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**BONDING GEOMETRY AND BONDING CHARACTER OF THIOCYANATE  
ADSORBED ON  
A Ag(100)**

by

**Gianfranco Pacchioni, Francese Illas,  
Michael R. Philpott and Paul S. Bagus**

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# BONDING GEOMETRY AND BONDING CHARACTER OF THIOCYANATE ADSORBED ON A Ag(100) SURFACE

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## ABSTRACT

The adsorption geometry and the nature of the interaction of the SCN molecule at an on top site of the Ag(100) surface have been investigated using ab initio cluster model wavefunctions. The SCN anion,  $\text{SCN}^-$ , is a bidentate ligand. If the SCN-Ag bond is ionic, we could expect, by analogy with thiocyanate-metal complexes, that SCN could be bound to a metal surface through either the N-end or the S-end. We show that the chemisorption bond for SCN/Ag is very ionic and that the interaction between chemisorbed SCN and the Ag surface is largely electrostatic. The most important bonding mechanism is the polarization of the Ag surface due to the presence of  $\text{SCN}^-$ . However, we do find that there is a small, but non-negligible, covalent interaction. There is a very small energetic cost to change the angle of SCN with respect to the surface between a perpendicular and a parallel orientation. We contrast this with the case of a covalently bonded adsorbate, CO/Ag(100), where the  $\pi$  bond strongly favors orientations near perpendicular. The flat potential energy curve for bending SCN suggests that the adsorption geometry at high SCN coverage may be largely determined by non-bonding interactions between adjacent adsorbates.

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## I. INTRODUCTION

The chemisorption geometry and the nature of the interaction of thiocyanate, SCN, adsorbed on a metal surface is of particular interest. In metal complexes, the SCN anion, SCN<sup>-</sup>, is an ambidentate molecule which can bond through either the N-end, the S-end, or both; see Fig. 1. However, there is very little precise experimental information about the bonding geometry of SCN to a metal surface.<sup>1</sup> There have been numerous experimental studies of SCN<sup>-</sup> adsorbed on noble metal electrodes from aqueous electrolyte solutions.<sup>2</sup> Differential capacitance measurements imply partial monolayer coverage at mM bulk solution concentrations at the potential of zero charge, rising to saturation coverage at the most positive potentials that the electric double layer will sustain without chemical reaction. Raman of rough surfaces and FT-IR of smooth surfaces are in agreement with thiocyanate being adsorbed oriented towards the surface normal at high surface coverage (i.e., positive of the potential of zero coverage) and flat otherwise. On the other hand, SCN is a well known ligand in transition metal coordination chemistry.<sup>3</sup> In metal complexes, the preference for bonding at N or at S has been attributed to electronic effects. In particular, it has been suggested that metal centers with high electron density prefer an S-bond SCN ligand because it can decrease the excess of negative charge on the metal through  $\pi$  back bonding. On the contrary, when the electron density on the metal is low the N-bound complex is expected to form.<sup>3</sup> It is worth noting that the N-bound species is linear while the S-bound form is usually bent.<sup>1,3</sup> Hence, the structural diversity of the thiocyanate ion may be the basis of very interesting surface chemistry.

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In this work, we have investigated the bonding nature and the geometry of SCN on a silver surface using the ab initio Hartree-Fock cluster model. Thiocyanate is studied interacting either N- or S-down at an on top site of a Ag(100) surface. We should note that we are concerned with the interaction of an SCN moiety with a silver surface. It is not important whether that moiety arrives at the surface as a neutral species or, as in an electrochemical cell, as an anion. The chemical nature of the adsorbed SCN will be the same in both cases since the Ag surface is an excellent source and sink of electrons. For the geometries considered, we shall show that the chemisorbed SCN molecule is  $\text{SCN}^-$ , an anion. The geometries studied have involved SCN at an on top site of a Ag(100) surface with either the N or the S atom directly above a surface Ag atom. The distance of the N or S atoms from the Ag have been varied. A range of polar angles of the internuclear axis of linear SCN with the Ag surface between  $180^\circ$ , perpendicular orientation, and  $\sim 70^\circ$  have been examined; we have also examined two azimuthal angles for the bent SCN molecule. See Fig. 1 for a schematic of the adsorption geometry. A cluster of 10 Ag atoms has been used. This cluster contains 5 atoms in the first, 4 atoms in the second, and 1 atom in the third layer; the Ag atoms are placed at their positions from the bulk and represent an unreconstructed Ag(100) surface. The cluster is denoted  $\text{Ag}_{10}(5,4,1)$ ; see Fig. 2. The SCN is added above the central Ag atom of the first layer to form the  $\text{Ag}_{10}\text{-L}$  cluster where L is either SCN or NCS. Results for  $\text{Ag}_{10}\text{-L}$  are compared with those for the simpler Ag-L and  $\text{Ag}_5(1,4)\text{-L}$  cluster models.<sup>3</sup>

