Eur. Phys. J. D **9**, 183–187 (1999)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences
© Società Italiana di Fisica
Springer-Verlag 1999

Structural and optical properties of small oxygen-doped- and pure-silver clusters

V. Bonačić–Koutecký[1], M. Boiron[1], J. Pittner[1,a], P. Fantucci[1,2], and J. Koutecký[3]

[1] Humboldt–Universität zu Berlin, Walther–Nernst–Institut für Physikalische und Theoretische Chemie, Bunsenstrasse 1, D-10117 Berlin, Germany
[2] Dipartimento di Biotecnologie, Università di Milano, Via Emanueli 12/B, I-20126 Milano, Italy
[3] Freie Universität Berlin, Institut für Physikalische und Theoretische Chemie, Takustrasse 3, D-14195 Berlin, Germany

Received: 22 September 1998 / Received in final form: 5 November 1998

Abstract. We present calculations of absorption patterns in large energy intervals for the stable structures of oxygen-doped- and pure-silver clusters using the linear-response-type approach which allows one to correlate all 11 and 6 electrons per Ag and O atoms, respectively. For this purpose, we designed a new 11-electron relativistic effective core potential (11e–RECP) for Ag atoms at the correlated level of theory, which, together with the associated AO basis set, provide an accurate description of excited states. This has been evidenced by the comparison of our results with available experimental data. We found that inclusion of d electrons in the RECP, as well as in the correlation treatment, is important for an accurate prediction of the complete absorption spectra. Moreover, the influence of d electrons of Ag atoms becomes pronounced, even for structural properties of Ag_nO clusters. Also, the electrons of oxygen are strongly involved in excitations besides those of Ag-valence electrons, leading to intense transitions spread in a large energy interval. The role O plays in Ag_nO clusters differs substantially from the one it plays in oxygen-doped alkali clusters, because of the participation of the d electrons of Ag atoms.

PACS. 31.15.Ar Ab initio calculations – 31.15.Dv Coupled cluster theory – 31.50.+w Excited states – 36.40.Mr Spectroscopy and geometrical structure of clusters

1 Introduction

Investigation of the influence of d electrons on structural and optical properties of small Ag_n and Ag_nO clusters motivated us to design a new relativistic 11-electron effective potential (11e–RECP) for the Ag atom. This 11e–RECP and its associated AO basis set were derived at correlated level of theory, and provide an accurate determination of excited states [1]. Therefore, comparison of optically allowed transitions and oscillator strengths calculated for the most stable structures of small Ag_n and Ag_n^+ ($n = 2-4$) clusters with the experimental absorption spectra permitted for identification of geometries responsible for the measured features. This gave us confidence to extend the study to oxygen-doped silver clusters, which are important for elucidating the role of the O atoms as precursors of reaction centers in small Ib metal oxidized clusters.

The experimental optical spectra of cationic Ag_n^+ clusters ($n = 9, 11, 15, 21$) were first obtained by photofragmentation of mass-selected clusters at very high temperature (estimated 2000–3000 K) [2,3]; these spectra are characterized by broad structureless bands. Absorption spectra for neutral Ag_n clusters ($n = 5, 7-9, 11, 13, 15-21$) have been recorded for mass-selected clusters embedded in rare gas matrices [4,5]. In spite of the low temperature ($T \approx 10$ K), the spectra are very broad. More recently, the optical spectra of Ag_n and Ag_n^+ clusters were obtained by photodepleting van der Waals complexes composed of silver clusters and rare-gas atoms [6,7]. These gas-phase experiments at $T = 100$ K gave rise to much narrower bands, in comparison with previous experiments, but the influence of rare-gas atoms remains an open question. New experimental results on optical absorption spectrum of Ag_4^+ in the gas phase have also become available [8]. In contrast, the absorption spectra of oxygen-doped silver clusters have not been recorded yet.

