

Detecting Weak Interactions between Au⁻ and Gas Molecules: A Photoelectron Spectroscopic and Ab Initio Study

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The finding of extraordinary catalytic activities of gold nanoparticles has aroused renewed interest in gold chemistry.^{1,2} Considerable effort to characterize the chemical interactions between gold clusters and a variety of molecules has been made.^{3–12} An earlier study of the interaction between gold clusters and O₂ by Cox et al.¹³ showed that Au_n⁺ cation clusters can react with O₂ only for *n* = 10, while gold anion clusters exhibit an odd–even effect toward O₂. This observation was later confirmed by Whetten and co-workers.¹⁴ Cox et al. also found that Au⁺ is reactive toward CH₄ but Au⁻ is not.¹³ Recently, Zhai et al.¹⁵ used photoelectron spectroscopy (PES) to elucidate the structure of AuO₂⁻ and found that it adopts a linear OAuO⁻ structure. The Au–H₂O complex has been studied extensively. Hrusák et al.,¹⁶ Hertwig et al.,¹⁷ and Feller et al.¹⁸ independently studied the structures of Au⁺(H₂O)_{*n*} (*n* = 1–4) using various high-level post-Hartree–Fock methods. Zheng et al.¹² recently carried out a PES experiment on Au(H₂O)_{*n*}⁻ (*n* = 1, 2). Enhancement of CO oxidation on a supported gold nanocluster by water was reported by Bongiorno and Landman,¹⁹ suggesting significant interactions between gold clusters and H₂O. Moreover, the bonding between a noble-gas (NG) atom and Au⁺ has attracted growing attention.^{4,20–22}

In this communication, we report a joint experimental and theoretical study of the interactions between gold anion, Au⁻, and an NG atom (NG = Ne, Ar, Kr, Xe) or a molecule of O₂, CH₄, or H₂O. Except for the Au⁻···H₂O interaction, which is comparable to strong hydrogen bonding, all of these are weak charge-induced intermolecular interactions. The observation of a weakly bound Au(O₂)⁻ complex shows the inertness of Au⁻ toward O₂, in line with the previous observation of the odd–even effect in the reactions of Au_{*n*}⁻ clusters and O₂. By comparing with results of high-level ab initio calculations, we demonstrate that anion PES is a good technique for probing weak charge-induced intermolecular interactions.

Weak intermolecular interactions are difficult to measure in a quantitative fashion. We have previously observed weakly bonded CO in Au_{*x*}(CO)_{*y*}⁻ complexes for large *y* beyond a saturation limit.^{7b,c} Recently, we were able to produce very cold anion clusters to form complexes of Au_{*n*}⁻ clusters with O₂ and Ar,^{23–25} allowing us to investigate physisorption using PES. The current experiment was carried out with a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which can be found in the Supporting Information (SI).

Figure 1 displays the 193 nm spectra for AuAr⁻, Au(H₂O)⁻, and AuO₂⁻ compared with that of Au⁻. The spectrum of AuAr⁻ (Figure 1b) is identical to that of Au⁻ (Figure 1a) except for a discernible blue shift (~35 meV) due to the weak interaction between Au⁻ and Ar. The spectral features of Au(H₂O)⁻ (Figure 1c) are also similar to

those of Au⁻, but there is a much larger blue shift (0.47 eV) as a result of the much stronger interaction between Au⁻ and H₂O. Notably, Zheng et al.¹² reported the PES spectrum of Au(H₂O)⁻ at 355 nm, allowing only the first band (X) to be observed (it was also vibrationally resolved). The spectrum of the AuO₂⁻ (Figure 1d) species is more complicated. Previously, we reported the PES spectra of pure OAuO⁻ using N₂O as a carrier gas.¹⁵ Features due to the gold dioxide anion are clearly present in Figure 1d (labeled as X' and A'–E'). In addition, we observed features similar to those of bare Au⁻, which are clearly derived from a Au(O₂)⁻ complex. In previous studies, we have reported Au_{*x*}(O₂)⁻ and Au_{*x*}Ar_{*y*}⁻ complexes under cold experimental conditions.^{23–25} In the current study, we found that the AuO₂⁻ spectrum was strongly dependent on our source conditions: the relative intensities of the Au(O₂)⁻ features increased as colder clusters were produced. We also measured the PES spectrum of AuO₂⁻ at 355 nm (3.496 eV) and observed a slight blue shift (~25 meV) of the first band of Au(O₂)⁻ relative to that of Au⁻ (Figure S1), suggesting the weak nature of the bonding between Au⁻ and O₂. As we suggested previously,¹⁵ Au⁻ does not react with O₂, and the formation of the OAuO⁻ dioxide species in our cluster source is from the reactions of Au⁻ with O atoms.

