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# COVALENT AND IONIC CONTRIBUTIONS TO THE BONDING OF ATOMIC AND MOLECULAR ADSORBATES ON METAL SURFACES. A CLUSTER MODEL APPROACH

by

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# COVALENT AND IONIC CONTRIBUTIONS TO THE BONDING OF ATOMIC AND MOLECULAR ADSORBATES ON METAL SURFACES. A CLUSTER MODEL APPROACH

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## ABSTRACT

The molecular cluster model approach for the description of processes at surfaces is presented. It involves using finite clusters which contain surface atoms interacting with atomic or molecular adsorbates. Accurate ab initio wavefunctions can be obtained for the clusters and thus makes it possible to describe the bonding in terms that are familiar for molecular systems. The adsorbate-substrate interaction can be analyzed by means of new techniques developed to characterize the bonding as covalent or ionic. This is shown for F on Ag(111) and O and CO on Cu(100) systems. The measures of adsorbate ionicity are (a) the expectation value of a projection operator giving an indication of the number of electrons associated with the adsorbate, (b) the analysis of the dipole moment curve as function of the distance, and (c) the effect of an external electric field on the adsorbate geometry. The consequences of ionic adsorbates on metal surfaces is discussed for two selected topics: adsorption of thiocyanate on Ag electrodes and coadsorption of CO with ionic species.

## 1. Introduction

The concept of chemisorption is a key to the understanding of the catalytic reactions on solid surfaces. Heterogenous catalysis consists of elementary reactions occuring at the surface of the catalyst. In these reactions chemical bonds are formed between the surface atoms and the adsorbed molecules. These interaction cause rupture of chemical bonds within the adsorbing molecule and formation of new bonds between the resulting fragments and the surface. Thus, the first step for the understanding of catalysis is understanding of chemisorption phenomena.

The questions that are asked and answered, both experimentally and theoretically, about bonding at surfaces are very similar to those that are asked in molecular systems: bonding nature, bond distances, binding energies, vibrational frequencies, etc. The theoretical evaluation of these energy-related observables requires the computation of potential energy hypersurfaces (PHS, often called potential energy surfaces and abbreviated as PES) or of their sections along a particular direction (potential energy curves, PEC) for the interaction of the adsorbed molecule and the solid surface. However, other properties are often easily as interesting as the total energy of the system; for example, dipole moments provide useful information about the nature of the chemical bond, and the determination of dipole moment surfaces (curves) is required for the evaluation of infrared intensities.

From the theoretical point of view, a surface-adsorbate system represents a very complex quantum-mechanical many particle object which requires a large number of approximations in order to be treated. Various concepts and models have been developed for the

determination of electronic wave functions describing the interaction between the adsorbate and the substrate [1].

The cluster model approach

In the cluster model approach, a finite number of atoms is chosen to model a local site on the crystal surface [2]. In this model one focusses on the local nature of interaction between the adsorbate and a the solid substrate which involves primarily the nearest neighbor surface atoms. The coupling of the cluster wave function to the rest of the substrate (embedding) would have to be accounted for in a second step. Efforts have been made in this direction [3]. Alternatively, one could increase the size of the cluster by adding additional shells of substrate atoms until the chemisorption properties become independent of cluster size. When only a single adsorbate is considered, the large substrate cluster represents the limit of zero coverage, i.e. in absence of lateral interactions with other adsorbates. Both embedding and cluster convergence are formally and computationally very difficult probelms so that often isolated clusters of small or medium size have been studied with ab initio Hartree-Fock techniques [4]. The use of simplified versions of the Hartree-Fock method [5] or of techniques where the exchange potential is replaced by an approximate expression depending on the electron density [6] has allowed the treatment of larger systems at the cost of reducing the reliability and accuracy of the results. It must be noted that almost all theoretical approaches usually employed in quantum chemistry have been applied to the study of cluster-adsorbate systems.

Since in the cluster model approach one tries to simulate a

solid surface by means of a finite size cluster, one usually uses cluster geometries (and eventually electronic states) which are appropriate for bulk and surface geometries of the substrate. These clusters have little in common with the real geometries and electron distributions of free metal clusters [7]. Indeed, gas-phase clusters, often highly fluxional, exhibit a very cluster-dependent chemical reactivity which is in general difficult to rationalize in simple terms and which is different from that of bulk materials [8]. Also theoretical computations show an oscillating behaviour of the chemisorption properties with increasing cluster size, at least for clusters of less than 50 atoms [9].

The big advantage of the cluster model approach to the study of chemisorption, and eventually of surface chemical reactions, is that the interaction can be analyzed by means of standard quantum chemical methods. The local minima of the total energy $E_{tot}(R_1, R_2, R_3, \ldots)$ as function of the nuclear coordinates define possible equilibrium geometries of the cluster. Usually, the geometry of the substrate is kept fixed, giving a static representation of the surface; however, approaches to the chemisorption of atomic or molecular species in which the (partial) relaxation of the surface has been taken into account have been reported [10].

Cluster wave functions

In this work ab initio LCAO-Self Consistent Field (SCF) wave functions are used. The MO's are expanded in terms of Contracted Gaussian Type Orbitals (GTO) of double zeta quality or better. Effective Core Potential (ECP) operators [11] are employed to describe the inner shells of heavy atoms or of some of the

cluster metal atoms surrounding the chemisorption site. Of course, accurate values for many properties cannot be obtained unless correlation effects are included in the wave function, e.g. through the use of extended configuration interaction (CI). This is necessary in particular for the exact determination of PES (or curves) and related properties.

