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Relativistic Effects in Properties of Gold

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ABSTRACT: *Gold often shows unusual and sometimes surprising chemical and physical properties compared to its lighter group 11 elements (gold anomaly). Pyykkö and coworkers demonstrated in the mid seventies that this is due to effects from special relativity. Recent work in this field indeed indicates that the chemistry and physics of gold is dominated by relativistic effects.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:578–584, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10093

INTRODUCTION

It was long believed that valence electrons important for chemical reactions move rather slowly compared to the velocity of light ($v \ll c$) and should therefore not show significant effects coming from special relativity [1]. In contrast, the importance of relativistic effects for inner K- or L-shell electrons of heavy elements was long recognized. For example, Pincherle pointed towards the importance of such effects in the calculation of X-ray spectra of gold as early as 1935 [2]. Early Hartree calculations by Williams in 1940 on closed shell Cu^+ however pointed towards the importance of relativistic effects in the valence shell [3]: *The charge density of each single electron turns out to resemble that for the nonrelativistic case, but with the maxima "pulled in" and raised. ...The size of the relativistic corrections appears to be just too small to produce important corrections in atomic form factors or other secondary characteristics of the whole atom. .... It must be noticed that copper is a relatively light ion, and the corrections for such an ion as mercury would be enormously greater.* Fifteen years later, Cohen [4] and independently Mayers [5] pointed out that relativistic effects are very important even in the valence region for a heavy element like mercury. Mayers noticed an unusually large relativistic 6s-orbital contraction as well as a relativistic 5d-orbital expansion for mercury [5]. As a result of the pioneering work of Pekka Pyykkö and Jean-Paul Desclaux in the early seventies of the last century [6] the importance of relativistic effects in the quantum chemical treatment of heavy element containing compounds became apparent and widely accepted [7–10].

The chemistry of heavy elements can often not be understood without the inclusion of relativistic effects [11,12]. In 1979, Pyykkö and Desclaux [6] demonstrated that neutral gold shows an unusually large relativistic 6s-orbital contraction compared to its neighboring atoms in the periodic table, resulting in a significantly increased ionization potential of ca. 2 eV. This is now known as the "group 11 maximum of relativistic effects" (it is also seen for Cu and Ag to a lesser extent) and is depicted in Fig. 1. How can we explain such large relativistic effects in the valence shell?

Because relativistic perturbation operators act in the vicinity of the nucleus where also valence s-electrons have a significant part of its density [13], and diffuse orbitals are more sensitive to relativistic

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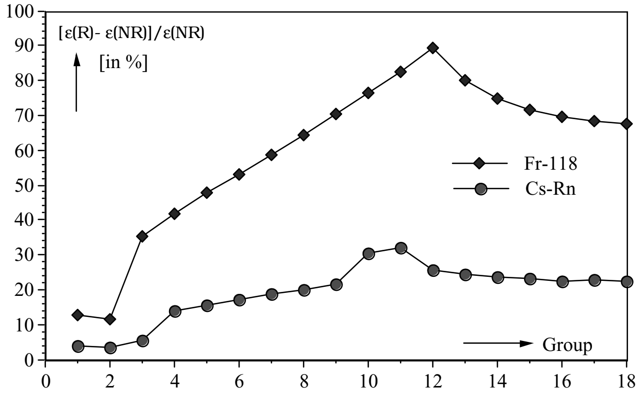

FIGURE 1 The relativistic stabilization of the 6s (7s) shell for the elements Cs to Rn (Fr to element 118). Cs to Rn redrawn from the data of Desclaux (Ref. [7]). The elements from Ra to 118, from Ba to Rn have a filled s-shell (s^2) except for Pt and Au. For the superheavy element series this causes a shift of the maximum from eka-Au to eka-Hg.

perturbations than the more compact inner shell electrons [14], the 6s-orbital of gold undergoes a rather large relativistic contraction (*direct relativistic effect*) as shown in Fig. 2. Such effects roughly increase with the square of the nuclear charge Z. Figures 1 and 2 also demonstrate that even larger relativistic changes can be expected for the group 11 element with nuclear charge 111, eka-gold.

Because of the relativistic contraction of all s-shells, the nucleus becomes more screened resulting in a smaller effective nuclear charge, and the higher angular momentum orbitals expand (*indirect relativistic effect*) [11]. The third most important relativistic effect is *spin-orbit coupling*, which also increases roughly like Z^2 and becomes especially important for the p-block heavy elements. All three relativistic effects can be clearly seen when orbital energies are compared for the heavy elements, for example for eka-Tl ($Z = 113$) as shown in Fig. 3.

