Ab initio pseudopotential study of cluster growth of coinage metal telluride clusters Au_nTe_m

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Abstract. The geometries of the lowest-lying isomers of small Au_nTe_m (n, m=1, 2) clusters are determined through the MP2 method. The aspect of gold-telluride interaction, the electron correlation and relativistic effects on geometry, and cluster growth are investigated at the MP2 and CCSD(T) theoretical levels. The results show that the gold-telluride interaction is strong enough to modify the known pattern of bare gold clusters. The electron correlation and relativistic effects are responsible not only for gold-gold attraction but also for additional gold-telluride interaction. Both electron correlation and relativistic effects are essential for determining the geometry and cluster growth of coinage metal telluride compound clusters Au_nTe_m.

1   Introduction

The study of coinage metal mixed clusters, especially the clusters consist of coinage metals mixed with 16 group atoms, is nowadays an important field of research in cluster science since the clusters are widely used in protein, catalysis, microelectronics and so on [1]. The relevant physical and chemical properties, greatly determined by the cluster size, represent great advantages compared to other molecular systems as far as nanostructured materials technology is concerned. The unique characters of this type of clusters are the dramatic effect of gold-mixed atom interaction, electron correlation and relativistic effects that directly influence the structure, stability and cluster growth.

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There exists a considerable amount of theoretical studies on different properties of clusters consisting of coinage metals mixed with 16 group atoms [2–4]. Recently, the structural properties of small clusters Au_nS (n=1-5) and Au_nS_2 (n=1-4), and the aspect of gold-sulphur interaction and its effects on the most stable geometries of the clusters, have been studied by Bravo-Prez *et al*. [5]. In Refs. [6–12], we investigated the small coinage metal telluride clusters $(M_2Te)_n$ (M=Cu, Ag, Au; n=1, 2, 3) and M_nPo (M=Cu, Ag, Au; n=1, 2) systems, and found out that the electron correlation has a strong influence on the bond angle of the clusters but does not change the bond length significantly. The relativistic effects lead to shorter M-Te bond length, lower energies, and increased vibrational frequencies. However, the cluster growth of coinage metal telluride clusters Au_nTe_m, especially the aspect of gold-telluride interaction, electron correlation and relativistic effects on cluster growth have not been studied systematically both by experiment and theoretical approaches.

In this paper, we investigate the aspect of cluster growth and structural properties of coinage metal telluride clusters Au_nTe_m up to n, m = 1, 2. From the calculation, we not only achieve an insight into the energetic of the various isomers that have not been measured experimentally, but also gain characteristics of the gold-telluride interaction, electron correlation and relativistic effects on cluster growth. As the calculated results are in good agreement with our previous results [2–12], we expect that these values are reasonable estimates, even though no experimental data are available at present.

In Section 2, we briefly describe our theoretical approach. Results for investigation are given in Section 3. Section 4 contains a summary of our results.

2   Computational details

The Møller-Plesset second order perturbation theory method (MP2) was used to determine the total energy of the lowest-lying isomers of the clusters. For the Au atom, the relativistic effective small-core pseudopotential (LANL2DZ) and the basis sets of Hay and Wadt (HW) [13] have been used. Under this approximation, the $5d^{10}6s$ outermost valence electrons of the Au atoms are described through a double-zeta (DZ) basis set $(3s3p3d)/[2s2p2d]$. The p exponents of the basis set were optimized considering the best agreement with the experimental spectroscopic values of the Au_2 dimer [14]. For the Te atom, an ECP and DZ basis set given by Hay and Wadt [15] has been used taking the $3s^23p^4$ as valence electrons, and one d function was also included with an optimized exponent.

