An Extended Hückel Calculation on the Interaction of 1,3,5-Trithian with Ag(111) Surface

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Received October 9, 1992

The interaction of 1,3,5-trithian molecule with Ag(111) surface is studied employing Extended Hückel method. The Ag(111) surface is modeled by the three layer metal clusters composed of 43 Ag atoms. We assume that the 1,3,5-trithian is lying flat on Ag(111) surface in the chair conformation. The geometry of 1,3,5-trithian itself is assumed to be the same as in the gas phase, which is obtained through the AM1 SCF-MO calculation with full geometry optimization. The calculation for 3-fold site adsorption leads to the weakening of C-S bond, which is compatible with the observed 5 cm^{-1} decrease of the C-S stretching frequency upon surface adsorption, while the on-top site adsorption leads to strengthening of C-S bond. The major component of the C-S bond of trithian is S $3p_\pi$ (S $3p_x$+S $3p_y$) and therefore only the 3-fold site adsorption causes the weakening of this bond. In addition, it is found that the trithian molecule binds to the 3-fold site more strongly.

Introduction

Understanding the interaction of organic sulfur compounds with metal surface is relevant to catalytic chemistry, as wall as to the boundary lubrication.[1] Recently several workers studied various organic sulfur compounds chemisorbed on silver[2-4] and gold[5] surfaces by surface-enhanced Raman scattering (SERS).[6] When a molecule is adsorbed on metal surface, its Raman scattering may be enhanced tremendously. This surface enhancement of Raman scattering decreases very rapidly with the increase of distance from the surface.[7] Hence, SERS provides a sensitive means to obtain the vibrational spectra of adsorbed molecules, their orientations with respect to the surface, and the metal-adsorbate interaction.[8-10]

It has been reported that aliphatic mercaptans are adsorbed dissociatively on silver surface by losing their thiol protons.[4,11,12] As expected, the adsorption of a thiolate thus formed occurred through its sulfur atom. The possible cleavage of the C-S bonds of organic sulfides upon surface adsorption has also been investigated by SERS. For example, Sandroff and Herschbach[13] reported the C-S bond cleavages of aromatic sulfides adsorbed on a silver surface. On the other hand, it has been reported that aliphatic sulfides did not undergo such surface-induced reactions.[14] In addition to the aliphatic sulfides, recent SERS investigations for the cyclic organosulfur compounds, pentamethylene sulfide, 1,4-dithian, and 1,3,5-trithian revealed that there is no surface-induced C-S bond dissociation for these compounds.[15] It has been reported[15] that 1,3,5-trithian is bound to the silver surface in the chair conformation *via* its three sulfur atoms. Upon surface adsorption, 5 cm^{-1} decrease of the C-S stretching frequencies and 8-19 cm^{-1} increase of the C-H stretching frequencies were reported.[15]

In this work, the interaction of 1,3,5-trithian molecule with Ag(111) surface is studied employing Extended Hückel (EH) method.[16] Since there is no further experimental information about the exact adsorption geometry of 1,3,5-trithian molecule adsorbed on single crystal silver surface, we assume that the 1,3,5-trithian is lying flat on Ag(111) surface in the chair conformation. The possible adsorption site of 1,3,5-trithian on Ag(111) surface is the on-top site and 3-fold site. For the case of on-top site adsorption, the three sulfur atoms of 1,3,5-trithian are located above the three silver atoms of the first layer of Ag(111) surface. For the case of 3-fold site adsorption, the three sulfur atoms are located above 3-fold hollow site.

We also carried out fragment molecular orbital transformation (FMO analysis) to investigate the role of each molecular orbitals of 1,3,5-trithian in the formation of chemisorption bond. The FMO analysis is a basis transformtion from C, S, H, and Ag atomic orbital basis to the 1,3,5-trithian molecular orbital basis and the silver cluster molecular orbital basis.

Computational Details

1,3,5-Trithian is the stable trimer of thioformaldehyde. Electron diffraction studies in the vapor phase,[17] dipole moments in the benzene solution,[18] and X-ray diffraction in the solid state[19] prove that it has the chair conformation. The bond lengths and bond angles, found by electron diffraction,[20] are shown in the Table 1. These are consistent with the sp^3 hybridization of the valence electrons of the sulfur atoms and, in the chair conformation, there will be lone pairs of the electrons available for donation in equatorial and axial directions. 1,3,5-trithian, therefore, could act as either a monodentate, bidentate, or tridentate ligand. In the silver complex of the 1,3,5-trithian molecule it is always in the chair conformation with little distortion from idealizaed C_{3v} sym-

Table 1. Geometry of the Free 1,3,5-Trithian Molecule

	Experimetal[a]	In this work[b]
d (C-S)	1.81 Å	1.73 Å
d (S-S)	3.05 Å	2.99 Å
d (C-H)	-	1.11 Å
<CSC	114.50°	192.10°
<SCS	106.50°	116.10°

[a] Ref. 20. [b] determined through AM1 calculation with full geometry optimization.