Despite the limitations due to the cluster size and the use of uncorrelated SCF wave functions, the MO cluster model can provide valuable information about surface chemical reactions. In particular, the MO cluster model is ideally suited for chemical interpretation of the bond at a surface in a way analogous to that used for molecular systems. Determination of SCF PES's is important therefore as a guide in identifying mechanisms which explain the surface bonding and in the use of these mechanisms to correctly interprete the significance of observable properties and dynamical processes.

Ionic versus covalent adsorbates

A very important aspect is the determination of the ionic or covalent nature of the adsorbate-surface chemical bond. This question is considerable fundamental importance. The amount of charge transfer from the surface to the adsorbate (or viceversa) dramatically influences the surface reactivity. We mention here a few selected examples. There is enough evidence that the formation of strong ionic bonds on metal surfaces can cause substantial surface reconstruction [12]; also the energy profile for the penetration of an atomic adsorbate below a solid surface can be strongly dependent on the ionic character of the bonding [13]; the determination of the charge associated to chemisorbed

alkali metal atoms on the surface of semiconductor materials is of basic importance in order to understand the significance of surface metallization and of the metal-insulator transition [14]; ionic or covalent adsorbates exhibit completely different behaviour on metal electrodes when an external potential is applied [15]; finally, the fascinating effect of promotion (inhibition) in catalysis is probably connected to the formation on the surface of ionic species [16].

The identification of the surface chemical bonding as covalent or ionic is thus of fundamental importance in surface chemistry. An analysis of the adsorbate-substrate binding is usually based on atomic population analysis. These are often misleading because of the arbitrary partitioning of electrons between different nuclear centers.

In this paper we present new techniques developed to characterize the chemical bonding at surfaces and we analyze the consequences of ionic surface bonding for two selected topics.The paper has been divided into two parts. In Section 2 we describe the techniques used to characterize the surface-adsorbate bonding for both atomic (F and O) and molecular (CO) adsorbates. In Sect. 3 we discuss a problem relevant to electrochemistry, the chemisorption of thiocyanate ions on Ag electrodes, and we present a new mechanism to explain the effect of coadsorbates promoting, or inhibiting, the catalytic activity of a metallic substrate.

## 2. Analysis of the surface chemical bonding

To determine the character of the bonding of an atomic or molecular adsorbate as covalent or ionic we apply three measures.

No single measure is sufficient to unambiguously characterize the bonding, but the three measures together can provide a reliable description of the interaction. The analysis is applied to the following problems: a) chemisorption of F on a $Ag_4$ cluster model of the three-fold symmetric site on the Ag (111) surface; details of the cluster geometry, basis set and ECP used can be found in Ref. 17b) Interaction of atomic oxygen with a $Cu_5(4,1)^-$ cluster model of the four-hollow site of a Cu(100) surface containing four atoms in the first and one atom in the second layer; the $Cu_5$-O cluster has been treated at all electron level using a [6s5p4d] [18c] and a [4s3p] [18a] contracted GTO basis sets for Cu and O atoms, respectively. c) Interaction of CO on $Cu_5$ and $Cu_{14}$ cluster models of the Cu(100) surface (details on Ref. 11a).

Projection operator

The first technique makes use of a projection operator for some or all the occupied orbitals of the adsorbate [19]. The expectation value of this projection operator using the wavefunction of the whole cluster+adsorbate system gives a measure of the extent to which the adsorbate orbitals are contained in the complex. Actually, three cases are possible: a) the expectation value $P\varphi$ of the projection operator $P(\varphi)$ for a given orbital $\varphi$ is close to 2, than $\varphi$ is completely occupied in the cluster wavefunction $\Psi$; b) $P\varphi$ is close to zero, thus $\varphi$ is unoccupied in $\Psi$; c) $P\varphi$ is between 0 and 2, indicating that a covalent bonding is formed. The sum of $P\varphi$ over all orbitals of physical interest, $N_P$, provides a measure of the number of electrons associated with the adsorbate. An example of this analysis is given in Table 1 for F on $Ag_4$, O on $Cu_5$, and CO on $Cu_5$. The data show that, for distances near $r_e$, the ionicity of

the F atom, defined as $Q_P = Z - N_P$, where Z is the nuclear charge, is very close to -1. F is close to be a perfect anion. For O on $Cu_3$, the 2s and 2p$\sigma$ orbitals are fully occupied, while P(2p$\pi$) is 3.87 (Table 1). In this case it is necessary to take into account the overlap between the orbitals of the isolated adsorbate and substrate when these two subunits are superposed at $r=r_e$. This overlap amounts to 0.41 and therefore the 2p$\pi$ occupancy is intermediate between 3.46 and 3.87. The oxygen ionicity can be estimated to be about -1.6; the bonding is covalent with large ionic character.

The analysis for the last case, CO on $Cu_3$, shows that the five $\sigma$ and the 1$\pi$ orbitals of CO are fully occupied in $Cu_3$-CO. The occupancy of the CO 2$\pi^*$ MO, $\Delta P(2\pi^*)$, has been corrected by the overlap of the two subunits and represents a measure of the increase in the ligand 2$\pi^*$ occupation due to metal back-donation (Table 1). P(2$\pi$) depends on cluster size. The projection is consistent with the CO bond being covalent, dominantly in $\pi$ space [11a].

