Chemisorption Studies of CH_3S on Ni(111)

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Abstract: The chemisorption of methanethiolate on Ni(111) is treated using a many-electron embedding theory, modeling the lattice as a 28-atom, three-layer cluster with the Ni atoms fixed at the positions from the bulk. Methanethiolate binds strongly to the Ni(111) surface at both high and low symmetry sites. Calculated adsorption energies are 61 kcal/mol for an equilibrium sulfur–surface distance of 1.99 Å at three-fold sites, 61 kcal/mol with a sulfur–surface distance of 2.06 Å at bridge sites, and 57 kcal/mol with a sulfur–surface distance of 2.13 Å at atop sites. Different equilibrium geometries are predicted for CH_3S at three-fold, bridge, and atop sites. The methanethiolate C–S axis is nearly perpendicular to the surface, inclined only about 5° from the surface normal, at the three-fold site. The C–S axis is found to be tilted away from the surface normal by 45° at the bridge site, and by 55° at the atop site. For the C–S axis perpendicular to the surface, the calculated C–S stretching vibration is 730 cm^{-1}, and the CH_3S–surface stretch is 281 cm^{-1} at the three-fold site. For a 45° tilt at the bridge site and a 55° tilt at the atop site, the C–S stretching vibrations are 677 and 698 cm^{-1}, respectively.

1. Introduction

Chemisorption studies of organosulfur compounds on transition metal and metal sulfide surfaces are important because of selective C–S bond activation in catalytic hydrodesulfurization (HDS) processes.[1,2] Methanethiol (CH_3SH) is the simplest thiol and its chemistry on nickel surfaces can provide insight into C–S and S–H bond activation. The adsorption and decomposition of methanethiol have been investigated on Ni(111),[3] Ni(100),[4–6] Ni(110),[7] Pt(111),[8–10] Cu(111),[5,11] Cu(100),[12] Fe(100),[13] W(211),[14] Au(111),[15] and polycrystalline aluminum.[16] Thermal decomposition of methanethiol and higher thiols on the Mo(110) surface has been studied by Friend and co-workers.[17–21] On most of these surfaces, the methanethiol decomposes by S–H bond cleavage to form a methanethiolate intermediate (CH_3S). The product distribution observed during the thermal decomposition varies with the surface under study; desorption of methane, ethane, dimethyl mercaptan, and hydrogen has been reported.

Castro and White have studied the adsorption and thermal decomposition of methanethiol on Ni(111) using temperature-programmed desorption (TPD), static secondary ion mass spectroscopy (SSIMS), and Auger electron spectroscopy (AES).[3] On Ni(111), CH_3SH decomposes below 150 K by S–H bond cleavage to form H (ads) and CH_3S (ads). Carbon–sulfur bond scission in CH_3S (ads) occurs between 160 and 210 K depending on the coverage. Desorption of H_2, CH_4, and C_2H_6 is observed above 200 K. In adsorption studies of CH_3SH on Ni(100)[4–6] and Ni(110),[7] CH_3S is also found to be the stable intermediate; desorption of CH_4 is observed on Ni(100)[4] and desorption of CH_4 and small amounts of C_2H_6 is found on Ni(110).[7] There is very little information concerning the nature of the binding sites and bonding geometries of CH_3S on nickel.

There have been some theoretical studies of methanethiolate–metal interactions.[22–27] An extended Hückel study of the electronic structure of methanethiol adsorbed on Ag(100) has shown that CH_3S is adsorbed at 4-fold hollow sites and bound on Ag(100) via its 3e symmetry orbitals.[22] Rodriguez has recently reported semi-empirical MO-SCF calculations (INDO-S) for methanethiolate and other oxygen and sulfur containing hydrocarbons on Cu and Mo clusters.[23,24] The heats of reaction and the molecular–orbital energy level spectrum upon adsorption have been reported. Performing *ab initio* cluster model calculations, Sellers has studied the adsorption of CH_3S on Pd(111) and Pt(111)[25] and the adsorption of CH_3SH on Au(111).[26] The C–S axis of CH_3S is calculated to be perpendicular to the surface on Pt(111) and is tilted away from the surface normal by 70° on Pd(111). Formation of σ and π bonds, resulting in an sp-hybridized S atom, characterizes the bonding of CH_3S to the Pt surface. sp^3-type sulfur is suggested in the interaction between CH_3S and Pd(111) surface. Calculated adsorption energy for CH_3S is 63 kcal/mol on Pt(111) and 79 kcal/mol on Pd(111).

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More recently, Sellers and co-workers have performed *ab initio* calculations of HS and CH_3S on cluster models of Au(111), Au(100), Ag(111), and Ag(100) surfaces, coupled with molecular mechanics simulations of self-assembled alkanethiolate monolayers on gold and silver surfaces.[27] The methanethiolate C–S axis is calculated to be perpendicular to the Au and Ag surface at hollow three-fold sites on the (111) faces and at hollow four-fold sites on the (100) faces, while the C–S axis is tilted away from the surface normal by about 70° at atop sites on the Au and Ag surfaces.[27] The bonding corresponds to sp- and sp^3-hybridization of the S atom for CH_3S adsorbed at high symmetry sites and at atop metal sites, respectively.

In this contribution, we describe the adsorption of CH_3S on the Ni(111) surface by a many-electron theory that permits an accurate description of bonding at the surface. The adsorbate and local surface region are treated as embedded in the remainder of the lattice electronic distribution which is modeled as a 28-atom, three-layer cluster with boundary atom potentials determined from a 62-atom cluster by an orbital localization transformation. Ni 3d orbitals are explicitly included on four nickel atoms of the surface region.