2 Computational

We derived the new 11e–RECP starting from the one proposed by Hay and Wadt [9], which was based on the HF wave function. Since the potential $\hat{V}^{\mathrm{ECP}}(r)$ involves

---

[a] *Permanent address*: J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

operators which are analytically expressed in terms of products of Gaussians and powers of r, the coefficients in the expansion and the exponentials can be considered as free fitting parameters. Therefore, we have carried out the optimization of these parameters for the atomic and diatomic properties at the correlated level of theory based on the configuration interaction (CI) method, using experimental and relativistic Dirac–Fock data as the reference.

The AO basis associated with the new 11e–RECP has also been newly optimized. The most satisfactory results have been achieved with a $(6s5p3d)$ AO basis set contracted to $(5s3p2d)$, which represents a relatively small AO basis, well suited for accurate description of excited states. Details of the method used to derive the new 11e–RECP and the associated AO basis are reported elsewhere [1]. For oxygen atoms the standard ECP [10] has been employed, and the standard $(3s1p/3s1p)$ AO basis set has been extended to $(5s5p1d/4s4p1d)$ in order to obtain accurate transition energies to atomic excited states.

Studies of the absorption spectra usually require the determination of a large number of electronic states of the same symmetry. In earlier work (cf. [11]) the multireference single double configuration interaction (MRD–CI) and the multiconfiguration linear response (MCLR) methods [12] have been employed to determine the absorption spectra of alkali metal clusters [13]. Both approaches can treat at the same footing the double and single excitations as reference configurations, but the application of these methods is limited to a relatively small number of electrons. Since all 11 valence electrons for each Ag atom need to be correlated, we have adopted in the present study the equation-of-motion coupled-cluster (EOM–CC) method [14], also known as the coupled-cluster linear response, which is based on the single-reference coupled-cluster method including single and double excitations (CCSD). In comparison with the full CI results available for the test examples, we found that the EOM–CCSD method gives reliable excitation energies and oscillator strengths for the transitions dominated by single excitations. Less accurate results are expected for the excited states, which have an appreciable double-excitation character. Due to the fact that the intense transitions are usually dominated by single excitations, the EOM–CCSD method is well suited for determination of absorption spectra.

Since the aim of this paper is to provide an adequate description of excited states of clusters, the most severe test for the accuracy of the new 11e–RECP is the comparison of our theoretical results for ground and excited states of the Ag_2 dimer with the corresponding experimental data. We found that the new 11e–RECP with associated AO basis set used in the framework of EOM–CCSD yields a description of excited states of Ag_2 in a large energy interval with an accuracy never achieved with previous versions of RECP. Therefore, the presented computational scheme is well suited for investigation of absorption spectra of small pure- and doped-silver clusters.

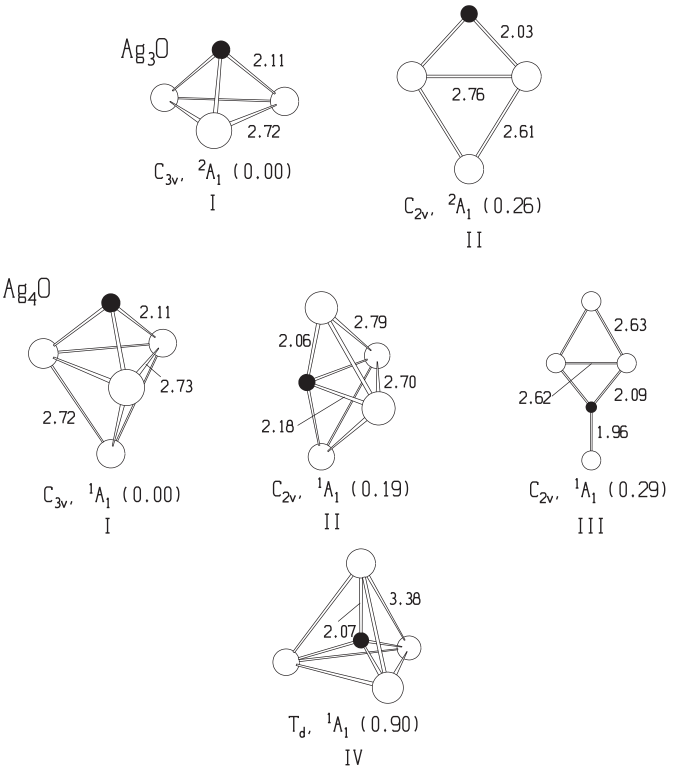

Fig. 1. The optimized structures of Ag_3O and Ag_4O clusters at the CCSD level of theory corresponding to the local minima on the ground-state energy surfaces. The relative energies in eV with respect to the most stable isomer I are also given.