Dipole moment curves

The second measure of bond character is based on the slope of the dipole moment curve as the distance of the adsorbate from the cluster is varied [17,19]. For an ionic molecule represented by two point charges +q and -q, with the negative charge on the positive z axis, the dipole moment is $\mu_z = -q \times r$, where r is the distance between the two point charges; thus the slope, or first derivative, of the curve is $d\mu/dr = -q$. For a fully ionic molecule with q=-1, $d\mu/dr=-1$ and the curve is a straigth line. Actually, in real systems, the polarization contributions can

change significantly the value of the slope because of the polarization of the subunits. This polarization, in particular of the metal substrate, can lead to a substantial decrease of the absolute magnitude of the dipole moment. This decrease is the reason why changes in the surface dipole or work function are not always a good measure of the ionicity of a chemisorbed atom on a surface [20]. It is also the reason why the absolute value of the dipole moment is not a measure of ionicity while the slope of the dipole moment curve can give a better estimate of the bond ionicity. In general, the slope is expected to be small for a covalent bonding and large for an ionic bonding. Indeed, the slope of the dipole moment curve as function of the metal-ligand distance for CO chemisorbed on $Cu_{10}$ and $Cu_{14}$ is -0.05 and -0.09 [15,21], respectively, consistently with the covalent interaction indicated by the projection operator analysis.

For the systems here considered, $Ag_4$-F and $Cu_3$-O, the dipole moment curve has been determined by a Taylor expansion about $r=r_e$

$$\mu(r) = M_0 + M_1 (r-r_e) + M_2 (r-r_e)^2 + \ldots$$

The first term, $M_0$, is $\mu(r_e)$; $M_1$ gives the slope at $r=r_e$, while small $M_2$ values indicate linear behaviour. For both F on Ag and O on Cu, the analysis has been repeated by replacing the real adsorbate atoms with a negative point charge, PC=-1 (Table 2). The F atom behaves very similarly to a -1 point charge: both dipole moment curves are linear and exhibit similar slopes (Table 2). The slopes differ from being exactly -1 because of the polarization of the subunits, in particular the $Ag_4$ metal cluster [17]. For O and PC on $Cu_3$, the dipole moment curves exhibit large negative slopes (Table 2), a sign of dominant ionic bonding. However, the slope for the $Cu_3$-O system is larger than that

obtained when we move the PC=-1 along the z direction, indicating that the negative charge associated with the O atom is larger than -1, in agreement with the result of the orbital projection analysis.

External electric field

A further proof of ionicity can be obtained by applying an uniform external electric field, F, normal to the cluster surface [15,21]. In fact, an electric field will produce large changes on the chemisorption geometry of ionic adsorbates but will have only small effects on covalently bonded adsorbates [15].

For a cluster in a uniform electric field, the SCF first order perturbation theory energy, $E_P(F)$, is obtained as the difference between the F=0 SCF energy and $\mu \times F$, where $\mu$ is the field-free dipole moment. This is a pure Stark effect and does not include any chemical change caused by the field. These electronic effects are explicitly considered in the SCF variational energy in the presence of the field, $E_{SCF}(F)$, obtained by addition of the term $(\Sigma\ r_i\ -\ \Sigma\ Z_N\ R_N) \times F$ to the field-free hamiltonian: i denotes electrons, N nuclei, and $Z_N$ the nuclear charges. The fields considered are +-0.01 a.u. = +-5 7 x $10^7$ V/cm. The sign of F is such that F < 0 attracts electrons from the surface towards the ligand.

Indeed, we found that the field has a large effect on the equilibrium geometry and vibrational frequency of F on $Ag_4$. In one case, F=-0.01 a.u., the $F^-$ ion is pulled away from the surface with consequent elongation of the $r_e$ value and decrease of $\omega_e$. For F=+0.01 a.u. the adsorbate ligand is pushed against the surface and the metal-ligand vibrational frequency increases

because $F^-$ stretches against the "well" represented by the surface charge distribution (Table 3).

In agreement with the picture of covalent bonding, the field has almost no influence on the adsorption geometry of CO adsorbed on a $Cu_{14}$ cluster [21]. In fact, the equilibrium bond distance and the vibrational frequency are virtually unaffected by the external field (Table 3).

For both F/Ag and CO/Cu, the Stark and full SCF values of $r_e$ and $\omega_e$ are extremely close, indicating that elctrostatic effects are much more important than chemical effects, at least for fields of magnitude +- 0.01 a.u.

## 3. Consequences of ionic adsorbates on metal surfaces

### 3.1 Thiocyanate on silver electrodes

In this section we summarize the results of calculations designed to provide a logical explanation of the behaviour of N- and S-bound thiocyanate species in Ag electrochemical cells. To this end we consider a simple model. The thiocyanate ion is assumed to bind N- or S-down on an on-top Ag(100) site. The simplest systems considered are $[Ag\text{-}NCS]^{0,-1}$ and $[Ag\text{-}SCN]^{0,-1}$; the total charge of the clusters has been changed to obtain a very simple model of the change in electrode charging as the potential is made positive, $Ag^0\text{-}L^- \dashrightarrow Ag^+\text{-}L^-$. The interaction of the $SCN^-$ ligand on the top site of an $Ag_5$ cluster containing one Ag atom in the first and four Ag atoms in the second layer has also been considered (Fig. 1). The metal atoms are fixed at their bulk positions and the metal-ligand geometry has been optimized for N- and S-down coordination modes. The same 19 electron ECP and basis set [10] used for the study of the $Ag_4\text{-}F$

cluster has been employed. In $Ag_5$, the four Ag atoms in the second layer have been treated with an ECP operator which includes in the valence only the 5s electron [10c]. C, N, and S atoms have been treated at all electron level; the basis set for C and N is a 4s3p contracted GTO basis [18a], the basis set for S is contracted to 5s4p [18b].

