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A density functional study of the adsorption of methane-thiol on the (111) surfaces of the Ni-group metals: I. Molecular and dissociative adsorption

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Abstract

The molecular and dissociative adsorption of methane-thiol (CH₃SH) in the high-coverage limit on the (111) surfaces of the Ni-group metals has been investigated using ab initio density functional techniques. In molecular form, methane-thiol is bound to the surface only by weak polarization-induced forces in a slightly asymmetric configuration with the C–S axis tilted by 35–60° relative to the surface normal. On Ni and Pd surfaces the S atom occupies a position close to a bridge site; on Pt it is located close to an on-top position. The length of the S–H bond is only slightly stretched relative to its value in the gas phase, indicating only a very modest degree of activation for dehydrogenation. A strong covalent adsorbate/substrate bond is formed upon adsorption of a methane-thiolate (CH₃S) radical. On Ni(111) in the energetically most favorable configuration the S atom occupies a position in a threefold hollow, slightly displaced towards a bridge site. The C–S axis is tilted by about 35° across the bridge. On Pd(111) and Pt(111) the S atom of thiolate occupies a position between a hollow and a bridge site, with the C–S axis tilted even more strongly across a neighboring threefold hollow. On all three surfaces our calculations demonstrate the existence of multiple metastable adsorption configurations, including upright CH₃S bound in the center of a threefold hollow as reported in some earlier studies. Dehydrogenation of the adsorbed methane-thiol to form co-adsorbed methane-thiolate and atomic hydrogen is an exothermic process, which is not activated on Ni(111) but activated on Pd(111) and Pt(111).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the pioneering work of Nuzzo and Allara [1] the formation and properties of supported monolayers of functional organic molecules have received increasing attention. Nowadays these systems are usually referred to as self-assembled monolayers (SAMs), and they find application in widely different fields ranging from materials science (corrosion protection) to molecular electronics (tuning the work function of inorganic electrodes) to molecular recognition [2–4]. In many SAMs thiol-based functional groups are used to anchor the molecule to the surface, and therefore functionalized chain-like molecules such as alkanethiols have received particular attention. Experimental studies of alkane-thiol SAMs [5–11] suggest that the interaction between the functional head group and the substrate plays a decisive role in the formation of the equilibrium structure. At low temperatures alkane-thiols are adsorbed molecularly, but at modest temperatures thermal decomposition by S–H bond cleavage leading to co-adsorption of an alkane-thiolate and atomic hydrogen has been observed [9, 12–14]. On Ni(111) and Pt(111) surfaces, decomposition of methane-thiol is already observed at temperatures below 150 K [12, 13]; the adsorption on Au(111) surfaces does not involve cleavage of the S–H bond [14]. While the molecular adsorption of a thiol is promoted only by the formation of a weak physisorptive
bond, a thiolate is bound to the substrate by a strong, partially covalent bond.

The importance of precise characterization of the adsorbate/substrate bond has motivated a number of ab initio density functional studies of the adsorption of alkane-thiols on close-packed surfaces of noble and transition metals. Most of these studies have focused on methane-thiolate on the (111) surfaces of the noble metals [15–28]. Except for the early work of Sellers [29] and Yang et al [30] based on quantum-chemical methods, the investigations have only recently been extended to methane-thiolate on the (111) surfaces of face-centered cubic (fcc) (Ni, Pd, Pt, Rh) [25, 26, 31, 32], the (0001) surfaces of hexagonal close-packed (hcp) (Ru, Cu) [31, 33], the (110) surface of body-centered cubic (bcc-Mo) metals [31], and to other low-index surfaces of noble metals [28]. Some investigations have also included longer n-alkane-thiols [20, 21] and more complex conjugate thiols [34, 35]. The results available for methane-thiolate on transition- and noble-metal surfaces are somewhat contradictory. While Ghiringhelli et al [26] report adsorption in a hollow with a C–S bond almost perpendicular to the surface on both groups of metals (maximum tilt angle 1.4° on Pt(111), 0.2–0.3° on Ag(111) and Au(111) at the highest coverage of Θ = 1/3) and similar results are also reported by Jiao et al [31] for the Ni-group metals, Akinaga et al [16], Hayashi et al [17], Gottschalk and Hammer [18], Yourdashyan and Rappe [19], De Renzi et al [22], Maksymyvych et al [23] and Carro et al [27] found a strong tilt of the C–S bond relative to the surface normal of 47–61° for methane-thiol adsorbed on Au(111).

