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Au(CN)$_n$ Complexes: Superhalogens with Pseudohalogen as Building Blocks

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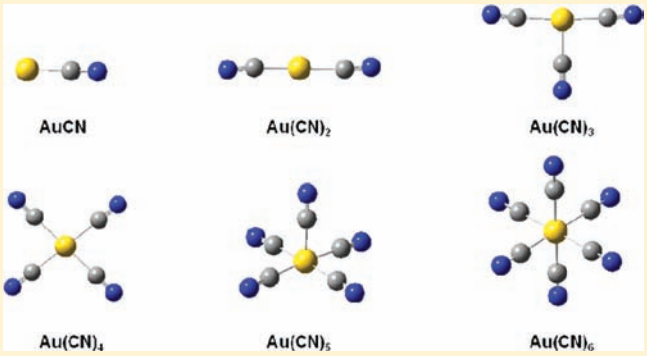

ABSTRACT: Electron affinity (EA) is one of the most important factors that govern reactivity of atoms and molecules. Chlorine, with the highest electron affinity (3.6 eV) of all elements in the periodic table, is a classic example of reactive elements. Over past thirty years, much research has been done to expand the scope of molecules with electron affinities even larger than that of Cl. These molecules, called superhalogens, have the general formula MX_{n+1} where M is a metal atom, X is a halogen atom, and n is the valency of the metal. In this paper we explore the potential of pseudohalogens such as CN, which mimic the chemistry of halogens, to serve as building blocks of new superhalogens. Using calculations based on density functional theory, we show that when a central Au atom is surrounded by CN moieties, superhalogens can be created with electron detachment energies as high as 8.4 eV. However, there is a stark contrast between the stability of these superhalogens and that of conventional AuF_n superhalogens. Whereas AuF_n complexes are stable up to $n = 5$ for neutrals and $n = 6$ for anions, Au(CN)$_n$ complexes (with CN moieties attached individually) are metastable beyond $n = 1$ for neutrals and $n = 3$ for anions. We investigate the nature and origin of these differences. In addition, we elucidate important distinctions between electron affinity (EA) and adiabatic detachment energy (ADE), two terms that are often used synonymously in literature.

I. INTRODUCTION

Electron affinity (EA) is the energy released when an electron is added to a species. It is one of the major factors that govern reactivity. Molecules with high electron affinity form very stable negative ions which are important in the chemical and health industry as they purify air,[1,2] lift mood,[3] and most importantly, act as strong oxidizing agents.[4] They can oxidize species with high ionization potential, thereby forming novel and unusual salts. It is well-known that noble gases have closed electronic shell structure and hence have high ionization potentials and low electron affinities, due to which they are chemically inert and resistant to salt formation under most conditions. This changed in 1962 when Bartlett synthesized the first salt of xenon, $XePtF_6$.[5] This was possible since PtF_6 has a very high electron affinity value of 7.00 ± 0.35 eV[6] rendering it able to ionize xenon.

In the periodic table, halogens have the highest electron affinities since they have ns^2np^5 configuration and need only one electron to attain the noble gas configuration. In fact, the electron affinity of Cl, 3.6 eV,[7] is the largest among all the elements. The discovery of Bartlett[5] and co-workers has led to a search for other molecules that also can have large electron affinities. In 1981, Gutsev and Boldyrev showed that when a central metal atom is decorated with halogen ligands, the electron affinity of the resulting species is much above that of Cl.[8] They called these species superhalogens and proposed the general formula for one class of superhalogens, namely MX_{n+1}. Here, M is a metal atom, X is a halogen atom, and n is the maximum valence of the metal atom. Since X is monovalent, MX_n is a closed shell species, and MX_{n+1} needs only one electron to close its shell. The extra electron in MX^-_{n+1} cluster can then delocalize over $(n + 1)$ halogen atoms as opposed to just one halogen atom because of which a resonance stabilized negative ion is formed. Hence, the corresponding neutral has a large electron affinity. This generalization has led to a number of studies where simple metals with multiple valence as well as transition metal atoms have been used as core atoms. Furthermore, oxygen atoms have been added to the list of electronegative atoms that surround the metal core. Experimental studies have also been carried out to validate the theoretical prediction.[9−12]

In this paper we consider a different class of electronegative moieties, called pseudohalogens, as building blocks of superhalogens. Like halogens, these molecules also need one electron to close their electronic shell, and form very stable singly charged negative ions. Thus, they mimic the chemistry of halogens.[13] Pseudohalides are composed of two or more atoms, and the

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nature of bonding between these atoms is not affected in chemical reactions where they resemble halogens. Typical examples of such moieties include CN, NCO, SCN, N_3, and so forth. Because of the similarity in chemical reactivity with halogens, it can be expected that pseudohalogens can also be used as building blocks of superhalogens. In a recent paper, Smuczynska and Skurski have shown that Li, Na, Be, Mg, Ca, B, and Al can be used as core atoms to form superhalogens with pseudohalogens as building blocks.[14]