Adsorption geometry

For the calculation of the molecular geometry a two-dimensional PES has been determined by varying simultaneously the metal-ligand (M-L) distance, r, and the M-N-C or M-S-C internal angles, $\alpha$. The C-N and C-S bond distance have been fixed at 2.20 and 3.20 a.u., respectively. The $r_e$ and $\alpha_e$ values have been determined from a two-dimensional polynomial fit. When the thiocyanate molecule is bound at nitrogen a perpendicular orientation is preferred for both Ag-L and $Ag_5$-L clusters (Table 4). When sulphur forms the thiocyanate-surface bond, the molecule assumes a bent conformation forming a Ag-S-C angle of about 100° (Table 4 and Fig. 1). The same bonding modes have been observed in organometallic complexes [22]. The nature of the Ag-SCN potential surface is very different for the bending of negatively charged and neutral Ag-L systems. In particular, it is very shallow for the $Ag-L^-$ case while for neutral Ag-L the PES exhibits a more pronounced minimum (Fig. 2), indicating a stronger directionality of the bond.

The N-down configuration is slightly preferred in both neutral and charged systems. However, the energy difference is always smaller than 0.2 eV (Table 4); this result hold for both Ag-L and $Ag-I^-$ clusters. It suggests that the two coordination modes can

coexist at least in the limit of low coverage.

Bonding nature

To characterize the nature of the Ag-thiocyanate bonding we applied the projection operator technique described in Sect. 2. First we projected the $SCN^-$ orbitals on the $[Ag\text{-}NCS]^{0,-1}$ and $[Ag\text{-}SCN]^{0,-1}$ wavefunctions for a geometry close to equilibrium. It turns out that in charged Ag-L complexes the thiocyanate ligand carries a full negative charge for both bonding modes (N or S down). For neutral Ag-L, there is a deviation from an ionicity -1, indicating that there is a small covalent contribution (Table 5) for Ag-L. However, $Ag\text{-}L^-$ is a better representation for chemisorbed SCN since other Ag atoms will reduce the local positive charge on the chemisorption site Ag atom.

A measure of the relative importance of various charge rearrangements contributions to the Ag-SCN bonding can be obtained by performing a Constrained Space Orbital Variation (CSOV) analysis [23]. In particular, this makes it possible to distinguish between intra-unit polarization, inter-unit charge transfer and electrostatic effects.

We start, CSOV step 0, with the superposed Ag ($Ag^+$) and $SCN^-$ charge distributions; this gives the frozen-orbital (FO) interaction. Then we let vary the Ag ($Ag^+$) orbitals in response to the presence of the $SCN^-$ anion (CSOV step 1); this allows the Ag orbitals to polarize in the presence of $SCN^-$. The next step, (CSOV step 2) is the Ag orbitals variation in the full space, indicating the amount of charge transfer from Ag to $SCN^-$. In step 3 the Ag orbitals are fixed as they are in step 2, and the $SCN^-$ orbitals are varied in their own space. This permits the $SCN^-$

unit to polarize in the presence of Ag. In CSOV step 4 this variation occurs in the full virtual space, so that both $SCN^-$ to Ag donation or dative covalent bonding as well as $SCN^-$ polarization are possible. The result of step 4 is compared to the full unconstrained SCF result and, if they are nearly the same, this means that all important bonding contributions have been considered. For each step, we consider the interaction energy, $E_{int}$, with respect to separated Ag ($Ag^+$) and $SCN^-$ fragments (Table 6).

The nature of the silver-thiocyanate interaction in charged and neutral Ag-L complexes is basically different. In the first case the bonding originates mainly from the polarization of the metal (CSOV step 1) in response to the presence of the $SCN^-$ ligand; of course, the larger $Ag_3$ cluster is much more polarizable than a single Ag atom and the bonding in $[Ag_3-L]^-$, 1.2-1.4 eV depending on the $SCN^-$ orientation, is considerably stronger than in $[Ag-L]^-$ (0.5-0.6 eV, Table 4). The Ag polarization dominates the bonding in the ionic complexes, but small bonding contributions come also from thiocyanate polarization (CSOV step 3) and from $SCN^-$ to Ag charge transfer (CSOV step 4) (Table 6).

For neutral Ag-L complexes we start the CSOV analysis, step 0, with the superposed $Ag^+$ and $SCN^-$ charge distributions. This is justified by the previous projection operator analysis which has shown the large ionicity of the bonding. Here the bonding is dominated by the attractive, FO, electrostatic interaction, CSOV step 0 (Table 6). Of course, the polarization of the $Ag^+$ fragment, step 1, is negligible, but this is an artifact of

representing the metal surface through a single metal atom. Again, this contribution is expected to be much larger for a real metal surface. A considerable contribution to $E_{int}$ in Ag-NCS and Ag-SCN cames also from the SCN polarization and from SCN to metal charge transfer, CSOV steps 3 and 4 (Table 6). These effects, together with the result of the orbital projection (Table 5), suggest that some degree of covalency is present in this essentially ionic bond.