It is known since a long time that gold exhibits unusual features compared to its lighter congeners [15]. Some of these are shown in Table 1. Such anomalies down the group 11 elements have often been rationalized in terms of the lanthanide contraction. Early one-center expansion techniques applied by Pyykkö and Desclaux to heavy element hydrides indicated that most of these unusual features in gold and its compounds can be traced back to relativistic effects [11], which are reviewed in this mini article. In the following we define relativistic effects on a specific atomic or molecular property P as $\Delta_R P = P_{NR} - P_R$, where P_{NR} is determined in the usual way using nonrelativistic quantum theory (the Schrödinger equation), and P_R from a variety of different relativistic procedures currently in use (the Dirac equation or its two-component or scalar relativistically derived forms including relativistic pseudopotentials). For a more detailed discussion on relativistic methodology see Ref. [17]. A few short accounts on relativistic effects in the chemistry of gold have been published elsewhere [18]. There are also two recent related highlights on gold compounds to be published in Angewandte Chemie [19].

ATOMIC PROPERTIES

What can we learn from relativistic effects in atomic properties with respect to the chemistry of gold? From Fig. 2 it is obvious that the relativistic valence s-contraction/stabilization results in an increase in

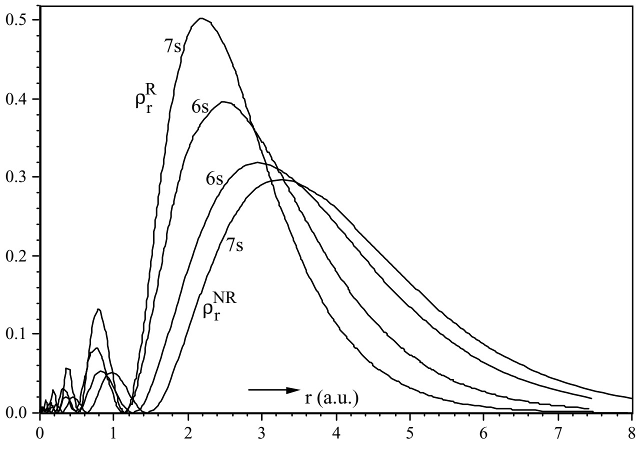

FIGURE 2 Relativistic and nonrelativistic radial valence s-densities for Au (6s) and eka-Au (7s).

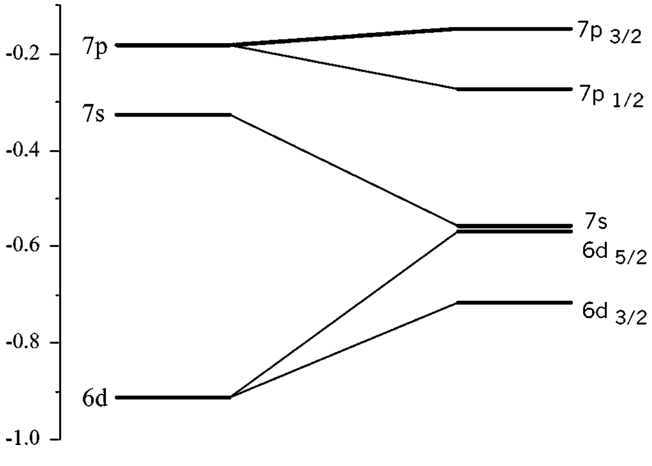

FIGURE 3 Nonrelativistic (on the left) and relativistic (on the right) orbital energies (in a.u.) of eka-Tl ($Z = 113$).

TABLE 1 A Comparison of Properties of Group 11 Elements (Ref. [16])