We have examined clusters which are neutral,  $[\text{Ag}_n\text{-SCN}]^0$  and  $[\text{Ag}_n\text{-NCS}]^0$  and clusters which have a net negative charge of 1 electron,  $[\text{Ag}_n\text{-SCN}]^-$  and  $[\text{Ag}_n\text{-NCS}]^-$ . These two total charge states for the cluster represent extreme cases for

sources of the charge required to form an adsorbed SCN anion. When the cluster has a negative charge, the charge to form the SCN anion comes from other than the Ag atoms explicitly included in the cluster. It could be that the SCN arrives at the surface as an anion or that the charge comes from other, more distant, Ag atoms of the substrate. When the cluster is neutral, the charge to form an adsorbed SCN anion would come entirely from the Ag atoms explicitly included in the cluster. For an anionic adsorbate, the actual situation at the surface will be intermediate between these two cases but closer to the case of the cluster with a net negative charge. The change in the total charge of the cluster can also be considered as a very simple model of changing the electrode charging in an electrochemical cell as the potential across the electrodes is changed. An accurate representation of the effect of the cell potential requires the application of an external electric field.<sup>5</sup>

We found that the bonding of SCN to the Ag surface is dominantly ionic and does not involve a substantial covalent interaction; in effect SCN on a Ag surface is SCN<sup>-</sup>. We have found this to be the case for neutral clusters as well as for clusters with a net negative charge. The fact that the SCN is an anion independent of the total cluster charge is compelling evidence that SCN chemisorbed on a surface is an anion. An important consequence of the fact that the SCN-surface bond is ionic is that SCN can be bound N- or S-down with similar interaction energies.<sup>13</sup> In addition, an ionic adsorbate is expected to be very mobile on a metal surface. In particular, it should be easy for the SCN to change its orientation from perpendicular to parallel to the surface as other conditions, e. g. the surface coverage, change. The bending mode for the ionically bonded SCN is compared with that for the covalently bonded CO molecule.

## II. COMPUTATIONAL DETAILS

Ab initio self-consistent field, SCF, electronic wavefunctions have been determined using the MO-LCAO procedure. The five first-layer Ag atoms of the Ag<sub>10</sub> cluster have been treated with an 11-electron Effective Core Potential, ECP, which explicitly includes the Ag 4d and 5s electrons.<sup>6b</sup> The remaining Ag atoms have been described by means of a 1-electron ECP.<sup>7</sup> For the cases of Ag<sub>5</sub>(1,4)-SCN and Ag-SCN, see Ref. 4, the Ag atom directly interacting with the SCN ligand has been treated with a 19-electron ECP.<sup>6a</sup> The S, C, and N atoms of the SCN adsorbate have been treated with all their electrons. The Gaussian Type Orbital, GTO, basis sets used are flexible enough to make the Basis Set Superposition Errors,<sup>8</sup> BSSE, small. The 11-electron ECP Ag atoms are described by a [3s,4p,4d/2s,2p,1d] contracted GTO basis set; the 1-electron Ag atoms are treated with a [3s,3p/2s,1p] basis set.<sup>6,7</sup> The basis sets for C and N atoms consist of [9s,5p/4s,3p] GTO's,<sup>9</sup> while the S atom basis set is [13s,9p/5s,4p].<sup>10</sup>

The metal atoms of the substrate cluster have been fixed and the metal-ligand geometry has been optimized for N- and S-down coordination modes. The metal-ligand distance and angle have been varied independently. We have optimized first the r(Ag-N) or r(Ag-S) distances; then we fixed r at r<sub>c</sub> and we varied the angle  $\alpha$  formed by the on top Ag atom and the N- and S-ends of the SCN<sup>-</sup> ion. For the optimal angle  $\alpha$  the Ag-thiocyanate distance has been reoptimized. During the optimization procedure the S-C and the C-N distances were fixed at their optimal values for free SCN<sup>-</sup>, r(S-C) = 3.27 bohr, r(C-N) = 2.21 bohr. We have chosen to bend the SCN molecule so that it is directly overhead a nearest neighbor surface Ag atom.

see Fig. 2; the corresponding azimuthal angle is  $\phi=0$ . In this way, when the SCN molecule is flat on the surface, the N and S atoms can interact directly with the two surface Ag atoms. In fact, the N-S distance in SCN, 5.477 bohr, is almost coincident with the nearest neighbor Ag-Ag distance, 5.449 bohr. The bending of SCN for  $\phi=45$  degrees has also been considered for the  $[\text{Ag}_{10}\text{-SCN}]^{0,-1}$  case (Table 1).

