REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER
Technical Report No. 27

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
CLUSTER-MODEL STUDY OF THE INTERACTION OF
HALOGEN ATOMS WITH Ag CLUSTERS

5. TYPE OF REPORT & PERIOD COVERED
Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
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8. CONTRACT OR GRANT NUMBER(s)
N00014-82-C-0583

9. PERFORMING ORGANIZATION NAME AND ADDRESS
IBM Research, Almaden Research Center
650 Harry Road
San Jose, CA 95120-6099

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

12. REPORT DATE
1987

13. NUMBER OF PAGES
11

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION ST ENT (of abstract entered in Block 20, if different from Report)

DTIC
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18. SUPPLEMENTARY TES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (C

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OFFICE OF NAVAL RESEARCH

Contract ONR-N00014-82-C-0583 NR-359-824

R & T Code 4133011

Technical Report No. 27

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Prepared for Publication

in

Z. Phys. D.

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RJ 6529 (63330) 11/9/88
Surface Science

CLUSTER-MODEL STUDY OF THE INTERACTION OF HALOGEN ATOMS WITH Ag CLUSTERS

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ABSTRACT: Analysis of ab initio wave functions shows that the interaction between halogen atoms (F, Cl, and Br) and Ag clusters is ionic, and that the halogen ionicity is essentially −1. The interaction and the bonding arise, almost entirely, from the Coulomb attraction between the charged halogen and the metal and from polarization of the two subunits. Large shifts in equilibrium bond distances and vibrational energies are caused by an external electric field. These changes arise form a dominant Stark effect.

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The nature of the bonding between halogen atoms and silver is a subject of considerable interest in surface science and electrochemistry [1-4], and the nature of the bonding interaction, if more ionic or more covalent, is still a matter of controversy.

We studied the interaction between F, Cl, and Br atoms and an Ag_4 cluster modeling the three-hollow site of the Ag(111) surface using ab initio Hartree-Fock wavefunctions. Attention has been focused on the character of the bonding and on the importance of the polarization effects for the dipole moment changes resulting from the bond formation. In addition we have considered the effect of an external electric field on the metal-adsorbate properties.

A major concern in adsorbate cluster-model studies is the dependence of the properties on the number of substrate atoms in the cluster. However, the analysis of the interaction of F atoms with Ag_6, Ag_7, and Ag_{10} clusters confirms the basic features of the bonding derived for Ag_4 [5]. Here we discuss only the results for Ag_4, but we believe that our conclusions about the character of the bonding will be valid for more general cluster geometries.

The molecular wave functions have been determined using flexible basis sets of contracted Gaussian type orbitals. In order to facilitate the calculations, the core electrons of Ag have been replaced by Effective Core Potentials [6] including explicitly in the valence only the $4s^2$ $4p^6$ $4d^{10}$ $5s^1$ electrons. The valence basis set for Ag is contracted to [4s4p3d]. The halogen atoms have been treated at all electron level and the contracted basis sets used are [5s4p1d], [5s4p2d], and [9s7d3d] for F, Cl, and Br, respectively [7]. The basis sets optimized for the neutral atoms [7] were extended with diffuse s, p, and d functions whose exponents have been determined in order to obtain a better approximation for the SCF electron affinity (EA), and for the dipole polarizability, α_D, of the respective anions.

The halogen atom to surface distance in Ag_n-X has been varied along the C_{3v} axis: the distance of X from the surface plane (r), the dissociation energy (D_e), the vibrational frequency (ω_e) and the dipole moment (μ) have been determined (Table 1).

For distances close to the equilibrium Ag-halogen distance, the ground state configuration is $(1a_1)^2\,(2a_1)^2\,(3a_1)^2\,(1e)^4\,(2e)^1\,(^2E)$; the halogen cores as well as the Ag $1s^2$ to $4d^{10}$ cores are not explicitly given. This state arises from the combination of the Ag_4 ground state $(a_1)^2\,(e)^2$ with the seven valence ns and np electrons of X in configuration $(a_1)^2\,(a_1)^2\,(e)^2$. The main bonding effects are in the outer e shells and can be either covalent or ionic. In this latter case the bonding can be considered as originating from the interaction of the ionized $Ag_4^+\,(a_1)^2\,(e)^1$ cluster and the closed shell anion $X^-\,(a_1)^2\,(a_1)^2\,(e)^4$. In the covalent view, a filling bonding $(1e)^4$ and a singly occupied antibonding $(2e)^1$ MOs are formed.

