

Predicted Chemical Bonds between Rare Gases and Au⁺

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Abstract: The valence isoelectronic series of the known PAuP⁵⁻, SAuS³⁻, and ClAuCl⁻ is continued to the predicted gas-phase or matrix species RgAuRg⁺, where Rg is a rare gas. The diatomic species AuRg⁺ are also studied. Quasirelativistic pseudopotential studies, at levels up to CCSD(T), including a counterpoise correction, predict Au–Xe bond energies of up to 0.9 eV and bond lengths of about 276 pm, close to the sum of covalent radii. Substantial electron transfer from Xe to Au⁺ occurs. Over half of the Au–Xe bond energy comes from relativistic effects. The bonds to Rg = Ar and Kr are weaker than those to Rg = Xe, while He and Ne form weak complexes. At large distances the AuXe⁺ potential curve coincides with that of AuXe⁻.

Noble metals, such as gold, actually have a rich chemistry. Likewise, chemical bonds to the rare gases, Rg = He–Xe, are known. However, we are not aware of any earlier discussions of systems with Au–Rg bonds, apart from a mass-spectrometric report on AuNe⁺ in 1977.¹ Several lines of thought suggest that such bonds could actually be quite stable, for example, the gold(I) dihalide anions, XAuX⁻, X = Cl–I, are experimentally known. So are the alkali metal salts of their isoelectronic chalcogen and pnictogen analogs, EAuE³⁻, E = S,² and EAuE⁵⁻, E = P, As,³ respectively. The next members of this isoelectronic series are the triatomic cations RgAuRg⁺.

Secondly we note that gold is almost as electronegative as hydrogen and that the species ArHAr⁺, KrHKr⁺,⁴ and XeHXe⁺⁵ have been observed in matrix spectroscopy.

Thirdly, the copper analogs CuRg⁺ and RgCuRg⁺ have been studied earlier. Calculations with large basis sets (triple- ζ + two-polarization functions) give D_e values approaching the present (double- ζ + two-polarization) ones for Au, e.g., 0.405⁶ and 1.212 eV⁷ for CuKr⁺ and KrCuKr⁺, respectively.

Finally, the first ionization potentials, IP1, of He, Ne, Ar, Kr, and Xe are 24.587, 21.564, 15.759, 13.999, and 12.130 eV, respectively.⁸ The last three ones are bracketed by the electron affinity and IP of Au⁺ (= IP1 and IP2 of Au), 9.225 and 20.5 eV, respectively. Therefore, one can expect a degree of covalent bonding between Au⁺ and the heavier rare gases.

Several examples on chemical bonds between other heavy metals and rare gases are experimentally known. The experimental D_0 of HgXe⁺ is 0.748(13) eV.⁹ The Xe–M bond energy in XeM(CO)₅ has been measured to be 0.36 eV for all M (Cr, Mo, W).¹⁰ The calculated values for the observed Rg–BeO complexes with G = Ar, Kr, Xe are 0.30, 0.43, and 0.56 eV.¹¹ The experimental D_0 of MgXe⁺ is 0.519 eV.¹²

As to interactions between Au⁺ and other closed-shell species, the complex Au–OH₂ is calculated to have a CCSD(T) dissociation energy of 1.56 eV.¹³

Method

The calculations were done using Gaussian 92. For Au and Ar–Xe, 19 and 8 valence-electron quasirelativistic pseudopotentials (PP) were used, respectively, with corresponding basis sets. He and Ne were treated at the all-electron (AE) level.¹⁴ As technical tests, AuAr⁺ was also run with AE Ar and AuXe⁺ with a nonrelativistic Au PP. The AuAr⁺ results closely agree with those using a PP at Ar.

The effects of the method (MP2–MP4, CCSD(T)), the counterpoise correction for the basis-set superposition error (BSSE), and the relativity are shown in Table 1 and Figure 1 for AuXe⁺. The MP2, MP4, and CCSD(T) results are all quite close. The BSSE effect is comparable at all three levels. The effect of the BSSE correction increases toward the lighter Rg and reaches a factor of three in the D_e of Rg = He and Ne. Consequently, only the results for the triatomic species with Rg = Ar–Xe are included in Table 2. These results were obtained at MP2 level, without BSSE corrections.

Results and Discussion

The calculated bond lengths, vibrational frequencies, and atomization energies are given in Tables 1 and 2 for AuRg⁺ and RgAuRg⁺, respectively. The Mulliken and natural bond orbital analyses are given in Table 3.