The nature of the Ag-SCN and Ag-NCS chemical bonding has been analyzed by means of the Constrained Space Orbital Variation, CSOV, technique.<sup>10</sup> This allows one to establish the relative importance of the different bonding contributions, in particular of the electrostatic versus the covalent interactions. The CSOV decomposition has been studied for different Ag-L bond lengths and angles.

### III. RESULTS AND DISCUSSION

#### 3.1 The Ag/SCN System

A very important consideration is the ionicity of SCN adsorbed on Ag. We have analyzed this ionicity using a projection operator technique to obtain a measure of the effective charge associated with the SCN fragment, or sub-unit, of the  $\text{Ag}_n\text{-L}$  clusters. Especially for ionic interactions, projection gives a more reliable measure of this charge than the standardly used Mulliken population analysis.<sup>12</sup> The projection operator for an orbital  $\phi$  is simply  $\phi\phi^\dagger$ . A measure of the occupation of an adsorbate orbital,  $\phi_\Lambda$ , in the total cluster wavefunction,  $\Psi_{\text{Cluster}}$ , is given by the expectation value<sup>13</sup>  $P(\phi_\Lambda)$  of the projection operator for  $\phi_\Lambda$ :

$$P(\phi_A) = \langle \Psi_{\text{Cluster}} | \phi_A \phi_A^\dagger | \Psi_{\text{Cluster}} \rangle.$$

If  $P(\phi_A)$  is very close to 2 (4 for degenerate orbitals), then the orbital  $\phi_A$  is fully occupied in  $\Psi_{\text{Cluster}}$ .

For the analysis of the SCN interaction with Ag, we have used the orbitals,  $\phi_A$ , for the free SCN<sup>-</sup> ion. We have examined both orientations of SCN, S- and N- down, for the perpendicular ligand geometry,  $\alpha = 180^\circ$ , and we have considered both 0 and -1 charge states for the total cluster,  $[\text{Ag}_n\text{-L}]^{0,-1}$ . Further, we obtained projections for the Ag-L, Ag<sub>5</sub>-L, and Ag<sub>10</sub>-L clusters for a range of distances about the equilibrium Ag-L bond distance. In all cases, the sum of  $P(\phi_A)$  over all the occupied orbitals of SCN was close to 30 showing that SCN is fully ionic; in no case was the sum less than 29.90. The projections provide definitive evidence that the charge of thiocyanate chemisorbed at an on-top site of Ag(100) is essentially -1.

The geometrical parameters and the interaction energy,  $E_{\text{INT}}$ , for the clusters considered in this work are summarized in Table I. For the geometry, we give the Ag-L equilibrium bond distance,  $r$ , and the equilibrium polar angle,  $\alpha$ ;  $r$  is given as the Ag-S or the Ag-N distance depending on the SCN orientation. For the Ag<sub>n</sub>-SCN, S-down, orientation, we give results for both  $\phi = 0$  and  $\phi = 45^\circ$  azimuthal angles; for Ag<sub>n</sub>-NCS, only  $\phi = 0^\circ$  was considered. For this latter orientation, the equilibrium polar angle was normally  $180^\circ$ . However for neutral Ag<sub>10</sub>-NCS with  $r(\text{Ag-N}) = 4.50$  bohr and  $\phi = 0$ , we found an equilibrium  $\alpha = 105^\circ$  with an energy 0.13eV lower than for  $\alpha = 180^\circ$  with equilibrium  $r = 4.41$  bohr. The interaction energy is given as the difference of the SCF energy of Ag<sub>n</sub>-L and the SCF energies of Ag<sub>n</sub> and L sub-units.

For the neutral  $[\text{Ag}_n\text{-L}]^0$  clusters, the sub-units were  $\text{Ag}_n^+$  and  $\text{L}^-$ ; for the negatively charged  $[\text{Ag}_n\text{-L}]^-$  clusters, the sub-units were  $\text{Ag}_n^0$  and  $\text{L}^-$ :

$$E_{\text{INT}}([\text{Ag}_n\text{-L}]^0) = E(\text{Ag}_n^+) + E(\text{L}^-) - E([\text{Ag}_n\text{-L}]^0).$$

$$E_{\text{INT}}([\text{Ag}_n\text{-L}]^-) = E(\text{Ag}_n) + E(\text{L}^-) - E([\text{Ag}_n\text{-L}]^-).$$

