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DOI:
10.1063/1.4901109

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Citation for published version (Harvard):
Shayeghi, A, Johnston, RL & Schäfer, R 2014, 'Global minimum search of Ag+10 with molecular beam optical spectroscopy', Journal of Chemical Physics, vol. 141, no. 18, 181104. https://doi.org/10.1063/1.4901109

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The following article appeared in Communication: Global minimum search of Ag+10Ag10+ with molecular beam optical spectroscopy and may be found at: http://scitation.aip.org/content/aip/journal/jcp/141/18/10.1063/1.4901109

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Citation: The Journal of Chemical Physics **141**, 181104 (2014); doi: 10.1063/1.4901109

View online: http://dx.doi.org/10.1063/1.4901109

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THE JOURNAL OF CHEMICAL PHYSICS **141**, 181104 (2014)

Communication: Global minimum search of Ag_{10}^{+} with molecular beam optical spectroscopy

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(Received 17 September 2014; accepted 24 October 2014; published online 13 November 2014)

The present study is focused on the optical properties of the Ag_{10}^{+} cluster in the photon energy range $\hbar\omega = 1.9$–4.4 eV. Absorption spectra are recorded by longitudinal molecular beam depletion spectroscopy and compared to optical response calculations using time-dependent density functional theory. Several cluster isomers obtained by the new pool-based parallel implementation of the Birmingham Cluster Genetic Algorithm, coupled with density functional theory, are used in excited state calculations. The experimental observations, together with additional simulations of ion mobilities for the several geometries found within this work using different models, clearly identify the ground state isomer of Ag_{10}^{+} to be composed of two orthogonal interpenetrating pentagonal bipyramids, having overall D_{2d} symmetry. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4901109]

The transition metal silver has the particular property of a filled *d*-shell causing its chemistry to be mainly dominated by the *s*-valence electron. As the most “alkali-like” group-11 element, it has been well studied in a number of theoretical investigations,[1–3] especially due to the strong surface plasmon absorption in the visible regime observed in silver clusters and nanoparticles.[4–9,52] In order to understand the size-dependent physical and chemical properties of such nano-sized silver particles, small clusters consisting of only a few atoms are ideal model systems.[10–13] The relatively large *s-d* separation means that the optical response is mainly associated with *s*-electrons while *d*-electrons are only partially involved in the excitations.[14] The Nilsson-Clemenger model,[15] taking only the 5*s*-electrons into account, leads to absorption spectra in good qualitative agreement with experiments.[16] Further, it has been shown that the jellium model is valid at high temperatures, whereas a molecular picture is more appropriate at low temperatures.[17] However, especially at small sizes, a quantum chemical treatment becomes important since the electronic structure of the sub-nanometer particles becomes more discrete. In order to probe the optical response of small silver clusters, photodissociation spectroscopy[18–24] and rare-gas matrix spectroscopy[14,16,25] have been reported previously. Very recently, Ito *et al.* presented optical spectra of Ag_{n}^{+} (n = 8–14) clusters in the range $\hbar\omega = 3.7$–4.4 eV.[26] However, the absorption spectrum of Ag_{10}^{+}, to the best of our knowledge, has not been reported in the literature yet.

Previously, Weis *et al.* performed ion mobility measurements on Ag_{n}^{+} (n<12) clusters and compared their results to theoretical predictions from density functional theory (DFT), employing the BP-86 functional and Møller-Plesset (MP2) perturbation theory both with RI-J quadrature using a svp basis set augmented by additional polarization and diffuse functions.[27] In order to identify global minimum (GM) structures for the different investigated cluster sizes, they applied the exact hard spheres scattering (EHSS)[28] model to their ground state structure candidates and calculated collision cross sections in good agreement with their experimental data. However, the ion mobility does not enable a clear identification of the ground state isomer in the case of Ag_{10}^{+}. Photodissociation spectroscopy, combined with quantum chemical investigations, therefore is indispensable for the sake of a clear structural assignment.

In this article, we present the photodissociation spectrum of the Ag_{10}^{+} cluster in the photon energy range $\hbar\omega = 1.9$–4.4 eV combined with calculations of optical spectra for several isomers in the framework of time-dependent density functional theory (TDDFT).[29] Initial cluster geometries are obtained by the Birmingham Cluster Genetic Algorithm (BCGA),[30] coupled with DFT (GADFT),[31] in a recently developed parallel pool modification.[32] The long-range corrected (LC) exchange correlation (xc) functional, LC-ωPBEh,[33] is used throughout our whole analysis. It has been shown to perform well for the calculation of ground and excited state properties of gold,[24,34] silver,[24] and mixed silver gold clusters,[35] where it leads to the reliable prediction of optical absorption spectra.