Our goals are to calculate the energetics of CH_3S adsorption as a function of surface site and to obtain the CH_3S bonding geometry.

2. Theory and Calculations

The objective of the embedding theory employed in this work is to use an accurate configuration interaction method to treat the adsorbate–surface region, while at the same time allowing a response of the bulk electrons to the surface processes. A local region is defined as an N-electron subspace extracted from the remainder of the lattice by a localization transformation.[28–31] The adsorbate and local region are then treated at high accuracy as embedded in the Coulomb and exchange field of the remainder of the electronic system. Calculations are carried out at an *ab initio* configuration interaction (CI) level, *i.e.*, all electron–electron interactions are explicitly calculated and there are no exchange approximations or empirical parameters. The details of the method are extensively discussed in refs 31–33.

Summarizing briefly the approach, the initial cluster consists of 62 atoms in three layers (28, 17, and 17 atoms). The embedding procedure is used to reduce this cluster to the 28-atom embedded cluster, model-depicted as shaded atoms in Figure 1. The embedding construct begins with the delocalized SCF solution of the Ni 4s-band and makes use of an orbital localization transformation,

$$\begin{array}{ccc} \text{s-band (delocalized)} & {\scriptstyle \Psi' = U\Phi} & \text{localized “s-band” orbitals} \\ \Psi = A(\varphi_1\varphi_2\varphi_3\ldots\varphi_N) & \longrightarrow & \Psi = A(\varphi'_1\varphi'_2\varphi'_3\ldots\varphi'_m\ldots\varphi'_N) \end{array}$$

to identify orbitals that are primarily localized outside the 28-atom embedded cluster. These orbitals have tails that extend into the embedded cluster, but mainly these tails lie on the boundary atoms of the embedded cluster. These tails can be thought of as the fraction of the 28-atom cluster strongly bound to the remainder of the lattice. The objective is to modify these boundary atoms to take into account the fact that they should be bonded to the remainder of the lattice; this is accomplished by effective potentials.

In the present work, that fraction of the boundary atom density that is tightly bound to the remainder of the lattice is described by a spherical density $fs(1)s(1)$ where s is a normalized linear combination of gaussians and f is the fraction of assigned charge. The Coulomb and exchange fields of the bulk electron distribution are represented by neutral atom potentials including a Phillips-Kleinman term, $\Sigma_k|\phi_k\rangle\langle\phi_k|(-\epsilon_k)$, where ϕ_k is an atomic orbital. As would be expected, the boundary atom charge assignments determined from the localization analysis qualitatively agree with a calculation based simply on the number of nearest neighbors removed from bonding with a given atom when the cluster is reduced in size. Figure 1 gives the fraction of charge for each boundary atom assigned to the effective potential and depicts the three-layer geometry. Further details are given in refs 31–33.

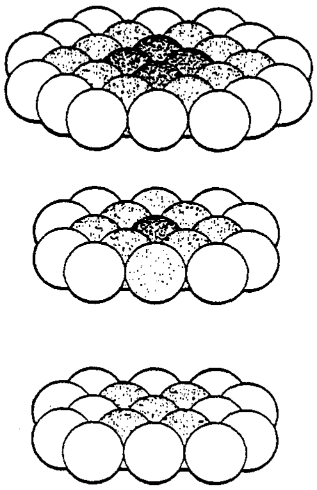

Figure 1. Cluster geometry and local region of the nickel cluster used to model the (111) crystal face of nickel. The three-layer, 62-atom cluster consists of a surface layer of 28 atoms, a second layer of 17 atoms, and a third layer of 17 atoms. Embedding theory is used to reduce the Ni_{62} cluster to a 28-atom model depicted as shaded atoms. Atoms surrounding the four central atoms in the surface layer and those surrounding the one central atom in the second layer are described by effective potentials for (1s-3p core)$(3d)^9(4s)^{0.5}$ and (1s-3p core)$(3d)^9(4s)^{0.25}$ configurations, respectively. Effective potentials for the shaded atoms in the third layer describe the (1s-3p core)$(3d)^9(4s)^{0.6}$ configuration. Unshaded atoms have neutral atom (1s-3p core)$(3d)^9(4s)^1$ potentials. All atoms have Phillips–Kleinman projectors $\Sigma|Q_m\rangle\langle Q_m|(-\epsilon_m)$ for the fixed electronic distribution. The nearest neighbor Ni–Ni distance is 2.48 Å.

The treatment of the adsorbate–surface system is then carried out by augmenting the basis in the region around the surface sites of interest to include functions describing polarization and correlation contributions. Nickel 3d functions on surface atoms are introduced explicitly at this stage. Final electronic wave functions including the adsorbate are constructed by configuration interaction,

$$\Psi = \sum_k \lambda_k A(\chi_1{}^k\chi_2{}^k\ldots\chi_n{}^k\varphi'_1\ldots\varphi'_p)$$
$$\approx \sum_k \lambda_k A(\chi_1{}^k\chi_2{}^k\ldots\chi_n{}^k)$$

and the coupling of the local electronic subspace and adsorbate to the bulk lattice electrons, $\{\varphi'_j,\ j = 1,\ p\}$, is represented by the modified Hamiltonian,

$$H = \sum_i^n -{}^1/{}_2\Delta_i^2 + \sum_i^n\sum_k^Q -Z_k/r_{ki} + \sum_{ij}^n 1/r_{ij}$$
$$+ \sum_m \{|r_{12}{}^{-1}\varphi_m(2)\rangle - |r_{12}{}^{-1}\gamma_m(1,2)\rangle\} + \sum_m \epsilon_m|q_m\rangle\langle q_m|$$

where φ_m, γ_m, and q_m denote atomic functions or densities derived from the orbital tails that extend onto the boundary atoms of the embedded cluster.