3 Structural and optical properties of oxygen-doped- and pure-silver clusters

The most stable structures of Ag_3O and Ag_4O assume C_{3v} symmetry with the oxygen atom occupying the face-bridge position (μ_3, isomer I). The isomers corresponding to the local minima on the energy surfaces obtained in the framework of CCSD geometry optimization are given in Fig. 1. Notice that in the case of oxygen- doped silver clusters, the explicit inclusion of d electrons in the RECP, as well as in the correlation treatment, is of crucial importance for the determination of geometries. In the second isomer of Ag_3O with the C_{2v} symmetry, the side-bridge (μ_2) coordinated O atom also takes peripheral position, but this isomer has an energy higher by 0.26 eV than that of the isomer I. In contrast, alkali metal-doped trimers such as Li_3O and Na_3O assume planar C_{2v} structures with centrally placed O atoms [15].

In the case of Ag_4O, we found, in addition to the lowest energy isomer I with a μ_3 oxygen atom (C_{3v}), two local minima with a four-coordinated O atom of C_{2v} and T_d symmetry, as well as a planar C_{2v} isomer with a three-coordinated O atom, as is depicted in Fig. 1. Again the T_d structure with the centered O atom has very high energy (0.9 eV) with respect to the isomer I, in contrast to the Li_4O and Na_4O, in which case the T_d structures are the lowest energy isomers [15].

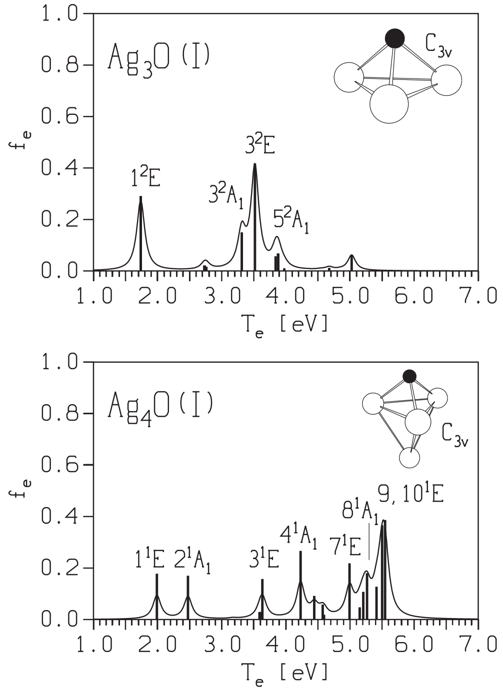

Fig. 2. Optically allowed transitions T_e in eV and oscillator strengths f_e obtained from the EOM–CC calculations for the lowest-energy structures of Ag_3O and Ag_4O.

A special role played by the O atom in the silver coordination environment is particularly pronounced in spectroscopical patterns. The calculated spectra for the lowest energy isomers of Ag_3O and Ag_4O are shown in Fig. 2. The peripheral oxygen participates in the leading excitations, giving rise to the intense transitions. Therefore, neither structural nor optical properties indicate separation into “oxide” and “metallic” parts. Also, the sum of oscillator strengths for the transitions calculated in the sufficiently large energy intervals exceeds values of excess valence electrons (1 or 2) for Ag_3O and Ag_4O, respectively. For both C_{3v} structures of Ag_3O and Ag_4O, it is characteristic that the first intense transitions lie in a low-energy visible region ≤ 2 eV. The calculated spectrum of Ag_3O is dominated by two transitions to 3 ^{2}E and 1 ^{2}E states located at 3.5 and 1.7 eV, respectively. In the case of Ag_4O, the intense transitions are distributed over a large energy interval, giving rise to a very rich spectroscopic pattern. The fact that the dominant transition lies at 5.5 eV indicates that it is important to carry out the calculations in a large energy interval. Correspondingly, the recorded spectra can reflect structural properties in a more complete way if the large energy interval is accessible. The experimental absorption spectra for oxygen-doped silver clusters are not yet available.