The experimental setup is described in detail elsewhere.[24] Briefly, cluster cations are produced by pulsed laser vaporization and separated with time-of-flight mass spectrometry. The optical response is probed by longitudinal photodissociation spectroscopy with a tunable ns-laser pulse from an optic parametric oscillator, pumped by the third harmonic of an Nd:YAG laser. Spectra are recorded by monitoring the ion signal depletion upon photon absorption using the Lambert–Beer law and assuming perfect overlap between the dissociation laser and molecular beam.

In the search of the decamer cation configuration space, the pool-BCGA uses the plane-wave self consistent field code within the Quantum Espresso[36] package in local optimizations, where 11 electrons for each Ag atom are

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treated explicitly and the remaining 36 core electrons are captured by ultrasoft Rabe-Rappe-Kaxiras-Joannopoulos pseudopotentials,[38] employing the Perdew-Burke-Ernzerhof (PBE)[39] xc functional. Local optimization is performed with an electronic self consistency criterion of 10^{-5} eV, and total energy and force convergence threshold values of 10^{-3} eV and 10^{-2} eV/Å, respectively. The lowest lying putative GM candidates are subsequently locally optimized using NWChem v6.3,[40] employing an extensive 19-electron def2-tzvpp basis set and the corresponding effective core potential (def2-ecp) of Weigend and Ahlrichs.[41] The long-range corrected xc functional LC-ωPBEh[33] is used in order to accurately recover the asymptotic behaviour of the exchange correlation potential, since this has proven to reliably reproduce vertical electronic excitation spectra.[4,6,8,24,33,34] The theoretical description of optical properties of clusters based on TDDFT calculations is easily applicable and widely used, in particular due to the low computational costs associated with the single-reference character.[42] In minimizations the BP-86[43,44] and M06-L[45] functionals are also studied for comparison purposes. The energy is calculated using a grid of high density (*xfine* integration grid, *tight* optimization criterion). The integral precision is set to 10^{-9} eV while the tolerance on linear dependencies in the overlap matrix has been set to 10^{-6} eV since diffuse basis sets are prone to linear dependencies. Additionally, harmonic frequency analyses are performed in order to verify whether the considered geometries are true minima on the potential energy surface.

Isomers of Ag_{10}^{+} lying within 0.25 eV of the lowest energy structure, sorted by increasing energy at the LC-ωPBEh/def2-tzvpp level of theory, are presented in Figure 1. Beside the isomers **g** and **h** found by Weis *et al.*, the pool-BCGA finds several lower lying isomers (**a-f**). The comparison of relative energies obtained with LC-ωPBEh, BP-86, and M06-L, sorted by increasing LC-ωPBEh energy, is displayed in Figure 2. The employed functionals give the same local minima with minute distortions of bond lengths and angles and they all agree upon the D_{2d} isomer **a** as the GM. However, they differ substantially in the energetic ordering of the higher lying geometries. Isomer **h**, which was predicted to be the GM from ion mobility experiments, becomes the highest lying geometry at the LC-ωPBEh level while it is the second lowest isomer from calculations with the local meta-GGA functional M06-L, recommended for transition metal systems. Thus, our calculations exclude isomer **h** as the GM but also demonstrate the strong dependence of the energetic ordering on basis set and xc functional, as can be seen at the M06-L/def2-tzvpp level, where isomer **h** becomes the second lowest geometry.

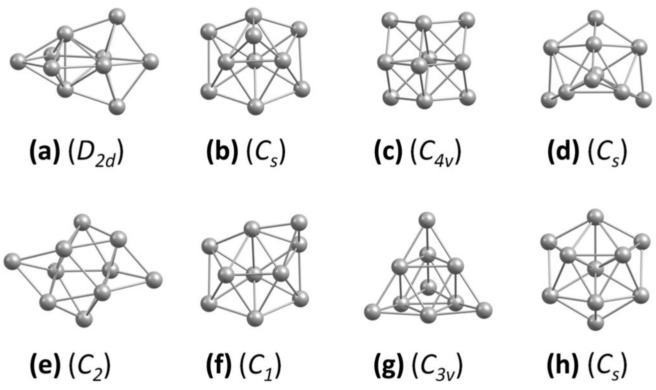

FIG. 1. Lowest lying pool-BCGA isomers of the Ag_{10}^{+} cluster (**a–h**) within 0.25 eV sorted by increasing energy at the LC-ωPBEh/def2-tzvpp level of theory. Point group symmetries are given in brackets. The atomic coordinates are available in the supplementary material.[37]