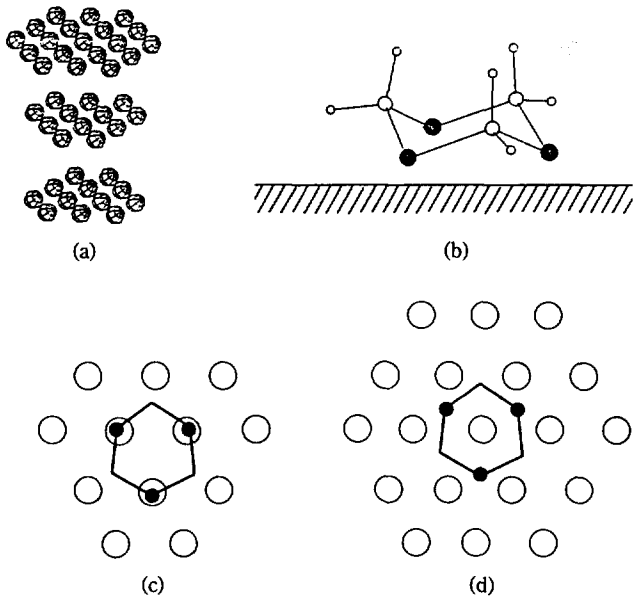

Figure 1. (a) The geometry of the Ag_{43} (19, 12, 12) cluster used in this study. (b) The adsorption geometry of 1,3,5-trithian molecule on Ag surface. (c) On-top site adsorption. Large white circles denote 1st layer Ag atoms and small black circles Sulfur atoms. (d) 3-fold site adsorption.

metry, as found in the crystals of 1,3,5-trithian itself by Moerman and Wiebenga[19] and by Hassel and Viervoll[17] using electron diffraction. The Ag-S bond length in the silver complexes has been reported to be bracketed in the range of 2.4-2.6 Å.[20-22]

It has been reported[15] that 1,3,5-trithian is bound to the silver surface *via* its three sulfur atoms in the chair conformation. To the best of our knowledge there is no further experimental information about the exact adsorption geometry of 1,3,5-trithian on single crystal silver surface. The comparison of the dimension of 1,3,5-trithian molecule and the nearest neighbor distance of the silver atoms shows a nearly perfect match from which one would expect a parallel orientation of 1,3,5-trithian with respect to the Ag(111) surface. From the 3-fold symmetry and the size of the 1,3,5-trithian molecules one is tempted to assume on-top site and 3-fold site adsorption geometry.

The geometry of 1,3,5-trithian molecule adsorbed on siver surface is assumed to be the same as in the gas phase with chair conformation, which is obtained through the AM1 SCF-MO calculation[23] with full geometry optimization. The detailed geometry of 1,3,5-trithian used in this work is given in Table 1 with the experimentally determined geometry.[20]

Model clusters used in this work are shown in Figure 1. The three layer model has been known to be a reasonable compromise between a convenient size of the calculaton and an adequate representation of the surface.[24] The Ag-Ag distance is taken as 2.89 Å, which is the nearest neighbor distance in bulk silver.[25] The bondlength of Ag-S is set equal to 2.50 Å for adsorbed 1,3,5-trithian. In our study, we varied the Ag-S distance between 2.45 and 2.55 Å, observing only very small changes in the chemisorption properties examined in present work.

Table 2. Comparison of the Results of EH Calculation Employing Various Ag H_{ii} Parameters and That of *ab initio* CPF SCF Calculation of Reference 26 for AgS Diatomic Molecule[a]

	Ag H_{ii} (eV)			Populations			Net charge of Ag atom
	5*s*	5*p*	4*d*	Ag 5*s*	Ag 5*p*	Ag 4*d*	
CPF[b]	–	–	–	0.52	0.17	9.86	0.35
	−11.8	−7.2	−15.9	0.59	0.18	9.88	0.35
	−12.3	−7.2	−15.9	0.69	0.16	9.87	0.28
	−12.8	−7.2	−15.9	0.79	0.15	9.87	0.19
	−13.3	−7.2	−15.9	0.90	0.14	9.86	0.10
EHT	−11.8	−7.7	−15.9	0.57	0.21	9.88	0.34
	−11.8	−8.2	−15.9	0.55	0.25	9.88	0.33
	−11.8	−8.7	−15.9	0.53	0.29	9.88	0.30
	−11.8	−7.2	−16.4	0.59	0.18	9.89	0.34
	−11.8	−7.2	−16.9	0.59	0.18	9.90	0.33
	−11.8	−7.2	−17.4	0.59	0.18	9.90	0.00

[a] *d* (Ag-S) is set equal to 2.3739 Å. [b] Ref. 26.