In contrast, the calculated spectra for small neutral and cationic pure silver clusters can be compared with the experimental results, as shown in Fig. 3 for the example of tetramers. It is known from the previous work using 1e–RECP with core valence correlation [16] that the most stable isomers of Ag_4 and Ag_4^+ assume rhombic structures. In fact, the structural properties of pure silver clusters remain qualitatively unchanged by the inclusion of *d* electrons in the RECP and in the correlation treatment for geometry optimization. We confirmed this by identifying the isomers at the CCSD level of theory using the new 11e–RECP. The question addressed in this contribution concerns mainly the influence of *d* electrons on absorption spectra of Ag_4 and Ag_4^+.

The calculated spectrum for the rhombic structures of Ag_4 is characterized by (a) a dominant transition to the 1 $^1B_{1u}$ state located at ~ 3.2 eV; (b) two transitions to 2 $^1B_{2u}$ and 1 $^1B_{3u}$ state with the same energies ~ 4.2 eV but different oscillator strengths ($f_e = 0.66$, $f_e = 0.27$); and (c) a large number of higher energies transitions with considerable intensities (e.g., 12 $^1B_{1u}$ state at ~ 6.7 eV with $f_e = 0.56$). The analysis of the leading excitations contributing to dominant transitions indicates that a direct involvement of *d* electrons is present in the wave function of 2 $^1B_{2u}$ and 12 $^1B_{1u}$ states (with considerably larger contributions for the latter one), but not in the case of 1 $^1B_{1u}$ and 1 $^1B_{3u}$ states. In fact, the location of the lowest-energy intense transition to 1 $^1B_{1u}$ remaines unchanged in the simplified treatments, allowing one only to correlate *s* electrons or to use 1e–RECP, but this is not the case for other, higher-energy intense transitions.

The calculated spectrum for the rhombic structure of Ag_4^+ is characterized by the dominant transition to the 2 ^2A_g state located at 3.25 eV and the considerably weaker transitions to 3 $^2B_{2g}$, 4 $^2B_{2g}$, and 7 $^2B_{3g}$ states at 4.25, 4.7, and 6.1 eV, respectively. The direct involvement of *d* electrons in the leading excitations is present in the wave function of the lowest-energy intense transition (2 ^2A_g), although the contribution is significantly lower than in the case of 4 $^2B_{2g}$ and 7 $^2B_{3g}$ states.

The experimental depletion spectra, obtained by depleting van der Waals complexes of Ag_4 and Ag_4^+ with Kr atoms, as shown in Fig. 3, are limited to the energy interval below 5.0 eV, and the influence of the number of Kr atoms has been found only in the case of cationic complexes. The measured features of both Ag_4Kr_2 and $Ag_4Kr_2^+$ complexes are characterized by one transition with high intensity at 3.0 and 3.1 eV, respectively, and by one weaker band located at 4.2 and 4.6 eV, respectively. The cross sections are smaller in the case of the cationic complex. The measured global features are well reproduced by the calculated spectra for the D_{2h} lowest-energy isomers of Ag_4 and Ag_4^+ clusters, as shown in Fig. 3. The question that remains is to what extent the presence of Kr atoms causes geometry changes which might be responsible for the slight deviation in locations of the intense transitions at ~ 3 eV and ~ 4.2 eV with respect to our prediction of ~ 3.2 eV and ~ 4.3 eV for the rhombic structure of Ag_4. Also, the rhombic structure of Ag_4^+, with dominant transition at ~ 3.2 eV, and weaker ones at 4.2 and 4.7 eV, reproduces in a very satisfactory way the recorded spectrum.