The sign is such that a positive  $E_{\text{INT}}$  indicates a bound system. The absolute values of  $r$ ,  $\alpha$ , and  $E_{\text{INT}}$  for the  $\text{Ag-L}$ ,  $\text{Ag}_5\text{-L}$ , and  $\text{Ag}_{10}\text{-L}$  clusters change significantly for the different cluster sizes; this is hardly surprising. We note two factors which make important contributions to the strong size dependence of  $E_{\text{INT}}$ . The polarization of the  $\text{Ag}_n$  or  $\text{Ag}_n^+$  charge distributions due to the presence of  $\text{SCN}^-$  should increase with cluster size because of the larger number of "conduction" band Ag electrons and of the more diffuse character of these electrons. For the charged  $\text{Ag}_n^+$  clusters, the position of the center of charge may be quite different as a function of cluster size. In particular for small clusters, this will change the large electrostatic interaction between the  $\text{Ag}_n^+$  and  $\text{SCN}^-$  sub-units. However while the absolute values change with cluster size, the ionic character of the bond and the general features of the chemisorption geometry are common for all cluster sizes.

In particular,  $\text{SCN}$  can bond either N-down or S-down, Table I, with very similar binding energies. Given the limitations of the approximations used in this work, principally cluster size and SCF wavefunctions, it is not possible to determine the preferred orientation of  $\text{SCN}$  on a Ag surface. For both N-down and S-down orientations, the bending of the  $\text{SCN}$  from  $\alpha = 180^\circ$  to  $90^\circ$  is accompanied by small energy changes showing that the potential surface is rather flat.

To determine the importance of electrostatic and polarization effects compared to covalent contributions to the Ag-SCN interaction, we have decomposed the total  $E_{\text{INT}}$  following the Constrained Space Orbital Variation, CSOV, procedure.<sup>11</sup> The CSOV analysis is reported for anionic  $[\text{Ag}_{10}\text{-NCS}]^-$  and  $[\text{Ag}_{10}\text{-SCN}]^-$  as a function of  $r(\text{Ag-L})$  for  $\alpha = 180^\circ$  and as a function of  $\alpha$  for fixed  $r(\text{Ag-L})$  and  $\phi = 0$ , see Figs. 3-5. We also give, in Tables II and III, values of  $E_{\text{INT}}$  at the various steps of the CSOV analysis for a few SCN geometries. With the CSOV analyses, we have determined how the bonding contributions vary as a function of adsorbate geometry.

The starting point of the CSOV analysis is the interaction between the frozen orbital, FO, charge densities of the  $\text{Ag}_{10}$  and  $\text{SCN}^-$  sub-units. The fixed charge densities for these two separated components are superimposed at the geometry of interest for SCN/Ag and no electronic rearrangement is allowed. This step, Step 0, is the sum of two contributions which cannot easily be further separated: (1) The electrostatic interactions between the multipoles of the charge distributions of the substrate Ag cluster and the adsorbate  $\text{SCN}^-$ . And, (2) the Pauli repulsion arising from the non-bonding overlap of the two frozen electron distributions. The Pauli repulsion depends strongly on the distance of the adsorbate from the surface; i. e., on the extent to which the  $\text{SCN}^-$  and surface charge clouds interpenetrate. As  $r(\text{Ag-L})$  decreases, the Pauli repulsion must dominate and it leads to a repulsive FO  $E_{\text{INT}}$  which increases exponentially as  $r$  becomes smaller, see Fig. 3. In fact even for distances near equilibrium, see Tables II and III, the FO  $E_{\text{INT}}$  is already significantly repulsive due to the Pauli repulsion.

The Pauli repulsion is offset by the polarization of the metal charge distribution which is taken into account in the next CSOV step,  $V(\text{Ag};\text{Ag})$  or Step 1. At this step,

the Ag cluster orbitals are allowed to vary in their own space but cannot mix with the virtual SCN orbitals; the occupied SCN orbitals remain fixed or frozen. The energetic importance of the Ag polarization is given by the change of  $E_{\text{INT}}$ ,  $\Delta E_{\text{INT}}$ , at this CSOV step. The polarization of  $\text{Ag}_n$  in response to the presence of  $\text{SCN}^-$  is large for all Ag clusters and for all SCN geometries; it gives the largest attractive contribution to the Ag-SCN bond. As the ligand approaches the Ag surface,  $\Delta E_{\text{INT}}$  due to the metal polarization becomes larger but not as rapidly as the Pauli repulsion increases, see Fig. 3. In CSOV step 2,  $V(\text{Ag};\text{All})$ , the SCN occupied orbitals are still fixed but the Ag cluster orbitals are now allowed to mix with the SCN virtual orbitals. The changes in the cluster wavefunction at this step provide, in principle, a measure of the charge donated from Ag to  $\text{SCN}^-$ ; of course, charge flow to the already negatively charged  $\text{SCN}^-$  is hardly expected to be important. Indeed,  $\Delta E_{\text{INT}}$  at this step is very small,  $\sim 0.01\text{-}0.07$  eV, see Tables II and III. At CSOV step 2, the basis set for the Ag orbitals has been increased to include the SCN virtual space. Because of the finite size of the Ag cluster basis set, this larger basis set could lead to a better description of the  $\text{Ag}_n$  orbitals. In other words, the  $\Delta E_{\text{INT}}$  at CSOV Step 2, albeit small, could arise from a computational artifact described as Basis Set Superposition Error,<sup>11a</sup> BSSE, rather than from a physical motion of charge from  $\text{Ag}_n$  to  $\text{SCN}^-$ . A measure of the charge motion between Ag and SCN at this CSOV step is given by the change in the cluster dipole moment,<sup>12</sup>  $\Delta\mu$ ; we have found that, at this step,  $\Delta\mu$  is quite small. The small change in  $\mu$  confirms that the  $\Delta E_{\text{INT}}$  at this step arises from BSSE artifacts.<sup>11a,12</sup>