Table 3. Extended Hückel Parameters

Atom	Orbital	H_{ii} (eV)	ξ_1	ξ_2	c_1	c_2
Ag[a]	5*s*	−11.80	2.244			
	5*p*	−7.20	2.202			
	4*d*	−15.90	6.070	2.663	0.5591	0.6047
S[b]	3*s*	−20.00	1.817			
	3*p*	−13.30	1.817			
	3*d*	−8.00	1.500			
C[b]	2*s*	−21.40	1.625			
	2*p*	−11.40	1.625			
H[b]	1*s*	−13.60	1.300			

[a] Orbital exponents ξ, and the coefficients in a double-ξ expansion of metal *d*-orbitals are taken from reference 27. See text for the determination of H_{ii}'s. [b] Ref. 28.

The results of calculation for AgS diatomic molecule employing various Ag H_{ii} parameters are compared with that of *ab initio* coupled-pair functional (CPF) SCF calculation of Bauschlicher *et al.*[26] to test the reliability of EH parameters used in this work. Table 2 shows some calculated quantities and their comparison with the CPF-SCF results.

Among the sets of parameters given in Table 2, the first set (−11.8, −7.2, −15.9) seems to be the most acceptable one. We have chosen this parameter set as reference parameter set for the detailed calculation although the calculations empolying all sets of parameters given in Table 2 are also carried out.

The Ag-S bond is known to have more covalent character than the Ag-O bond.[26] Too large charge transfor from silver to sulfur is calculated when we have adopted the same values of Ag H_{ii} used in the O_2/Ag(110) system.[27] Other EH parameters used in this study except Ag H_{ii} valuces are the same as that of the O_2/Ag(110) system, and these EH parameters are given in Table 3.

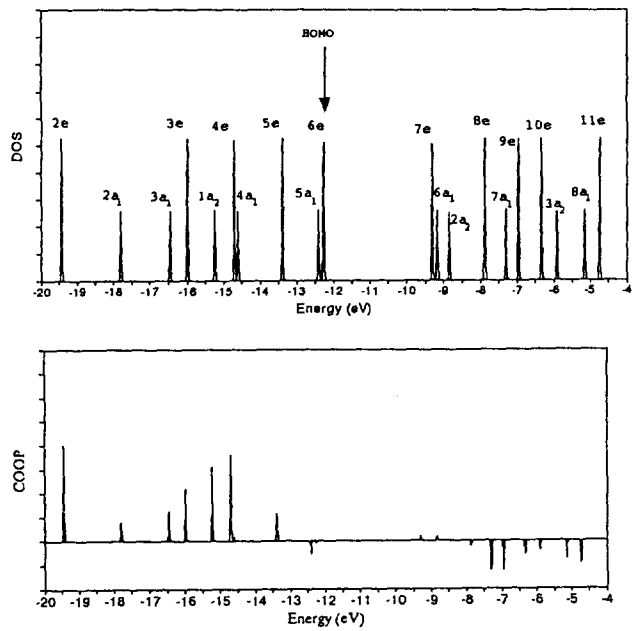

Figure 2. (a) DOS curve of free 1,3,5-trithian molecule with MO assignment. (b) COOP curve of C-S bond of free 1,3,5-trithian molecule.

Results and Discussion

The density of states (DOS) curve and the crystal orbital overlap population (COOP) curves for the free 1,3,5-trithian molecule are shown in the Figure 2.

The DOS curve shown in Figure 2(a) is a plot of the number of orbitals per unit energy as abscissa versus energy as ordinate. The crystal orbial overlap population (COOP) curve is a plot of the overlap-population-weighted density of states versus energy.[29] Integration of the COOP curve up to the Fermi energy gives the total overlap population. The positive regions of the COOP curve represent bonding and the negative regions antibonding. The amplitude of the COOP curve depends on the number of states in an energy interval, the magnitude of the coupling overlap, and the size of the coefficients in the MO's.[30] The definition of COOP curve of a bond *A-B* is given in the Eq. (1), where c_{ji} is the *j*th coefficient of *i*th MO and s_{jk} is an overlap integral of *j*th basis and *k*th basis.

COOP (Crystal Orbital Overlap Population)

$$=\sum_i 2\,\delta(E-E_i)\sum_{j\in A}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk} \qquad (1)$$

The COOP curve of the *A-B* bond can be resolved into the contribution of each atomic orbitals of the atom *A* as in Eq. (2), where COOP (*A*, *p*) of Eq. (2) represents the contribution of *p* atomic orbital of the *A* atom to the COOP curve of *A-B* bond.