Property	*Cu*	*Ag*	*Au*
Color	Bronze	Silver	Yellow
Specific resistivity ($10^{-8}\Omega$ m)	1.72	1.62	2.4
Thermal conductivity (J cm^{-1} s^{-1} K^{-1})	3.85	4.18	3.1
Electronic heat capacity (10^{-4} J K^{-1} mol^{-1})	6.926	6.411	6.918
Melting point (°C)	1083	961	1064
Boiling point (°C)	2567	2212	3080
Atomic volume (cm^3 mol^{-1})	7.12	10.28	10.21
Electronegativities	1.9	1.9	2.4
Cohesive energies (kJ mol^{-1})	330	280	370
Energy of O_2-chemisorption (eV)	2212	6.0	3.6
Desorption temperature of CO on metal (K)	190–210	40–80	170–180
Common oxidation states	I,II	I	I,III
MF fluorides (solid)	Unknown	AgF	Unknown
Superconductors	Many	Rare	Rare

both the first ionization potential (IP) and the electron affinity (EA) for all group 11 series of elements, as shown in Fig. 4 [22]. According to Mulliken, the electronegativity (EN) is $\lambda(\mathrm{IP}+\mathrm{EA})$($\lambda$ being an adjustable factor) and increases for gold by ca. 0.4–0.5 because of relativistic effects [23] . Thus, we obtain electronegativities of 1.9 for Cu and Ag, and 2.4 for Au. Gold is therefore as electronegative as iodine (EN = 2.2) and may be regarded as a pseudohalide.

As a result of the relativistically increased electronegativity of gold we obtain an ionic bonding situation for the semiconductor Cs^+Au^- (EN(Cs) = 1.2) and not a metallic bond as one expects (two metals do not form necessarily a metallic bond) [24]. CsAu can be dissolved in liquid ammonia like several other ionic alkali or alkaline earth halides [19]. Moreover, solid-state calculations by Christensen and Kolar revealed large relativistic effects in the electronic band structures with nonrelativistic CsAu being a metal [25]. The coordination compound $AuCs\cdot NH_3$ has recently been isolated by Jansen and coworkers [26].

The (direct) relativistic stabilization of the 6s shell together with the (indirect) relativistic destabilization of the 5d shell leads to a substantially decreased 5d/6s gap, as shown in Fig. 5. For element 111 the strong relativistic 6s stabilization leads to a change in the electronic configuration from $^2S_{1/2}$ ($d^{10}s^1$) to $^2D_{5/2}$ (d^9s^2) [24]. Hence, d-participation in group 11–ligand bonding becomes more pronounced for gold (and eka-gold) leading to the stabilization of the higher oxidation states +3 and +5. Figure 6 shows the stability of group 11 fluorine complexes MF_4^- and MF_6^- towards decomposition into the lower oxidation states calculated at the coupled cluster level of theory [27]. At the nonrelativistic level the stability of the oxidation state +3 for the fluorides decreases with increasing nuclear charge of the central atom. This trend is reversed for gold and eka-gold because of relativistic effects. Interestingly, the stability of the highest oxidation state +5 increases at both levels of theory, but for gold and eka-gold, we again see a substantial relativistic stabilization. Of all group 11 elements only gold is known so far to form a compound in the oxidation state +5, AuF_6^-. Entropy effects shift further the equilibrium towards decomposition and the synthesis of unknown AgF_6^- might not be feasible so easily. The calculations also reveal a substantially increased 5d-participation in the MF bond

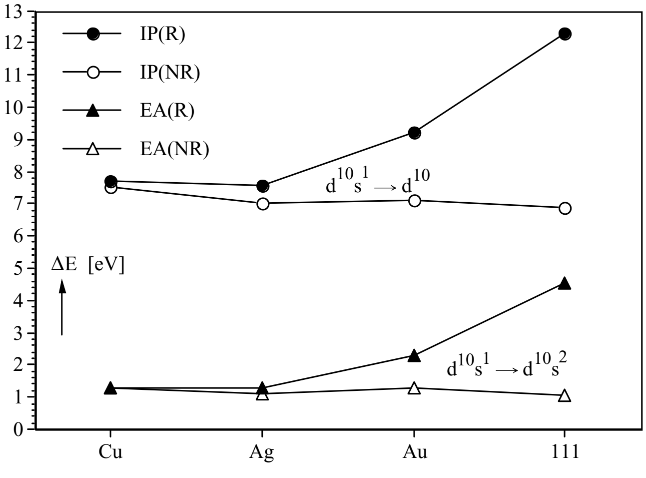

FIGURE 4 Nonrelativistic (NR) and relativistic (R) ionization potentials and electron affinities of the group 11 atoms. Data from Refs. [20] and [21].