Here we present an ab initio density functional investigation of the adsorption of methane-thiol (CH3SH) and methane-thiolate (CH3S−) on the (111) surfaces of Ni, Pd, and Pt. The investigation of alkane-thiols adsorbed on the surfaces of the Pt-group metals is of interest because the thiolate SAMs supported on these surfaces are expected to show a higher resistance to reductive desorption than those adsorbed on noble-metal surfaces. Experimental studies of methane-thiol adsorption on Ni(111) using secondary ion mass spectroscopy (SIMS), temperature-programmed desorption (TPD) and Auger electron spectroscopy (AES) [12, 36] have demonstrated molecular adsorption at 100 K and thermal decomposition into co-adsorbed CH3S and H atoms at 150 K. At low thiol coverage complete decomposition into carbon, sulfur and desorbed hydrogen is observed. The structure of methane-thiolate on Ni(111) has been investigated using TPD, x-ray photoemission spectroscopy (XPS) and high-resolution electron energy loss (HREELS) spectroscopy [5, 6]. At low temperatures and coverage CH3S adsorbs mainly on bridge sites. In the temperature range from 150 to 250 K, some of the bridge-bonded thiolate is converted to hollow sites. CH3S bound to hollow sites is the dominant surface species at higher temperatures and coverage. For the bridge-bonded species the C–S bond is tilted towards the surface, while for the hollow site it has been suggested that the C–S axis is more closely aligned with the surface normal. Above room temperature methane desorption has been observed, leaving S on the surface. For lower coverage it was suggested [37] that the adsorption of CH3S induces a surface layer reconstruction similar to that reported for methane-thiolate adsorption on Cu(111) [38] and for the adsorption of atomic sulfur on Ni(111) [39]. For the more open Ni(100) surface it was reported [40] that alkane-thiols start to decompose at low temperatures to form adsorbed thioliates and that further heating results in the formation and desorption of alkanes, olefins and hydrogen and leaves sulfur adsorbed on the surface. Information on alkane-thiolates on Pd surfaces is rather scarce. Investigations have concentrated on monolayers formed by long-chain molecules [7, 41, 42] and the formation of thiol-capped Pd nanoparticles [43], confirming the expected increased bond strength between the thiolate and the substrate. Molecular and dissociative adsorption of methane-thiolate on Pt(111) has been investigated using TPD, HREELS, low energy electron diffraction (LEED), NEXAFS and normal-incidence x-ray standing wave (NIXSW) techniques [8, 9, 13, 44–46]. Molecular adsorption is found below room temperature, leading to a fairly ordered overlayer producing a diffuse (√3 × √3)R30° LEED pattern. Heating above 373 K leads to dehydrogenation and formation of an ordered methane-thiolate layer with a sharp (√3 × √3)R30° LEED pattern. Further heating in the presence of molecular hydrogen results in the activation of the C–S bond and desorption of methane, and at a temperature of 360 K C–S bond breaking and carbon removal from the surface is almost complete [8]. The hydroxylase is an activated process with a low apparent activation energy of 18 kcal mol−1. The experimental investigations have also been extended to long-chain n-alkane-thiols [47, 48].

In our work we have used methane-thiol as a model system to study the molecular adsorption of the thiol molecule and the dehydrogenation and formation of an adsorbed thiolate on the (111) surfaces of the three Pt-group metals. A forthcoming publication will be devoted to the theoretical vibrational spectroscopy of the stable adsorbate/substrate complexes of both thiol and thiolate.