The gas-phase results on Ag_4^+ by Terasaki, Kondow, *et al.* [8] exhibit intense transitions at 3.1, 4.0, and 4.35 eV, which are slightly red-shifted with respect to our results. Based on the comparison between experimental and theoretical results, we propose the assignment of rhombic structures to the measured features of Ag_4 and Ag_4^+ clusters.

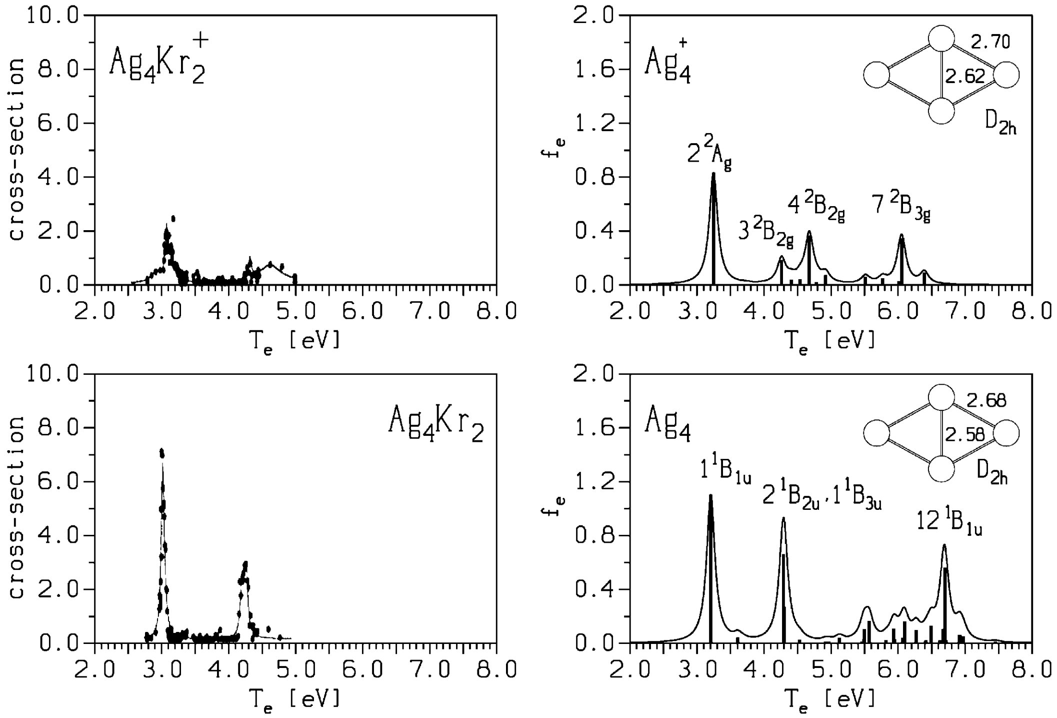

Fig. 3. Optically allowed transitions T_e in eV and oscillator strengths f_e, obtained from the EOM–CC calculations using new 11e–RECP with associated AO basis for the lowest-energy structures of Ag_4 and Ag_4^+. The optimized geometries at the CCSD level of theory with bond lengths in Å are drawn. For comparison, photodepletion spectra of Ag_4 and Ag_4^+, obtained by depleting van der Waals complexes of the silver clusters with Kr atoms [7], are presented.

4 Conclusions

The new 11e–RECP for Ag atoms derived at the correlated level of theory and the associated AO basis set provide an accurate description of excited states of pure- and oxygen-doped-silver clusters. This has been evidenced by calculations of absorption patterns in large energy intervals for the stable cluster structures based on the linear-response-type approach EOM–CCSD, allowing us to correlate all 11 and 6 valence electrons per Ag and O atoms. Notice that small silver and sodium (neutral and cationic) clusters have common structural properties but that their spectroscopic patterns exhibit important differences.

