

# Using calculated vibrational shifts to map cooperative effects in CO oxidation on Au atoms



**Angela N. Smith**, Alex D. Hunter, David T. Moore  
Department of Chemistry, Lehigh University, Bethlehem, PA 18015



## Introduction

The oxidation of CO on gold nanoclusters has been extensively studied computationally and experimentally, but many questions still remain as to the details about the reaction mechanism. An essential step in this reaction is the initial binding of the reactants (CO and O<sub>2</sub>) to the metal. It has been observed previously that there is a cooperative enhancement of the binding of both reactants in the ternary complex relative to the respective binary complexes.<sup>1-3</sup> It has been proposed that arises because CO is an electron donor, while O<sub>2</sub> is an electron acceptor, and so there is a net transfer of charge through the complex, increasing the overall binding.<sup>3</sup> Here we present a comprehensive computational investigation of the binding of CO and O<sub>2</sub> to gold atoms and ions, in order to elucidate the underlying factors contributing to the cooperative effect.

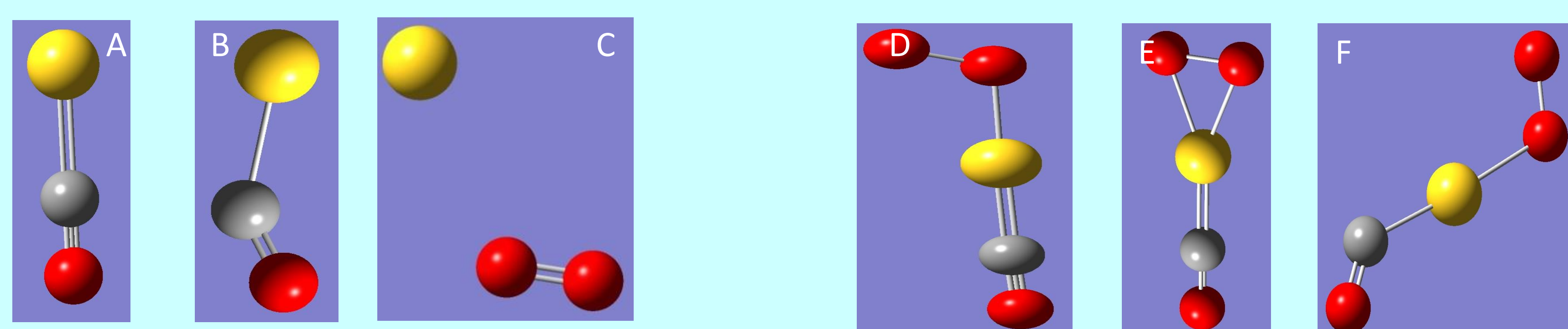
## Computational Methods and Results

DFT Geometry optimizations and frequency calculations were performed for the binary [AuCO]<sup>q</sup> and [AuO<sub>2</sub>]<sup>q</sup> complexes, and ternary [O<sub>2</sub>AuCO]<sup>q</sup> complexes, for charge states q=1,0, and -1. The results reported here are for mPW1PW91 hybrid functional and mixed SDD/6-311+G(2d) basis set for Au/C,O respectively. Identical calculations done using the B3LYP functional revealed with no qualitative deviations from the mPW1PW91 results.

**Spin-states:** In general, for each complex there was a clearly identifiable “best” spin-state, giving a lower energy than all others, as noted in the tables below. The notable exception is the anionic ternary complex for which the singlet and triplet states energies are within 1 kcal/mol, and so results are reported for both spin states.