2. Computational setup

Our investigations are based on density functional theory as implemented in the Vienna ab initio simulation package VASP [49, 50]. VASP performs an iterative solution of the Kohn–Sham equations in a plane-wave basis; the interaction of the valence electrons with the ionic cores is described within the projector-augmented wave (PAW) formalism [51]. The PAW method achieves a high accuracy at a relatively modest cut-off-energy of 400 eV. Electronic exchange and correlation are described by the gradient-corrected PW91 functional proposed by Perdew et al [52]. The self-consistency cycle was terminated when the total energies in the next step only changed by less than 10−6 eV per cell. Brillouin-zone integrations were performed on Monkhorst–Pack grids [53] adapted to the size of the supercell and a modest Methfessel–Paxton smearing [54] of σ = 0.2 eV, final total energies being extrapolated to σ → 0. The metallic substrates were modeled by periodically repeated five-layer slabs with a (√3×√3)R30° surface cell; the vertical extension of the supercell is 30 Å such that there is a minimum separation of about 15 Å between the top of the adsorbed molecule and the bottom of the periodically
repeated slab. We have placed a single molecule into each cell, leading to a surface coverage of $\Theta = 1/3$. Molecules were adsorbed on one side of the slab only.

Gas-phase molecules were treated by placing an isolated molecule into the center of a large orthorhombic box measuring about 15 Å in diameter. The geometry of the gas-phase molecules of the two top layers of clean and adsorbate-covered surfaces was relaxed using a quasi-Newton algorithm until all forces on the atoms are converged to $F \leq 10^{-2}$ eV Å$^{-1}$. The optimization of the adsorbate/substrate complexes was performed in two steps: the system was pre-converged using a $3 \times 3 \times 1$ $k$-point grid and final accurate relaxations were performed using a finer $6 \times 6 \times 1$ grid (corresponding to 54 $k$-points).

We have also determined the barrier for the dehydrogenation of absorbed methane-thiolate to co-adsorbed methanethiolate and atomic hydrogen. The transition state search was performed using the improved dimer method proposed by Heyden et al [55, 56]. In the improved dimer method the reaction path connecting reactant to transition and product states is constructed by following the vector of the imaginary eigenmode identified at the transition state in the forward and backward directions up to the corresponding potential energy minima. The potential energy profile along the intrinsic reaction coordinate (IRC) [57, 58] represents the steepest descent path in mass weighted coordinates that connects the transition state to reactant and product. The intrinsic reaction coordinate was determined using the damped velocity Verlet algorithm [59] as implemented in VASP by Bučko [60].

3. Clean metal surfaces

For the bulk face-centered cubic metals we calculate the following lattice constants, bulk moduli and cohesive energies (experimental values from [61, 62] are given in parentheses): Ni $a = 3.52(3.52)$ Å, $B = 187(180)$ GPa, $E_{\text{coh}} = 4.87(4.44)$ eV/atom; Pd $a = 3.96(3.89)$ Å, $B = 162(180)$ GPa, $E_{\text{coh}} = 3.71(3.89)$ eV/atom; Pt $a = 3.99(3.92)$ Å, $B = 243(230)$ GPa, $E_{\text{coh}} = 5.85(5.84)$ eV/atom. The calculated equilibrium lattice constants have been used for the frozen part of the slabs modeling the substrate. We realize that certain functions such as PBEsol [63] produce slightly better lattice constants for the heavy metals Pd and Pt [64]. However, the improvement is realized at the expense of biasing the coefficient of the exchange gradient expansion so as to improve the performance for solids at the expense of less accurate results for molecules. Therefore we decided to stick to the PW91 functional [52]. For Ni surfaces and for adsorption complexes on these surfaces, spin-polarized calculations have been performed. However, the influence of the magnetism of the substrate on the adsorbate properties was always found to be negligible.

The results for the relaxation of the near-surface interlayer distances, the surface energies and the work function, calculated for a five-layer slab and a $(\sqrt{3} \times \sqrt{3})R30'$ surface cell, are compiled in table 1. A critical analysis of DFT predictions for surface relaxations, surface energies and work functions for a number of metals, including Pd and Pt, has recently been presented by Singh-Miller and Marzari [65] and we find good agreement with their results. For Ni(111) the spin-polarized calculations are presented, and we find good agreement with the earlier results of Mittendorfer et al [66], including a slightly enhanced magnetic moment of 0.68 $\mu_B$ at the surface. The comparison of the predicted surface relaxations with experiment is hampered by the wide scatter of the experimental results, but the overall trend of a modest inward relaxation of the Ni surface, the absence of relaxation on Pd(111) and the small outward relaxation of Pt(111) are in good agreement with experiment. For the work functions our calculations predict an increase in the series form Ni to Pt, in semiquantitative agreement with experiment.