The electron correlation effects are investigated at the Møller-Plesset second order perturbation theory method (MP2) and the coupled cluster formalism restricted to single and double excitation augmented by a perturbational estimate for triple excitation (CCSD(T)) theoretical levels employing the above mentioned pseudopotential and basis sets (HW) [13–15]. In order to elucidate the role of relativistic effects on structure and stability, we carried out further relativistic and nonrelativistic calculations on the most

Table 1: Bond lengths r(Å), vibrational frequencies ν (cm^{-1}), dissociation energies D_0 (eV) and generalenergies E (a.u.) of stable states for Te$_2$ and AuTe dimers calculated at the MP2 level

Species	Structure	State/Group	r	ν	D_0	E
Te$_2$	(Te-Te)	$^3\sum_g / D_{\infty h}$	2.56	191	2.59	-15.777
			2.56[a]	2.49[a]	2.63[a]	
		$^1\sum_g / D_{\infty h}$	2.78	171	3.20	-15.753
		$^5\sum_u / D_{\infty h}$	3.80	45	2.15	-15.687
AuTe	I(Au-Te)	$^2\sum^+ / C_{\infty h}$	2.60	190	3.12	-142.502
				212[b]	242[b]	
		$^4\sum^- / C_{\infty h}$	2.78	112	2.09	-142.464

[a]Taken from Ref. [26]

[b]Taken from Ref. [27]

stable structures of the clusters with the relativistic (R) and nonrelativistic (NR) energy-consistent pseudopotentials (RECP and NRECP) and basis sets [16, 17] at the MP2 theoretical level.

All calculations are performed using Gaussian 03 program package [18].

3 Results and discussion

3.1 Dimers Te$_2$ and AuTe

The calculated total energy E, equilibrium distance r, vibational frequency ν, and dissociation energy D_0 for dimer Te$_2$ and AuTe are reported in Table 1.

Our calculations indicate that the ground state of dimer AuTe is $^2\sum^+$, dissociating into Te (^{3}P$_g$) + Au (^{2}S$_g$), and the $^4\sum^-$ state corresponds to the first excited state. For molecule Te$_2$, the ground state is $^3\sum_g$, dissociating into Te (^{2}S$_g$) + Te (^{2}S$_g$), and the $^1\sum_g$ state corresponds to the first excited state.

Both the equilibrium bond length and vibrational frequency of dimer AuTe, in the ground state, have an intermediate value with respect to those of the Au$_2$ [19,20] and Te$_2$ molecules. On the other hand, the dissociation energy of AuTe dimer shows a weaker bond as compared to the homonuclear molecules, but still reflecting a relatively strong gold-telluride interaction.

3.2 Trimers Au$_2$Te and AuTe$_2$

Fig. 1 shows the results of all stable isomers obtained by one and two Te atom substitutions on the Au$_2$ and Au$_3$ clusters [19,20]. The properties of all stable isomers in different spin multiplicities are given in Tables 1 and 2 respectively. The results show that the ground state of both trimer, Au$_2$Te and AuTe$_2$, is bent structure (isomer II and IV) of C$_{2v}$ symmetry being Au$_2$Te more stable than AuTe$_2$. The bent structure of both trimer, II and IV, shows a relaxed Au-Au and Te-Te distances with respect to the equilibrium distances

of Au_2 [19, 20] and Te_2 (Table 1), but the Au-Te bond length remains unaltered essentially compared to the calculated values for dimer AuTe (Table 1). This reflects the strong gold-telluride interaction in this type of binary Au_nTe_m clusters.
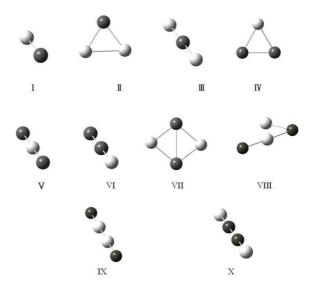

Figure 1: The locally stable structures of isomers; the tellurium atom is designated by black ball and the coinage atom by white ball.

Except for bent structures II and IV, linear structures III, V and VI are detected also as stable isomers. For both trimers, linear structures III (Au-Te-Au) and V (Te-Au-Te) that break the Au-Au and Te-Te bond come next in energy. For $AuTe_2$, except for structures V (Te-Au-Te), another linear structure VI (Te-Te-Au), which does not break the Te-Te bond, appeared as the least stable isomer. These results are consistent with the relatively strong gold-telluride interaction of the dimer AuTe and the higher stability of AuTe than Te_2.

These structural aspects reflect the degree of distortion that the Te atom can produce on the geometry of bare gold cluster and the gold-telluride interaction is strong enough to modify the known pattern of bare gold clusters.

