Journal of Molecular Structure: THEOCHEM 717 (2005) 91–97

THEO CHEM

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Ab initio study of coinage metal telluride clusters $(M_2Te)_n$ ($M=Cu$, Ag, Au; $n=2, 3$)

Qi-Mu Su Rong[a,b], Yongfang Zhao[a,*], Xiaogong Jing[a], Xinying Li[a], Wenhui Su[a]

[a]Department of Physics, Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, People's Republic of China
[b]Institute of Computational Physics, Inner Mongolia University for Nationalities, Tongliao 028043, People's Republic of China

Received 2 April 2004; revised 9 September 2004; accepted 9 September 2004
Available online 22 January 2005

Abstract

Coinage metal telluride clusters $(M_2Te)_n$ ($n=2, 3$; $M=Cu$, Ag, Au) are studied by ab initio calculations including electron correlation at the Møller–Plesset second-order perturbation theory (MP2) level. The relativistic and non-relativistic pseudopotentials are employed to describe the core electrons. Various stable isomers are found for clusters, and the energy separations are rather small with energy hypersurfaces that are very shallow. The electron correlation and relativistic effects on geometrical structures and relative stabilities of various isomers are discussed.

Keywords: Coinage metal telluride cluster; Electron correlation; Relativistic effect

1. Introduction

Coinage metal clusters, especially clusters containing copper, silver and gold, are of great importance since the clusters are widely used in catalysis, microelectronics and light-sensitive non-linear optical materials. The structures of the clusters $(Cu_2Se)_n$ have been characterized experimentally. They have short Cu–Cu distances (down to 2.40 Å) and small Cu–Se–Cu angles (below 70°) [1]. The clusters Ag_nS_m and Au_nS_m were already examined by mass spectrometry [2]. Theoretically, the Cu_2S, Ag_2S and $(Cu_2Se)_n$ ($n=1$–6) systems were already studied in detail by Ahlriichs et al. [3–7], and Dixon et al. [8]. Li and Pyykkö have performed calculations for the related Ag_2Se $(AgPH_3)_2Se$, Au_2Se and $(AuPH_3)_2Se$ [9], while Alemany et al. considered only Ag_2Se and Au_2Se [10]. They found that the inclusion of electron correlation does not essentially change the electronic structure of clusters, but has a strong influence on geometries. Not long ago, small semiconductor silver and gold sulfide clusters $(Ag_2S)_n$ and $(Au_2S)_n$ ($n=1$, 2) were studied in detail by Bagatur'yants et al., using relativistic and non-relativistic pseudopotentials, and the understanding of relativistic effect and electron correlation effects on geometrical structure and stability has been obtained [11].

The new research direction opened by previously mentioned groups was to study systematically the whole $(M_2Te)_n$ series ($M=Cu$, Ag, Au; $n=1, 2, 3$), in order to have an insight into the evolution of the structure and stability of these types of clusters. Recently, we studied [12, 13] the monomers M_2Te ($M=Cu$, Ag, Au) and found out that electron correlation has a strong influence on the bond angles but does not change the bond lengths of the monomers significantly. The relativistic effects lead to shorter M–Te bond length, lower energies, and increased vibrational frequencies. Therefore, the relativistic effects make the monomers more stable. To our knowledge, the telluride clusters containing copper, silver and gold $(M_2Te)_n$ ($n=2, 3$; $M=Cu$, Ag, Au) have not been studied both by experiment and by theoretical approaches. However, these clusters should have a close relationship with the above mentioned clusters $(M_2S)_n$ and $(M_2Se)_n$ ($M=Au$, Ag, Cu) because of their analogous valence electron configuration.

In the present work, we extend the recent investigation on monomers M_2Te ($M=Cu$, Ag, Au) [12,13] to $(M_2Te)_n$

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* Corresponding author. Fax: +86 451 8641 2828.
E-mail address: xgjing@hope.hit.edu.cn (Y. Zhao).

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doi:10.1016/j.theochem.2004.09.026

(n = 2, 3; M = Cu, Ag, Au). Characteristic structural features of the clusters are deduced to help rationalize the relative stability of various isomers. From the calculations, we achieve insight into the energetics of the clusters that is not measurable experimentally, and elucidate the role of relativistic and electron correlation effects on structures of various isomers. In particular, we present results for bonding energies of $(M_2Te)_n$ (n = 2, 3; M = Cu, Ag, Au) from which the energetic instability towards further cluster growth can be assessed. Considering our calculated results are in good agreement with the available data of above mentioned clusters [1–11], which have analogous valence electron configurations, we expect that the values for whole $(M_2Te)_n$ (n = 1, 2, 3; M = Cu, Ag, Au) are reasonable estimates, even though no experimental data are available at present.