In our work, we have performed a systematic study of $Au(CN)_n$ complexes where $n = 1$ to 6 and calculated their equilibrium structure, nature of bonding, and spectroscopic properties. We have chosen gold since it is a noble metal and because of the aurophilic interaction its chemistry is of interest to a vast range of disciplines. Moreover, gold has a high electronegativity and can have a range of oxidation states from −1 to +5, the +1 and +3 states being the most widely prevalent.[15] The oxidation state of +6, however, is highly debated. Though Au has an oxidation state of +6 in AuF_6 neutral, some argue that it will either soon transform to AuF_6^- because of its large electron affinity or dissociate. We chose to study the interaction of CN (EA 3.82 eV[16]) with Au since cyanide is the simplest pseudohalogen and gold cyanides have an extensive chemistry. In fact, cyanidation is one of the major methods for extraction of gold from its ore in the form of water-soluble $Au(CN)_2^-$ complex.[17] Gold cyanides are also used in electroplating.[18] The objectives of this work are 2-fold. First we demonstrate that noble metals like Au can also form superhalogens when decorated by CN ligands. Second, we study the extent to which the CN ligand mimics the halogen ligands with respect to its interaction with Au in forming superhalogens. For the first phase, we have done extensive calculations using density functional theory (DFT), and for the second we have compared our data with those available for AuF_n complexes,[19] which are traditional superhalogens.

II. METHODS

The total energies and geometries of the low lying isomers of both anions and corresponding neutral clusters were calculated using DFT with hybrid functional B3LYP[20] for exchange-correlation potential. The 6-311+G*[21,22] basis set was used for C and N while the Stuttgart pseudo potential SDD[23,24] basis set was used for Au. This procedure has already been shown to yield results in good agreement with experiments.[25,26] To find the global minimum structure we have considered several initial geometries by attaching Au to N or C atom of CN as well as allowing CN molecules to cluster. In all cases, the structures were optimized within the given symmetry. For each optimized structure no imaginary frequencies were found indicating that they are dynamically stable. The convergence in the total energy and force were set at 1×10^{-6} eV and 1×10^{-2} eV/Å, respectively. The output symmetries were kept at a tolerance of 0.1 using Gaussview. All calculations were done using the Gaussian 03 package.[27]

The calculated energies of the optimized clusters are used to probe their spectroscopic properties. These results can be compared with those of photoelectron spectroscopy (PES) experiments where a mass selected cluster anion is crossed with photons of fixed frequency, ν, and the kinetic energy, E_{kin} of the photoejected electron is measured. Spectroscopic properties are studied by using the energy conserving equation, $E_{anion} + h\nu = E_{neutral} + E_{kin}$, where $h\nu$ is the energy of the photon, E_{anion} is the energy of the anion, and $E_{neutral}$ is the energy of the neutral that results following photodetachment. The electron binding energy, EBE = $E_{neutral} - E_{anion} = h\nu - E_{kin}$.

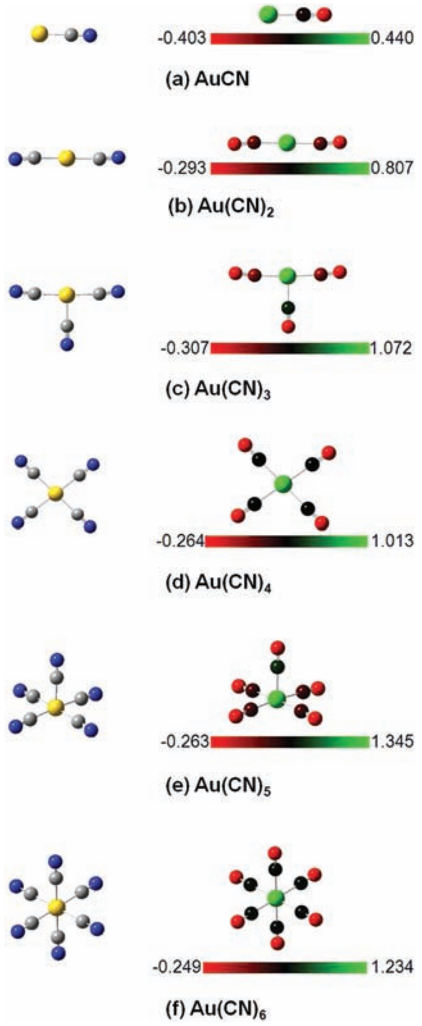


Figure 1. Optimized structures (left) and natural bond orbital (NBO) charge distribution (right) of $Au(CN)_n$ neutral complexes. Yellow represents Au, blue represents N, and gray represents C.

The vertical detachment energy (VDE) is the electron binding energy (EBE) corresponding to optimal Franck−Condon (FC) overlap between the ground state of the anion and the corresponding neutral at the structure of that anion, that is, straight up or vertically from the anion's ground state. For an electronic transition, the VDE is taken as the EBE of the peak of that transition, that is, the maximum FC overlap of the anion's and neutral's wave functions producing a maximum in electron intensity. Theoretically, it is calculated as the energy difference between the lowest energy isomer of the anion and its neutral at this anion geometry. The adiabatic electron affinity (EA), on the other hand, is the energy difference between the ground vibronic state of the lowest energy anion isomer and that of the corresponding lowest energy neutral isomer. It is the thermodynamic EA. With vibrational spectral structure and an assignment, one can identify the transition in the vibronic envelope that corresponds to the EA. Without it, one is left to estimate its location near the low EBE side of the ground anion to ground neutral transition. With no vibrational hot bands, it is at the threshold, but the problem is that there are often some hot bands. The problem gets further complicated if the anion possesses energetically nearly degenerate isomers and/or if the geometries of the lowest energy anion and the lowest energy neutral isomers are very different. In the latter case, the neutral resulting from the photodetached anion will be in an electronically excited state. Its geometric structure may not be that of the lowest