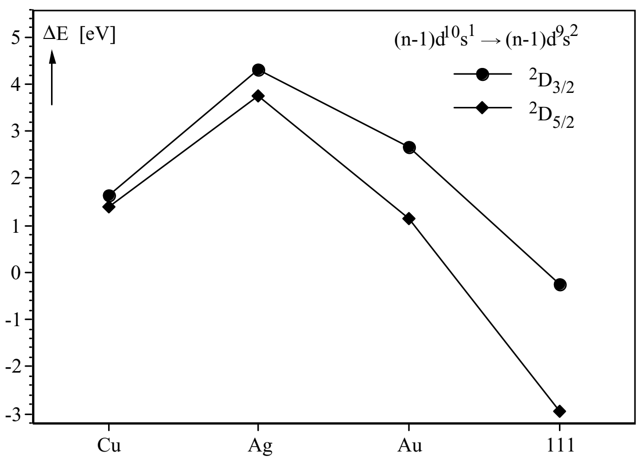

FIGURE 5 $^2S_{1/2} \rightarrow {}^2D_{5/2}$ ($^2D_{3/2}$) excitation energies for group 11 atoms. Data from Refs. [20] and [21].

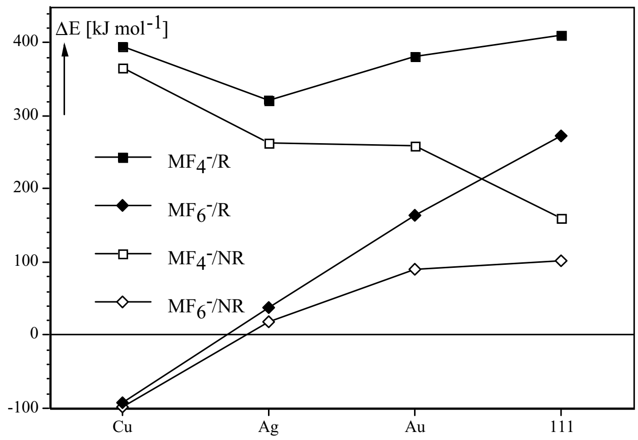

FIGURE 6 Decomposion energies for the group 11 fluorides in the oxidation state +5 ($MF_6^- \rightarrow MF_4^- + F_2$) and +3 ($MF_4^- \rightarrow MF_2^- + F_2$). All data from Ref. [27].

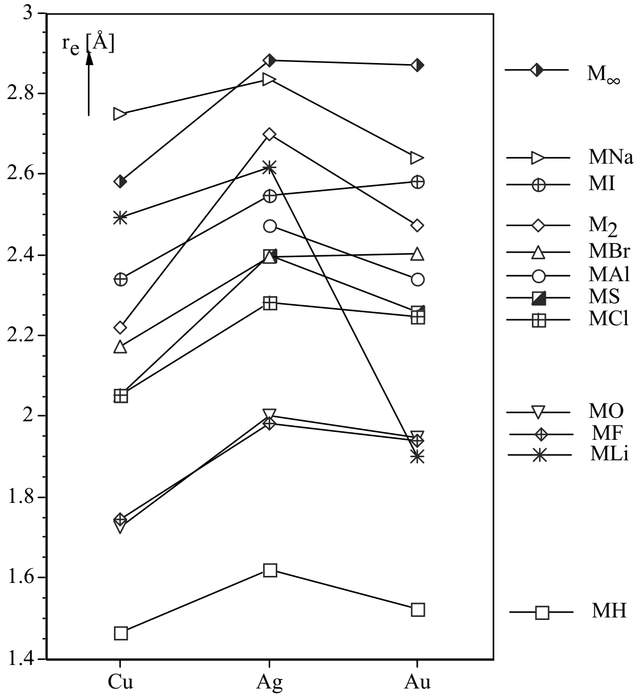

FIGURE 7 Bond distances for a number of diatomic group 11 compounds. Data from Refs. [36] and [37].

when going from Cu to eka-Au because of relativistic effects [27].