The results of the CSOV analysis help to understand the different bonding geometry of the N- or S-bound surface complexes. We performed the CSOV analysis for various distances and angles of the $[Ag-NCS]^-$ and $[Ag-SCN]^-$ systems. Keeping in mind that the most important contribution to $E_{int}$ are the FO Pauli repulsion, CSOV step 0, and the metal polarization, CSOV step 1, the results can be summarized as follows. In general, as the Ag-L distance decreases, both Pauli repulsion and metal polarization increase. However, the Pauli repulsion increases more rapidly than the polarization as r becomes smaller. For $Ag-NCS^-$ a compromise between the two tendencies is found for r=4.5 a.u. where the potential energy curve exhibits a minimum. For a linear orientation of the $Ag-SCN^-$ system we observe a similar competition between attractive and repulsive contributions and the minimum of the potential energy curve is found at r=5.3 a.u. because of the larger spatial extension of the sulphur with respect to nitrogen charge distribution. However, bending the $SCN^-$ ligand towards the Ag atom stabilizes the complex, while in the N-down case where this motion is unfavoured. In both cases the bending moves the center of charge of the $SCN^-$ ligand closer to the surface, thus increasing the metal polarization; however,

in Ag-NCS this effect is overcompensated by the increasing repulsive interaction between the $SCN^-$ $1\pi$ MO, mainly localized on C and N centers, and the Ag metal orbitals. The overall result is a destabilization of the bent Ag-NCS structure. When SCN is bound at sulphur, the bending is not accompanied by a similar increase of the Pauli repulsion because the charge distribution around the S atom is more spherical and the repulsive interaction between the S and Ag charge distributions is practically independent on Ag-S-C angle. The result is a minimum in the PES for $\alpha = 100°$.

Field effects on the thiocyanate adsorption geometry

The different geometry of N- and S-bound thiocyanate ligand is the reason of a different behaviour of the two conformations as the metal electrode potential is changed. This effect has been simulated by applying an external electric field parallel to the Ag-SCN axis of magnitude +-0.01 a.u.

The main effect of the field for N-bound thiocyanate is to move the ion up and down depending on the sign of F without changing its orientation (Table 7). When the bent $[Ag-SCN]^-$ system is considered, a field F=+0.01 a.u., such that electrons are attracted toward the metal, further bends the molecule to form an Ag-S-C angle of 82 degrees. On a real metal surface this bending motion is limited by the presence of other Ag atoms and the $SCN^-$ ligand will lie flat on the surface. The opposite field, F=-0.01 a.u., orients the $SCN^-$ ligand parallel to the field direction changing the shape of $[Ag-SCN]^-$ from bent to linear, with consequent destabilization of the complex, and pushes the $SCN^-$ ion away from the metal to such an extent that no minimum is found for a field of this magnitude. The same behaviour was found

for the more stronlgy bound $[Ag_2-SCN]^-$ cluster; here too the $SCN^-$ ion is unstable in a field F=-0.01 a.u.

Thus, the present results provide evidence that thiocyanate adsorbs on Ag electrodes at both S and N sites in the double layer region; however, as the potential is changed the S-down configuration orients increasingly towards the normal, and, eventually, dissociates for large negative fields. When positive fields are applied the S-bound configuration is adsorbed flat and cannot be detected by IR spectroscopy.

3.2 Interaction of CO with ionic coadsorbates

One of the most challenging areas in catalysis is the interaction occuring between an ad-molecule and co-adsorbates which increase (promoters) or reduce (inhibitors) the catalytic activity of the metal substrate.

Several theories [24,25] have been proposed in terms of simple concepts to rationalize the role of promoters, and in particular to explain the observed large shifts in vibrational frequency of molecules like CO adsorbed in the presence of electropositive (e.g. alkali metals) or electronegative (S, P, Cl, etc.) atoms. The proposed mechanisms are essentially based on electronic factors or on steric site blocking. Here, we consider an additional mechanism, purely electrostatic, which is shown to make an important contribution to the CO vibrational shifts.

The basic idea is that an electropositive (electronegative) adatom forms a bond with the surface with large ionic character. In image charge theory, the electrons of a metal substrate redistribute in the presence of a positive (negative) charge above the surface in such a way that the electric field within the metal is zero. This electron redistribution can be

represented by an image charge below the surface of opposite sign to the "test" charge. The image and test charges are equidistant from the surface plane and generate an electric field which will interact with the coadsorbed molecule. Thus, we model the ionic adatoms with a pair of point charges. Specifically, we consider the interaction of positive and negative point charges (PC) pairs which are simple models of ionic adatoms and their image charges with the $Cu_3$-CO cluster. The geometry of the cluster with PCs is shown in Fig. 3; further details can be found in ref. 16.