To determine the character of the Ag-halogen bonding as covalent or ionic we apply two measures. First, we make use of a projection operator [8] for the occupied orbitals of the free halogen anion X^-. The expectation value of the projection operator for a given spatial orbital of X^-, $\phi_{n\,l\,m}\phi^+_{n\,l\,m}$, is a measure of the extent to which $\phi_{n\,l\,m}$ is occupied in the total cluster wavefunction, $\psi(Ag_nX)$. In the case that this projection gives a value close to 2, it is clear that $\phi_{n\,l\,m}$ of X^- is completely occupied in $\psi(Ag_nX)$ [8]. For all X and for a wide range of distances about the minimum of the Ag_4-X energy curve, the projection of all $\phi_{n\,l\,m}$ is about 2. Summing over all the orbitals of X, we find 9.98, 17.95, and 35.92 electrons for F, Cl, and Br, respectively, in Ag_4-X; these values are for the halogen near the minimum. They provide very strong evidence for an ionic interaction where the silver cluster is Ag_4^+ and the halogen is X^-.

A second measure of the bonding nature is based on the slope of the dipole moment curve as the distance of X from the cluster is varied [8]. For an ionic bond, the absolute magnitude of the slope should be -1. In fact, the non-zero component of the dipole moment of an ionic molecule represented by two point charges $+q$ and $-q$ will be $\mu = -q\,r$ and $d\mu/dr = -q$. Therefore, for an ideal fully ionic molecule where $q = 1$, $d\mu/dr = -1$ and the curve is a straight line. Generally, on the other hand, a small slope is characteristic of a covalent bond. Of course, in a real system the polarization of the subunits, in our case the halogen and the cluster, can lead to a substantial change in the absolute magnitude of the dipole moment. In our case, this polarization must be quite important because we find a slope greater than 1, see Table 1; it is impossible that the ionicity of the halogen is greater than 1.

The dipole moment curve as function of the distance has been determined by a cubic polynomial fitting:

$$\mu(r) = M_0 + M_1(r - r_e) + M_2(r - r_e)^2 + M_3(r - r_e)^3 .$$

For each value of r it is possible to transform the Ag_4X cluster orbitals into those which are most like X, $\phi_i(\mathrm{loc},X)$, and the orthogonal complement of the SCF canonical space. This corresponding orbital transformation [9,10] provides the transformation with maximally localized orbitals. The contribution to the total dipole moment of $\phi_i(\mathrm{loc},X)$ to the total cluster dipole is denoted by $\mu(X)$. The coefficients of the expansions of $\mu(Ag_4X)$ are reported in Table 1. The dipole moment curve, for a considerable distance about the equilibrium Ag-halogen bond, is a straight line (small M_2 and M_3) and the contribution from the chemisorbed X-halogen to the slope of the curve is almost exactly -1 thus supporting the view of an essentially ionic bond.

In order to understand the origin of the Ag_n-X interaction, we applied a constrained space-orbital variations CSOV [11]. In this way it is possible to determine the individual contributions to the bonding, i.e., electrostatic effects, intraunit polarization, charge transfer, and covalent bonding. We start, CSOV step 0, with the superposed Ag_4^+ and X^- charge distributions; this gives the frozen-orbital (FO) interaction. Given the strong evidence that the bonding is ionic, we analyze the effect of replacing the X^- ion with a unit point charge, PC = − 1, placed at the position of the halogen nucleus. In this case step 0 gives the pure electrostatic attraction with no repulsive contribution originating from non-bonding overlap of X^- and Ag_4^+ charge distributions (Pauli repulsion). Then we allow the Ag_4^+ orbitals to vary because of the presence of the X anion for both the PC and the extended representation of X^- (CSOV step 1); this allows the Ag_4^+ to polarize in the presence of X^-. The next step (step 2) is the Ag_4^+ orbital variation in the full space, indicating the amount of charge transfer from Ag_4^+ to X^-. In step 3 the Ag_4^+ orbitals are fixed and the X^- orbitals are varied in their own space. This permits the X^- unit to polarize as a result of the presence of Ag_4^+. In CSOV step 4 this variation occurs in the full space, so that both X^- to Ag_4^+ donation and X^- polarization are possible. In step 5 the covalent mixing between the valence e orbitals, $(1e)^4$ (X^-), and $(2e)^1$ (Ag_4^+), is allowed; all other orbitals are fixed as determined in step 4. The result of step 5 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. Of course, steps 2-6 have no meaning when X^- is replaced by a point charge. For each step, we consider the interaction energy E_{int}, with respect to separated Ag_4^+ and X^- fragments, and the dipole moment μ. In Table 2 the results of this analysis are reported for Ag_4-F at $r_e = 3.2$ near equilibrium bond distance. Clearly, the most important contribution comes from the electrostatic interaction. The difference between the PC and F^- values, 1.5 eV, represents the Pauli repulsion contribution. The electrostatic attraction is followed by the cluster polarization, about 2 eV, which reduces the repulsive contribution to the bonding. These two contributions alone account for about 90% of the whole binding energy. The other CSOV steps, X^- polarization and covalency, only slightly improve E_{int} (Table 2). Similar data have been obtained for Ag_4Cl and Ag_4Br [5]. The main difference is that, because of the larger equilibrium bond distances, the electrostatic interaction and the cluster polarization are smaller than in Ag_4F. On the other hand, the contribution from the Cl^- and Br^- polarization is higher, as expected on the basis of the larger dipole polarizabilities of these anions (Table 1).