It is notorious the lack of a clear pattern relating the cluster stability and spin multiplicity. From Table 2 we can see that the ground state is bent structure II and IV of the lowest spin multiplicities. However, for linear structures III, V and VI, their stable isomers are in the quintet and quartet spin multiplicities. These results show the importance of considering different spin multiplicities when investigate this type of binary Au_nTe_m clusters.

3.3   Tetramers Au_2Te_2

The trial geometries used in the geometry optimizations of the Au_2Te_2 were the isomers of the Au_4 previously investigated: rhombic, $T(C_{2v})$, and tetrahedral geometries [19, 20].

Table 2: Geometries (r in Å, θ in deg.), general energies E (a.u.) and relative energies ΔE (kJ/mol) of all stable states for trimers Au_2Te and $AuTe_2$ calculated at the MP2 level.

Species	Structure[a]	State / Group	r(Au-Te)	r(A-A)[2]	θ(A-B-A)[b]	E
Au_2Te	II(Au-Te-Au)Bent	$^1A_1/C_{2v}$	2.62	3.06	71.54	-277.168
		$^3B_1/C_{2v}$	2.83	2.74	57.96	-277.124
		$^5B_1/C_{2v}$	2.91	2.75	56.48	-277.065
		$^7B_1/C_{2v}$	3.03	3.25	64.90	-276.875
	III(Au-Te-Au) Linear	$^5\sum_u/D_{\infty h}$	2.96		180.0	-277.048
$AuTe_2$	IV(Te-Au-Te) Bent	$^2A_2/C_{2v}$	2.73	3.03	67.59	-150.402
		$^4B_1/C_{2v}$	2.98	2.78	55.62	-150.378
		$^6A_1/C_{2v}$	3.19	2.77	51.42	-150.174
	V(Te-Au-Te) Linear	$^4\sum_u/D_{\infty h}$	2.62		180.0	-150.389
	VI(Te-Te-Au) Linear	$^4\sum/C_{\infty h}$	3.02	2.68	180.0	-150.364
Au_2Te_2	VII Rhombus	$^3B_{3u}/D_{2h}$	2.68	3.06	69.71	-285.082
	VIII Bent (Au-Te-Au-Te)	$^1A'/C_s$	2.63/2.59/2.51	3.04	71.29	-285.047
	IX Linear (Te-Au-Au-Te)	$^5\sum_u/D_{\infty h}$	2.62	2.69	180.0	-285.013
	X Linear (Au-Te-Te-Au)	$^5\sum_u/D_{\infty h}$	3.02	2.82	180.0	-284.957

[a] As illustrated in Fig. 1.

[b] A=Au, B= Te for structure II, III, VIII, IX and A=Te, B=Au for structure IV, V, VI, VII, X.

In addition, we also consider a trapezoidal form obtained from the parallel approach of the Au_2 and Te_2 dimers, and linear configurations. The calculated lowest-energy structures are shown in Fig. 1, and their properties are also reported in Table 2. The results indicate that the rhombic structure is the most stable isomer as it also occurred in the Au_4 cluster optimizations [19, 20].

We can see from the Table 2 that the importance of considering different spin multiplicities is emphasized again by the spin multiplicity for rhombus and linear structures is triplex and quintet.

3.4   Electron correlation effect

The results calculated at different theoretical levels of electron correlation are reported in the Table 3. The results obtained at the highest theoretical level CCSD(T)/PP may serve as reference values. Comparing the results of MP2 with CCSD(T), we find that the fluctuations of bond length and bond angle are fallen into an extremely small region of 0.05 Å, 0.07 e for Au_2Te, and 0.13 Å, 0.63 e for $AuTe_2$, respectively. It means that the MP2 method is sufficiently accurate and that it essentially can reflect the electron correlation effect within the theoretical level of performing calculation with the above methods. Schwerdtfeger and Boyd [21], as well as Li and Pyykk [22] also recommended the MP2 as a reliable method for the study of weak dispersion type interactions between coinage metal atoms. Therefore, we discuss the electron correlation and relativistic effects at the MP2 theoretical level.