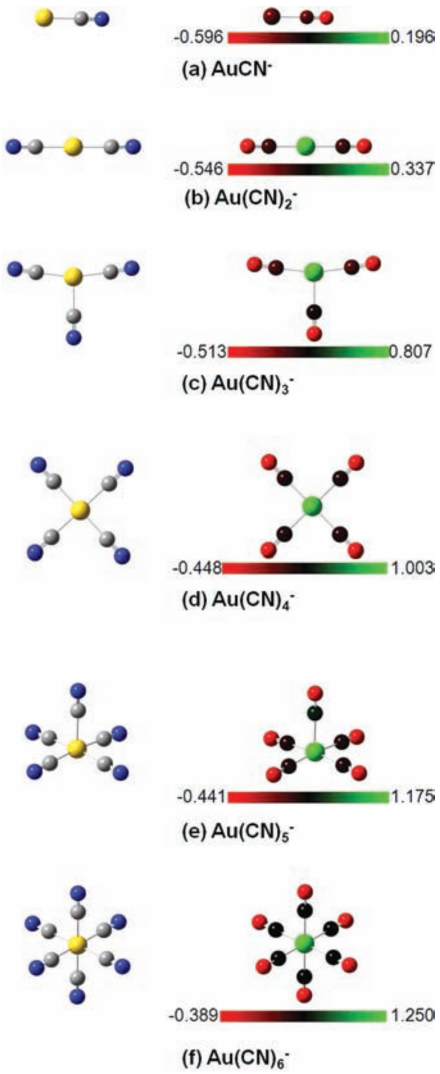


Figure 2. Optimized structures (left) and NBO charge distribution (right) of $Au(CN)_n^-$ complexes.

energy neutral isomer. What the experiment will then measure is not the EA, but what we term as the adiabatic detachment energy (ADE). We define this ADE as the transition energy from the ground vibronic state of an anion to the ground vibronic state of the structurally similar neutral isomer. This is calculated by optimizing the neutral geometry by starting with the geometry of the ground state of the anion isomer. The resulting neutral structure clearly belongs to one of the local minima on the potential energy surface. The geometry of the lowest energy neutral isomer, as mentioned before, is determined by starting from different initial structures and optimizing the geometry. This indeed is one of the hardest quantities to calculate since there may be numerous local minima on the potential energy surface. Several techniques such as genetic algorithm and basin hopping methods have been developed to make this task easier. However, geometries lying within 0.2 eV of each other are often referred to as nearly degenerate as this is beyond the accuracies of current computations. We will illustrate the distinction between EA and ADE in the following.

III. RESULTS AND DISCUSSIONS

A. $Au(CN)_n$ (n = 1−6) Superhalogens. First we have considered the dissociative attachment of CN ligands with Au, that is, attachment of CN without association into $(CN)_n$. Since CN is a well-known ambident ligand, it can attach with gold in two possible ways. It can either form gold cyanide clusters in which C atom of CN is bonded with Au (AuCN) or it can form gold isocyanide cluster where the N end of CN is bonded with Au (AuNC). For all the cases studied, we have found that gold cyanides (AuCN) are lower in energy than their isomeric gold isocyanide clusters (AuNC). All these structures are similar in geometry to the corresponding AuF_n clusters.[19] Furthermore, analogous to AuF_n clusters, $Au(CN)_n$ clusters have lowest energy for minimum spin multiplicities, that is, species with odd number of electrons prefer to be doublet while species with even number of electrons prefer to be singlet. This is expected since CN^- is known to be a strong field ligand according to the spectrochemical series.[28]

In Figure 1, we present the geometries and charge distributions of neutral $Au(CN)_n$ clusters. The Au−C bond length lies between 1.94 Å and 2.05 Å. The C−N bond length is about 1.16 Å in each case which is same as that in a free CN moiety. This means that the nature of the C−N bond is not affected when the CN ligand binds with Au as should be the case for a true pseudohalogen. AuCN is linear. $Au(CN)_2$ is pseudolinear and slightly trans in geometry, the Au−C−N angle being about 175° and the C−Au−C angle being about 180°. The Au−C bond lengths are 1.99 Å. An earlier calculation at the PW91/TZ2P level using DFT indicates that neutral $Au(CN)_2$ is linear.[29] When we forced the molecule to be linear, the total energy of the molecule was 0.09 eV greater. This is within the errors associated with DFT level theories. However, it is known that different levels of theory may result in different optimized structures. $Au(CN)_3$ is T-shaped with C_{2v} symmetry where all the Au−C bonds are not equivalent. The Au−C bond length between the Au atom and the CN ligands which form the head of the T is about 2.01 Å whereas, the Au−C bond length for the CN ligand attached perpendicular to the head is 1.94 Å signifying that this bond is stronger. $Au(CN)_4$ is planar with a D_{2h} symmetry and all bond lengths are about 2.02 Å. One pair of C−Au−C angles is about 80° while the other pair is about 100°. $Au(CN)_5$ has C_{4v} symmetry. Here, four of the CN ligands lie in the same plane as Au, and one CN ligand is perpendicular to this plane. As in case of $Au(CN)_3$, there are two kinds of Au−C bonds. The Au−C bonds between the Au and the CN in the same plane are all equivalent and about 2.03 Å whereas the remaining Au−C bond length is 1.98 Å. $Au(CN)_6$ has D_{3d} symmetry, and all the Au−C bonds are equivalent with a bond length of 2.05 Å. As indicated in section II, we have used a tolerance level of 0.1 in assigning cluster symmetry. Note that this assignment may vary depending upon the tolerance level chosen. For example, if this tolerance level is increased to 0.6, the symmetries of $Au(CN)_4$ and $Au(CN)_6$ are respectively D_{4h} and O_h.