We also carried out ab initio calculations to elucidate the structures and binding energies of the AuM⁻ complexes. We used the CCSD(T) method and the augmented Dunning correlation-consistent basis sets

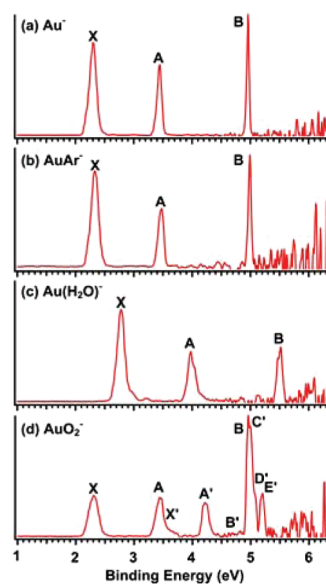


Figure 1. Photoelectron spectra of (a) Au⁻, (b) AuAr⁻, (c) Au(H₂O)⁻, and (d) AuO₂⁻ at 193 nm. Notably, the spectrum in (d) contains contributions from a physisorbed Au(O₂)⁻ complex (X, A, B) and the OAuO⁻ dioxide (X', A'–E').¹⁵

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(aug-cc-pVTZ and aug-cc-pVQZ) for H, C, O, Ne, Ar, and Kr and the same basis sets with pseudopotentials (aug-cc-pVTZ-PP and aug-cc-pVQZ-PP)²⁶ for Au and Xe. Geometry optimization was performed at the MP2/aug-cc-pVTZ(PP) level of theory. The basis-set superposition error (BSSE) was corrected using the counterpoise method. The equation used to evaluate the CCSD(T) complete-basis-set (CBS) limit and other computational details are given in the SI.

Table 1. Calculated Binding Energies and Vertical Detachment Energies of Au⁻-M Complexes (M = Ne, Ar, Kr, Xe, O₂, CH₄, H₂O) Along with Average M Polarizabilities^a

complex	binding energy (kcal/mol)			α_M^b	VDE (eV)	
	aug-cc-pVTZ	aug-cc-pVQZ	CBS(SI)		calcd	exptl
Au ⁻					2.296	2.309 ^c
Au ⁻ ...Ne	0.08	0.14	0.15	0.3956	2.297	
Au ⁻ ...O ₂	0.62	0.75	0.78	1.5812	2.306	2.33(3)
Au ⁻ ...Ar	0.71	0.85	0.89	1.6411	2.314	2.34(3)
Au ⁻ ...Kr	1.07	1.29	1.37	2.4844	2.325	
Au ⁻ ...CH ₄	1.62	1.75	1.77	2.593	2.343	
Au ⁻ ...Xe	1.68	2.05	2.15	4.044	2.335	
Au ⁻ ...H ₂ O	12.18	12.50	12.58	1.45	2.824	2.76 ^d

^a All energies were based on MP2/aug-cc-pVTZ-optimized structures and evaluated using the CCSD(T) method with the counterpoise BSSE correction. ^b Average polarizabilities (10⁻²⁴ cm³) taken from ref 27. ^c From ref 28. ^d From ref 12.

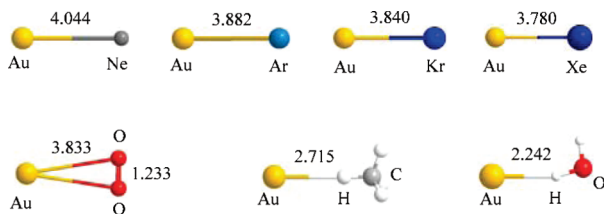


Figure 2. Optimized structures of Au⁻-M complexes (bond lengths in Å).

The calculated Au⁻-M binding energies and average M polarizabilities are given in Table 1, and the corresponding structures are displayed in Figure 2. For Au(O₂)⁻, the binding energy between Au⁻ and O₂ is only 0.78 kcal/mol, which is 0.11 kcal/mol smaller than that of AuAr⁻, consistent with the smaller PES spectral shift. The interaction between Au⁻ and H₂O is much stronger than the weak intermolecular interactions in the other species and comparable to a strong hydrogen bond (>10 kcal/mol). Mulliken charge analysis suggests that the charges of Au⁻ and the H atom closest to Au⁻ are -1.06e and 0.45e, respectively. Hence, electrostatic interactions between Au⁻ and H₂O play an important role, inducing the large blue shift in the PES spectrum (Figure 1c).

Since our theoretical results reproduced the experimental trend of the weak intermolecular interactions in Au(O₂)⁻, AuAr⁻, and Au(H₂O)⁻, we extended our calculations to the interactions in AuM⁻ (M = Ne, Kr, Xe, CH₄). As Table 1 shows, the binding energies calculated using two different basis sets show a consistent trend. In particular, the CCSD(T)/aug-cc-pVQZ results are very close to those in the CBS limit, indicating that the calculated binding energies are converged. Furthermore, the trend in the binding energies of these Au⁻-M species is correlated with the average polarizability of M (except in the case of H₂O). Notably, the binding energies of the corresponding neutral complexes at the anion geometries (Table S1) are significantly less than those of the optimized anion species (Table 1), which implies that electrical induction plays a major role in these anion complexes (especially in Au⁻...H₂O, for which the binding energy increases by more than an order of magnitude compared with that of the neutral Au...H₂O complex). It should also be noted that

the trend of the calculated vertical detachment energies (VDEs) of Au⁻, Au⁻...O₂, Au⁻...Ar, and Au⁻...H₂O is consistent with the trends of the measured VDEs and binding energies (Table 1). The only exception is Au⁻...Xe, which has a larger binding energy but a slightly smaller VDE compared with Au⁻...CH₄. This exception might be due to the use of pseudopotential basis sets for Xe.

In summary, we have shown that PES can be a very sensitive tool for probing weak intermolecular interactions between Au⁻ (or gold clusters) and gas atoms (or molecules). High-level ab initio calculations confirm the trend in the relative interactions in various Au⁻-M complexes revealed by the PES results. Surprisingly, Au⁻ has stronger interactions with Ar than with O₂. The ability to form weakly bonded complexes has recently been exploited to probe the exact gold cluster sizes at which the 2D-to-3D²⁴ and cage-to-pyramid²⁵ structural transitions occur.

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Supporting Information Available: Experimental and computational methods, binding energies, and PES spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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