Since our concern is primarily directed to the C-O stretch vibrational frequency, we consider geometry variations along an internal coordinate for this stretch. As discussed in Sect. 2, both Stark and full SCF shifts can be determined (Table 8). Two PC distributions have been considered: positive charges above and negative charges below the surface, hereafter denoted as (+/-) PC, and the reverse case, (-/+) PC, representing, respectively, electropositive and electronegative coadsorbates. The PC orientation (+/-) creates an electric field which draws electronic charge from the surface toward CO and correspond to a field $F < 0$. This PC distribution induces large CO $\omega_e$ shifts, about 400 $cm^{-1}$, to lower frequencies. The C-O distance is substantially elongated (Table 8). These $\Delta\omega$ values represent about 70% of the $\Delta\omega$ experimentally observed for coadsorption of CO and K [26,27]. The effect of the (-/+) PC distribution is opposite and raises the CO vibrational frequency by 200-300 $cm^{-1}$, thus reinforcing the CO bonding and justifying a reduction of the catalytic activity. The changes in $r_e$ and $\omega_e$ due to the PCs are dominated by electrostatic Stark effects, but they are

accompanied by significant electronic rearrangements mainly due to a change in Cu to $2\pi^*$ back-donation [16].

The limitations of the present model preclude our obtaining quantitative results for $\Delta r_e$ and $\Delta\omega_e$; moreover, the field created by the PCs, about $13 \times 10^7$ V/cm, is probably too large with respect to a real situation. Nevertheless, we have shown that without invoking any electronic mechanism, the electrostatic interaction alone causes remarkable shifts in CO $\omega_e$. This can be a first step in the activation of the CO molecule accompanied by other, non negligible, electronic or steric mechanisms.


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Table 1 - Projection of $F^-$ on $Ag_4F$, $O^{2-}$ on $Cu_5O$, CO on $Cu_5$-CO, for $r=r_e$

| $F/Ag_4$-F | | O/$Cu_5$-O | | CO/$Cu_5$-CO | |
|---|---|---|---|---|---|
| P(2s) | 2.00 | P(2s) | 1.99 | P(5$\sigma$) | 1.99 |
| P(2p$\sigma$) | 1.99 | P(2p$\sigma$) | 1.96 | P(1$\pi$) | 4.00 |
| P(2p$\pi$) | 3.99 | P(2p$\pi$) | 3.87 | P(2$\pi^*$) | 0.32 |
| | | $\Delta$P(2p$\pi$) | 3.46[a] | $\Delta$P(2$\pi^*$) | 0.21[a] |
| $N_P$ | 9.98 | | 9.83 | | 14.21 |

[a] $\Delta P(\varphi)$ are the values of the difference of $\varphi$ projection from $Cu_5$-L (L=O, CO) and $Cu_5$ + L subunits at $r=r_e$.

Table 2 - Dipole moment curves for $Ag_4$-F, $Ag_4$-PC, $Cu_3$-O and $Cu_3$-PC systems (PC = -1 point charge, see text)

| | $Ag_4$-F | $Ag_4$-PC | $Cu_3$-O | $Cu_3$-PC |
|---|---|---|---|---|
| $M_0$ | -1.09 | -1.65 | +0.24 | +0.20 |
| $M_1$ | -1.39 | -1.32 | -1.17 | -0.72 |
| $M_2$ | -0.09 | -0.08 | -0.37 | -0.27 |

Table 3 - Field induced shifts in metal-ligand equilibrium bond distances and vibrational frequencies for $Ag_4$-F and $Cu_{14}$-CO clusters

| F | method | $Ag_4$-F | | $Cu_{14}$-CO[a] | |
|---|---|---|---|---|---|
| | | $r_e$, au | $\omega_e$, $cm^{-1}$ | $r_e$, au | $\omega_e$, $cm^{-1}$ |
| 0 | SCF | 3.31 | 277 | 3.95 | 184 |
| -0.01 | Stark | 3.64 | 213 | 3.96 | 185 |
| | SCF | 3.62 | 215 | 4.00 | 172 |
| +0.01 | Stark | 3.10 | 322 | 3.95 | 186 |
| | SCF | 3.09 | 323 | 3.97 | 180 |

[a] From Ref. 21.

Table 4 - Optimized geometries and dissociation energies of N- and S-bound thiocyanate on Ag atom and $Ag_3$ cluster

| | r(Ag-L), au | α, degrees | $D_e$, eV |
|---|---|---|---|
| [Ag-NCS]$^-$ | 4.47 | 180 | 0.64 |
| [$Ag_3$-NCS]$^-$ | 4.25 | 180 | 1.41 |
| Ag-NCS | 4.04 | 180 | 5.27 |
| $Ag_3$-NCS | 4.11 | 180 | 4.12 |
| [Ag-SCN]$^-$ | 5.39 | 107 | 0.49 |
| [$Ag_3$-SCN]$^-$ | 5.09 | 105 | 1.17 |
| Ag-SCN | 4.82 | 98 | 5.17 |
| $Ag_3$-SCN | 4.91 | 97 | 3.99 |

Table 5 - Projection of $SCN^-$ orbitals on $[Ag\text{-}NCS]^{0,-1}$ and $[Ag\text{-}SCN]^{0,-1}$.

| | [Ag-NCS]⁻ | Ag-NCS | [Ag-SCN]⁻ | Ag-SCN |
|---|---|---|---|---|
| $N_P$ ($\sigma$) | 7.98 | 7.93 | 8.00 | 8.00 |
| $N_P$ ($\pi$) | 8.00 | 7.98 | 7.97 | 7.89 |
| $Q_P$ | -0.98 | -0.91 | -0.97 | -0.89 |