The anionic clusters shown in Figure 2 have similar geometry as that of the neutrals. This is reflected in the small difference between the calculated vertical detachment energies (VDE) and the adiabatic detachment energies (ADE) as discussed below. The average C−N bond distance is 1.16 Å as in the case of the neutrals. However, the Au−C distances are slightly longer compared to those in the neutrals and lie between 2.02 Å and 2.26 Å. The symmetries of $Au(CN)_n$ are $C_{\infty v}$, $D_{\infty h}$, C_{2v}, D_{4h}, C_{4v}, and C_{4h} for n = 1 to 6 respectively. These are the lowest energy structures for dissociative attachment of CN.

The adiabatic detachment energies (ADE) and vertical detachment energies (VDE) of the complexes were computed.

Table 1. Theoretical and Experimental ADE and VDE of $Au(CN)_n$ Complexes for Dissociative Attachment of CN Ligands

	ADE (eV)		VDE (eV)	
complex	theo	expt	theo	expt
AuCN	2.12	2.07[30]	2.25	2.19[30]
$Au(CN)_2$	6.08	6.09[29]	6.10	6.09[29]
$Au(CN)_3$	5.07		5.44	
$Au(CN)_4$	7.61		7.95	
$Au(CN)_5$	7.02		7.45	
$Au(CN)_6$	8.40		8.48	

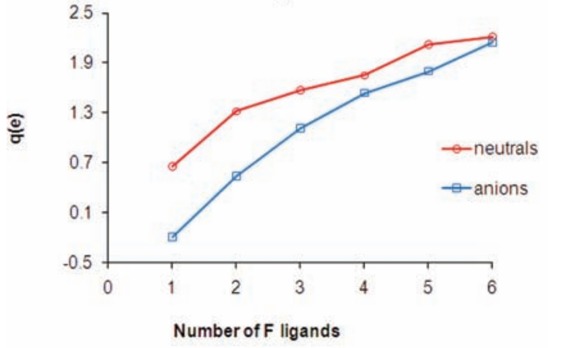
ADE provides a measure of the stability of the anion over the neutral and its electron accepting capacity. The ADE and the VDE values are given below in Table 1 and compared with available experimental data. Note that the ADE of $Au(CN)_2$ is almost a factor of 3 larger than that of AuCN and a factor 2 larger than that of Cl. Hence, it is a superhalogen. These results are in excellent agreement with previous theoretical and experimental data.[29] The ADEs of clusters for $n \geq 3$ are more than twice the electron affinity of Cl and reach values as high as 8.4 eV in $Au(CN)_6$. This indicates that these $Au(CN)_n$ complexes are indeed superhalogens. We also note that Smuczynska and Skurski[14] recently studied $Na(CN)_2$, $Mg(CN)_3$, and $Al(CN)_4$ and found these to be superhalogens as well.

The difference between the ADE and VDE is a measure of the geometry change of the anion when the electron is removed. The small magnitude of this (between 0.02 and 0.43 eV) signifies that the neutrals and anions studied here are analogous in symmetry and structure as is evidenced from Figure 1 and 2.

From the above data we observe that very high ADEs, much higher than that of Cl, are obtained. These values are comparable with those of corresponding AuF_n complexes (2.46 to 8.38 eV for $n = 1$ to 6).[19] We further notice that there is an odd−even alternation in the electron affinities. When n is odd, the ADE is low and when n is even the ADE is high. The explanation is simple. For odd n, the neutrals have an even number of electrons and a closed shell. Thus, the ADE is comparatively small when an extra electron is added. When n is even, the neutrals have an odd number of electrons and an open shell. Since their anions have an even number of electrons and a closed shell, energies are lowered when the electron is attached. This increases their ADE values.

To understand the nature of bonding we also calculated the NBO charges $[q(e)]$ on the Au atom in both the neutral and the anionic structures (see Figure 1 and 2). The results are plotted in Figure 3 and compared with that in AuF_n clusters. As we can see, gold is positively charged in all the neutral clusters and all the anionic clusters except in $AuCN^-$. CN, because of its high electron affinity, withdraws electron density from Au, thus rendering it a positive charge in the clusters. However, AuCN is a small closed shell molecule. Thus, on addition, the extra electron in $AuCN^-$ is delocalized over all the three atoms. This process is further facilitated since Au, though a metal, has quite a high electronegativity. In fact, the closed shell nature of AuCN explains why its ADE is low. The charge on the Au atom increases with the number of ligands in both the neutral and the anionic clusters. However, the difference between the charges gets smaller as the number of ligand atoms increases and becomes vanishingly small at $n = 4$. This is to be expected when one considers the oxidation state of Au to be +3. In $Au(CN)_4^-$, the extra electron is distributed over the CN moieties and hence the charge on Au is the same as that in neutral $Au(CN)_4$. The charge distribution in $Au(CN)_n$ compares well with that in AuF_n, although the magnitudes are different. This shows that as long as CN moieties are bound to Au dissociatively, the pseudohalogen behaves like a halogen. Moreover, we see that the charges on Au are greater when F is attached than when CN is attached. It should also be mentioned that the small NBO charges on Au in AuCN and $Au(CN)_2^-$ establishes the covalent nature of the Au−C bond corroborating earlier experimental work.[29,30]