By definition, the electron correlation corrections of structure parameters, such as

Table 3: Geometries (r in Å, θ in deg.), vibrational frequencies ν (cm^{-1}), dipole moments μ(debye) and dissociation energies D_0 (eV) of the most stable states for Au$_n$Te$_m$ (n, m=1, 2) clusters calculated at the different correlation levels

Species	Method	Structure[a]	S	r(Au-Te)	r(Au-Au)	r(Te-Te)	θ(A-B-A)[b]	ν	μ	D_0
AuTe	HF	I	2	2.64				166	3.49	2.51
	MP2	I	2	2.60				190	3.48	3.12
	CCSD(T)	I	2	2.62				179	3.48	3.44
Au$_2$Te	HF	II Bent	1	2.63	3.81		93.11	36/176/180	4.16	3.44
	MP2	II Bent	1	2.62	3.06		71.54	51/156/201	4.66	5.35
	CCSD(T)	II Bent	1	2.63	3.07		71.47	48/152/195	4.70	5.22
	HF	III Linear	5	4.41			180.0	3/4/5/5	0.00	1.37
	MP2	III Linear	5	2.96			180.0	19/19/26/44	0.00	2.12
	CCSD(T)	III Linear	5	2.91			180.0	16/16/54/66	0.04	2.86
AuTe$_2$	HF	IV Bent	2	2.83		2.83	60.06	41/109/195	3.75	1.65
	MP2	IV Bent	2	2.73		3.03	67.59	96/183/207	2.98	5.72
	CCSD(T)	IV Bent	2	2.74		3.07	68.22		2.98	6.37
	HF	V Linear	4	2.62			180.0	16/16/122/194	0.00	1.34
	MP2	V Linear	4	2.62			180.0	39/40/133/217	0.00	5.39
	CCSD(T)	V Linear	4	2.64			180.0	39/41/140/198	0.07	6.77
	HF	VI Linear	4	4.80		2.62	180.0	3/4/4/249	0.01	1.38
	MP2	VI Linear	4	3.02		2.68	180.0	28/32/32/260	0.38	4.69
	CCSD(T)	VI Linear	4	2.89		2.72	180.0		0.54	5.42
Au$_2$Te$_2$	HF	VII Rhombus	3	2.74	3.40	4.31	76.62	38/44/98/105 113/146	0.00	5.16
	MP2	VII Rhombus	3	2.68	3.06	4.39	69.71	51/68/119/129 182/192	0.00	9.16
	CCSD(T)	VII Rhombus	3	2.63	3.08	4.41	70.84			
	HF	VIII Bent	1	2.62/2.61/2.64	3.85		94.84	10/22/54/121 180/201	4.73	4.26
	MP2	VIII Bent	1	2.63/2.59/2.51	3.04		71.29	20/30/68/148 190/255	4.85	8.19
	CCSD(T)	VIII Bent	1	2.48/2.51/2.33	3.12		77.39			
	HF	IX Linear	5	2.71	2.81		180.0	11/26/32/37 73/145/162	0.00	4.42
	MP2	IX Linear	5	2.62	2.69		180.0	13/14/34/45 89/173/199	0.00	7.29
	CCSD(T)	IX Linear	5				180.0			
	HF	X Linear	5	4.84		2.62	180.0	1/1/3/4 5/5/248	0.00	3.58
	MP2	X Linear	5	3.02		2.82	180.0	10/10/38/152 725/765/765	0.00	5.75
	CCSD(T)	X Linear	5	2.89		2.72	180.0			

[a] As illustrated in Fig. 1.
[b] A=Au, B= Te for Au$_2$Te and Au$_2$Te$_2$, and A=Te, B=Au for AuTe$_2$.