In the CI calculations, the occupied and virtual orbitals of the SCF solution are transformed separately to obtain orbitals with varying degrees of localization about the four-atom surface region. This unitary transformation of orbitals which is based upon exchange maximization with the valence orbitals of atoms in different parts of the cluster enhances convergence of the configuration interaction expansion. Examples of the present approach applied to nickel surfaces and hydrocarbon adsorbates can be found in refs 34–40.

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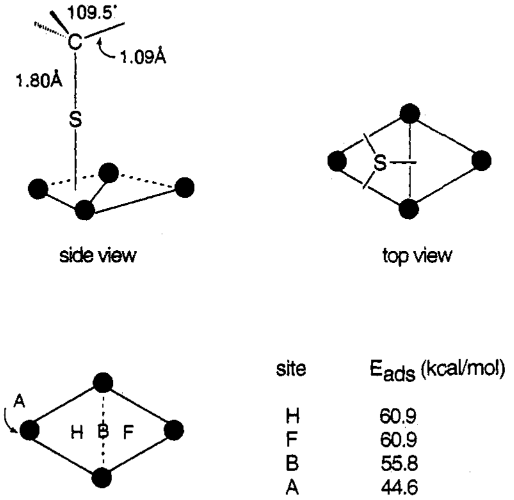
The CI calculations involve single and double excitations from multiple parent configurations within a 33-electron subspace to 28 possible localized virtual orbitals. All configurations arising from excitations with an interaction energy greater than 1 × 10^{-5} hartree with the parent SCF configuration and several other reference configurations with CI coefficients >0.05 are explicitly retained in the expansion; contributions of excluded configurations are estimated using second-order perturbation theory. For all sites and geometries calculated, the SCF solution is the dominant configuration. Details of the procedure are given in ref 41. Basis superposition contributions to the total energy were taken into account by calculating the energy of the Ni cluster with the adsorbed species' virtual basis present (but not the adsorbate nuclei). Calculated basis superposition corrections to the total energy are very small, between 1 to 2 kcal/mol. All energies reported in the present work include the basis superposition contributions.

The cluster geometry and surface region of the Ni(111) surface are shown in Figure 1. The three-layer, 62-atom cluster consists of a surface layer of 28 atoms, a second layer of 17 atoms, and a third layer of 17 atoms. Embedding theory is used to reduce the Ni_{62} cluster to a 28-atom model depicted as shaded atoms: the surface layer of 14 atoms, a second layer of 9 atoms, and a third layer of 5 atoms. For the local surface region of four nickel atoms, an effective [1s-3p] core potential and valence 3d, 4s, and 4p orbitals are used. Other Ni atoms are described by an effective core potential for [1s-3d] electrons, and a single 4s orbital. For all boundary atoms, and those in the third layer, the core potential is further modified to account for bonding to the bulk as defined by the embedding procedure (see refs 31-33).

In calculating the energies for thiolate bonding at various sites on the nickel cluster, the positions of the Ni atoms in the cluster model were held fixed with a nearest neighbor Ni-Ni distance of 2.48 Å from the bulk. The triple-ζs and p basis for carbon is taken from Whitten[42] and augmented with a set of d polarization functions with an exponent of 0.626. The triple-ζs and p basis for sulfur is taken from ref 43 and augmented with a set of d polarization functions with an exponent of 0.58. The basis orbitals of Ni and H are the same as those used in previous chemisorption studies of H/Ni(111)[37] and NiCO.[44] The exponent of H 2p functions is 0.6. The same basis and core potentials are used in all subsequent calculations on the Ni(111) surface for CH_3S adsorption calculations.

The reference total energy is computed for CH_3S at a distance of 25 au above the surface using the same occupied and virtual space for the configuration interaction. This procedure is effective in minimizing CI size inconsistency errors.[34-40,45-48]

The present embedding approach allows us to calculate accurately the energetics and geometries of adsorbed species on various types of adsorption sites on nickel surfaces. In the case of hydrogen adsorbed on the same 28-atom Ni(111) cluster,[36] the calculated adsorption energy of 62 kcal/mol for H at three-fold sites is in agreement with a thermal desorption value of 63 kcal/mol.[49] The calculated H-Ni distance of 1.86 Å at three-fold sites is in excellent agreement with both the low-energy electron diffraction (LEED) value[50] of 1.84 ± 0.06 Å and a very recent He-atom diffraction value[51] of 1.86 ± 0.07 Å for H on Ni(111). In addition, the calculated H-surface vibrational frequency and H orbital levels are also consistent with electron energy loss spectroscopy (EELS) and ultraviolet photoelectronn spectroscopy (UPS) results. Thus, our previous calculations demonstrated that the characteristic features of H chemisorption on Ni(111) obtained from different experiments are well reproduced by the present embedding theory.



site	E_{ads} (kcal/mol)
H	60.9
F	60.9
B	55.8
A	44.6

Figure 2. CH_3S adsorption sites on Ni(111) and calculated adsorption energies for the methanethiolate C–S axis perpendicular to the surface. The notations H, F, B, and A refer to filled three-fold, hollow three-fold, bridge, and atop sites, respectively. All C–H bond lengths are 1.09 Å, and HCH angles are 109.5°, unless otherwise indicated. CH_3S adsorbed at both filled and hollow three-fold sites shows no energetic difference. Adsorbed CH_3S at bridge and atop sites are stabilized by tilting the C–S axis away from the surface by 45° and 55°, respectively (see text and Figure 3). Only four Ni atoms of the surface layer are shown.