Because of the relativistic 6s-contraction in gold the 6s shell becomes more compact (inert, hence the nobility of gold) and the (static dipole) polarizability α_D decreases substantially from 9.5 a.u. (NR) to 5.2 a.u. (R) [28]. This can easily be rationalized from the well-known dependence of α_D on the first ionization potential, i.e. $\alpha_D \sim IP^{-2}$. As expected, the core polarizability increases from 1.4 a.u. (NR) to 1.7 a.u. (R) for Au^+ (compared to Cu^+ with 0.9 a.u. and Ag^+ with 1.2 a.u.) [23]. Despite the relativistic decrease in the Au polarizability, dispersive type of interactions between two gold units in compounds can increase substantially since $V_{disp} \sim \alpha^2/r^6$ and the Au–Au distance r decreases because of relativistic effects. Moreover, the relativistic increase in the Au^+ dipole polarizability leads to an increase in dispersive type d^{10}–d^{10} interactions between Au^+ units. Schmidbaur calls these interactions between Au^+ units aurophilicity [29,30]. Such aurophilic interactions can reach bond energies of up to 30 kJ mol^{-1}. In contrast, cuprophilic interactions are much weaker (roughly 1/3 of the aurophilic interaction) [31]. Pyykkö and coworkers demonstrated that aurophilic interactions are of dispersive nature enhanced substantially by relativity [32]. These aurophilic interactions may also be responsible for chemiluminescence properties often found in compounds with close Au–Au contacts [33,34].

MOLECULAR PROPERTIES

As a result of the relativistic 6s contraction gold–ligand bond distances are shorter than expected [35]. In some cases very large relativistic bond contractions are found ($\Delta_R r_e > 0.3$ Å) yielding gold–ligand bond distances as small (or even smaller) as copper–ligand bond distances (see Fig. 7) [36]. This relativistic bond contraction is critically dependent on the occupancy of the gold 6s orbital. Electropositive ligands like Li or Na (intermetallic gold compounds) increase the charge density in gold (M^+Au^-) and therefore lead to large relativistic bond contractions. For electronegative ligands (Au^+X^-) charge density in the 6s orbital is diminished and relativistic bond contractions are accordingly small. In fact, for the diatomic compounds the size of the relativistic bond contraction nicely correlates with the electronegativity of ligand [38]. For gold compounds in the higher oxidation state (e.g. $AuCl_4^-$, AuF_3) we find rather small bond contractions because the 6s density is further depleted and 5d-participation becomes important (remember that the 5d orbitals expand due to relativistic effects) [39]. As an interesting result the crystal structure of $Cs_2[AuCl_2][AuCl_4]$ shows one short Au–Cl distance for the $[AuCl_2]^-$ unit and one longer distance for the $[AuCl_4]^-$ unit [40], which reverses at the nonrelativistic level of theory [41].

The diatomic compounds AuH and Au_2 have been studied intensively by quantum chemists in the past [42–44] since they present ideal test cases for different relativistic approximations. For the most accurate calculations we obtained $\Delta_R r_e(AuH) = 0.22$ Å and $\Delta_R r_e(\mathrm{Au_2}) = 0.26$ Å [43,44]. An interesting fact is that for the bulk metals we have $r_e(\mathrm{Au}_\infty) \approx r_e(\mathrm{Ag}_\infty)$ in contrast to the diatomics. This indicates a reduced relativistic bond contraction for solid gold compared to $\mathrm{Au_2}$, which is not so easily understood [45]. However, in a linear chain of gold atoms we have nonbonding orbitals close to the Fermi surface, and relativistic effects in nonbonding orbitals are usually smaller [10] (relativistic effects in the band structure of solid gold have been investigated by Christensen and Seraphin [46]). Note that for $\mathrm{Au_3}$ we already have a smaller relativistic bond contraction of $\Delta_R r_e(\mathrm{Au{-}Au}) = 0.22$ Å [44].

Relativistic effects for gold–ligand stretching force constants are usually very large for all oxidation states. Figure 8 demonstrates this for the group 11 hydrides. The reason for such large effects are not so well understood, since gold–ligand force constants increase even for cases where relativistic bond contractions are relatively small, i.e. for the gold fluorides [27]. Relativistic changes in dissociation energies for diatomic gold compounds are more easily understood either from the Pauling formula [36] or from the relativistic 6s stabilization at both the atomic and molecular level comparing nonrelativistic with relativistic potential energy curves for ligands of different electronegativities [11]. Anomalies in the stability of group 11 series of compounds, like the increased stability of all intermetallic gold compounds, can easily be explained in this way [47]. As a curiosity, $\mathrm{AuBa^-}$ consists of two interacting closed $6s^2$ shell atoms with a dissociation energy of 143 kJ mol^{-1} [48]. It is therefore the strongest closed-shell interaction predicted so far and a result of an increased charge induced dipole interaction at a relativistically decreased bond distance. For comparison, the s^2–p^6 interaction between $\mathrm{Au^-}$ and Xe is much weaker (5 kJ mol^{-1}) [49].