The ionic nature of the silver-halogen interaction suggests that an external electric field F will produce large changes on the chemisorption properties. For a cluster in a uniform electric field F, 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 μ is the field-free dipole moment [12,13]. This is a pure Stark effect and does not include chemical changes 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 $(\Sigma r_i - \Sigma Q_N R_N) \times F$ to the field-free hamiltonian; i denotes electrons, N nuclei, and Q_N the nuclear charges [12,13].

The fields considered are ± 0.01 a.u. $= \pm 5.7 \times 10^7$ V/cm. The sign of F is such that $F < 0$ attracts electrons from the surface towards the ligand. Indeed, we observe that for $F = -0.01$ the X^- ions are pulled away from the surface giving a large increase in r; similarly, $F = +0.01$ pushes the ion toward the surface (Table 3). Consequently, the vibrational energies decrease for $F = +0.01$ and considerably increase for $F = -0.01$ (Table 4). This occurs because the adsorbed ligand is stretched against the wall represented by surface charge density. The changes caused by the external field are dominantly stark effects, while the chemical changes make only minor contributions (Tables 3 and 4).

In conclusion, we have shown that the bonding of F, Cl, and Br with Ag clusters is almost entirely ionic. We believe this is true also for surfaces in particular considering that the SCF wave function underestimates the electron affinities of the atoms and that a silver surface is more polarizable than a small cluster.

Table 1

Properties of Ag_4-X Clusters

		Ag_4-F	Ag_4-Cl	Ag_4-Br
EA (X)	eV SCF	1.35	2.08	2.52
	exp	3.40	3.62	3.36
α_n	Å^3 SCF	1.35	3.77	6.19
	HFL*	1.71	5.89	8.18
r (Ag-X)	au	3.310	4.347	4.721
ω_e	cm^{-1}	277	180	115
$D_e(Ag_4 + X)$	eV	2.72	2.68	2.76
<u>μ(r) (Ag_4-X) au</u>				
M_0		-1.09	-1.72	-2.00
M_1		-1.39	-1.60	-1.59
M_2		-1.09	-0.04	-0.01
M_3		1.01	0.03	-0.03
<u>μ(r) (X) au</u>				
M_0		-2.90	-3.31	-3.43
M_1		-1.00	-1.10	-1.11
M_2		0.10	-0.03	-0.04
M_3		-0.01	0.04	-0.01

*HFL = Hartree-Fock Limit [14]

Table 2

CSOV Analysis for Ag_4-F and Ag_4-PC (PC = Point charge)[a]

Step		E_{int}	ΔE_{int}	μ	$\Delta\mu$
0. Frozen orbital	PC	+4.82	...	−4.49	...
	F^-	+3.37	...	−4.21	...
1. Ag_4^+ polarization (Ag_4 basis)	PC	+6.92	+2.10	−1.52	+2.97
	F^-	+5.25	+1.88	−1.37	+2.84
2. Ag_4^+ polarization (full basis)	F^-	+5.35	+0.10	−1.43	−0.06
3. X^- polarization (X basis)	F^-	+5.59	+0.24	−1.15	+0.28
4. X^- polarization (full basis)	F^-	+5.84	+0.25	−1.05	+0.10
5. Covalent e sym. interaction	F^-	+5.85	+0.01	−1.04	+0.01
6. Full SCF	F^-	+5.88	+0.03	−0.94	+0.10

[a] Interaction energies E_{int} in eV are computed with respect to separate ions; μ in au

Table 3

Equilibrium Bond Distances in Bohrs for Halogens Chemisorbed on Ag_4. When a Field F = ±0.01 au is Applied Both SCF and Stark Values Are Given. Δr are Also Given

F		Ag_4-F	Ag_4-Cl	Ag_4-Br
0.00	SCF	3.310/...	4.347/...	4.721/...
+0.01	Stark	3.098/−0.21	4.055/−0.29	4.405/−0.32
	SCF	3.092/−0.22	4.058/−0.29	4.418/−0.30
−0.01	Stark	3.637/+0.33	4.893/+0.55	5.375/+0.65
	SCF	3.620/+0.31	4.904/+0.56	5.410/+0.69

Table 4

Vibrational Frequencies in cm^{-1} for Halogens Chemisorbed on Ag_4. When a Field $F=\pm0.01$ au is Applied, both SCF and Stark Values are Given. $\Delta\omega$ are Also Given

F		Ag_4-F	Ag_4-Cl	Ag_4-Br
0.00	SCF	277/...	180/...	115/...
0.01	Stark	322/+45	222/+42	144/+29
	SCF	323/+46	222/+42	144/+29
−0.01	Stark	213/−64	118/−62	66/−49
	SCF	215/−62	116/−64	65/−51

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*THIS RESEARCH HAS BEEN SUPPORTED IN PART BY THE OFFICE OF NAVAL RESEARCH.