3. CH_3S Adsorption on Ni(111)

The calculated structural parameters of gaseous CH_3S using the present basis are the following: C–H bond lengths of 1.09 Å, a C–S bond length of 1.80 Å, and HCH angles of 104°. These values are in good agreement with the very recent free-jet-cooled laser-induced fluorescence values of 1.10 Å, 1.77 Å, and 102.5°, respectively.[52] Our calculations show that the CH_3 group in the gas phase of CH_3S remains nearly tetrahedral. In fact, the energy change with respect to the HCH angles between 109.5° and 102° is less than 0.1 kcal/mol. Thus, in the initial sulfur–surface distance optimization, the C–H bond lengths of the CH_3 group are fixed at 1.09 Å, the HCH angles are fixed at 109.5°, and the C–S bond length is fixed at 1.80 Å. The sites considered for CH_3S adsorption are as follows: a hollow three-fold site with no second-layer Ni atom underneath (fcc extension of the lattice); a filled three-fold site with a second-layer Ni atom underneath (hcp extension of the lattice); and a bridge site and an atop Ni site, denoted by F, H, B, and A, respectively, in Figure 2. Sulfur distances from the surface are fully optimized for all the adsorption sites studied.

Calculated adsorption energies, sulfur–surface equilibrium distances, C–S stretching frequencies, and methanethiolate sulfur–surface perpendicular stretching vibrations are reported in Table 1. For a methanethiolate C–S axis perpendicular to the surface, our calculations show that there is no energetic difference between the fcc hollow and the hcp filled three-fold sites. The calculated adsorption energies are 61 kcal/mol, with a sulfur–surface distance of 1.99 Å, for CH_3S at both three-fold sites. For CH_3S adsorbed at a bridge or an atop Ni site, with the C–S axis normal to the surface, the adsorption energies are 56 or 45 kcal/mol with sulfur–surface distances of 2.06 and 2.13 Å, respectively.

Figure 3 shows the adsorption energy changes as a function of the angle, β, between the C–S axis and the surface normal. The surface normal is the z axis, and the C–S bond is tilted in the yz plane. As depicted in Figure 3, the C–S bond is tilted toward the $+y$ direction, resulting in one of the hydrogens being toward the surface. These H-surface distances are, for example, 2.84, 2.54, and 2.12 Å for β = 45°, 55°, and 65°, respectively. Results shown in Figure 3 indicate that the equilibrium geometry for

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Table 1. CH_3S Adsorption on Ni(111)

	site						
	3-fold		bridge		atop		
	$\beta^a = 0°$	$\beta = 5°$	$\beta = 0°$	$\beta = 45°$	$\beta = 0°$	$\beta = 55°$	expt
$E_{ads}{}^b$ (kcal/mol)	60.9	61.4	55.8	61.0	44.6	56.8	
$R_{S\text{-surface}}{}^c$ (Å)	1.99	1.99	2.06	2.06	2.13	2.13	
$R_{S\text{-Ni}}{}^c$ (Å)	2.46	2.46	2.40	2.40	2.13	2.13	
C–S stretch (cm^{-1})	730	727	707	677	723	698	670[d] 710[e]
CH_3S–Ni stretch[f] (cm^{-1})	281		305		365		300[d]

[a] β is the angle between the methane thiolate C–S axis and the surface normal. [b] E_{ads} is relative to CH_3S at infinite separation on Ni(111). Positive values are exothermic. Results are from configuration interaction calculations and are corrected for basis superposition effects (about 1 or 2 kal/mol). [c] $R_{S\text{-surface}}$ is the perpendicular distance from sulfur to the Ni surface, and $R_{S\text{-Ni}}$ is the distance from sulfur to the nearest surface Ni. [d] Recent EELS values for CH_3S on Ni(111), see ref 53. [e] EELS value for CH_3S on Ni(100), see ref 6. [f] CH_3S–surface perpendicular stretch.

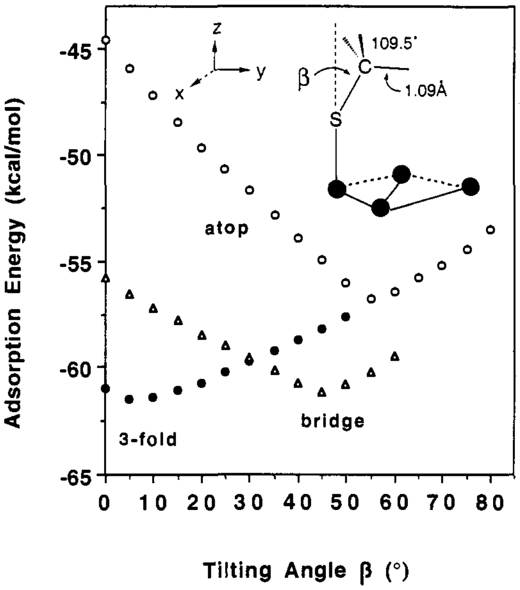

Figure 3. Adsorption energy versus β, the angle between the methanethiolate C–S axis and the surface normal. Negative values are exothermic. The minimum energy (equilibrium) geometries correspond to $\beta = 5°$ at the three-fold site, 45° at the bridge site, and 55° at the atop site, and the corresponding adsorption energies are 61.4, 61.0, annd 56.8 kcal/mol, respectively. Only CH_3S adsorbed at an atop site on the four Ni atoms of the surface layer is depicted. The C–S bond is in the yz plane and is tilted toward the $+y$ direction.