The inclusion of *d* electrons in the correlation treatment is important for an accurate prediction of the complete absorption spectra, although their direct involvement in leading excitations is not always present or dominant, in particular in lower-energy intervals. The influence of *d* electrons of Ag atoms becomes pronounced even for structural properties of Ag_nO $(n = 3, 4)$ clusters. The oxygen atom prefers a μ_3 peripheral position in Ag_3O and Ag_4O clusters, in contrast to the case of the Na_nO and Li_nO $(n = 3, 4)$ species, where the O atom is at the center of the metal cage.

For the lowest-energy C_{3v} structures of Ag_3O and Ag_4O, the electrons of the oxygen atom are strongly involved in the excitations, as well as the Ag *s* valence electrons. The resulting intense transitions are spread in a large energy interval. There is no evidence for segregation into non-metallic (oxide) and metallic parts; this is certainly due to the small size of the considered clusters. The oxygen atom's role in Ag_nO clusters differs substantially from the one played in Na_nO and Li_nO clusters, due to the participation of *d* electrons of Ag atoms.

The investigation of structural and optical properties of oxygen-doped silver complexes reported here represents a first step in a more general study of the possible catalytic role of Ib clusters for oxidation reactions.

This work has been supported by the Deutsche Forschungsgemeinschaft (Sfb 337, Energy transfer in molecular aggregates) and the Consiglio Nationale delle Ricerche (CNR, Rome). We thank Professor P.A. Hacklett and Professor T. Kondow for communicating their results prior to publication.

References

1. V. Bonačić–Koutecký, J. Pittner, M. Boiron, P. Fantucci: J. Chem. Phys. **110**, 3876 (1999)
2. J. Tiggesbäumker, L. Köller, H.O. Lutz, K.H. Meiwes–Broer: Chem. Phys. Lett. **190**, 42 (1992)
3. J. Tiggesbäumker, L. Köller, K.H. Meiwes–Broer, A. Liebsch: Phys. Rev. A **48**, R1748 (1993)
4. W. Harbich, S. Fedrigo, J. Buttet: Chem. Phys. Lett. **195**, 613 (1992)
5. S. Fedrigo, W. Harbich, J. Buttet: Phys. Rev. B **47**, 10 706 (1993)
6. B.A. Collings, K. Athanassenas, D.M. Lacombe, D.M. Rayner, P.A. Hackett: J. Chem. Phys. **101**, 3506 (1994)

7. M. Rayner, K. Athanassenas, B.A. Collings, St.A. Mitchell, P.A. Hackett: in press
8. A. Terasaki, S. Minemoto, M. Iseda, T. Kondow: in *Proceedings of ISSPIC 9,* 1998
9. P.J. Hay, W.R. Wadt: J. Chem. Phys. **82**, 299 (1985)
10. J.W. Stevens, H. Basch, H. Krauss: J. Chem. Phys. **81**, 6026 (1984)
11. V. Bonačić–Koutecký, P. Fantucci, J. Koutecký: Chem. Rev. **91**, 1035 (1991); V. Bonačić–Koutecký, L. Češpiva, P. Fantucci, C. Fuchs, J. Koutecký, J. Pittner: "Quantum chemical interpretation of optical response of small metal clusters", in *Comments on Atomic and Molecular Physics*, **31**(3–6), 233 (1995), and references therein
12. C. Fuchs, V. Bonačić–Koutecký, J. Koutecký: J. Chem. Phys. **98**, 3121 (1993)
13. V. Bonačić–Koutecký, J. Pittner, C. Fuchs, P. Fantucci, M.F. Guest, J. Koutecký: J. Chem. Phys. **104**, 1427 (1996)
14. J.F. Stanton, R.J. Bartlett: J. Chem. Phys. **98**, 7029 (1993)
15. V. Bonačić–Koutecký, J. Pittner, R. Pou–Amerigo, M. Hartmann: Z. Phys. D **40**, 445 (1997)
16. V. Bonačić–Koutecký, L. Češpiva, P. Fantucci, J. Koutecký: J. Chem. Phys. **98**, 7981 (1993)