COOP (Crystal Orbital Overlap Population)

$$=\sum_i 2\,\delta(E-E_i)\sum_{j\in A,\,p}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk}$$

$$+\sum_i 2\,\delta(E-E_i)\sum_{j\in A,\,q}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk}$$

$$+\sum_i 2\,\delta(E-E_i)\sum_{j\in A,\,r}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk}+\cdots$$

$$=\mathrm{COOP}\ (A,\ p)+\mathrm{COOP}\ (A,\ q)+\mathrm{COOP}\ (A,\ r)+\cdots \qquad (2)$$

The reduced overlap population (ROP) of a bond *A-B* is defined as in Eq. (2), where n_i is the occupation number of the *i*-th MO. It has been used successfully as an indication of the strength of a given bond and has been correlated with such properties as force constants, vibrational frequencies, and dissociation energies.[31,32]

Reduced Overlap Population (ROP)

$$=2\sum_i n_i\sum_{j\in A}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk} \qquad (3)$$

The ROP can also be resolved into the contribution of each atomic orbitals as follows. The ROP (*A*, *p*) of Eq. (4) represents the contribution of *p* atomic orbital of the *A* atom to the *A-B* bond stregth. This ROP (*A*, *p*) can be resolved again into the contribution of each molecular orbital of a given molecule to ROP (*A*, *p*). ROS (S 3*s*; 2*e*), for example, represents the contribution of 2*e* molecular orbital to the ROP (S 3*s*) of C-S bond.

Reduced Overlap Population (ROP)

$$=2\sum_i n_i\sum_{j\in A,\,p}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk}$$

$$+2\sum_i n_i\sum_{j\in A,\,q}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk}$$

$$+2\sum_i n_i\sum_{j\in A,\,r}\sum_{k\in B} c_{ji}\,c_{ki}\,s_{jk}+\cdots$$

$$=\mathrm{ROP}\ (A,\ p)+\mathrm{ROP}\ (A,\ q)+\mathrm{ROP}\ (A,\ r)+\cdots \qquad (4)$$

Of particular interest for the results presented below are the occupied $3a_1$, 3*e*, $1a_2$, 4*e*, $4a_1$, 5*e*, $5a_1$, 6*e* (HOMO) orbitals and the empty 7*e* (LUMO) orbital. Their energies and the fact that they have large contributions from the atomic orbitals of the sulfur atoms make these MO's ideal for bonding with the silver surface.

The $3a_1$ orbitial is rather strong bonding orbital of C-S bond due to the bonding interacting of S $3p_\pi$ and S $3d_\pi$ with carbon atom. There is also small bonding interactiong of S 3*p* with carbon atom. The 3*e* orbital is strong bonding orgital of C-S bond due to the bonding interaction of S $3p_\pi$ and S $3p_\sigma$ with carbon atom. The $1a_2$ orbital is very strong bonding orbital of C-S bond. This strong bonding character results exclusively from the bonding interaction of S $3p_\pi$ with carbon atom. The 4*e* orbital orbital is also very strong bonding orbital of C-S bond due to the strong bonding interaction of S $3p_\pi$ and $3d_\pi$ with carbon atom. The $4a_1$ is composed of the antibonding interaction between S 3*s* and carbon atom and the bonding interaction between S $3p_\pi$ and carbon atom. The contribution of this orbital to the C-S bond strength is negligible due to the cancellation between the bonding and the antibonding interaction. The 5*e* orbital is composed of antibonding interaction between S 3*s* and carbon atom, weak bonding interaction between S $3p_\pi$ and carbon atom, and bonding interaction between S $3p_\sigma$ and carbon atom. The contribution of this orbital to the C-S bond strength is very small as can be seen in Figure 2(b). The $5a_1$ orbital is rather strong antibonding orbital between S $3p_\sigma$, S $3p_\pi$ and carbon atom. The 6*e* orbital (HOMO) is very weak antibonding orbital of C-S bond. This is due to the comparable