4. Gas-phase CH₃SH and CH₃S

To create a reference for the geometric data of the adsorbed species, calculations of the molecular geometry of methane-thiol (CH₃SH) and of a methane-thiolate radical (CH₃S) have been performed for a single species placed into a large orthorhombic box, using the Γ point of the supercell only. To check the reliability of our plane-wave approach we also optimized the molecular geometry using the GAUSSIAN03 suite of programs [77], with the PW91 exchange–correlation functional and the 6-31G(d) basis set. The results are compiled in table 2 and compared with earlier quantum-chemical calculations at the MP2 level of theory [78] and with experiment. Bond lengths and angles predicted by VASP are found to be in excellent agreement with experiment (which can, however, not resolve the slight differences in the C–H bond lengths and H–C–H and C–S–H angles resulting from the violation of C₃v symmetry) with a maximum error in the bond length of 0.01 Å. Results obtained with GAUSSIAN03 are found to be slightly less accurate, probably due to insufficient convergence with the standard basis. The MP2 calculation yields perfect agreement with the experimental values, but preserves the threefold symmetry of the methyl group.

The methane-thiolate radical could have full C₃v point group symmetry. However, as the highest occupied molecular

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta d_{12}$</th>
<th>$\Delta d_{33}$</th>
<th>$\gamma$</th>
<th>$\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>-0.9</td>
<td>0.2</td>
<td>1.96</td>
<td>5.13</td>
</tr>
<tr>
<td>Pd</td>
<td>-1.2</td>
<td>0.0</td>
<td>2.38</td>
<td>5.15</td>
</tr>
<tr>
<td>Pt</td>
<td>0.1</td>
<td>-0.3</td>
<td>1.34</td>
<td>5.30</td>
</tr>
<tr>
<td>Exp. a</td>
<td>0.25</td>
<td>-0.34</td>
<td>1.31</td>
<td>5.25</td>
</tr>
<tr>
<td>Exp. b</td>
<td>0.0 ± 4.4</td>
<td>0.0</td>
<td>1.20</td>
<td>5.55</td>
</tr>
<tr>
<td>Exp. c</td>
<td>1.3 ± 1.3</td>
<td>1.3 ± 1.3</td>
<td>1.50</td>
<td>5.78</td>
</tr>
<tr>
<td>Exp. d</td>
<td>0.2</td>
<td>-0.7</td>
<td>1.49</td>
<td>5.69</td>
</tr>
<tr>
<td>Exp. e</td>
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<td>-0.56</td>
<td>2.49</td>
<td>6.10</td>
</tr>
<tr>
<td>Exp. f</td>
<td>1.1 ± 4.4</td>
<td></td>
<td>6.08</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Surface-induced relaxation of the interlayer distances $\Delta d_{ij}$ (in % of the bulk interlayer distance), surface energy $\gamma$ (in J m$^{-2}$) and work function $\varphi$ (in eV) for the (111) surfaces of Ni, Pd and Pt. (Note: experimental surface energies after [72], work functions after [73] (Ni), [74] (Pd), [75, 76] (Pt).)

- Present work. b Reference [67]. c Reference [65].
- Reference [68]. d Reference [69]. e Reference [70].
- Reference [71].
Figure 1. Charge distribution of the HOMO (a) and LUMO (b) states of methane-thiol (isodensity contours for values of $0.15 \text{e Å}^{-3}$ (HOMO) and $0.05 \text{e Å}^{-3}$ (LUMO)). C and S atoms are represented by large green and yellow spheres and H atoms by smaller blue ones. The dark gray surfaces show the charge distributions.

Table 2. Equilibrium geometry (bond lengths in Å, angles in deg) CH$_3$SH and CH$_3$S as optimized using VASP and GAUSSIAN (G03), compared to theoretical calculations at the MP2 level of theory [78, 79] and to experiment [84].