For XeAu⁺, a calculation was also performed using a nonrelativistic (NR) PP on Au. The bond length increases by 34 pm, a not unusual value for gold compounds.¹⁵ The total

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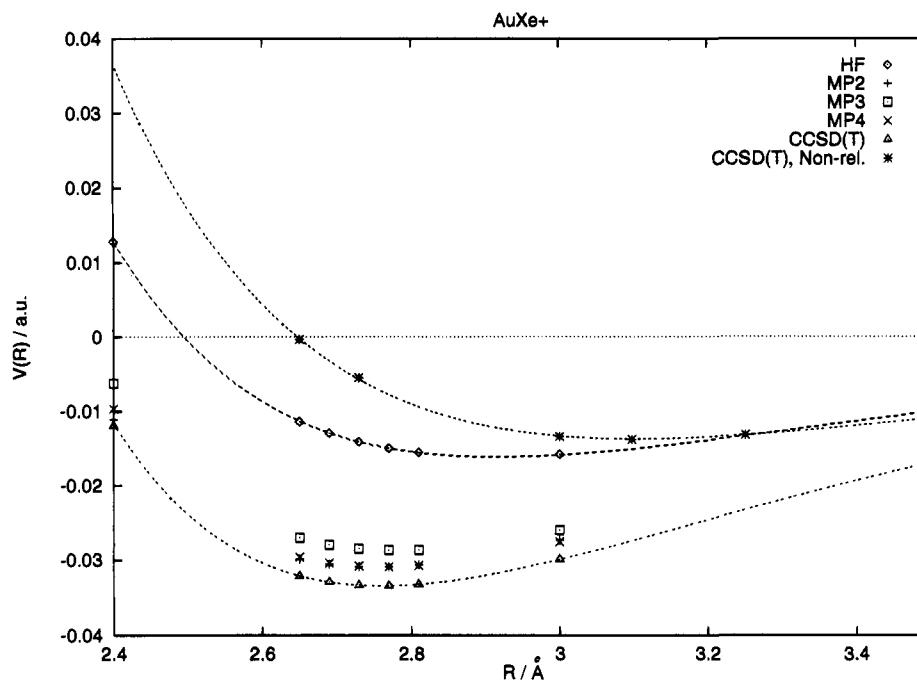


Figure 1. Calculated, counterpoise corrected AuXe^+ potential curves $V(R)$ at HF-CCSD(T) levels. Note the near overlap of the MP2 and MP4 points. A nonrelativistic reference calculation at the best level (CCSD(T)) is included. The curves are fits to a Morse potential.

Table 1. Calculated Properties of the Diatomic Species, AuRg^\pm , $\text{Rg} = \text{He-Xe}$, with and without BSSE Corrections at Various Levels of Approximation^a

species	method	uncorrected			corrected		
		Au-Rg	ν	D_e	Au-Rg	ν	D_e
AuHe^+	MP2	244	186	0.078	281	83	0.022
	CCSD(T)	239	209	0.091	275	93	0.0265
AuNe^+	CCSD(T)	267	112	0.151	290	71	0.052
AuAr^+	MP2	263.5	148	0.409			
	CCSD(T)	261.7	157	0.460	274.0	118	0.272
	CCSD(T) ^b	264.3	150	0.432	273.0	123	0.292
AuKr^+	MP2	264.4	135	0.647			
	CCSD(T)	263.7	141	0.713	271	120	0.510
AuXe^+	HF				291.4	90	0.439
	MP2	269.1	142	1.063	275.1	127	0.842
	MP3	271.9	135	1.013	278.1	122	0.781
	MP4	269.9	141	1.085	276.3	127	0.841
	CCSD(T)	269.8	145	1.16	276.1	129	0.910
AuXe^-	MP2	403	25	0.112	310	79	0.376
	CCSD(T)	418	21	0.083	453	17	0.048

^a Bond lengths in pm, frequencies in cm^{-1} , and atomization energies, D_e , in eV. ^b All-electron Ar. ^c NR PP on Au.

Table 2. Calculated Properties of RgAuRg^+ , $\text{Rg} = \text{Ar-Xe}$

Rg	method	Au-Rg	$\nu(\pi_u)$	$\nu(\sigma_g)$	$\nu(\sigma_u)$	D_e
Ar	MP2	254	33	141	201	0.91
Kr	MP2	257	36	126	186	1.43
Xe	MP2	266	35	120	182	2.25

^a Bond lengths in pm, frequencies in cm^{-1} , and atomization energies, D_e , in eV.