There are many other examples where relativistic effects substantially influence physical and chemical properties of gold: for example to mention the unusual lattice geometries of AuCl, AuBr, and AuI showing chain-like tetragonal structures with linear $\mathrm{AuX_2}$ units and rather short Au—Au distances caused by relativistic effects [50]. The predicted low stability of solid AuF is also due to relativity [50]. The unusual photochemical cis to trans conversion in dinuclear gold halide bis(diphenylphosphino)ethylene complexes has also been related to relativistic effects [51]. Gold forms a wide range of different cluster compounds in contrast to copper and silver [52]. Many of these gold clusters are unique in structure and chemical properties [53]. Gold clusters are generally stabilized by phosphine ligands and the Au–Au bonding in such clusters is stabilized by relativistic effects [54]. Properties of bare gold clusters in the gas phase have been studied intensively in the past and the ionization potentials with changing cluster size of the group 11 metals are shown in Fig. 9. We see that the $\mathrm{Au_n}$ ionization potentials are about 2 eV above the Cu_n and Ag_n values up to the bulk (work function). It has been demonstrated recently that this is due to relativistic effects [44]. A similar situation is found for the group 11 cluster electron affinities [44]. Very recently, Häkkinen et al. studied negatively charged group 11 cluster $\mathrm{M_7^-}$ (M=Cu, Ag, and Au) applying relativistic density functional theory with surprising results [56]. The simulated thermally weighted photoabsorption spectra showed that $\mathrm{Au_7^-}$ is dominated by planar structures while $\mathrm{Cu_7^-}$ and $\mathrm{Ag_7^-}$ give predominantly 3D arrangements.

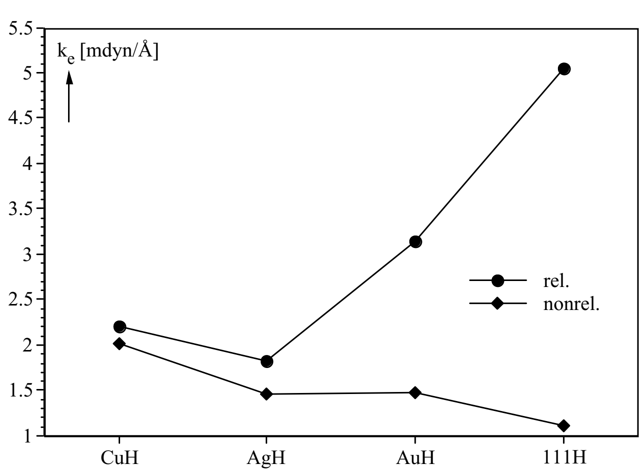

FIGURE 8 Calculated nonrelativistic and relativistic force constants for group 11 hydrides.

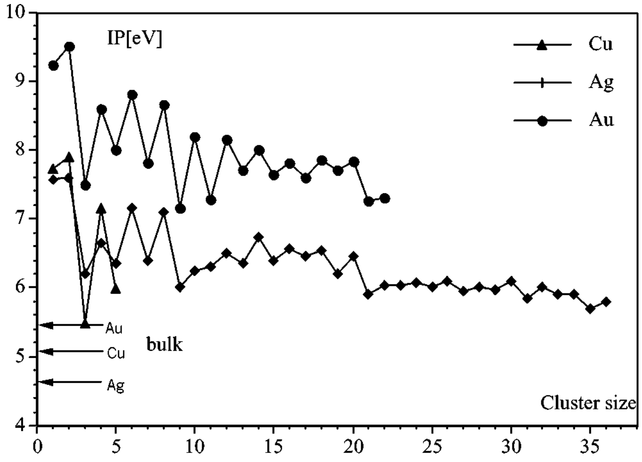

FIGURE 9 Ionization potentials (IP) of group 11 clusters. The bulk metal work functions for the (100) plane are also shown on the left-hand side. Experimental values from Ref. [55].

Nonrelativistic Au_7^- behaves similar to the analogues copper and silver species [56].

To summarize, the chemistry and physics of gold cannot be understood without the inclusion of relativistic effects because gold is dominated by relativistic effects. Future investigations into gold chemistry and physics might lead to quite surprising results. Some of these very recent surprises include new compounds like $[AuXe_4]^{2+}$ (a bulk compound with short covalent Au—Xe bonds of 2.74 Å and a calculated average Au—Xe bond energy of more than 200 kJ mol^{-1}) [57], and nano-wires of gold with an unexpected helical structure [58].

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