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$SH</th>
<th>CH$_3$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–S</td>
<td>1.822</td>
<td>1.835</td>
</tr>
<tr>
<td>S–H</td>
<td>1.350</td>
<td>1.359</td>
</tr>
<tr>
<td>C–H$_1$</td>
<td>1.102</td>
<td>1.099</td>
</tr>
<tr>
<td>C–H$_2$, C–H$_3$</td>
<td>1.099</td>
<td>1.090</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles</th>
<th>CH$_3$SH</th>
<th>CH$_3$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–S–H</td>
<td>97.0</td>
<td>96.6</td>
</tr>
<tr>
<td>S–C–H$_1$</td>
<td>106.1</td>
<td>106.1</td>
</tr>
<tr>
<td>S–C–H$_2$(H$_3$)</td>
<td>111.5</td>
<td>111.6</td>
</tr>
<tr>
<td>H$_1$–C–H$_2$(H$_3$)</td>
<td>108.7</td>
<td>108.6</td>
</tr>
<tr>
<td>H$_2$–C–H$_3$</td>
<td>110.3</td>
<td>110.2</td>
</tr>
</tbody>
</table>

orbital is twofold degenerate and only partially occupied, it is unstable against a Jahn–Teller distortion lowering the symmetry to C$_2$ and the total energy per molecule by 55 meV. The fully relaxed ground state is double-degenerate, with one long and two slightly shorter C–H bonds in the methyl group, corresponding to one S–C–H angle which is slightly lower and two which are larger than average and corresponding changes in the H–C–H angles of the methyl group. The two degenerate ground states are separated by a saddle point which also has C$_2$ symmetry, but two slightly longer (1.102 Å) and one shorter (1.096 Å) C–H bond and corresponding changes in the bond angles. The saddle point energy is only 0.5 meV above the ground state. In this case the C–S bond length calculated using VASP is in definitely better agreement with experiment and with MP2 calculations [79] than the GAUSSIAN result. The difference in the C–H bond lengths induced by the Jahn–Teller splitting is predicted to be largest in the GAUSSIAN calculations and distinctly lower if calculated using VASP or MP2. The predictions based on GAUSSIAN could possibly be improved by choosing a larger basis set, but this was not attempted here. The Jahn–Teller induced splitting is too small to be resolved by experiment.

We have also examined whether the use of a hybrid functional (B3LYP [81]) instead of a conventional gradient-corrected functional influences the molecular geometries. For CH$_3$SH the C–S bond length is increased by 0.0007 Å, while the S–H and C–H bond lengths shrink by 0.008 Å and 0.006 Å, respectively. For CH$_3$S the C–S bond is stretched by 0.006 Å and the C–H distances are shortened by 0.008 Å. The bond angles remain unchanged.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the CH$_3$SH molecule are shown in figure 1. The HOMO is a non-bonding sulfur-p (S p) state perpendicular to the C–S–H plane; the LUMO is essentially an antibonding linear combination of in-plane p orbitals on the S atom with some weight on the C and H atoms. The HOMO–LUMO gap is 4.52 eV. The gap width is 0.93 eV lower than the value of 5.45 eV estimated from ultraviolet photoemission [80].

The HOMO of the CH$_3$S radical with full C$_3v$ symmetry is a doubly degenerate eigenstate consisting of S p states oriented perpendicular to the C–S bond, occupied by three electrons. The next occupied molecular eigenstate (HOMO-1) located at a binding energy of $-3.34$ eV is a pp bonding state between C and S, the HOMO-2 state located at $-4.80$ eV is again twofold degenerate and consists of bonding linear combinations of C p and H s states. The LUMO located at 4.70 eV is an antibonding pp state. The HOMO is split by 0.17 eV if the symmetry is lowered to C$_2$ by the Jahn–Teller distortion.