(a) Charge on Au atom as a function of number of F ligands



(b) Charge on Au atom as a function of number of CN ligands

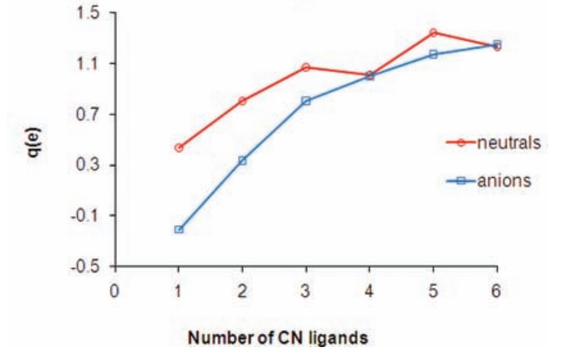


Figure 3. NBO charge on Au in (a) AuF_n and (b) $Au(CN)_n$ complexes.

B. Stability with Respect to Fragmentation. Since none of the molecular structures studied above have imaginary frequencies, they at least belong to minima on the potential energy surface. However, to test their stability against fragmentation, we have considered several dissociation pathways of structures given in Figures 1 and 2. Here, the neutral clusters can fragment by ejecting a CN or $(CN)_2$. In the case of anions, we also have to consider whether the charge is carried by the CN or the $Au(CN)_n$ moiety. In Table 2 we list the dissociation energies corresponding to the most thermodynamically preferred channel. When dissociation energy is positive, fragmentation will be endothermic implying that the parent cluster is stable. Both AuCN and $AuCN^-$ are stable. However, $Au(CN)_n$ complexes are unstable with respect to dissociation for $n > 1$ in case of neutrals and $n > 3$ in case of anions. This is in stark contrast with AuF_n complexes which are stable with respect to dissociation up to $n = 5$ for neutrals and $n = 6$ for anions. This difference arises because of the difference in the F−F bond energy in F_2 molecule and C−C bond energy in cyanogen gas (NCCN). The binding energy of

Table 2. Fragmentation Energies for Neutral and Anionic $Au(CN)_n$ Clusters

complex (A)	preferred fragmentation product (B)	fragmentation energy/eV (energy of B-A)
AuCN	Au + CN	3.65
$AuCN^-$	Au + CN^-	1.70
$Au(CN)_2$	Au + $(CN)_2$	−0.49
$Au(CN)_2^-$	Au^- + $(CN)_2$	3.39
$Au(CN)_3$	AuCN + $(CN)_2$	−1.42
$Au(CN)_3^-$	$AuCN^-$ + $(CN)_2$	1.53
$Au(CN)_4$	Au + $2(CN)_2$	−2.44
$Au(CN)_4^-$	$Au(CN)_2^-$ + $(CN)_2$	−0.42
$Au(CN)_5$	AuCN + $2(CN)_2$	−5.03
$Au(CN)_5^-$	$Au(CN)_3^-$ + $(CN)_2$	−1.65
$Au(CN)_6$	Au + $3(CN)_2$	−6.32
$Au(CN)_6^-$	$Au(CN)_2^-$ + $2(CN)_2$	−3.50

$(CN)_2$ (NCCN), namely, 5.84 eV,[31] is about 3.5 times the binding energy of F_2, namely, 1.82 eV.[32] Moreover the Au−F bond energy (2.65[19]) > F−F bond energy (1.82 eV) whereas, the Au−CN bond energy (3.65 eV) < NC−CN bond energy (5.84 eV). Hence, CN would preferentially bind to itself than with Au whereas F would preferentially bind to Au than with itself. Similarly $Au(CN)_n^-$ are less stable against fragmentation than corresponding AuF_n^-.

This brings us to examine the case of $Au(CN)_2$ more closely. We note from Table 2 that while neutral $Au(CN)_2$ is unstable and fragments to Au and NCCN, its anionic counterpart is stable. The question then arises: What prevents the neutral following electron detachment of the anion to remain in the metastable state. To gain further insight we have calculated the energy barrier between the metastable and the dissociated lower energy state by keeping the C−Au−C fixed at a particular angle and optimizing all other parameters. Partial geometry optimizations were carried out by varying the ∠C−Au−C angle from 30° to 180° in 10° increments. This simple procedure gave us the potential energy diagram for fragmentation (Figure 4). We also calculated the structure and energy of the transition state. The difference in the energy of the TS and $Au(CN)_2$ gave the barrier height. This energy barrier is 1.86 eV which is substantial indicating that though $Au(CN)_2$ is metastable, it has a long lifetime. In this connection, it should also be mentioned that fragmentation through other pathways such as $Au(CN)_2 \rightarrow$ AuCN + CN are thermodynamically unlikely, as in this case the energy of the fragmented products is 2.12 eV higher than that of $Au(CN)_2$. This is even higher than the energy barrier for fragmentation into Au + $(CN)_2$.

Note that Wang et al. probed the nature of bonding in $Au(CN)_2^-$ using PES and found the spectrum to be quite narrow indicating that the anion and neutral have similar geometries. We want to emphasize that what Wang et al. measured[29] is the adiabatic detachment energy (ADE) which should not be confused with the electron affinity (EA).