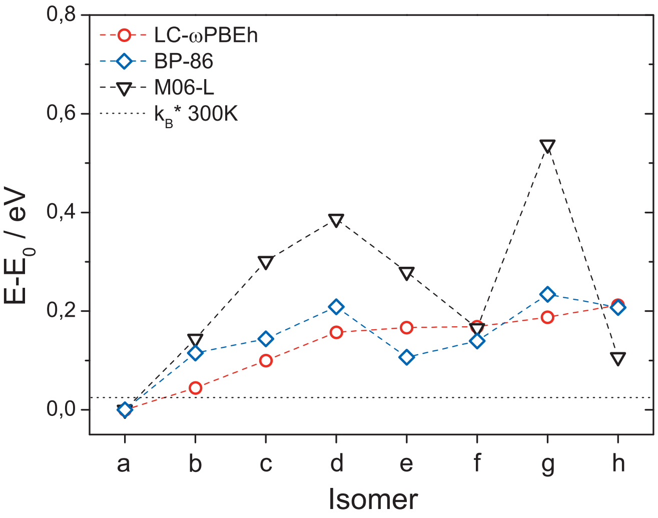

FIG. 2. Lowest lying isomers of the Ag_{10}^{+} cluster relaxed at the LC-ωPBEh/def2-tzvpp level of theory and their relative energies in eV (circles) compared to relative energies from the BP-86 (diamonds) and the M06-L (triangles) xc functional. Dashed lines connecting the data points are a guide to the eye. The horizontal (dotted) line represents the thermal energy at 300 K.

For all geometries resulting from the DFT optimizations, electronic excitation spectra are calculated using spin-unrestricted TDDFT (at the LC-wPBEh/def2-tzvpp level with NWChem v6.3.[40]) with 50 excited state roots to be determined. The optical response calculations are compared to the experimental photodissociation spectrum in Figure 3. It is clear that only isomer **a** qualitatively reproduces the signature of the experimental spectrum, while all other isomers show features which do not match the experimental observation. The pool-BCGA results and local relaxations, as well as the measured absorption spectrum point to isomer **a** being the GM and the only species present in the molecular beam experiment.

In order to compare these results to previous ion mobility experiments, three commonly used theoretical models for calculating the collision cross section of a given ion structure have been used. The EHSS model, the trajectory method including either partial charges (CT-TR) or a uniform charge distribution (EQ-TR), and the projection approximation (PA) are used in order to elucidate the structure of Ag_{10}^{+}. For all structure candidates minimized with the LC-ωPBEh functional, collision cross sections are calculated within the MOBCAL code of Mesleh *et al.*,[46] using the same potential parameters as Weis *et al.*: $\epsilon = 1.35$ meV, $\sigma_{AgHe} = 3.0$ Å, $r_{HardSphere} = 2.57$ Å for Ag–He and $\alpha_{He} = 0.205$ Å^3. For each TR simulation 2×10^6 classical trajectories are run. The partial charges in CT-TR calculations are determined by the Löwdin method,[47] using the LC-ωPBEh functional. Here the smaller def2-svp basis set is used in order to counter the