At this point, the Ag orbitals are fixed as they are at CSOV Step 2 and in the following two CSOV steps only the SCN orbitals are varied. In CSOV Step 3,  $V(\text{SCN};\text{SCN})$ , the  $\text{SCN}^-$  occupied orbitals are varied in the virtual space of  $\text{SCN}^-$ .

This step measures the extent of the SCN polarization which is modest for the N-down orientation and negligible for the S-down orientation, see Figs. 2 and 4 and Tables II and III. For the latter orientation, the SCN polarization is small, at least in part, because the Ag-S distance is rather large,  $r \approx 5.80$  bohr. In CSOV Step 4, V(SCN;All), the variational space is expanded to include the Ag cluster virtual orbitals; this step measures the importance of the dative covalent bonding of SCN<sup>-</sup> with Ag. The  $\Delta E_{\text{INT}}$  for V(SCN;All) can have BSSE artifacts just as we discussed for V(Ag;All). However, the values of  $\Delta E_{\text{INT}}$  at this step are much larger than they were for V(Ag;All), see Tables II and III. In fact, the  $\Delta E_{\text{INT}}$  for the SCN donation, or dative covalent bonding with Ag, is the next largest contribution to the SCN-Ag bond after the Ag polarization, V(Ag;Ag). This is good evidence that SCN<sup>-</sup> does form dative covalent bonds which are of modest importance and which are responsible for the small reduction of adsorbed SCN from a fully anionic character. In Figs. 2-5, the results of the V(SCN;All) CSOV step are denoted by "covalency". Finally, the unconstrained SCF, Full SCF, energy is compared with the energy at the V(SCN;All) step. The small difference of the Full SCF values of  $E_{\text{INT}}$  from the values at the V(SCN;All) CSOV step, see Tables II and III, shows clearly that all the important bonding effects have been included in the series of CSOV steps.

The CSOV analysis shows that for both [Ag<sub>10</sub>-NCS]<sup>-</sup> and [Ag<sub>10</sub>-SCN]<sup>-</sup> the leading contributions to the interaction are given by the Ag Polarization and, to a smaller amount, the SCN<sup>-</sup> to Ag donation or dative covalent bonding. The analysis gives definitive proof that intra-unit polarization of the Ag and SCN<sup>-</sup> sub-units dominates over classical covalent chemical bonding for SCN on a Ag surface. The CSOV analyses together with the projections described earlier give conclusive evidence

that the interaction between SCN and Ag is ionic with SCN chemisorbed on a Ag surface being almost a full anion.

We analyze now how the main contributions to the interaction depend on the adsorbate geometry. First, we consider the change of the Ag-SCN distance for SCN normal to the surface. This variation is shown in Fig. 2 for the N-down case but the same general features are also found for the S-down case. As already mentioned, the Pauli repulsion term increases very rapidly as the Ag-N distance is reduced. For distances larger than the equilibrium, the Ag intra-unit polarization leads to an attractive interaction. However, for distances less than equilibrium, the Pauli repulsion grows faster than the attraction due to the Ag polarization. For a wide range of distances,  $r(\text{Ag-N}) = \sim 4.0$  to  $\sim 5.2$  bohr, the intra-unit polarization of SCN increases only by a very small amount. The contribution of the dative covalent interaction increases as  $\text{SCN}^-$  approaches the Ag surface; this is to be expected since there is a larger overlap of the Ag and SCN orbitals for shorter  $r$ . However, we have not established a precise magnitude of the covalent bonding, especially at the shorter distances, because the BSSE artifact, see above, also increases when the Ag-SCN distance decreases.