C. More Stable Isomers and the Importance of Metastability. Since neutral $Au(CN)_2$ structure shown in Figure 1 is not the global minimum and clusters with larger CN concentration are metastable, we searched for lower energy isomers where CN molecules may dimerize to form $(CN)_2$ or trimerize to form $(CN)_3$. We concentrated our search only on $Au(CN)_3$ and $Au(CN)_4$ where strong bonding is observed. We have not considered van der Waals type clusters in which cyanogen gas molecules can also dimerize to form $(CN)_4$ and then interact with Au.

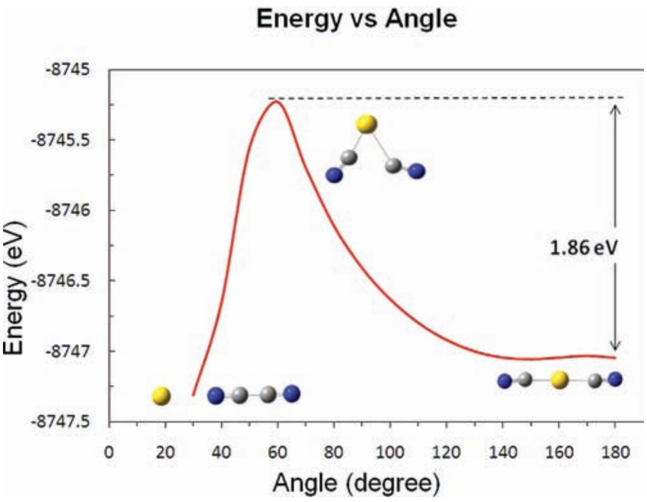


Figure 4. Calculation of energy barrier for the fragmentation of $Au(CN)_2$ to Au and $(CN)_2$.

First, we determined the minimum energy structures of $(CN)_n$ for $n = 2$ and 3. This gave an indication of the relative C−C, C−N and N−C bond strengths in the $(CN)_n$ moieties and accordingly we proceeded in our search for lowest energy $Au(CN)_n$ structures. The geometries of some isomers of $(CN)_2$ and $(CN)_3$ are given in Figure 5. It is to be noted that none of the structures were found to have imaginary frequencies indicating they are dynamically stable. In case of neutral $(CN)_2$, we found that cyanogen (NCCN) has lower energy than isocyanogen (NCNC), which in turn, has lower energy than diisocyanogen (CNNC). This indicates that when cyanide binds with gold after dimerization, it will preferentially attach as NCCN moiety. The N−C bond lengths are 1.16 Å and the C−C bond length is 1.38 Å. In case of $(CN)_2^-$, we found that again, $NCCN^-$ with C_{2h} symmetry has the lowest energy. The N−C bond lengths increase to 1.20 Å and the C−C bond length remains at 1.38 Å. Our results agree with previous reports.[33−35] We found several isomers for $(CN)_3$, some of which are shown in Figure 5. Of these, the NCNCCN structure with C_s symmetry has the lowest energy, in both neutral and anionic forms. Here, a cyanide moiety is attached to the cyanogen molecule. The energies of the different isomers relative to the ground state (ΔE) isomers are listed in Figure 5. ΔE is defined as the energy of the converged structure minus the energy of the lowest energy structure.

With these results in mind, we proceeded to the investigation of lower energy structures of $Au(CN)_n$ clusters. We expected that structures where $(CN)_2$ and $(CN)_3$ attach as NCCN and CNNCCN, respectively, will have lower energy. We did not find any energetically lower isomers of AuCN and $Au(CN)_2$ than those given in Figures 1 and 2. However, for $Au(CN)_3$, $Au(CN)_3^-$, and $Au(CN)_4$ we were able to find lower energy structures, in accordance with our expectations. These are shown in Figure 6. The energies of these structures are lower from those given in Figure 1 and 2 by 2.69, 0.08, and 2.97 eV, respectively. No structures of $Au(CN)_4^-$ with energies lower than that shown in Figure 2 were found.

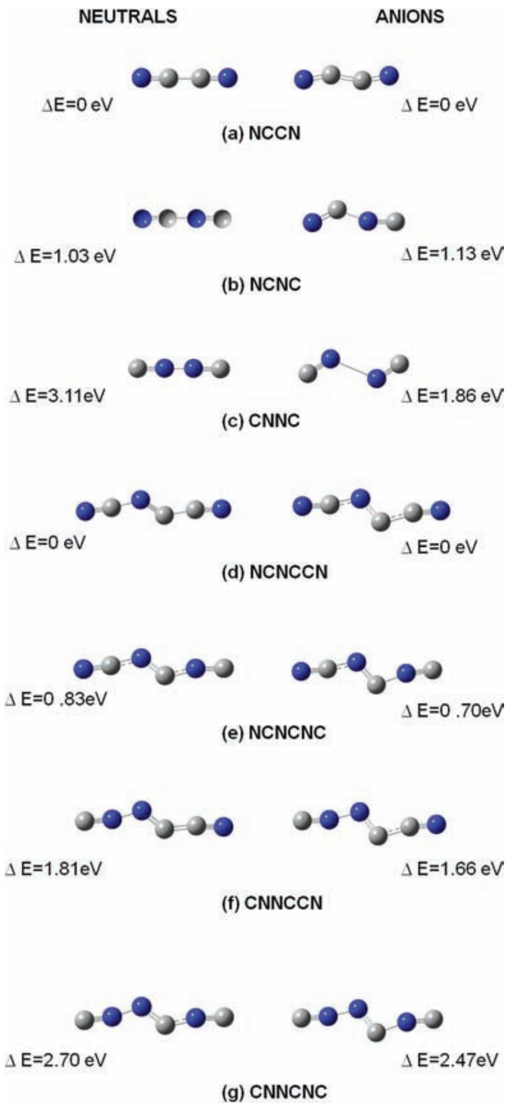


Figure 5. (a−c) Some low energy isomers of $(CN)_2$; (d−g) some low energy isomers of $(CN)_3$.

