal functional, are eliminated in a similar way as has been done in Ref. \(\text{[14]}\). Trial geometries were fully optimized without symmetry and geometry constraints for different multiplicities using the Broyden-Fletcher-Goldfarb-Shanno algorithm \(\text{[17]}\). The multiplicities were ranged from 1 to 11 and in all reported structures the singlet state was favored energetically. During the optimization, the convergence criterion for the norm of the energy gradient was fixed to 10\(^{-4}\) a.u. while it was 10\(^{-7}\) a.u. for the energy and 10\(^{-9}\) a.u. for the charge density. For the latter, after inserting the atomic coordinates of the converged structures provided by DEMON-KS3P5 all the dynamical quantities are computed by evolving the electronic wave functions in real time and real space \(\text{[13]}\). The electron-ion interaction is described through the Hartwigsen-Goedecker-Hutter relativistic separable dual-space gaussian pseudopotentials \(\text{[18]}\) and the XC effects were treated in the GGA, implemented via the Perdew-Burke-Ernzerhof functional \(\text{[18]}\). The grid in real space to solve the Kohn-Sham equations consists in a sum of spheres around each atom of radius 5.5 Å and a mesh spacing of 0.23 Å. The time step for the propagation of the electronic orbitals was fixed to 0.0013 fs, which ensures the stability of time-dependent propagation. An artificial electronic temperature of 10 K was included according to the Fermi-Dirac function used to distribute the electrons among the accessible states.

After a review of the literature on silver clusters \(\text{[4, 5, 6, 7, 8]}\), we have decided to optimize, as a good candidate to the structural minimum of the octamer, the following isomers of Ag\(_8\): a D\(_{2d}\) dodecahedron (D\(_{2d}\)-DD), which can also be viewed as a distorted bicapped octahedron, a T\(_d\) tetracapped tetrahedron (T\(_d\)-TT) and a C\(_s\) 1-pentagonal bipyramid (C\(_s\)-PBP) in Fournier’s notation \(\text{[4]}\). The main results (density of states (DOS), optimized structures, polarizabilities, ground state energies, ...) of the electronic structure calculations are collected in Table \(\text{[4]}\) and Fig. \(\text{[4]}\). The LCGTO-KSDFM calculations clearly show that the C\(_s\)-PBP geometry is energetically far from the lowest energy structure by an amount of 181.25 meV. Therefore, we will concentrate our attention in D\(_{2d}\) and T\(_d\) structures.

Despite the fact that the lowest energy isomer corresponds to a D\(_{2d}\) symmetry, it should be noted that the ground-state energy difference between D\(_{2d}\)-DD and T\(_d\)-TT isomers is very small \((\Delta E_{D_{2d} \rightarrow T_d} = 6.12 \text{ meV})\) compared to 0.19 eV which is the averaged energy difference between the ground-state structure and the second stable structure of Ag\(_n\) (2\(\leq n\leq 12\) \(\text{[4]}\)). Furthermore, the polarizabilities and the HOMO-LUMO gaps (HLg) do not offer a clear picture for elucidating the structural minimum of the octamer. That is, it is well known that the Ag\(_8\) cluster is a closed-shell system and it was demonstrated experimentally and theoretically that the closure of electronic shell manifest itself in particularly large HLg (see \(\text{[4]}\) and references therein), consequently the HLg reported in Table \(\text{[4]}\) are on the side of stabilization of the T\(_d\)-TT isomer. As far as the reported polarizabilities are concerned, in molecular electronic distribution studies under the influence of an external electric field, the relevant quantities are the mean static polarizability \(\tilde{\alpha} = (\sum_{i=1}^{3} \alpha_{ii})/3\) and the polarizability anisotropy \(\Delta \alpha\), defined as:

\[
\Delta \alpha = \frac{1}{2} \sum_{i,j=1,2}^{2,3} \left( \alpha_{ii} - \alpha_{jj} \right)^2 + 6 \sum_{i,j=1,2}^{2,3} \alpha_{ij}^2
\]

where \(\alpha_{ij} = \partial(\mu_{\text{e}})_{ij}/\partial E_j\) is the ij-component of the polarizability tensor under the action of an external electric field \(E_j\). It is not a common procedure to express the polarizability anisotropy such as it was defined in Eq. \(\text{(4)}\). The commonly-used definition omits the second term \((6 \sum_{i,j=1,2}^{2,3} \alpha_{ij}^2)\) and thus neglects the important influence that the off-diagonal elements of the second-rank polarizability tensor play in the symmetry considerations of the electric charge distribution \(\text{[20]}\). The mean static polarizabilities, reported in Table \(\text{[4]}\) are quite similar to each other showing in average that the electron charge is nearly equally distributed among the three isomers. However, only the polarizability anisotropy of the

| Symmetry | \(\Delta E_{D_{2d}}\) (meV) | \(E_f\) (eV) | \(\Delta \xi\) (eV) | \(\tilde{\alpha}\) (\(\text{\AA}^3/\text{atom}\)) | \(\Delta \alpha\) (\(\text{\AA}^3/\text{atom}\)) |
|----------|-----------------|---------|---------------|----------------|----------------|
| D\(_{2d}\) | 0.00 | -4.302 | 1.719 | 6.32 | 1.22 |
| T\(_d\) | 6.14 | -4.574 | 2.335 | 6.46 | 0.01 |
| C\(_s\) | 181.25 | -4.048 | 1.327 | 6.45 | 1.71 |