The total potential energy curve for the N-down interaction of SCN with a perpendicular orientation at an on-top site of a Ag(100) surface, denoted by "Total BE" in Fig. 2, results from the sum of these contributions. For  $r(\text{Ag-N}) > 4$  bohr, the Total BE curve is rather flat; this is well inside the equilibrium  $r_e = 4.56$  bohr. Of course for  $r < r_e$ , the Pauli repulsion is growing most rapidly; for  $r < \sim 4$  bohr, the potential rises very rapidly. For S-down SCN, the  $r_e(\text{Ag-S})$  is larger than  $r_e(\text{Ag-N})$  because the S atom has a larger spatial extent than the N atom. For variation of

$r(\text{Ag-S})$  in a broad range of  $r$  about  $r_e$ , all the CSOV curves are smoother than for the N-down case. The final result is a very flat potential energy curve for the variation of the Ag-SCN distance.

The same analysis has been performed for variation of the Ag-N-C and Ag-S-C angles with fixed  $r(\text{Ag-N})=4.5$  bohr and  $r(\text{Ag-S})=5.8$  bohr, respectively; this variation is for  $\phi=0$ . The bending of the Ag-NCS bond requires virtually no energy as shown by the total interaction energy curve in Fig. 4. The value of  $E_{\text{INT}}$  decreases by only 0.1 eV by changing the angle  $\alpha$  from  $180^\circ$  (perpendicular orientation) to  $100^\circ$  (nearly flat orientation). The decrease is even smaller for bending from  $180^\circ$  to  $120^\circ$ ; for this range,  $E_{\text{INT}}$  changes by only 0.06 eV. None of the bonding contributions are significantly affected by the bending of SCN. For a wide range of angles, 180-120 degrees, the Pauli repulsion does not increase at all. Only when the angle is decreased below  $120^\circ$  and the S-end of the adsorbate molecule becomes close to a surface Ag atom, see Fig. 2, the Pauli repulsion increases rapidly. The Ag and SCN polarizations and the covalent bonding are also basically independent of the SCN angle between 180-120 degrees. A direct consequence of this very flat potential curve for bending SCN is that the actual geometry of the N-down thiocyanate on a surface is likely to be determined by the non-bonding interactions between adjacent adsorbates. For very low coverage, i. e., in the absence of lateral interactions, the present calculations indicate a slight preference for the perpendicular orientation. However, the bending motion has a very low vibrational energy. A flat potential curve for bending is also found for the neutral  $\text{Ag}_{10}\text{-NCS}$  cluster. In this case, the interaction energy between the  $\text{Ag}_{10}^+$  and  $\text{SCN}^-$  components is large,  $>3$  eV (Table I), but, nevertheless, the bending requires virtually no energy. In fact for neutral  $\text{Ag}_{10}\text{-NCS}$ , when SCN is nearly parallel to the Ag surface at  $\alpha=105^\circ$ , the system is actually slightly, 0.14 eV,

more stable than for the perpendicular orientation, see Table I. This suggests that charging a Ag electrode in an electrochemical cell positive might cause an adsorbed SCN molecule to assume a parallel orientation even for the N-down geometry.

The bending of the S-down  $\text{SCN}^-$  ion shows a somewhat different behavior (Fig. 5). The potential energy curve exhibits a minimum for an angle  $\alpha$  of about 90 degrees; the energy difference between  $E_{\text{int}}$  at  $\alpha = 180^\circ$  and  $\alpha = 90^\circ$  is about 0.2 eV. The reason why the S-down ligand prefers to bend is clear from the analysis of the different bonding contributions as function of  $\alpha$ , the bending angle. The Pauli repulsion does not increase as  $\alpha$  goes from 180 to 100 degrees; for smaller angles, the N-end of the SCN molecule goes too close to one of the Ag surface atoms, see Fig. 2. However, as the molecule bends, both the metal polarization and the covalent interaction increase so that the total potential energy curve presents a minimum when SCN lies flat on the surface. The bending motion occurs at low energy cost and it can be concluded that this bonding mode, preferred at low-coverage, can easily change as more molecules approach the surface. Indeed, IR measurements seem to indicate that at higher coverages adsorbed thiocyanate lies normal to the Ag surface.<sup>14</sup>

For SCN adsorbed parallel to the surface with an azimuthal angle of  $\phi = 45^\circ$ , the N-end of the molecule is not on top of a Ag surface atom, as for  $\phi = 0$ , but in a bridge position between two surface Ag atoms (Fig. 2). This orientation exhibits a similar but slightly, 0.1 eV, smaller binding energy and a slightly different Ag-SCN distance from the  $\phi = 0$  case (Table 1). At first glance, this could be attributed to the possibility that the N atom forms a direct covalent bond with an Ag atom for  $\phi = 0$ , see Fig. 2. However, the CSOV analysis performed for a geometry close to equilibrium for

$\phi = 0$  and  $\phi = 45^\circ$  does not show any appreciable difference in the bonding mechanism (Table 3). Again, the bonding arises in large part from the metal polarization and to a smaller extent, from the  $\text{SCN}^-$  donation. These two contributions are virtually the same for both azimuthal angles  $\phi = 0$  and  $\phi = 45^\circ$ .