**Complex Structures:** There were several different binding motifs exhibited in the complexes for both CO and O<sub>2</sub>, as illustrated in the images below. These general structure types are correlated to the complexes as follows:

A) [AuCO]<sup>+</sup> B) [AuCO]<sup>0</sup> and [AuCO]<sup>-</sup> C) [AuO<sub>2</sub>]<sup>+</sup> all charges  
D) [O<sub>2</sub>AuCO]<sup>+</sup> and [O<sub>2</sub>AuCO]<sup>0</sup> E) [O<sub>2</sub>AuCO]<sup>-</sup>, singlet state F) [O<sub>2</sub>AuCO]<sup>-</sup>, triplet state



- CO binds in linear [AuCO]<sup>+</sup>-like orientation in all ternary complexes (except triplet anion)
- Singlet [O<sub>2</sub>AuCO]<sup>-</sup> has C<sub>2v</sub> structure; only complex with η<sub>2</sub>-binding motif for O<sub>2</sub>
- Despite similar energies, singlet and triplet [O<sub>2</sub>AuCO]<sup>-</sup> complexes have qualitatively different structures

## Vibrational Frequencies (cm<sup>-1</sup>, uncorrected)

	AuCO	O <sub>2</sub> AuCO		AuO <sub>2</sub>	
	CO frequency	CO frequency	O <sub>2</sub> frequency	O <sub>2</sub> frequency	
<b>Cationic (triplet)<sup>a</sup></b>	2309	2337	1647	1658	
<b>Neutral (doublet)</b>	2105	2250	1210	1674	
<b>Anionic</b>	<b>Singlet<sup>b</sup></b>	1975	<b>2042</b>	<b>874</b>	1241
	<b>triplet</b>		<b>1850</b>	<b>1230</b>	1436
<b>Reference frequencies<sup>c</sup></b>	CO - 2240	O <sub>2</sub> - 1702	O <sub>2</sub> <sup>-1</sup> - 1240	O <sub>2</sub> <sup>-2</sup> - 749	

<sup>a</sup>[AuCO]<sup>+</sup> is singlet, while other cationic complexes are triplets

<sup>b</sup>lower energy spin state

<sup>c</sup>calculated at same level of theory

- Ternary complex CO frequencies blue-shifted relative to binary complexes
- Ternary complex O<sub>2</sub> frequencies are red-shifted relative to binary complexes; drastic effect for neutral and anionic complexes, which show O<sub>2</sub> frequencies comparable with superoxide and peroxide ions
- Both trends consistent with model of cooperative charge transfer through complex from CO to O<sub>2</sub>
- CO and O<sub>2</sub> frequencies for singlet and triplet anionic ternary complex are qualitatively different

## Bond Lengths (Å)

	AuCO		O <sub>2</sub> AuCO				AuO <sub>2</sub>		
	Au-C bond	C-O bond	Au-C bond	C-O bond	Au-O bond	O-O bond	Au-O bond	O-O bond	
<b>Cationic (triplet)<sup>a</sup></b>	1.939	1.117	1.934	1.113	2.188	1.199	2.294	1.195	
<b>Neutral (doublet)</b>	2.030	1.136	1.902	1.124	2.014	1.314	3.042	1.198	
<b>Anionic</b>	<b>singlet<sup>b</sup></b>	2.430	1.160	1.83	1.159	1.934 <sup>d</sup>	1.478	2.379	1.271
	<b>triplet</b>			1.999	1.181	2.135	1.313	3.036	1.224
<b>Reference lengths<sup>c</sup></b>	C-O	1.123	O-O (O <sub>2</sub> )	1.196	O-O (O <sub>2</sub> ) <sup>-</sup>	1.328	O-O (O <sub>2</sub> ) <sup>-2</sup>	1.533	

<sup>a</sup>[AuCO]<sup>+</sup> is singlet, while other cationic complexes are triplets

<sup>b</sup>lower energy spin state

<sup>c</sup>calculated at same level of theory

<sup>d</sup>Perpendicular distance to O-O bond center in C<sub>2v</sub> complex.