TABLE I: Ground-state energies relative to the most stable isomer (D\(_{2d}\)-DD) and electronic structure properties of the DFT-optimized Ag\(_8\) cluster isomers. The Fermi level is denoted by \(E_f\) and \(\Delta \xi\) stands for the HOMO-LUMO gap. The mean static polarizability \(\tilde{\alpha}\) and the polarizability anisotropy \(\Delta \alpha\) were calculated under the influence of an external electric field of strength 0.0005 a.u.
The T_d-TT isomer is clearly reduced. This result tends to stabilize the T_d symmetry over D_{2d} because the less polarizability anisotropy is, the more spherically symmetric charge distribution is and the latter condition is favored by a closed-shell system like the silver octamer. Indeed, the delocalized molecular orbitals for the higher-lying occupied levels of the D_{2d} and T_d geometries, presented in Fig. 1 exhibit a hybridization of the atomic 5s levels with the 5p levels leading to a nearly spherical shape whereas for the lower-lying unoccupied levels, the spherical symmetry becomes less important. The proximity in energy and the corresponding superposition of the spatial distribution of the higher-lying occupied molecular orbitals of the T_d-TT isomer with respect to the ones of the D_{2d}-DD isomer, contribute to a spherical symmetrization of the T_d-TT charge distribution.

The balance of the aforementioned contrary tendencies does not allow a reliable prediction of the structure, such as it was discussed in literature [4, 6, 7, 8, 10]. The TDDFT calculations using the structural parameters provided by the LCGTO-KSDFM as starting point can shed some light on the better understanding of this vexing controversy on the structure of Ag_8. In this respect, as it is shown in Fig. 2, the calculated spectrum for D_{2d} symmetry is in excellent agreement with the resonant two-photon ionization spectrum reported by F. Federmann et al. [21], whereas the T_d-TT calculated spectrum only shows one resonant peak and it is about 0.31 eV blue-shifted with respect to the experimental measurements. Thus, the LCGTO-KSDFM predicted structure is confirmed by the TDDFT calculations of the optical response when it is compared to the experimental evidences.

Some of the relevant states involved in the transitions that populate the peaks of Fig. 2 are provided through the calculated DOS depicted in Fig. 1. For the D_{2d} isomer, the eigenvalues of the HOMO and HOMO-1 states are both close together in energy and the HOMO-2 state is 0.7 eV further down meanwhile for the T_d-TT isomer, this three states were grouped together in a window energy of only 3 meV. It is worthwhile to mention here that the T_d-TT isomer has high symmetry, so many states will be degenerate. However, because of small numerical errors, it is quite possible that states that should strictly be degenerate will show as being within very small energy windows. In the energy range displayed in Fig. 2 for D_{2d} symmetry, the TDDFT calculations predict four electronic transitions starting from the twofold degenerate HOMO and HOMO-1 states to two excited states separated 0.07 eV in energy and it gives rise to two peaks because of the nearness in energy of the HOMO-1 and HOMO states. In the case of the T_d symmetry, six transitions are predicted giving rise to only one peak because
FIG. 2: Comparison between two experimental recorded spectra and the calculated spectra for both (solid line) D$_{2d}$-DD and (dashed line) T$_{d}$-TT isomers at a temperature of 10 K. Open circles correspond to the resonant two-photon ionization (R2PI) spectroscopy on Ag$_8$ clusters in He droplets [21] while the solid triangles are for the excitation spectrum of Ag$_8$ excited with monochromatic Xe light in an Ar matrix [22]. The D$_{2d}$-DD isomer spectrum is in excellent agreement with the experiment whereas the T$_{d}$-TT isomer spectrum is around 0.31 eV blue-shifted compared to the R2PI spectrum.

the two excited states that electronic transitions populate are only 1 meV separated, as commented above.

Some consequences can be extracted going further in the analysis of the calculated spectrum for D$_{2d}$-DD isomer when it is compared with the experimental references reported in Fig. 2. On one hand, for the case of R2PI experiment we attribute the slight difference in peak position (∼3 meV) to the helium environment through the formation of electron bubble states that significantly blue shift the transition [22]. As already mentioned above, our TDDFT calculations also confirm the authors’ feeling of Ref. [21] that the asymmetry of the peak involves more than one transition. On the other hand, the comparison between the excitation spectrum in Ar matrix [22] and the calculated D$_{2d}$ isomer spectrum allow us to measure the interaction of the Ar matrix with the Ag$_8$ cluster. Thus, the shift of energy probably due to Ar matrix effects is estimated to be about 25 meV that is great enough compared to the slight difference in peak position (∼3 meV) attributed to the helium surrounding the Ag$_8$ clusters in R2PI experiment. Consequently, the use of liquid helium droplets as a spectroscopic matrix has the advantage over argon matrix of providing an environment more suitable for study the electronic excitations of small and free silver clusters.

In conclusion, we have shown that a combination of a LCGTO-KSDFM and TDDFT approach is able to reproduce the measured optical response of the silver octamer and allow us to elucidate its lowest energy structure below 10 K. Our calculation thus confirms that the structural minimum of Ag$_8$ is the D$_{2d}$-DD isomer, whose geometrical structure is depicted in Fig. 1. The TDDFT calculations have provided a number of electronic transitions involving the resonant peaks showed in Fig. 2 and demonstrate that the R2PI experiment is a good technique to measure experimentally the electronic excitations of bare silver clusters because it is less aggressive than, for example, the experiments that consider argon as the spectroscopic matrix.

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