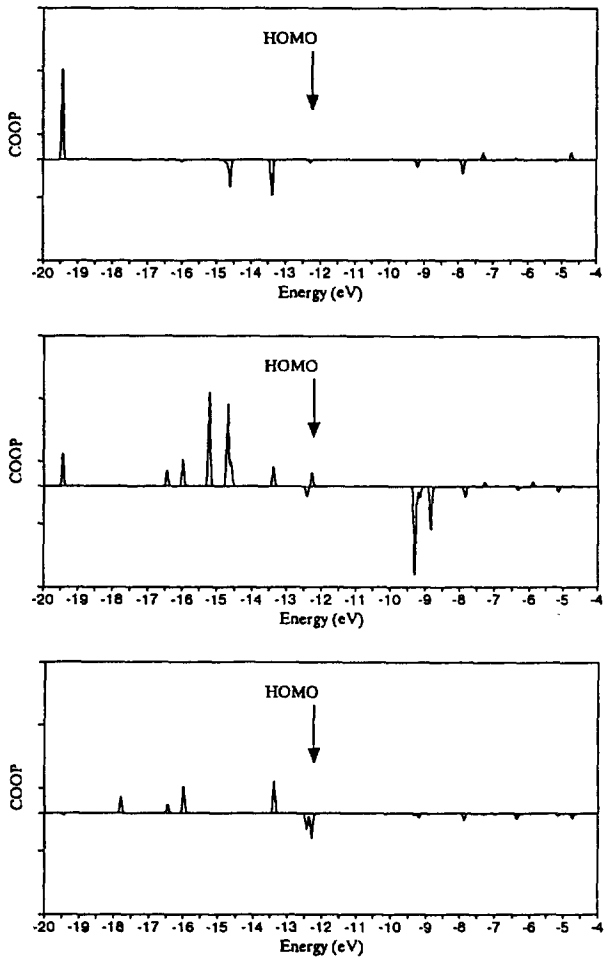

Figure 3. Resolved COOP curve of C-S bond of free 1,3,5-trithian molecule. (a) Contribution of S 3*s* atomic orbital. (b) Contribution of S $3p_\pi$ (S $3p_x$+S $3p_y$) atomic orbital. (c) Contribution of S $3p_\sigma$ (S $3p_z$) atomic orbital.

magnitude of the bonding interaction of S $3p_\pi$ and the antibonding interaction of S $3p_\sigma$ with carbon atom. The *7e* orbital (LUMO) is very weak bonding orbital of C-S bond due to the cancellation between the antibonding interaction of S $3p_\pi$ and the bonding interaction of S $3d_\pi$ with carbon atom.

The contributions of S 3*s*, S $3p_\pi$ (S $3p_x$+S $3p_y$), and S $3p_\sigma$ (S $3p_z$) to the COOP curve of C-S bond of free 1,3,5-trithian moleucle is shown in Figure 3. The figures corresponding to the contributions of S 3*d* atomic orbitals are omitted since their contributions to C-S bond are very small. One can understand the nature of each moleular orbitals of free 1,3,5-trithiane molecule through the comparison of each peaks shown in Figures 2 and 3 carefully. In short, one might say that the C-S bond of free 1,3,5-trithian moleucle is mainly composed of the interactions between S $3p_\pi$ (S $3p_x$+S $3p_y$) and atomic orbitals of carbon.

The result of calculation for 1,3,5-trithian adsorbed on Ag clusters empolying reference parameter set is given in Table 4.

There is no experimental data about the preferred adsorption site of 1,3,5-trithian on Ag(111) surface. Considering the binding energy and ROP between 1,3,5-trithian and Ag cluster given in Table 4, however, it can be claimed that the

Table 4. Results of Calculation Employing Reference Parameter Set

	On-top site	3-Fold site
HOMO (eV)	−11.45	−11.33
Net charge of 1,3,5-trithian	1.565	2.150
Binding Energy (eV)[a]	4.926	6.046
ROP (adsorbate-substrate)[b]	1.7138	2.8380
ROP (C-S)	0.9034	0.8775
ROP (C-H_{axial})	0.6913	0.7013
ROP (C-$H_{equatorial}$)	0.6943	0.7151

[a]Binding Energy is calculated as follows. B.E.=*E* (1,3,5-trithian) +*E* (silver cluster)−*E* (total system). [b]This is calculated through FMO analysis.

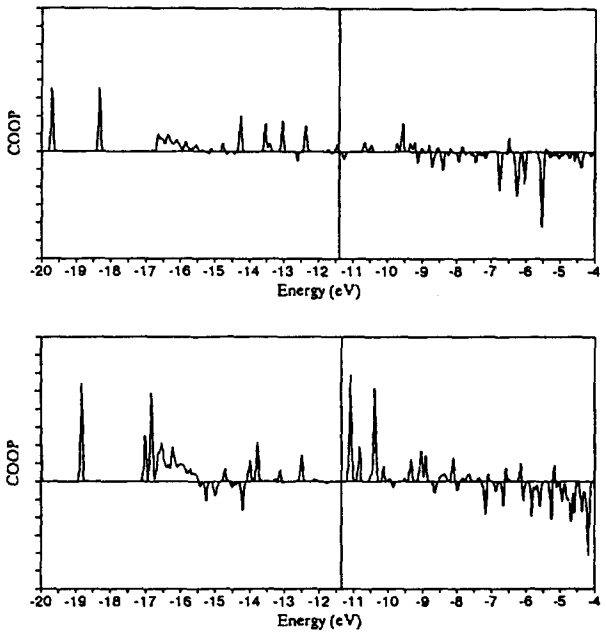

Figure 4. COOP curve of the chemisorption bond adsorbate-substrate. The vertical line around −11.5 eV represents the Fermi energy. (a) on-top site adsorpton. (b) 3-fold site adsorption.

1,3,5-trithian molecules are adsorbed on the 3-fold site preferentially.

To elucidate which molecular orbitals of 1,3,5-trithian are involved in the bonding between the adsorbate and the substrate, COOP curve of this chemisorption bond is shown in Figure 4. The contribution of each MO's of 1,3,5-trithian molecule to the ROP between the adsorbate and the substrate is also given in Table 5. The 5*e*, $5a_1$, and 6*e* MO's of 1,3,5-trithian molecule contribute heavily to the chemisorption bond regardless of the adsorption site as can be seen in Table 5. At first sight of Figure 4, one may think that the large peak located below the energy of −17 eV, which are originated from the 2*e* and $2a_1$ orbitals, play an important role in making the chemisorption bond. These orbitals which located considerably below the Fermi energy of silver surface, however, lead only to the occupied MO-occupied MO interactions with the metal MO's and therefore these contributions to the chemisorption bond are very small.