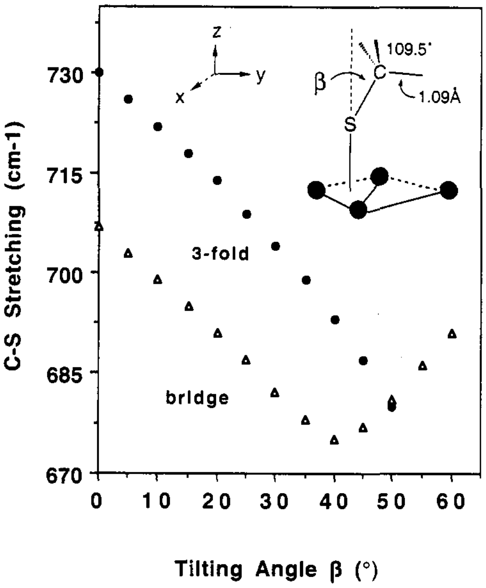

Figure 4. Methanethiolate C–S stretching frequency versus β, the angle between the methanethiolate C–S axis and the surface normal. Only CH_3S adsorbed at a three-fold site on the four Ni atoms of the surface layer is depicted. The C–S bond is in the yz plane and is tilted toward the $+y$ direction.

adsorbed CH_3S on Ni(111) varies with respect to binding site. For CH_3S adsorbed at three-fold sites, our calculations show that the methanethiolate C–S axis is nearly perpendicular to the surface or is inclined 5° from the surface normal. A 5° tilting stabilizes the CH_3S species by only 0.5 kcal/mol, and the energy slightly increases with increasing tilting angle. For a 30° tilt, the energy increases only by 1.1 kcal/mol compared to the perpendicular geometry. This suggests a floppy CH_3 motion that could easily be influenced by adsorbate–adsorbate interactions.

For CH_3S adsorbed at the bridge site, the C–S axis is found to be tilted away from the surface normal by 45°. This tilt stabilizes the CH_3S species by 5.3 kcal/mol compared to the perpendicular structure. Thus, the energy difference between the three-fold site and the bridge site is only 0.4 kcal/mol.

For CH_3S adsorbed at the atop site, the C–S axis is found to be tilted away from the surface normal by 55°. The calculated binding energy at the 55° tilt is 57 kcal/mol compared to the value of 45 kcal/mol with the C–S axis normal to the surface. However, CH_3S adsorbed at the three-fold site is still 4.3 kcal/mol more stable than that adsorbed at the atop site.

On the basis of the above results, we conclude that the adsorption of CH_3S at three-fold and bridge sites on Ni(111) shows very little energetic difference, and the geometries are very different. Our calculations suggest that for methanethiolate adsorbed at the three-fold sites the local geometry can be either C_{3v} or C_s symmetry, and at bridge sites the symmetry is C_s.

Figure 4 reports the calculated methanethiolate C–S stretching frequency with respect to the tilting angle β for CH_3S adsorbed at three-fold and bridge sites. Our calculations show that the C–S stretching vibration gradually decreases with an increase of the tilting angle. For the methanethiolate C–S axis normal to the surface, the calculated C–S stretching frequencies are 730, 707, and 723 cm^{-1} at three-fold, bridge, and atop sites, respectively. For a 45° tilt at the bridge site, *i.e.* the minimum energy geometry, the methanethiolate C–S stretching vibration shifts to 677 cm^{-1}. For CH_3S adsorbed at the atop site with a 55° tilt, the calculated C–S stretching vibration shifts to 698 cm^{-1} (not shown in Figure 4). The calculated C–S stretching frequency for CH_3S adsorbed at bridge sites is about 20 cm^{-1} lower than that adsorbed at three-fold sites with up to 40° tilt. When the tilting angle is greater than 45°, the calculated C–S stretching frequency for CH_3S adsorbed at the bridge site slightly increases. The calculated C–S stretching frequencies are close to the very recent EELS values of 670 cm^{-1} for CH_3S on Ni(111),[53] 710 cm^{-1} on Ni(100),[6] and 670 cm^{-1} on Pt(111).[8,10]

For the C–S axis normal to the surface, the calculated CH_3S–surface perpendicular stretch is 281 cm^{-1} at the three-fold site, 305 cm^{-1} at the bridge site, and 365 cm^{-1} at the atop site. These

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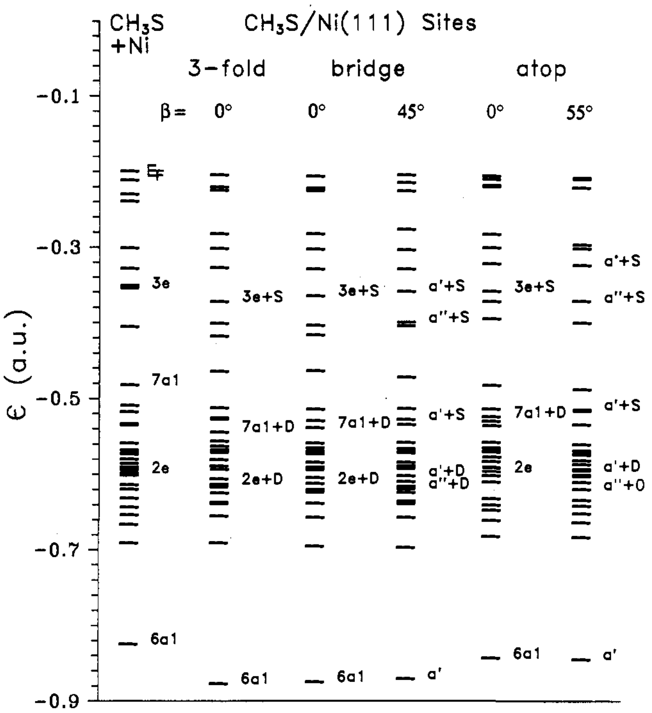