Table 6 - CSOV analysis for $[Ag\text{-}NCS]^{0\cdots1}$ and $[Ag\text{-}SCN]^{0\cdots1}$ for a geometry close to equilibrium (see Table 4)

| Step | [Ag-NCS]⁻ $E_{int}/\Delta E_{int}$ | Ag-NCS $E_{int}/\Delta E_{int}$ | [Ag-SCN]⁻ $E_{int}/\Delta E_{int}$ | Ag-SCN $E_{int}/\Delta E_{int}$ |
|---|---|---|---|---|
| 0. F.O. | -0.68/... | +3.86/... | -0.25/... | +4.02/... |
| 1. V(Ag;Ag) | +0.22/+0.90 | +4.09/+0.23 | +0.24/+0.49 | +4.11/+0.09 |
| 2. V(Ag;all) | +0.26/+0.04 | +4.14/+0.05 | +0.25/+0.01 | +4.12/+0.01 |
| 3. V(SCN;SCN) | +0.42/+0.16 | +4.82/+0.68 | +0.30/+0.05 | +4.41/+0.29 |
| 4. V(SCN;all) | +0.59/+0.17 | +5.21/+0.39 | +0.44/+0.14 | +5.06/+0.65 |
| 5. full SCF | +0.64/+0.05 | +5.26/+0.05 | +0.49/+0.05 | +5.16/+0.10 |

Table 7 - Equilibrium bond distances (a.u.) and bond angles (degrees) for [Ag-NCS]$^-$ and [Ag-SCN]$^-$ in the presence of an external electric field F (in a.u.). Only variational SCF values are given

| Field | [Ag-NCS]$^-$ | | [Ag-SCN]$^-$ | |
|---|---|---|---|---|
| | $r_e$ | $\alpha$ | $r_e$ | $\alpha$ |
| 0.00 | 4.47 | 180 | 5.39 | 107 |
| -0.01 | 4.92 | 180 | ....[a] | 180 |
| +0.01 | 4.29 | 180 | 5.34 | 82 |

[a] This geometry is not stable in a repulsive electric field F=-0.01 a.u.; the molecule becomes linear and than dissociates.

Table 8 - Equilibrium CO bond distances, $r_e$ in a.u., and vibrational frequencies, $\omega_e$, in $cm^{-1}$, for CO chemisorbed on $Cu_5$ in the presence of point charges (PC). Changes from the no PC values, $\Delta r_e$ and $\Delta\omega_e$, are also given.

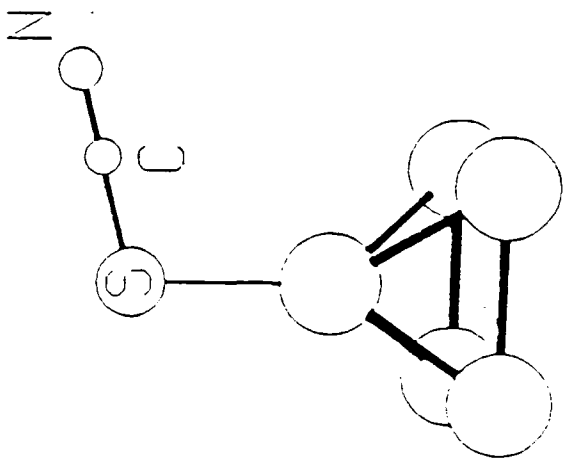
| | | $r_e / \Delta r_e$ | $\omega_e / \Delta\omega_e$ |
|---|---|---|---|
| no PC | | 2.119/... | 2275/... |
| (+/-) PC | Stark | 2.193/+0.074 | 1859/-416 |
| | SCF | 2.206/+0.087 | 1824/-451 |
| (-/+) PC | Stark | 2.069/-0.050 | 2572/+297 |
| | SCF | 2.086/-0.033 | 2461/+186 |

FIGURES CATIONS

Fig. 1 - Schematic representation of the adsorption geometry of N- and S-bound thiocyanate ligand on the on top site of an $Ag_5$ cluster model of the Ag (100) surface.

Fig. 2 - (a) Potential energy surface for the interaction of the Ag atom and the $SCN^-$ ligand as function of Ag-S distance and Ag-S-C bond angle. (b) Potential energy surface for the interaction of the $Ag^+$ ion and the $SCN^-$ ligand as function of Ag-S distance and Ag-S-C bond angle.

Fig. 3 - Geometry of the $Cu_5$-CO cluster interacting with point charges (PC) modeling ionic coadsorbates. The Cu-CO bond distance is 3.70 a.u.. The PCs are 6 a.u. above and below an hypotetical Cu atom on the Cu(100) surface; the distance of this point from the top Cu atom in $Cu_5$-CO (9.6 a.u.) is twice the nearest neighbor distance in bulk Cu.