those of bond length and bond angle, are

$$\triangle r(A\text{-}B) = r(A\text{-}B)_{\text{MP}} - r(A\text{-}B)_{\text{HF}}$$

and

$$\triangle\theta(A\text{-}B\text{-}A) = \theta(A\text{-}B\text{-}A)_{\text{MP2}} - \theta(A\text{-}B\text{-}A)_{\text{HF}}$$

at the MP2 theoretical level, where A=Au, B=Te for Au_2Te and Au_2Te_2, and A=Te, B=Au for $AuTe_2$. The results show that electron correlation effects exert strong influence on the bond angle $\theta(A\text{-}B\text{-}A)$, but an extremely small influence on the Au-Te bond length for the most stable structures II and IV of both trimers. From Table 3 we can see that the bond angle θ(Au-Te-Au) is reduced from 93.11 deg. to 71.54 deg. for trimer Au_2Te, and the θ(Te-Au-Te) is increased from 60.06 deg. to 67.59 deg. for trimer $AuTe_2$ at the MP2 theoretical level. However, the Au-Te bond length of both trimers remains unaltered essentially. Therefore, the electron correlation effect in the most stable structures II and IV of both trimers, Au_2Te and $AuTe_2$, can be explained as an Au-Au or Te-Te interaction, which only change the bond angle $\theta(A\text{-}B\text{-}A)$, but dose not change the Au-Te bond length.

In the linear structure III (Au-Te-Au) of trimer Au_2Te, the bond length Au-Te is reduced significantly due to the electron correlation effect: it is reduced from 4.41 Å to 2.96 Å at the MP2 theoretical level. Contrarily, in the linear structure V (Te-Au-Te) of trimer $AuTe_2$, the bond length Au-Te remains almost unaltered, but in another linear structure VI (Te-Te-Au) of isomer $AuTe_2$, it is reduced significantly due to the electron correlation effect, which reduced from 4.80 Å to 3.02 Å at the MP2 theoretical level. Therefore, the electron correlation effect in linear structure of both trimers can be explained as an attraction of Te atom for Au atom. In the linear structure V(Te-Au-Te), because the attractions of two Te atoms just balance on one Au atom, so the Au-Te distance remains unaltered. But in structure III (Au-Te-Au) and VI (Te-Te-Au), the attractions can not balance on the Au atom, therefore the bond length Au-Te is reduced significantly. Such structural variations of the clusters indicate the part origin of the gold-telluride interaction in these types of clusters.

Finally, we point out that the electron correlation effects make the clusters more stable since the electron correlation effects lead to lower energies and increased vibrational frequencies (Table 3). In summary, the electron correlation effects make these types of clusters more stable and more compact.

3.5   Relativistic effect

A comparison between relativistic and nonrelativistic results shows rather clear general trend. From Table 4 we can see that the relativistic effect on all structure parameters is pronounced. Generally speaking, all relativistic Au-Te bond lengths are shorter than nonrelativistic bond lengths. Strangely, in the most stable structures II and IV of both trimers, the relativistic effects show different variation of bond angle. It can be seen from Table 4 that the bond angle θ(Au-Te-Au) of isomer Au_2Te is reduced from 73.76 deg. to 69.91 deg., but the bond angle θ(Te-Au-Te) of isomer $AuTe_2$ is increased contrarily: it is increased from 59.43 deg. to 69.86 deg. due to relativistic effect.

The vibrational frequencies of clusters also increased slightly due to relativistic effects. From the Table 4 we can see that the increment in all vibrational modes of the most stable

Table 4: Relativistic and nonrelativistic geometries (r in Å, θ in deg.) vibrational frequencies ν (cm^{-1}), dipole moments μ(debye) and dissociation energies D_0 (eV) of the most stable states for Au$_n$Te$_m$ (n, m=1, 2) clusters calculated at the MP2 level