Figure 5. SCF eigenvalues for the clean surface plus gaseous CH_3S and for CH_3S adsorbed on Ni(111). The symmetry of orbitals ($6a_1$, 2e, $7a_1$, and 3e) for adsorbed CH_3S (C_{3v} classification) is indicated. For tilted CH_3S, C_{3v} symmetry reduces to C_s, and the degenerate e symmetry orbitals split into a′ and a″ levels. The left most eigenvalue spectrum is for the clean surface plus CH_3S (C_{3v} classification). β is the angle between the methanethiolate C–S axis and the surface normal. E_F is the surface Fermi level. Ni 3d orbitals are in the range –0.50 to –0.70 hartree.

values are not far from the ELLS data of 300 cm^{-1} for CH_3S on Ni(111)[53] and 320 cm^{-1} on Pt(111).[8,10]

Figure 5 shows the SCF eigenvalue spectra for the clean surface plus gaseous CH_3S and for CH_3S adsorbed at different surface sites. These results and the Mulliken populations from the SCF calculations provide considerable information about orbital interactions on CH_3S adsorption on Ni(111). While adsorbed on the surface with the C–S axis normal to the surface, the 2e, $7a_1$, and 3e symmetry orbitals of CH_3S (C_{3v} classification) are the orbitals principally involved in bonding with the surface. For methanethiolate adsorbed at the three-fold site, the degenerate 2e orbitals mix mainly with Ni 3d orbitals with populations (in percent) of [74% (2e), 26% (3d)] at 11.2 eV below the Fermi level, E_F, as calculated by Koopmans' theorem; the $7a_1$ orbital mixes with Ni 3d and 4s and 4p orbitals with populations (in percent) of [33% ($7a_1$), 40% (3d), 27% (4s + 4p)] at 9.2 eV below the E_F; the higher degenerate 3e orbitals strongly interact with Ni 4s and 4p orbitals with populations (in percent) of [41% (3e), 59% (4s + 4p)] at 4.5 eV below the E_F. The $6a_1$ orbital of CH_3S retains its gas-phase molecular character, with a Mulliken population of 94%, upon adsorption on Ni(111).

For CH_3S adsorbed at the bridge site with the C–S axis normal to the surface, the calculated 2e, $7a_1$, and 3e orbitals are 11.0, 9.0, and 4.3 eV below the E_F with populations (in percent) of [60% (2e), 40% (3d)], [25% ($7a_1$), 50% (3d), 25% (4s + 4p)], and [49% (3e), 51% (4s + 4p)], respectively. If the C–S axis is tilted away from the surface normal, the local bonding geometry of CH_3S reduces the symmetry from C_{3v} to C_s. The degenerate e levels split into a′ and a″ levels. For a 45° tilt at the bridge site, the energy separation between the a′ and a″ levels from the 2e orbitals is less than 0.3 eV. However, the energy separation between the a′ and a″ levels from the 3e orbitals is about 1.2 eV (see Figure 5). The eigenvalue spectra of the tilted geometry and the upright configuration for CH_3S adsorbed at bridge sites is expected to be different. The $7a_1$ orbital level at 9.0 eV below the E_F for the perpendicular case becomes the a′ orbital at 8.7 eV below the E_F on a 45° tilt with resulting populations of [40% (a′), 15% (3d), 45% (4s + 4p)]. This indicates that tilting 45° allows the $7a_1$ orbital of CH_3S to interact more strongly with the Ni 4s and 4p orbitals increasing the ionic character. For CH_3S adsorbed at atop sites, the bonding is similar. In addition to the splitting of 2e and 3e orbitals with the C–S axis tilted away from the surface normal by 55°, the $7a_1$ orbital becomes the a′ which bonds more strongly with the Ni 4s and 4p orbitals. This is supported by the change of the orbital populations from [38% ($7a_1$), 56% (3d), 16% (4s + 4p)] at $\beta = 0°$ to [50% (a′), 8% (3d), 42% (4s + 4p)] at $\beta = 55°$. Table 2 summarizes the CH_3S populations and orbital levels upon adsorption on Ni(111).

The strong interactions of CH_3S/Ni(111) also involve electron transfer between the adsorbate and substrate. Charges in units |e| from a Mulliken populations analysis of CI wave functions of about 3500 configurations are listed in Table 3. For CH_3S adsorbed at the three-fold site with the C–S axis normal to the surface, the net charge gained by methanethiolate (mainly by S atom) is 0.31 |e| (mainly from the Ni 4s and 4p, only 0.03 |e| from Ni 3d). The transferred electron mainly fills the unpaired 3e orbital and makes the methanethiolate more ionic. Defining the perpendicular methanethiolate C–S axis as the z axis, the calculated cumulative charge population for sulfur $3p_x$ and $3p_y$ orbitals is 1.74 |e| each, while the gas-phase values are 1.98 |e| and 1.04 |e|, respectively.[54] After CH_3S adsorption at the three-fold site, the surface layer loses 0.19 |e|; the second layer loses 0.33 |e|; and the third layer gains a net charge of 0.21 |e|. For CH_3S adsorbed at the atop site with the C–S axis tilted away from the surface normal by 55°, the net charge gained by CH_3S is 0.38 |e|. The surface layer loses 0.33 |e|; the second layer loses 0.18 |e|; and the third layer gains a net charge of 0.13 |e|. These results suggest that lattice polarization effects accompanying adsorption for CH_3S on Ni(111) extend beyond the second layer.