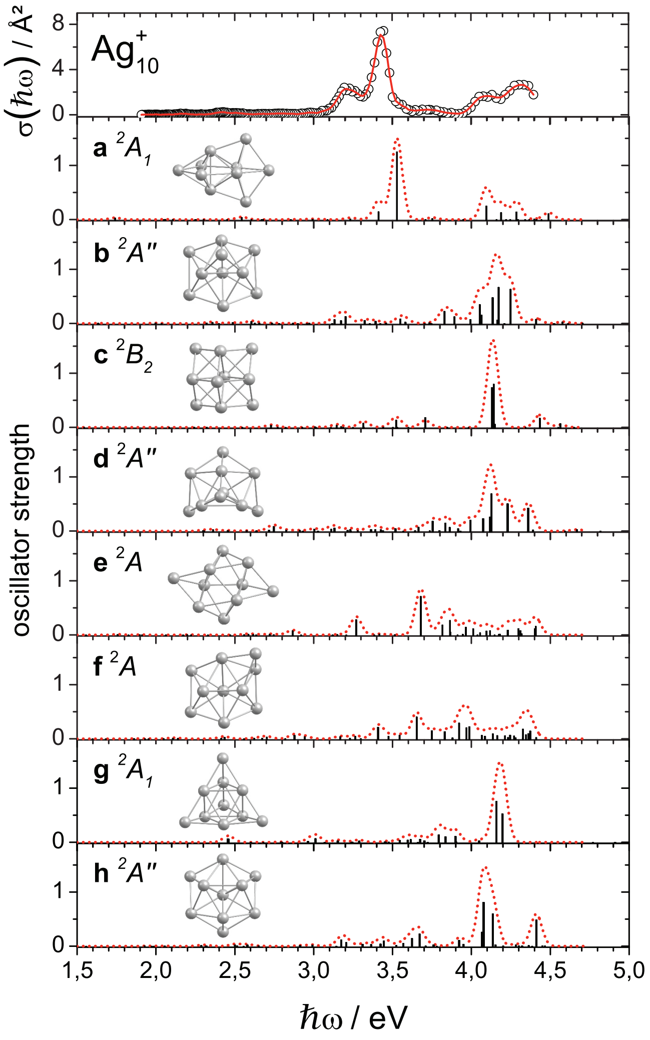

FIG. 3. Experimental Ag_{10}^{+} absorption cross section $\sigma(\hbar\omega)$ data points (open circles) and a 3-pt adjacent average of these to guide the eye (solid line) compared to TDDFT calculations for the lowest lying isomers relaxed at the LC-ωPBEh/def2-tzvpp level of theory. The irreducible representations of the electronic ground states are given. The calculated line spectra (vertical lines) are convoluted with Gaussian functions with a full width at half maximum of 0.1 eV (dotted lines).

common problem of population analyses, based on partitioning the wave function: to predict unphysical charges when using diffuse basis functions.[48] The calculated collision cross sections are shown in Figure 4. The dashed line represents the experimental value within the experimental error range of 5% (pale dotted lines). The EHSS model takes multiple collisions into account but generally overestimates collision cross sections due to neglect of dispersion and ion-induced dipole interactions between the positively charged cluster and the polarizable He atom. The PA tends to underestimate collision cross sections due to the simple projection of the possible hard sphere contact area, which is only a good approximation for convex molecules. In concave molecules multiple collisions must be considered.[49] The trajectory method (TR) includes attractive interactions and allows a specific charge distribution to be taken into account. Here, the comparison of CT-TR (including Löwdin charges) and the EQ-TR (uniform charge distribution) shows only small deviations. This is not surprising since the charge distribution becomes less relevant for larger clusters though the total charge has to be taken into account.

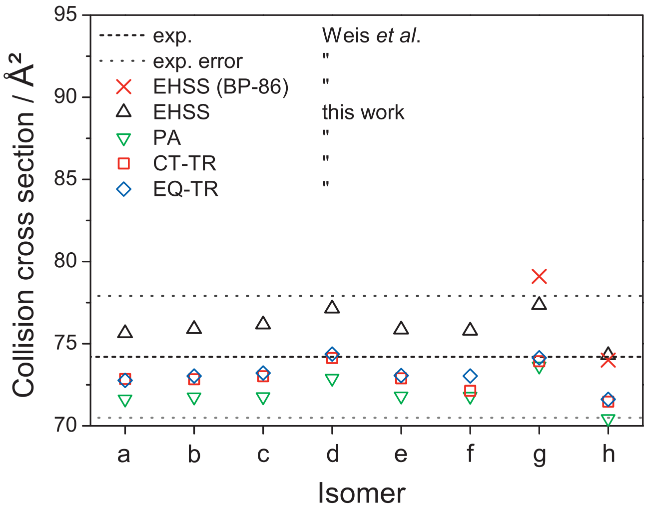

FIG. 4. Experimental collision cross section of Ag_{10}^{+} (dashed line) compared to calculated collision cross sections using the EHSS model for the lowest lying isomers obtained at the BP-86/aug-SVP level (crosses) with RI-J quadrature (experiments and calculations taken from Ref. 27) compared to calculated collision cross sections for cluster geometries from this work obtained with LC-ωPBEh using the EHSS model (triangles), the PA (inverse triangles), the EQ-TR (diamonds), and the CT-TR method (squares) including Löwdin partial charges.

In general, all of the postulated isomers can fit the experimental ion mobility data as nearly all collision cross section calculations, for the different models, remain in the experimental error range. Hence, spectroscopy is necessary for the unambiguous assignment in the case of Ag_{10}^{+}, since the structural differences have a dominant influence on optical absorption spectra.[50]

In conclusion, we have strong evidence that we have identified the true GM structure of the Ag_{10}^{+} cluster from the combination of photodissociation spectra with systematic structural global optimization using genetic algorithms and spectral simulation based on LC-TDDFT calculations. We are therefore confident that the GM structure for Ag_{10}^{+} is composed of two interpenetrating pentagonal bipyramids, generating a structural motif with overall D_{2d} symmetry.

We acknowledge financial support by the DFG (Grant No. SCHA 885/10-2) and the Merck'sche Gesellschaft für Kunst und Wissenschaft e.V. The calculations reported here have been performed on the following HPC facilities: The University of Birmingham BlueBEAR facility (Ref. 51); the MidPlus Regional Centre of Excellence for Computational Science, Engineering and Mathematics, funded under EPSRC Grant No. EP/K000128/1; and via our membership of the UK's HPC Materials Chemistry Consortium, which is funded by EPSRC (EP/F067496), this work made use of the facilities of ARCHER, the UK's national high-performance computing service, which is provided by UoE HPCx Ltd at the University of Edinburgh, Cray Inc. and NAG Ltd, and funded by the Office of Science and Technology through EPSRC's High End Computing Programme.

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