Table 5. Contributions of Some Molecular Orbitals of 1,3,5-trithian to the ROP (adsorbate-substrate)[a]

	On-top	3-Fold
ROP	1.7138	2.8380
$2a_2$	0.0312(2)[b]	0.0888(3)
$6a_1$	0.0582(3)	0.0809(9)
$7e$	0.0936(5)	0.2167(7)
$6e$	0.2528(13)	0.2927(10)
$5a_1$	0.3452(17)	0.7520(25)
$5e$	0.5477(27)	0.7520(25)
$4a_1$	0.0640(3)	0.2063(7)
$4e$	0.0122(1)	0.0703(2)
$1a_2$	0.0021(0)	0.0960(3)

[a] This is calculated through the FMO analysis. [b] The value in parathesis is the percentage of each contribution to the ROP (adsorbate-substrate).

Table 6. Contributions of Atomic Orbitals of Sulfur Atom to the ROP(C-S)

	C-S bond of free adsorbate	Ag-S bond	
		On-top	3-Fold
ROP	0.8945	0.6038	1.0587
S $3s$	0.2281(25)[a]	0.1138(19)	0.2154(22)
S $3p_x$	0.1211(13)	0.0095(2)	0.1451(15)
S $3p_y$	0.3194(35)	0.0078(1)	0.1082(11)
S $3p_z$	0.0584(6)	0.3222(54)	0.3511(35)
S $3d_{x^2-y^2}$	0.0598(7)	0.0038(1)	0.0140(1)
S $3d_{z^2}$	0.0254(3)	0.0641(11)	0.0555(6)
S $3d_{xy}$	0.0380(4)	0.0057(1)	0.0324(3)
S $3d_{xz}$	0.0083(1)	0.0345(6)	0.0644(6)
S $3d_{yz}$	0.0361(4)	0.0425(7)	0.0725(7)

[a] The values in parathesis are the percentage of the total ROP value.

The fact that the net charge of 1,3,5-trithian given in Table 4 is positive on both adsorption site implies that there is charge transfer from the adsorbate to the silver surface. This direction of charge transfer is consistent with the fact[20] that 1,3,5-trithian could act as a Lewis base.

Upon adsorption of 1,3,5-trithian on the 3-fold site, the reduced overlap population (ROP) of C-S bond is decreased while the ROP of C-H bond is increased compare with those of free 1,3,5-trithian. Accepting the existence of relationship between ROP and vibrational frequency as proposed by other workers, this is consistent with the experimental result of the red shift of C-S stretching frequency and the blue shift of C-H stretching fequency upon surface adsorption. On the other hand, on-top site adsorption shows opposite behavior to the experimental results.

This adsorption site dependence of C-S bond strength is originated from the nature of C-S bond itself. The contribution of atomic orbitals of sulfur to the bond strength of C-S bond is given in the first column of Table 6. It should again be emphasized that the contribution of S $3p_\pi$ (S $3p_x$+S $3p_y$) to the C-S bond is very larger than that of the S $3p_\sigma$ (S $3p_z$).

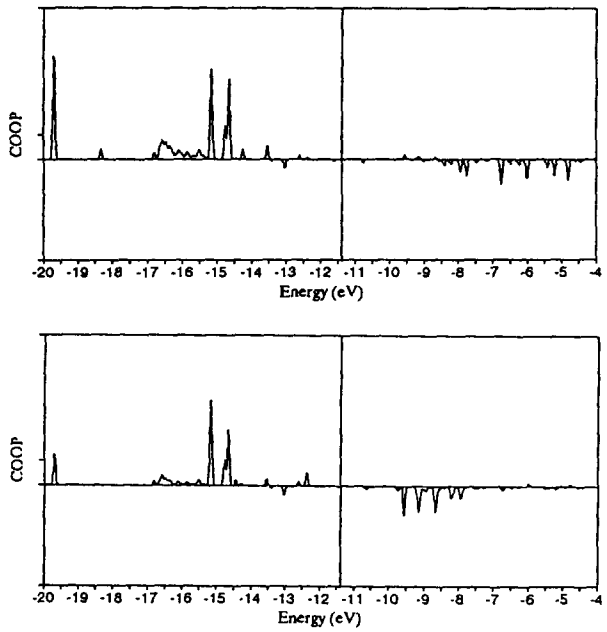

Figure 5. (a) COOP curve of C-S bond when the 1,3,5-trithian is adsorbed on on-top site. (b) Contribution S $3p_\pi$ to this C-S bond. The vertical line around −11.5 eV represents the Fermi energy.