Since there is only very little Ni 3d electron transfer to the CH_3S, the bonding between CH_3S and Ni 3d orbitals is mainly covalent. In fact, the main reason for the comparable stabilizing of tilted CH_3S at bridge and atop sites with CH_3S at three-fold sites is the much stronger $7a_1$–Ni (4s + 4p) ionic bond due to the tilting of the C–S axis. Thus, we may conclude that the bonding of methanethiolate to the Ni surface is characterized as a combination of ionic and covalent bonding with substantial mixing with the Ni 3d orbitals.

Our conclusion is qualitatively consistent with the bonding pictures deduced from other theoretical cluster treatments that metal valence s and p orbitals are more important to the bonding of CH_3S than the d orbitals.[23,25,27] Using semi-empirical MO-SCF cluster calculations (INDO/S),[23] Rodriguez found that the CH_3S–Cu surface bonding is mainly a consequence of the interaction between the 3e symmetry orbitals and the Cu 4s and 4p orbitals. Although many geometries were studied, relative energies were not reported since the method was not parametrized to provide reliable values of bond energies.[23] An adsorption energy of 52 kcal/mol for CH_3S on Cu is estimated in ref 23, by using the bond order conservation Morse potential (BOC-MP) method.

Assuming a C–S bond dissociation energy of 74 kcal/mol[55] and using the BOC-MP method developed by Shustorovich,[56] an adsorption energy of 67 kcal/mol is calculated for methanethiolate on Ni(111), which is in good agreement with the values obtained in the present study.

Performing *ab initio* Hartree–Fock plus correlation from second-order perturbation theory (MBPT2) cluster calculations, Sellers has studied the adsorption of CH_3S on Pt(111) and Pd-

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[54] There is a singly occupied molecular orbital in gaseous CH_3S. This orbital has mainly either sulfur $3p_x$ or $3p_y$ character.

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Table 2. Ionization Energies, Calculated by Koopmans' Theorem, of Higher Occupied CH_3S Orbitals Adsorbed on Ni(111) and Corresponding Mulliken Populations (Energies Referenced to the Fermi Level[a])

3-Fold Site, β[b] = 0°						
orbitals	6a$_1$	2e		7a$_1$	3e	
$-\epsilon_k$ (eV)	18.2	11.2		9.2	4.5	
Ni populations[c]	6% (sp)	26% (d)		40% (d) + 27% (sp)	59% (sp)	
Bridge Site, β = 0°						
orbitals	6a$_1$	2e		7a$_1$	3e	
$-\epsilon_k$ (eV)	18.1	11.0		9.0	4.3	
Ni populations[c]	6% (sp)	40% (d)		50% (d) + 25% (sp)	51% (sp)	
Bridge Site, β = 45°						
orbitals	a′	a′	a″	a′	a′	a″
$-\epsilon_k$ (eV)	18.0	11.2	10.9	8.7	5.3	4.1
Ni populations[c]	6% (sp)	40% (d)	40% (d)	15% (d) + 45% (sp)	30% (sp)	48% (sp)
Atop Site, β = 0°						
orbitals	6a$_1$	2e		7a$_1$	3e	
$-\epsilon_k$ (eV)	17.3	10.6		8.6	4.2	
Ni populations[c]	4% (sp)	6% (d)		56% (d) + 16% (sp)	49% (sp)	
Atop Site, β = 55°						
orbitals	a′	a′	a″	a′	a′	a″
$-\epsilon_k$ (eV)	17.2	11.2	10.6	8.4	4.5	3.2
Ni populations[c]	4% (sp)	66% (d)	12% (d)	8% (d) + 42% (sp)	49% (sp)	40% (sp)

[a] Calculated SCF + CI ionization energy or work function of CH_3S at the three-fold site on Ni(111) is 5.50 eV, while the work function for the clean surface is 5.29 eV (Koopmans' theorem values are 5.60 and 5.35 eV, respectively). [b] β is the angle between the methanethiolate C–S axis and the surface normal. [c] The corresponding CH_3S populations are omitted. sp and d refer to the Ni 4s + 4p and 3d orbitals, respectively.

Table 3. CH_3S and Nickel Charge Distributionn[a]

				Ni layers		
site	S	C	3-H[b]	first (Ni 3d)[c]	second	third
3-fold (β[d] = 0°)	–0.37	+0.05	+0.01	+0.19 (+0.03)	+0.33	–0.21
bridge(β = 0°)	–0.39	+0.06	+0.02	+0.20 (+0.02)	+0.28	–0.17
(β = 45°)	–0.36	+0.05	–0.01	+0.19 (+0.04)	+0.29	–0.16
atop(β = 0°)	–0.42	+0.04	+0.02	+0.37 (+0.01)	+0.16	–0.17
(β = 55°)	–0.34	+0.02	–0.06	+0.33 (+0.01)	+0.18	–0.13

[a] Net charge is in units |e| from a Mulliken population analysis of CI wave functions of about 3500 configurations compared to the infinite separation between CH_3S and the cleann surface with basis superposition corrections. In gaseous CH_3S, the absolute charges for 3-H, C, and S atoms are 2.94 |e|, 5.89 |e|, and 16.17 |e|, respectively. [b] Total net charge for 3 H atoms. [c] Total amount of Ni 3d electrons are transferred from the neighboring 3 Ni atoms, 2 Ni atoms, and the underneath Ni atom at the 3-fold, bridge, and atop sites. [d] β is the angle between the methanethiolate C–S axis and the surface normal.