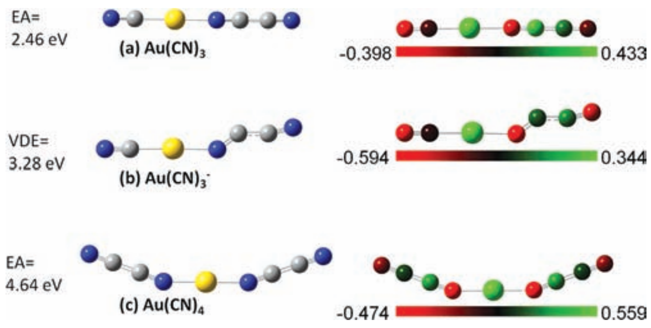


Figure 6. Ground state geometries of $Au(CN)_3$, $Au(CN)_3^-$, and $Au(CN)_4$.

Neutral $Au(CN)_3$ is linear with $C_{\infty v}$ symmetry. The Au−C bond length is 1.96 Å which is slightly longer than that in AuCN (1.94 Å). The N−Au bond length is 2.04 Å signifying that this bond is much weaker. The structure of $Au(CN)_3^-$ is quite different. The Au−C bond length is 1.98 Å, and the Au−C−N atoms lie in a plane. However, the $(CN)_2$ moiety on the other side has a slight trans nature with the Au−N bond length of 2.04 Å. Considering Au to be in +1 oxidation state, we see that AuCN has a closed shell. Hence, most of the negative charge (−0.755) in $NCAuNCCN^-$ goes to the $(CN)_2$ moiety and thus its structure is similar to that of free $NCCN^-$. Moreover, the difference between VDE and ADE (which is also the EA in this case) of $NCAuNCCN^-$ is 0.82 eV which is equal to the VDE of $NCCN^-$. We note that the $Au(CN)_3^-$ isomer in Figure 6 is only 0.08 eV lower in energy than that in Figure 2 where CN moieties bind dissociatively. This energy difference is less than the accuracy of DFT methods and hence the two geometries are nearly degenerate. The PES spectra of $Au(CN)_3^-$ would be very revealing. The ADE of $Au(CN)_3$ calculated from Figure 6 would yield 2.46 eV while that calculated from Figure 1 and 2 and given in Table 1 is 5.07 eV. Note that one is a superhalogen while the other is not. In addition, we would expect the PES spectra to be narrow irrespective of whether the $Au(CN)_3^-$ has the structure given in Figure 6 or in Figure 2c as the corresponding neutral geometries are quite similar to their anion counterparts. Since both the anion isomers of $Au(CN)_3$ are nearly degenerate, it will be interesting to see if experimental PES spectra would reveal that.

Neutral $Au(CN)_4$ has C_{2v} symmetry with two linear cyanogen groups in a cis conformation, the C−N−Au angles being 159° each and the N−Au−N angle being about 180°. The Au−N bond length is 1.98 Å. It is interesting to note that while their isomers in which CN molecules have attached to Au dissociatively are unstable with respect to fragmentation, these lower energy structures are all stable and also have no imaginary frequencies. The fragmentation energies of the lower energy structures along the same path as for the metastable ones are 1.26, 1.60, and 0.53 eV for $Au(CN)_3$, $Au(CN)_3^-$, and $Au(CN)_4$, respectively.

We also found several energetically higher structures for these three complexes. These were obtained by permutations of the relative positions of the C and N atoms with respect to gold. Some of the structures are shown below in Figure 7. Optimization of $Au(CN)_4^-$, starting with different initial configurations led to structures all of which have higher energies than the structure in Figure 2 (d). However, these structures are also dynamically stable and belong to local minima on the potential energy surface. The energies of the higher energy structures relative to the ground state (ΔE) are incorporated in Figure 7. Beyond this limit, cyanogen dimerization sets in.

This suggests that what will be observed experimentally may depend on the initial reaction conditions. In gas phase synthesis of gold cyanide clusters, if the vapor pressure of CN molecules is low, the most likely products will have the structures shown in Figure 1 and 2. This is because reaction occurs when two species collide with each other. Lower CN vapor pressure minimizes the chances of CN-CN collisions. On the contrary, if the vapor pressure of CN is high, structures as shown in Figure 6 may form. However, it is likely that in both cases a mixture of isomeric products may exist.