Species	Method	Structure[a]	S	r(Au-Te)	r(Au-Au)	r(Te-Te)	θ(A-B-A)[b]	ν	μ	D_0
AuTe	NR	I	2	2.78				151	7.16	3.03
	R	I	2	2.56				198	3.76	6.88
Au$_2$Te	NR	II Bent	1	2.77	3.33		73.76	36/133/165	8.66	4.94
	R	II Bent	1	2.59	2.97		69.91	58/159/211	4.95	5.61
	NR	III Linear	5	3.68			180.0	4/9/9/16	0.00	1.75
	R	III Linear	5	2.84			180.0	23/23/51/51	0.00	2.25
AuTe$_2$	NR	IV Bent	2	2.93		2.91	59.43	107/117/170	6.19	6.09
	R	IV Bent	2	2.66		3.05	69.86	91/193/477	3.00	6.14
	NR	V Linear	4	2.87			180.0	2/26/83/1436	0.00	5.07
	R	V Linear	4	2.59			180.0	39/39/142/227	0.00	5.77
	NR	VI Linear	4	3.65		2.67	180.0	20/20/21/292	0.68	4.88
	R	VI Linear	4	2.89		2.67	180.0	40/40/45/244	0.32	4.98
Au$_2$Te$_2$	NR	VII Rhombus	3	2.86	3.73	4.32	81.63	27/30/105/115 135/139	0.00	7.73
	R	VII Rhombus	3	2.65	2.99	4.38	68.59	52/73/116/134 190/199	0.00	8.75
	NR	VIII Bent	1	2.82/3.14/2.79	3.12		61.25	25/48/63/113 142/160	11.64	7.19
	R	VIII Bent	1	2.64/2.61/2.49	2.75		63.14	30/35/99/142 197/254	4.38	7.96
	NR	IX Linear	5	2.85	2.96		180.0	8/9/25/27 61/133/143	0.00	5.47
	R	IX Linear	5	2.59	2.66		180.0	9/11/31/44 95/181/208	0.00	6.93
	NR	X Linear	5	3.30		2.78	180.0	11/28/29/50 170/205/259	0.00	5.10
	R	X Linear	5	2.92		2.79	180.0	13/43/93/159 243/953/989	0.00	5.26

[a] As in Fig. 1.

[b] A=Au, B=Te for Au$_2$Te and Au$_2$Te$_2$, and A=Te, B=Au for AuTe$_2$

bent structure II(Au-Te-Au) is in the range of 22-46 cm^{-1} and of the linear structure III (Au-Te-Au) is in the range of 19-42 cm^{-1} for the cluster Au$_2$Te. For the cluster AuTe$_2$, the increment in all vibrational modes of the most stable bent structure IV(Te-Au-Te) are in the range of 6-307 cm^{-1}, of the linear structure V(Te-Au-Te) is in the range of 13-84 cm^{-1} and of the linear structure VI (Te-Te-Au) is in the range of 20-38 cm^{-1}, respectively.

In summary, as the same as the electron correlation effects, the relativistic effects

make the bond length shorten, the vibrational frequency increase, the energy decrease etc. Hence, the clusters tends to be more stable and more compact due to relativistic effects. It is worth to emphasize that the relativistic effects in the containing gold compounds have been studied by Pyykk *et al*. [23–25] for some detail. The relativistic effects give rise to the stronger chemical bonds of the gold due to the stabilization of $6s$ shell and destabilization of $5d$ shell. Both of the trends can lead to stronger bonds.

4   Summary

Several stable geometrical configurations of the coinage metal telluride clusters Au_nTe_m (n, m=1, 2) originated from one and two Te atom substitutions in the Au_n (n=2, 3) clusters have been investigated in this work at the HF, MP2 and CCSD(T) theoretical levels. The $^2\sum^-$ and $^4\sum^-$ electronic states have been determined as the ground and first excited electronic state configurations for the dimer AuTe. For trimer Au_2Te, a bent (C_{2v}) and a linear ($D_{\infty h}$) isomer have been found, and the ground state is bent structure of singlet spin multiplicity. For trimer $AuTe_2$, a bent (C_{2v}) and two linear ($D_{\infty h}$) isomers have been found and the ground state is bent structure of doublet spin multiplicity.

The electron correlation and relativistic effects result in structural variation of all isomers. Based on the aspect of structural variation of all isomers, the electron correlation effects in bent structure can be explained as an Au-Au or Te-Te interaction, and in linear structures can be explained as an attraction of the Te atom for the Au atom. In general, both electron correlation and relativistic effects shorten the bond lengths, lower the energies, increase the vibrational frequencies, and make the clusters more stable and more compact. Both effects are responsible not only for gold-gold attraction but also for additional gold-telluride interaction. Therefore, the electron correlation and relativistic effects are essential for determining the geometry and cluster growth of coinage metal telluride compound clusters Au_nTe_m.

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