### 3.2 The Ag/CO System

It is known that CO bonds to metal surfaces mainly through a  $\pi$  dative bond arising from donation from the occupied metal orbitals to the empty  $2\pi^*$  MO of CO.<sup>11</sup> The CO-metal bond is due to covalent chemical bonds and contrasts with the Ag-SCN bond which is due, dominantly, to electrostatic and polarization effects. We have studied the Ag-CO bond for CO/Ag(100) with the  $\text{Ag}_{10}$ -CO cluster with C-end down at the same on top site used to study SCN. This allows us to directly compare the potential curve for the bending of CO with those for the bending of SCN and NCS. The Ag-CO distance has been chosen as  $r(\text{Ag-C}) = 4.0$  bohr; it has not been optimized. This choice is larger, by  $\sim 0.4$  bohr than the Cu-CO distance<sup>15</sup> for CO at the same site of Cu(100) to account for the larger size of the Ag atom. It is a rough estimate for the Ag-CO bond distance but the properties of the metal-CO bond are not strongly sensitive to this distance.<sup>16,17</sup> The C-O distance is fixed at 2.15 bohr; the same value has been used in extensive cluster model studies of CO/Cu, see Ref. 17 and references therein.

For the perpendicular orientation, CO is bound to  $\text{Ag}_{10}$  by 0.37 eV. The CO is bent by keeping the C position fixed and only rotating the O atom; the potential curve

for this bending is shown in Fig. 6. For a deviation of  $\sim 10^\circ$  from perpendicular,  $\alpha = 170^\circ$ , the total energy of the  $\text{Ag}_{10}\text{-CO}$  cluster does not change significantly. However, a further bending of the CO molecule has a considerable energetic cost. For a flat CO molecule,  $\alpha = 90^\circ$ , the interaction with Ag is strongly repulsive in contrast to the results for  $\text{SCN/Ag}$ . The reason for the repulsive interaction is that bending the CO molecule weakens the  $\pi$  covalent bond; in addition, there may also be a Pauli repulsion between the  $\text{CO}(1\pi)$  MO and the metal charge for the parallel orientation. The weakened  $\pi$  bond is not replaced by alternative bonding mechanisms, at least when the Ag-C and C-O distances and geometries do not change.

The very small energetic cost of the  $\sim 10^\circ$  bend of CO away from the normal suggests that, at higher CO coverages, the CO may be tilted, by a relatively small amount, with respect to the normal. This tilting could reduce the Pauli repulsion due to the non-bonding overlap of the charge distributions of adjacent adsorbed CO molecules.

#### IV. CONCLUSIONS

All the results above show conclusively that the bonding of SCN on  $\text{Ag}(100)$  is ionic. The most important rearrangement mechanism for the interaction is the polarization of the metal due to the presence of the  $\text{SCN}^-$  anion. The contribution of dative covalent bonding arising from the donation from  $\text{SCN}^-$  to unoccupied metal levels is much smaller than that from the metal polarization. In other words, electrostatic effects are dominant and covalent bonding is of secondary importance.

An important consequence of the ionic bonding of SCN with Ag is that the bond is not directional and the SCN can move between perpendicular and parallel orientations with a small energetic cost. Thus, the actual adsorption geometry for SCN may be determined by the non-bonding interactions between adjacent adsorbates and may depend on the SCN coverage. The flat potential surface for changing the SCN orientation is fundamentally different from that found for covalently bonded adsorbates where the bond has considerable directional character. For covalently bonded CO on Ag(100), the energetic cost of bending the molecule from a perpendicular,  $\alpha = 180^\circ$ , to a parallel,  $\alpha = 90^\circ$ , orientation is 1 eV. This is a large energetic cost, much larger than found for ionically bonded SCN on Ag(100).

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Table I. Optimized Ag-SCN geometrical parameters for several Ag<sub>n</sub>-SCN clusters; r is the Ag-SCN distance,  $\alpha$  is the polar, and  $\phi$  is the azimuthal angle. See Fig. 2 for the adsorbate geometry.