When the 1,3,5-trithian molecules are adsorbed on the on-top site of Ag(111) surface, S $3p_\sigma$ is the major component of the Ag-S bond as can be seen in Table 6. The contribution of S $3p_\pi$ to the Ag-S bond is negligible for the case of on-top site adsorption. On the other hand, S $3p_\pi$ is the major component of the Ag-S bond when the 1,3,5-trithian molecules are adsorbed on the 3-fold site. The contribution of S $3p_\sigma$ to the Ag-S bond is reduced considerably in the case of 3-fold site adsorption. Because the C-S bond is mainly composed of S $3p_\pi$, only the 3-fold site adsorption result in the weakening of C-S bond. The COOP curves of C-S bond of 1,3,5-trithian molecule adsorbed on on-top site and 3-fold site are shown in Figures 5 and 6 with the resolved COOP curves respectively. It is evident form the resemblance of Figure 5(a) and (b) and from that the Figure 6(a) and (b) that the C-S bond is mainly composed of S $3p_\pi$ regardless of adsorption site. Comparing the Figure 5(b) and Figure 6(b), however, one can see that the peak at −19.5 eV of Figure 5(b) moves to lower energy and the large peaks of Figure 5(b) around 15 eV are more broadened in Figures 6(b). This implies that S $3p_\pi$ is more heavily perturbed by silver surface when the 1,3,5-trithian molecule is adsorbed on the 3-fold site of Ag(111) surface.

The contribution of atomic orbitals of silver to the bond between the adsorbated and substrate is given in the Table 7. It is very interesting to note that the contribution of Ag $4d$ atomic orbital to the chemisorption bond is very small. Although the contribution of Ag $5s$ atomic orbital is very large, there is no adsorption site dependence (42% *vs.* 47%). It deserves to be mentioned, however, that the contribution of Ag $5p_\pi$ (Ag $5p_x$+Ag $5p_y$) and that of Ag $5p_\sigma$ (Ag $5p_z$) are very adsorption site dependent.

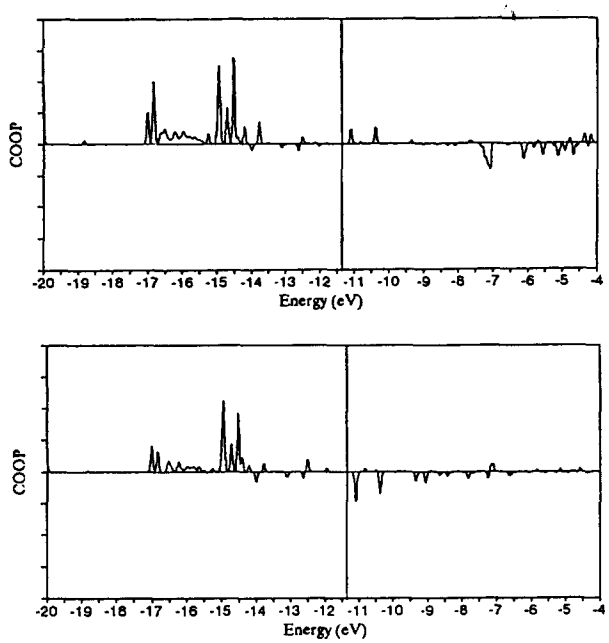

Figure 6. (a) COOP curve of C-S bond when the 1,3,5-trithian is adsorbed on 3-fold site. (b) Contribution S $3p_\pi$ to this C-S bond. The vertical line around −11.5 eV represents the Fermi energy.

Table 7. Contributions of Atomic Orbitals of Ag Atom to the ROP (Ag-S)

	On-top	3-Fold
ROP	0.6038	1.0587
Ag 5*s*	0.2526(42)[a]	0.4687(47)
Ag $5p_x$	0.0197(3)	0.1181(12)
Ag $5p_y$	0.0181(3)	0.0959(10)
Ag $5p_z$	0.2562(43)	0.2145(21)
Ag $4d_{x^2-y^2}$	−0.0004(−)	0.0114(1)
Ag $4d_{z^2}$	0.0209(3)	0.0404(4)
Ag $4d_{xy}$	−0.0007(−)	0.0128(1)
Ag $4d_{xz}$	0.0171(3)	0.0543(5)
Ag $4d_{yz}$	0.0204(3)	0.0425(4)

[a]The values in parathesis are the percentage of the total ROP value.

The results of calculations employing various parameter sets of Ag H_{ii}'s are given in Tables 8 and 9 for on-top site and 3-fold site adsorption respectively. One can see that the ROP (C-S) of 1,3,5-trithian adsorbed on the on-top site increase while that of 1,3,5-trithian adsorbed on 3-fold site decrease as the Ag H_{ii}'s of 5*s* and 5*p* move toward lower energy. One can also see that the effect of the variation of Ag H_{ii} (4*d*) is negligible. It is worth to note that the effect of Ag H_{ii} (5*p*) on the value of ROP (C-S) is more obvious than of Ag H_{ii} (5*s*) for the case of 3-fold site adsorption. This effect supports our explanation about the decrease of ROP (C-S) of 1,3,5-trithian when it is adsorbed on the 3-fold site of Ag(111) surface.