- O-O bonds show stronger increasing trend with negative charge in ternary relative to binary complexes; O-O bonds in neutral and anionic complexes comparable to peroxide and superoxide O-O bonds
- Au-C and Au-O bonds show decreasing trend with negative charge in ternary complexes, in contrast to increasing trend in binary complexes → suggests tighter binding of CO and O<sub>2</sub> as electron density increases?
- These trends also consistent with cooperative electron transfer model described above

## Binding Energies<sup>a</sup> (kcal/mol, uncorrected<sup>b</sup>)

	AuCO	AuO <sub>2</sub>	O <sub>2</sub> AuCO <sup>c</sup>	Coop. binding <sup>c,d</sup>
<b>Cationic<sup>+</sup></b>	-29.7	-11.1	-64.6	-23.8
<b>Neutral</b>	-10.5	0.03	-35.3 (-212.7)	-24.8 (-202.2)
<b>Anionic</b>	<b>singlet<sup>++</sup></b>	-2.9	-18.4 (-410.8)	-13.1 (-405.5)
	<b>triplet</b>		-2.4	-17.6 (-46.6)

<sup>a</sup>Computed relative to optimized values for component molecules, with charge (if any) localized on gold center

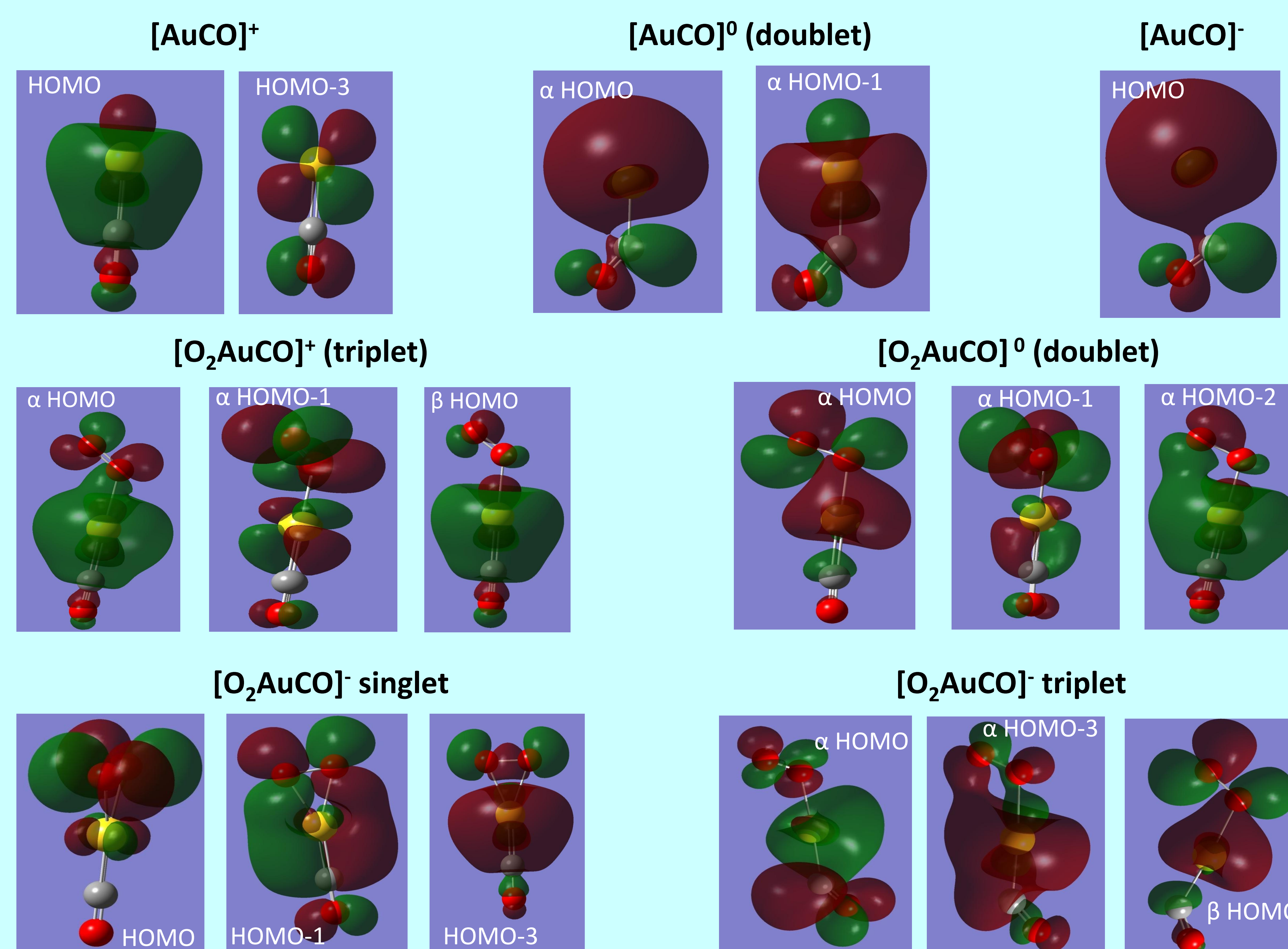
<sup>b</sup>BSSE effects and ZPE differences are within 1-2 kcal/mol for all systems studied