Cluster	r (bohr)	$\alpha$ (degrees)	E <sub>INT</sub>
Ag-SCN	4.82	98°	5.17
Ag <sub>5</sub> -SCN	4.91	97° ( $\phi = 0$ )	3.99
Ag <sub>10</sub> -SCN	5.61	86° ( $\phi = 0$ )	3.61
	5.32	106° ( $\phi = 45^\circ$ )	3.40
[Ag-SCN] <sup>-</sup>	5.39	107°	0.49
[Ag <sub>5</sub> -SCN] <sup>-</sup>	5.09	105° ( $\phi = 0$ )	1.17
[Ag <sub>10</sub> -SCN] <sup>-</sup>	5.77	87° ( $\phi = 0$ )	0.92
	5.64	100° ( $\phi = 45^\circ$ )	0.81
Ag-NCS	4.04	180°	5.27
Ag <sub>5</sub> -NCS	4.11	180°	4.12
Ag <sub>10</sub> -NCS	4.41	180°	3.30
	4.50	105° ( $\phi = 0^\circ$ )	3.43
[Ag-NCS] <sup>-</sup>	4.47	180°	0.64
[Ag <sub>5</sub> -NCS] <sup>-</sup>	4.25	180°	1.41
[Ag <sub>10</sub> -NCS] <sup>-</sup>	4.56	180°	0.87

Table II - CSOV analysis of  $E_{\text{int}}$  (eV) for  $[\text{Ag}_{10}\text{-NCS}]$ : Angles in degrees, distances in bohr.

Step	$\alpha = 180^\circ, r = 4.50$	$\alpha = 100^\circ, r = 4.50$
	$E_{\text{Int}} / \Delta E_{\text{Int}}$	$E_{\text{Int}} / \Delta E_{\text{Int}}$
0. FO	-0.38/...	-0.87/...
1. V(Ag;Ag)	+0.38/ +0.76	+0.02/ +0.89
2. V(Ag;all)	+0.42/ +0.04	+0.09/ +0.07
3. V(SCN;SCN)	+0.60/ +0.18	+0.19/ +0.10
4. V(SCN;all)	+0.83/ +0.23	+0.71/ +0.52
5. Full SCF	+0.85/ +0.02	+0.72/ +0.01

Table III - CSOV analysis of  $E_{\text{int}}$  (eV) for  $[\text{Ag}_{10}\text{-SCN}]$ . Angles in degrees, distances in bohr.

Step	$\alpha = 180^\circ, r = 5.80$	$\alpha = 100^\circ, r = 5.80$	$\alpha = 100^\circ, r = 5.60$
	$\phi = 0$	$\phi = 0$	$\phi = 45^\circ$
	$E_{\text{Int}}/\Delta E_{\text{Int}}$	$E_{\text{Int}}/\Delta E_{\text{Int}}$	$E_{\text{Int}}/\Delta E_{\text{Int}}$
0. FO	-0.07/...	-0.05/...	-0.14/...
1. V(Ag;Ag)	+0.38/+0.44	+0.51/+0.56	+0.43/+0.57
2. V(Ag;all)	+0.38/=	+0.52/+0.01	+0.45/+0.02
3. V(SCN:SCN)	+0.43/+0.05	+0.56/+0.04	+0.49/+0.04
4. V(SCN:all)	+0.53/+0.10	+0.80/+0.24	+0.78/+0.29
5. Full SCF	+0.54/+0.01	+0.80/=	+0.79/+0.01

## Figure Captions

Figure 1. Schematic representation of SCN bonding geometries in metal complexes: (a) N-end down; (b) S-end down; and (c) bonding through both S and N-ends.

Figure 2. Geometry of SCN at an on top site of the  $\text{Ag}_{10}$  cluster. The bond distance,  $r$ , and the  $\alpha$  and  $\phi$  angles for the SCN orientation are indicated.

Figure 3. Bonding contributions in  $[\text{Ag}_{10}\text{-NCS}]^-$  as a function of  $r(\text{Ag-N})$  for  $\alpha = 180^\circ$ .

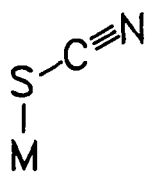
Figure 4. Bonding contributions in  $[\text{Ag}_{10}\text{-NCS}]^-$  as a function of  $\alpha$  for  $r(\text{Ag-N}) = 4.50$  bohr, see also Table II.

Figure 5. Bonding contributions in  $[\text{Ag}_{10}\text{-SCN}]^-$  as a function of  $\alpha$  for  $r(\text{Ag-S}) = 5.20$  bohr, see also Table III.

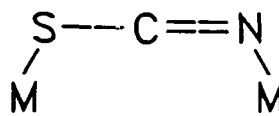
Figure 6. Potential energy curve for the bending of CO in  $\text{Ag}_{10}\text{-CO}$  for  $r(\text{Ag-C}) = 4.0$  bohr.



(a)



(b)



(c)