Conclusion

Table 8. Results of Calculation for 1,3,5-Trithian Adsorbed on On-top Site of Ag(111) Employing Various Parameter Sets

Ag H_{ii} (eV)			ROP			Net charge of 1,3,5-trithian
5*s*	5*p*	4*d*	C-S	C-H_{ax}	C-H_{eq}	
Free 1,3,5-trithian			0.8946	0.6946	0.6959	–
−11.8	−7.2	−15.9	0.9034	0.6913	0.6946	1.5652
−12.3	−7.2	−15.9	0.9052	0.6884	0.6944	1.7829
−12.8	−7.2	−15.9	0.9072	0.6848	0.6939	2.0345
−13.3	−7.2	−15.9	0.9615	0.6801	0.6908	3.1255
−11.8	−7.7	−15.9	0.9041	0.6903	0.6943	1.7152
−11.8	−8.2	−15.9	0.9046	0.6890	0.6934	1.7932
−11.8	−8.7	−15.9	0.9054	0.6872	0.6918	1.9210
−11.8	−7.2	−16.4	0.9034	0.6913	0.6950	1.5823
−11.8	−7.2	−16.9	0.9034	0.6912	0.6949	1.5965
−11.8	−7.2	−17.4	0.9034	0.6912	0.6949	1.6082

Table 9. Results of Calculation for 1,3,5-Trithian Adsorbed on 3-Fold Site of Ag(111) Employing Various Parameter Sets

Ag H_{ii} (eV)			ROP			Ne charge of 1,3,5-trithian
5*s*	5*p*	4*d*	C-S	C-H_{ax}	C-H_{eq}	
Free 1,3,5-trithian			0.8946	0.6946	0.6959	–
−11.8	−7.2	−15.9	0.8775	0.7013	0.7151	2.1504
−12.3	−7.2	−15.9	0.8753	0.6984	0.7154	2.4332
−12.8	−7.2	−15.9	0.8726	0.6952	0.7162	2.7847
−13.3	−7.2	−15.9	0.8700	0.6918	0.7155	3.6172
−11.8	−7.7	−15.9	0.8731	0.7000	0.7142	2.3549
−11.8	−8.2	−15.9	0.8685	0.6981	0.7131	2.6199
−11.8	−8.7	−15.9	0.8589	0.6952	0.7098	3.3318
−11.8	−7.2	−16.4	0.8772	0.7011	0.7152	2.1988
−11.8	−7.2	−16.9	0.8769	0.7011	0.7153	2.2388
−11.8	−7.2	−17.4	0.8767	0.7011	0.715	2.2721

We have carried out an EH calculation for the 1,3,5-trithian molecule adsorbed on Ag(111) surface. We have shown that the 1,3,5-trithian molecule interacts with the Ag(111) surface mainly through the 5*e*, $5a_1$, and 6*e* molecular orbitals. There is charge transfer from the adsorbate to substrate. The 3-fold site adsorption leads to the weakening of C-S bond while the on-top site adsorption leads to the strengthening of C-S bond. Since the C-S bond of 1,3,5-trithian is mainly composed of S $3p_\pi$ (S $3p_x$+S $3p_y$), only the 3-fold site adsorption can lead to the weakening of C-S bond. In addition, it is found that the 1,3,5-trithian molecule binds to the 3-fold site more strongly. We can thus conclude that the 1,3,5-trithian molecule adsorb on the 3-fold and that the weakening of C-S bond is occurred through the interaction between the silver surface and the S $3p_\pi$ components of C-S bond.

Acknowledgement. This work has been supported by the Korea Science and Engineering Foundation, the Ministry of Education, and the S.N.U. Daewoo Research Fund.

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Dual Capillary Column System for the Qualitative Gas Chromatography: 2. Comparison between Splitless and On-Column Injection Modes

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A dual capillary column system is described for the simultaneous analysis of a given sample and measurement of retention index (RI) and area ratio (AR) values of each peak on two capillary columns of different polarity, DB-5 & DB-1701 from a single injection. Both capillary columns were connected to either a splitless injector or an on-column injector *via* a deactivated fused-silica capillary tubing of 1 m length and a 'Y' splitter. Both injection modes allowed to measure RI and AR values with high reproducibility (<0.01% RSD) and high accuracy (<10% RE), respectively with the exception that the trace and high boiling solutes required the on-column mode for the accurate quantification and AR comparison. When the dual capillary column system in on-column injection mode was applied to the blind samples containing organic acids, each acid was positively indentified by the combined computer RI library search-AR comparison.

Introduction

Recent advances both in capillary column technology and in instrumentation of gas chromatography (GC) which is primarily a separation technique, make GC to be implemented into routine laboratory qualitative analyses of samples such