<sup>c</sup> Parenthetical values computed relative to [AuCO]<sup>+</sup> with O<sub>2</sub><sup>-</sup> or O<sub>2</sub><sup>-2</sup>, as described below

<sup>d</sup> difference between total binding energy of ternary complex and summed binary complexes

- Cationic complexes appear most stable relative to isolated components
- Net binding tends to decrease with increasing negative charge
- Cooperative binding effect > 10 kcal/mol for all ternary complexes
- Drastically larger estimated “effective binding energies” for neutral and anionic ternary complexes relative to peroxide and superoxide species (implied by vibrational & structure data)

## Molecular Orbitals



- [AuCO]<sup>+</sup> has linear structure with classic Dewar-Chatt-Duncanson bonding (σ-donation & π back-bonding)
- Neutral and anionic AuCO have bent structures, and HOMO's reflect Au s-CO π\* interactions, consistent with lower computed binding energies, and longer Au-C bond distances
- Ternary complexes (except triplet [O<sub>2</sub>AuCO]<sup>-</sup>) have linear Au-CO binding, and high-lying occupied orbitals reflect Dewar-Chatt-Duncanson bonding for CO, suggesting [AuCO]<sup>+</sup> character
- HOMO's of ternary complexes dominated by O<sub>2</sub> π\* character, consistent with charge transfer model, and observation of superoxide- and peroxide-like character in neutral and anionic O<sub>2</sub>AuCO

## Conclusions and Future Work

This study tends to support the model for the cooperative binding involving increased charge transfer to the oxygen moiety. Furthermore, our results suggest that this effect increases with increasing negative charge, such that the O<sub>2</sub> in the anionic complex may be expected to have superoxide or peroxide character. The molecular orbitals and calculated structures indicate that the electron withdrawing O<sub>2</sub> polarizes the electron density on the AuCO subunit, facilitating favorable Dewar-Chatt-Duncanson interactions between Au and CO.

Future computational work will include expanding the study to gold clusters, and computation of Hirshfeld charges to gauge extent of charge transfer. In addition, we plan to conduct experimental vibrational spectroscopic studies of these complexes under cryogenic conditions, which should help resolve the apparent singlet-triplet ambiguity for the anionic ternary complex.

## Acknowledgements

The NSF provided funding support for this research under CAREER award CHE-0955637.

<sup>1</sup>Wallace, W.T., Whetten, R.L. *J. Am. Chem. Soc.* **124**, (2002) 7499-7505.

<sup>2</sup>Yuan, D.W., Zeng, Z. *J. Chem. Phys.* **120**, (2004) 6574.

<sup>3</sup>Zhai, H.J., Wang, L.S. *J. Chem. Phys.* **122**, (2005) 051101.