CCSD(T) dissociation energy decreases from 0.910 to 0.376 eV if relativistic effects are omitted. This is not surprising. The calculated relativistic and nonrelativistic (R and NR) ionization potentials of Au are 9.086 and 6.981 eV, respectively.¹⁶ As relativistic effects increase IP1 of gold by 2.105 eV, they simply make the element much more electronegative. Other recent calculations^{17,18} of the same increase give 2.01 and 2.14 eV, respectively.

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Table 3. Mulliken (M) and Natural Bond Orbital (NBO) Charges on the Rare-Gas Atom Rg

Rg	AuRg^+ ^b		RgAuRg^+ ^c	
	M	NBO	M	NBO
He	0.014	0.0011		
Ne	0.039	0.0060		
Ar	0.142	0.036	0.217	0.082
Ar ^d	0.147	0.037		
Kr	0.253	0.080	0.345	0.149
Xe	0.394	0.167	0.466	0.240

^a All-electron Ar. ^b MP2 density at counterpoise corrected CCSD(T) R_e . ^c MP2 density at uncorrected MP2 R_e .

A comparison along the coinage metal series, group 11, suggests that the bonds to gold would be slightly stronger than those to copper: The calculated D_e are 0.405 and 0.510 eV for CuKr^+ ⁶ and AuKr^+ , respectively. While copper has a smaller covalent radius than gold, it also has a smaller IP1, 7.726 versus 9.226 eV. Silver has the smallest IP1 in the series, 7.576 eV, and it is a common experience that it has the smallest D_e in the series, while the values for Cu and Au are comparable.^{19,20}

The results confirm the expectation that He and Ne would form weak complexes with Au^+ while the three heavier rare gases show increasingly covalent character. The He dissociation energy is smaller than the Ne one; Partridge et al.⁶ found for Cu^+ and some other $3d^n$ ions the opposite behavior, He > Ne. While He has a smaller polarizability than Ne, it also has a smaller radius. Hence it obtains substantial binding energies to small metal ions, like the calculated D_e of 1.19 and 0.748 eV for AlHe^{3+} and the experimentally observed VHe^{3+} , respectively.²¹

For xenon, the calculated Au-Xe bond energy turns out to be about 0.9 eV/bond; the results without counterpoise correc-

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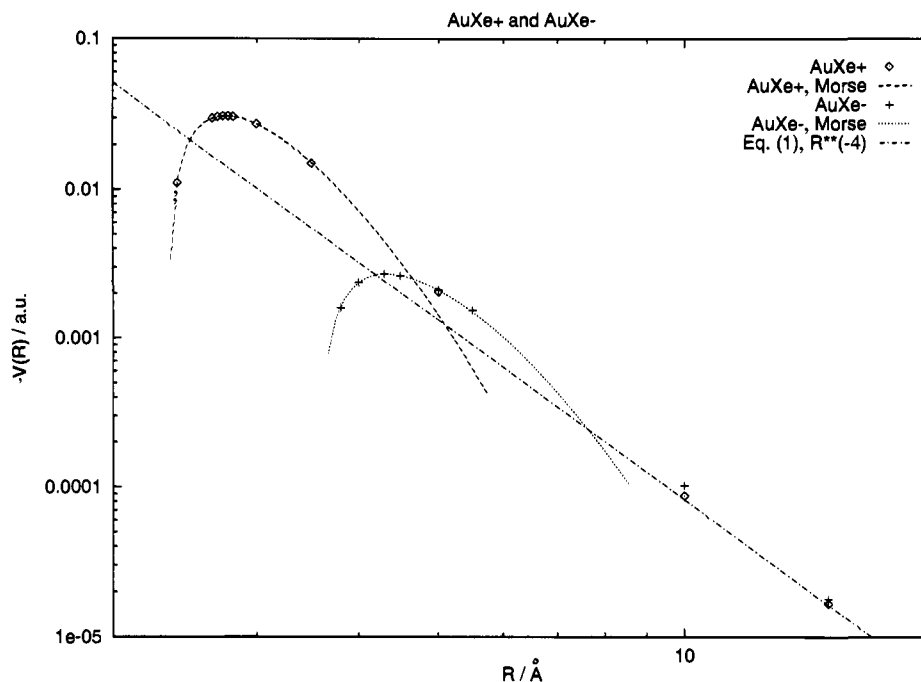


Figure 2. Calculated interaction potentials for AuXe[±] at MP2 level in a logarithmic scale, including counterpoise corrections. Note the transition to an R^{-4} behavior (eq 1 corresponding to the calculated MP2 α_{Xe}).