Our results also lead us to the important conclusion that there is a difference between the electron affinity (EA) and the adiabatic detachment energy (ADE). In fact, the EA of $Au(CN)_3$ is the energy difference between structures (a) and (b) in Figure 6 which is 2.46 eV. The energy difference between the structures in Figures 1c and 2c is simply an ADE. From Figure 6, we see that $Au(CN)_3$ can be considered to be composed of a pseudo closed-shell dipolar AuCN moiety which binds to the pseudo

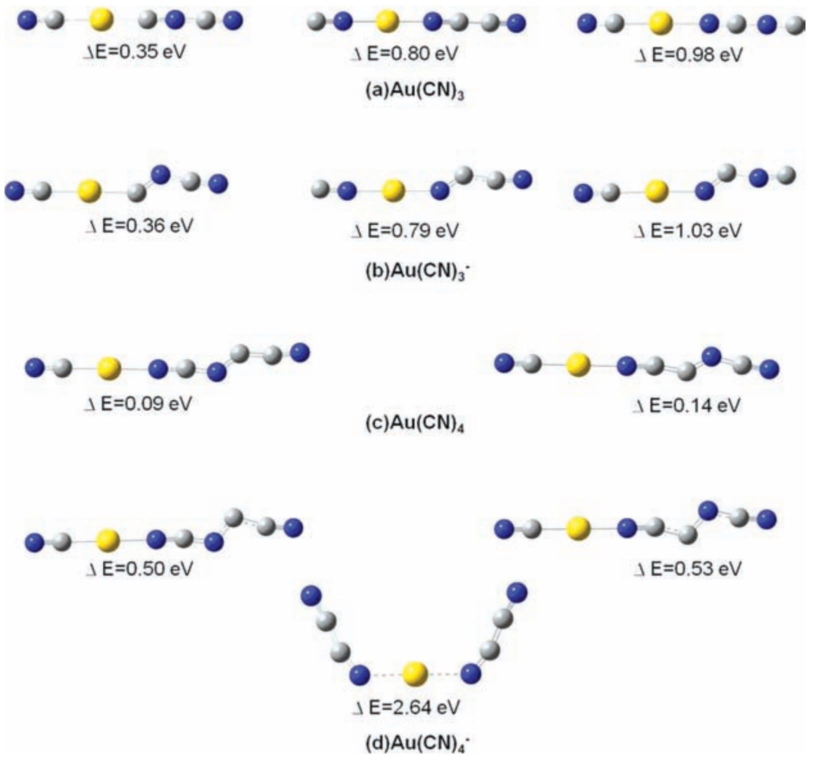


Figure 7. Some higher energy structures of $Au(CN)_3$, $Au(CN)_3^-$, $Au(CN)_4$, and $Au(CN)_4^-$.

closed-shell $(CN)_2$ moiety by inducing a dipole moment in it. This explains the low value of EA. The VDE is 3.28 eV. Similarly, the EA of $Au(CN)_4$ is 4.64 eV, the energy difference between the structures in Figures 2d and 6c. The VDE is 7.95 eV as tabulated in Table 1. The large difference of 3.3 eV between the EA and VDE accounts for the fact that the geometries of the neutral and the anion are drastically different in this case. Since we note that there is a substantial difference between the lowest energy structure of the neutral and the lowest energy structure of the anion in several cases, one has to be careful while assigning a value to the EA experimentally. If the structures shown in Figure 1 and Figure 2 are relevant to experimental conditions, one would measure ADE as the transition energy from the anion's ground state to the ground state of the structurally similar neutral isomer. We earlier demonstrated this to be the case for $Au(CN)_2$. Experimental studies of larger $Au(CN)_n$ complexes will be very useful.

A very important realization that we make from our data is that, to exhibit superhalogen behavior it is essential that the CN moieties attach dissociatively with Au so that effective electron delocalization can take place. Most of the structures studied are metastable, and their fragmented counterparts are lower in energy. However, to exploit the superhalogen properties of these clusters, it is these metastable clusters that are important. Experiments can tell us if the formation of $Au(CN)_n$ clusters will be driven kinetically or thermodynamically and if the spectroscopic properties carry the signature of metastable states.

IV. CONCLUSIONS

Our systematic study of $Au(CN)_n$ clusters shows several important results. (1) The calculated vertical and adiabatic detachment energies of AuCN and $Au(CN)_2$ agree with previous experiments. However, we show that neutral $Au(CN)_2$ is metastable, and the PES study only yields the adiabatic detachment energy and not the electron affinity as initially believed. (2) Our result confirms the earlier observation[14,29] that pseudohalogens can be used to build superhalogens. However, in our study we show that large electron affinities can be attained without changing the identities of the reactant molecules, simply by tuning the number of ligands allowed to interact with the central metal atom. Moreover, we observe a fundamental difference between how the halogens and pseudohalogens lead to the formation of superhalogens. For example AuF_n forms superhalogens up to $n = 6$. Pseudohalogens can do the same if experimental conditions are such that they bind individually to the metal atom. (3) The reaction of halogens and pseudohalogens with a metal atom is different which arises because pseudohalogens can dimerize more easily because of their large binding energy. (4) It is to be noted that for superhalogen behavior, it is essential to have ligands attaching dissociatively rather than after dimerization. This is demonstrated for $Au(CN)_3$ whose electron affinity corresponding to the lowest energy anion isomer is 2.46 eV while for its metastable isomer in Figure 6, the adiabatic detachment energy is 5.07 eV. Moreover, we show that the possible existence of metastable isomer can make the task of experimental determination of electron affinity difficult. In such cases, there may be a discrepancy between the electron affinity and the adiabatic detachment energy of a species, and theoretical work is essential. We hope our work will provide direction in the synthesis of new superhalogens and in a fundamental understanding of their behavior.

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