(111).[25] The calculated local bonding geometry of CH_3S adsorbed at the three-fold site on the 11-atom cluster of Pt(111) is the C–S axis normal to the surface with an adsorption energy of 63 kcal/mol. For CH_3S adsorbed near the three-fold center on the 11-atom cluster of Pd(111), the calculated methanethiolate C–S axis was found to be tilted away from the surface normal by 70° with an adsorption energy of 79 kcal/mol.[25] Formation of σ and π bonds, resulting in the sp-hybridized S atom, characterizes the bonding of CH_3S to the Pt surface. sp^3-type sulfur was suggested for the interaction between CH_3S and the Pd(111) surface. The mobility of the adsorption of methanethiolate on the Pt and Pd surfaces was not studied by Sellers.

It is worth noting that in their recent *ab initio* calculations of CH_3S on Au(111) and on Ag(111) Sellers *et al.* have shown that CH_3S adsorbed at three-fold and at atop sites has different bonding geometries.[27] The C–S axis is nearly normal to the surface at three-fold sites and is tilted away from the surface normal by about 70° at atop sites. They have interpreted their results as due to sp and sp^3 hybridizations of the S atom for CH_3S adsorbed at three-fold and atop sites.[27] They do not report the energy difference between the three-fold and atop sites for CH_3S, since different cluster models are used for these sites. The present calculated geometries of CH_3S on Ni(111) are similar to the CH_3S geometries on Au(111) and Ag(111). Our calculations show that for CH_3S adsorbed at bridge and atop sites on Ni(111) the energy minimum occurs where the C–S axis is tilted away from the surface normal by 45° and 55°, respectively. The S atom is close to the sp^3 hybridization at these sites.

In the chemistry of organosulfur complexes, there exists terminal bonding (such as NiS_2 fragments), μ_2 bridging (such as Ni_2S_2 fragments), and μ_3 bridging (such as Ni_3S_2 fragments), etc.[57–62] The average Ni–S distances in these Ni organosulfur compounds are betweenn 2.1 and 2.3 Å. The Ni–S–C bond angles in the organosulfur compounds are generally between 104° and 115°. Our calculated Ni–S distances for methanethiolate on Ni(111) are 2.46, 2.40, and 2.13 Å at the three-fold, bridge, and atop sites, respectively. The Ni–Ni distances in the organosulfur complexes range from 2.7 to 3.2 Å, about 0.2–0.7 Å longer than the bulk Ni–Ni distance of 2.48 Å.

While the possibility of surface reconstruction upon CH_3S adsorption has not been considered in these calculations (i.e. the positions of the surface atoms have been held fixed at the values from the bulk), we believe that any displacements of the surface atoms during CH_3S adsorption are small and that they will not significantly affect the absolute or relative adsorption energies that have been calculated. Indirect experimental evidence for a lack of significant surface reconstruction comes from the recent low-energy Li^+ ion scattering studies of Ku and Overbury.[63] They demonstrated that atomic sulfur (which is expected to bond even more strongly than CH_3S) on Ni(111) induces surface reconstructions only for coverages above 0.29 ML which is larger than the saturation coverage of about 0.25 ML for methanethiol on Ni(111).[53] A p(2×2) LEED pattern characteristic of a S overlayer on an unreconstructed Ni surface was observed after annealing to 600 K.[63] Therefore, since thiolates are stable on Ni(111) only below 300 K and since even after annealing to high temperatures the S coverage is not adequate to induce a reconstruction of the Ni surface, it seems very unlikely that significant displacement of the metal atoms would occur in this system.

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4. Conclusions

The chemisorption of CH_3S on the Ni(111) surface is studied using a many-electron embedding theory at an *ab initio* configuration interaction level, modeling the lattice as a 28-atom, three layer cluster with the Ni atoms fixed at the positions from the bulk. The results are summarized as follows:

(1) Methanethiolate on Ni(111) shows very little adsorption energy difference between three-fold and bridge sites. Calculated adsorption energies are 61 kcal/mol with a sulfur–surface distance of 1.99 Å at three-fold sites, and 61 kcal/mol with a sulfur-surface distance of 2.06 Å at bridge sites.

(2) Different geometries are predicted for CH_3S at three-fold and bridge sites. The methanethiolate C–S axis is nearly perpendicular to the surface, inclined only about 5° from the surface normal at three-fold sites. The 5° tilt stabilizes the methanethiolate by only 0.5 kcal/mol. The C–S axis is found to be tilted away from the surface normal by 45° at bridge sites. This tilt stabilizes the methanethiolate by 5.3 kcal/mol.

(3) For CH_3S adsorbed at atop Ni sites, the calculated adsorption energy is 57 kcal/mol with a sulfur–surface distance of 2.13 Å and the C–S axis is tilted away from the surface normal by 55°. The 55° tilt makes CH_3S more stable than the perpendicular CH_3S by 12.2 kcal/mol.

(4) The calculated C–S stretching frequency decreases slightly with an increase in tilting angle of the C–S axis at three-fold and bridge sites. For the C–S axis perpendicular to the surface, the calculated C–S stretching vibration is 730 cm^{-1}, and the CH_3S–surface stretch is 281 cm^{-1} at the three-fold site. For a 45° tilt at the bridge site and a 55° tilt at the atop site, the C–S stretching vibrations are 677 and 698 cm^{-1}, respectively.

(5) The bonding of CH_3S to the Ni surface involves ionic and covalent contributions and substantial mixing with the Ni 3d orbitals.

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