Table 4. Mulliken and NBO Atomic Orbital Charges

molecule	method	atom	population ^a								
			s	pσ	pπ	p ^b	dσ	dπ	dδ	d ^b	f ^b
KrAuKr ⁺	M	Au	0.51	0.17	0.02	0.21	1.93	1.98	1.99	9.89	0.08
		Kr	1.97	1.67	1.96	5.58	0.02	0.02	0.02	0.10	
AuXe ⁺	M	Au	0.29	0.09	0.01	0.12	1.97	1.99	1.99	9.95	0.04
		Xe	2.00	1.60	1.95	5.51	0.02	0.02	0.02	0.10	
XeAuXe ⁺	M	Au	0.73	0.20	0.03	0.27	1.90	1.99	1.99	9.86	0.08
		Xe	1.99	1.55	1.95	5.45	0.02	0.02	0.02	0.10	
	NBO	Au	0.54	0.02	0.01	0.05	1.90	1.99	1.99	9.87	0.02
		Xe	1.97	1.76	1.97	5.69	0.02	0.02	0.02	0.10	

^a Assuming filled 5s²5p⁶ semicore shells for Au. ^b Total.

tion, per bond, are comparable for the di- and triatomic species. At the same level of approximation (MP2 without counterpoise correction), the dissociation energy per bond is, however, slightly larger in RgAuRg⁺ than in AuRg⁺ (Rg = Ar–Xe), as found earlier for the copper species.^{6,7}

The long-distance attraction between Au⁺ and Rg follows the R^{-4} law

$$V(R) = -(\alpha Z^2/2R^4) \quad (1)$$

Here α is the polarizability of the Rg atom, Z the charge of the metal ion, and R the interatomic distance.

This large- R limit is the same for Au⁺ and Au⁻, as seen in Figure 2 for calculations using the same basis. The minimum occurs much earlier for the larger Au⁻ than for the smaller Au⁺. Consequently the ν and D_e of anion in Table 1 are much smaller. We note that the electronegativity of gold is almost comparable to that of iodine and that the species ArBr⁻, ArI⁻, and KrI⁻ have just been observed.²²

The calculated MP2 polarizability for Xe is 21.025 au. This is the contribution from the 5s²5p⁶ valence space. The total, experimental value is 27.29 au.²³

The Mulliken and natural bond orbital (NBO) population analysis results for the cations in Table 3 indicate substantial charge transfer from the Rg atom(s) to the metal cation, approaching 0.4–0.5 e for Rg = Xe. A more detailed analysis by atomic orbitals is given in Table 4. For XeAuXe⁺, the Mulliken populations are 6s^{0.73}6p^{0.20}5d^{0.10} for Au and 5p^{0.45} for Xe. In other words, the main feature is the donation of nearly 0.9 electron from the 5pσ orbitals of the two xenon atoms to a 6s–6p hybrid on Au. The NBO analysis of the other two systems in Table 4 is qualitatively similar.

While the D_e increases down the column, the bond lengths and vibrational frequencies remain roughly comparable for all the AuRg⁺ species; the increase in bond energy compensates the increase of atomic radii and masses down the column. For XeAuXe⁺, the calculated Au–Xe distance of 266 pm approaches the sum of the covalent radii, 130 + 127 = 257 pm for Xe²⁴ and Au,²⁵ respectively.

Higher coordination numbers than two were not considered because the isoelectronic counterpart of AuX₄⁻ would be AuRg₄³⁺, a different charge state. For the weak complexes CN > 2 is a likely option.

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Conclusions

If one first makes the original investment of atomization and ionization energies of gold, $3.816 + 9.225 = 13.04$ eV, about 0.3, 0.5, and 0.9 eV per bond can be gained by making the present Au-Rg bonds for Rg = Ar, Kr, and Xe, respectively. The latter noble metal-noble gas bonds have considerable covalent character and, as seen from Figure 2, are about two times stronger near R_e than the charge-polarizability interaction (eq 1).

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