2. Methods and basis sets

The suitability of methodological aspects is based on the results of Schäfer et al. [3,4] on copper–selenium clusters $(Cu_2Se)_n$ (n = 1–6), where they applied various quantum chemical methods up to high-level treatments, such as the coupled cluster formalism restricted to single and double excitations (CCSD) and augmented by a perturbational estimate for triple excitations (CCSD(T)). It turned out that the inclusion of dynamic electron correlation is essential for structures, with the Møller–Plesset second-order perturbation theory (MP2) being sufficiently accurate as compared to CCSD(T). Schwerdtfeger and Boyd [5], as well as Li and Pyykkö [9] also recommended the MP2 as a reliable method for the study of weak dispersion type interactions.

In our recent work on monomers M_2Te (M = Au, Ag, Cu) [12,13], we obtained the geometries, vibrational frequencies, dipole moments and dissociation energies at the levels of the Hartree–Fock (HF), MP2, CCSD and CCSD(T) with the effective small-core pseudopotential (LANL2DZ) given by Hay and Wadt [18–20]. In the LANL2DZ, the number of valence electrons is 19 for coinage metal atoms (Cu, Ag and Au) which are composed of valence-shell $(n-1)d^{10}$ ns and inner-shell $(n-1)s^2(n-1)p^6$ (n = 4 for Cu, n = 5 for Ag, and n = 6 for Au) configurations. The number of valence electrons is 24 for Te atom, including valence-shell $4d^{10}5s^25p^4$ and inner-shell $4s^24p^6$ configurations.

In order to elucidate the role of the relativistic effects, we performed further relativistic and non-relativistic calculations with the relativistic and non-relativistic energy-consistent pseudopotentials (RECP and NRECP) [14–17] for the stable structures of the clusters. The RECP and NRECP also include eight lower-lying electron shells $(n-1)s^2(n-1)p^6$ (n = 4 for Cu, n = 5 for Ag and n = 6 for Au) into the valence shell.

The basis sets given by Andrae et al. were used for Au and Ag atoms [21], and the one given by Dolg et al. was used for Cu atom [22]. The f-type diffuse functions, which $\alpha_f = 0.2$ for Au, $\alpha_f = 0.22$ for Ag and $\alpha_f = 0.24$ for Cu, are added to coinage metal atoms respectively. For Te atom, the basis set given by Bergner was used [23].

All calculations are performed using the GAUSSIAN 98 [24] program package.

3. Results and discussion

All stable isomers we have identified so far for clusters $(M_2Te)_n$ (n = 1, 2, 3; M = Au, Ag, Cu) are shown in Fig. 1. They are a bent structure I of C_{2v} symmetry for monomers; two distorted rhomboidal structures II, III of C_{2h}, C_{2v} symmetries and a bipyramidal structure IV of D_{4h} symmetry

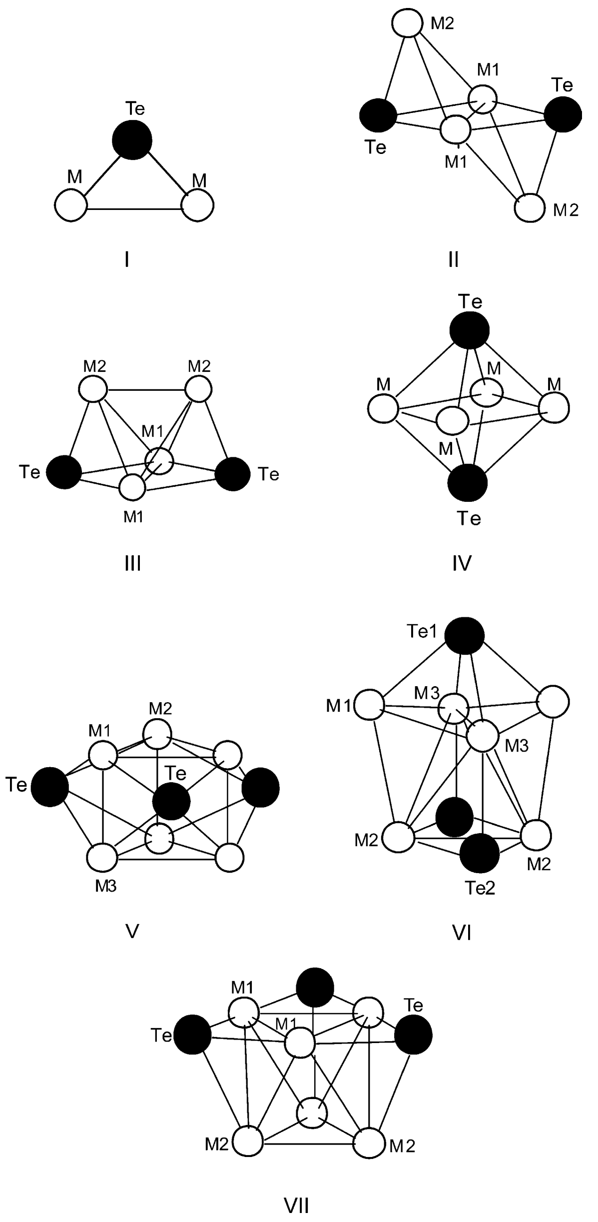

Fig. 1. The locally stable structures of isomers; the tellurium atom is designated by black circles and the coinage metal atoms by white circles.