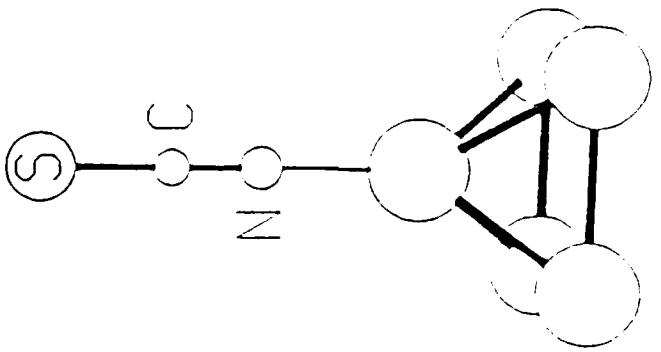




FIGURE 1

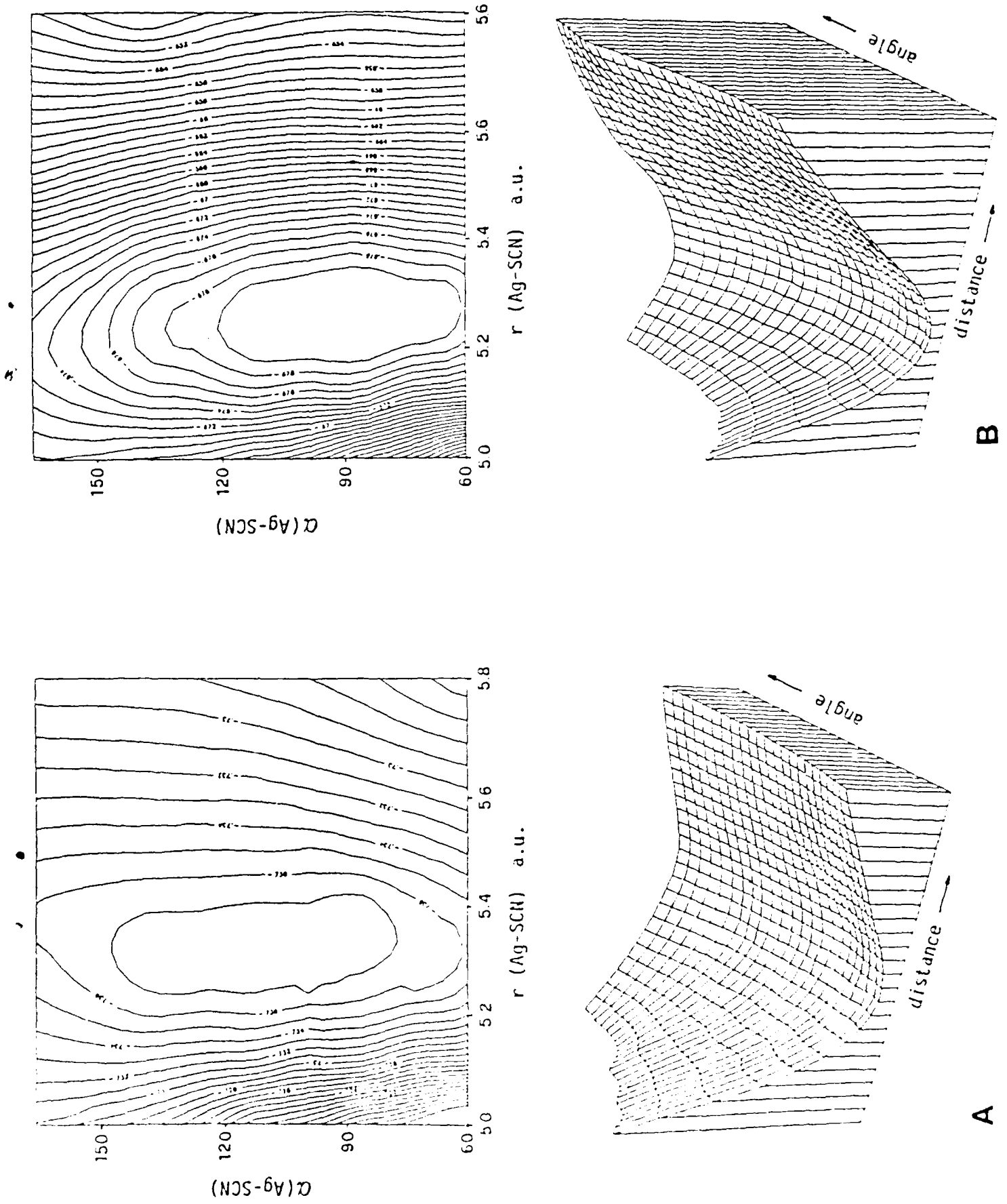



FIGURE 2

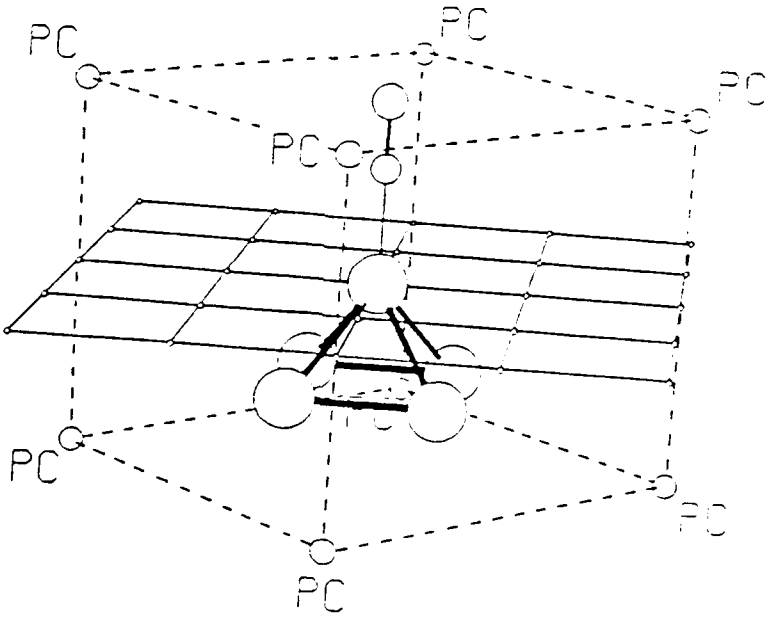



FIGURE 3