The total energies of the molecular species also allow us to derive the heat of reaction of the relevant gas-phase reactions. The dissociation of methane-thiol into a methane-thiolate radical and atomic hydrogen (CH$_3$SH $\rightarrow$ CH$_3$S + H) is endothermic, $\Delta H = 3.933$ eV (calculated relative to the spin-polarized radical and hydrogen atom). Experimentally this reaction has been studied by ultraviolet photodissociation.
Table 3. Adsorption energies and geometrical data for CH$_3$SH molecularly adsorbed on the (111) surface of Ni, Pd and Pt at a $\Theta = 1/3$ coverage. Adsorption energies ($E_{\text{ads}}$) are given in eV/molecule, $h_{S-M}$ measures the height of the S atom above the top layer of the substrate, $d_{S-M}$ the distances from the S atoms to the three nearest metal atoms, $d_{C-S}$ the C–S bond length, $d_{S-H}$ the S–H bond length and $d_{H-M}$ the distance between the H-atom bound to the sulfur and the nearest substrate atom (all bond lengths in Å). The tilt angle measures the angle between the C–S bond and a surface normal. $\Delta d_{12}$ and $\Delta d_{35}$ measure the relaxation of the first two interlayer spacings of the substrate (in % of the bulk interlayer distance). The energetically most favorable configurations are denoted in bold print.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Site$^a$</th>
<th>$E_{\text{ads}}$</th>
<th>$h_{S-M}$</th>
<th>$d_{S-M}$</th>
<th>$d_{C-S}$</th>
<th>$d_{S-H}$</th>
<th>$d_{H-M}$</th>
<th>Tilt angle</th>
<th>C–S–H angle</th>
<th>$\Delta d_{12}$/$\Delta d_{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>t–t/t</td>
<td>−0.33</td>
<td>2.31</td>
<td>3.35, 2.19, 3.32</td>
<td>1.84</td>
<td>1.36</td>
<td>2.55</td>
<td>42.2</td>
<td>93.6</td>
<td>−0.3/−0.1</td>
</tr>
<tr>
<td></td>
<td>b–h/t</td>
<td>−0.37</td>
<td>1.95</td>
<td>2.94, 2.37, 2.20</td>
<td>1.88</td>
<td>1.37</td>
<td>2.34</td>
<td>34.8</td>
<td>92.4</td>
<td>−0.4/−0.4</td>
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<tr>
<td></td>
<td>fcc–b/t</td>
<td>−0.26</td>
<td>1.77</td>
<td>2.37, 2.20, 2.29</td>
<td>1.88</td>
<td>1.37</td>
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<td>90.8</td>
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<td>hcp–b/t</td>
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<td>1.78</td>
<td>2.20, 2.40, 2.27</td>
<td>1.88</td>
<td>1.37</td>
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<td>91.1</td>
<td>−0.1/−0.2</td>
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<tr>
<td>Pd</td>
<td>t–t/h</td>
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<td>3.59, 2.32, 3.64</td>
<td>1.83</td>
<td>1.36</td>
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<td>96.5</td>
<td>+0.7/−0.3</td>
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<tr>
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<td>1.86</td>
<td>1.42</td>
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<td>1.92</td>
<td>2.39, 2.59, 2.58</td>
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<td>1.37</td>
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<td>Pt</td>
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<td>3.26, 3.17, 2.34</td>
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<td>2.37</td>
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<td>1.36</td>
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<td>74.2</td>
<td>94.8</td>
<td>+3.4/+0.6</td>
</tr>
<tr>
<td></td>
<td>hcp–b/t</td>
<td>−0.41</td>
<td>2.16</td>
<td>2.38, 2.73, 3.23</td>
<td>1.86</td>
<td>1.37</td>
<td>2.30</td>
<td>43.8</td>
<td>94.8</td>
<td>+3.4/+0.7</td>
</tr>
</tbody>
</table>

$^a$ We use the following nomenclature to characterize the adsorption geometry: initial position of the S atom (top, t; bridge, b; fcc hollow, fcc; hcp hollow, hcp); final position of the S atom (t, b or h)/C–S bond tilted towards t, b or h site.

experiments [82, 83], yielding $\Delta H = 3.74$ eV in reasonable agreement with the theoretical prediction. The alternative dissociation pathway produces methyl and thioxy radicals (CH$_3$SH $\rightarrow$ CH$_3$ + SH) at a lower heat of reaction, $\Delta H$ (theor.) = 3.61 eV, $\Delta H$ (exp.) = 3.16 eV. Although this is the energetically more favorable pathway, S–H cleavage was found to be dominant in all photodissociation experiments.

5. Molecular adsorption of methane-thiol

The molecular adsorption of methane-thiol, which has been experimentally confirmed for low temperatures, seems not to have been investigated theoretically as yet. Here we have studied the formation of a close-packed methane-thiol overlayer with a coverage of $\Theta = 1/3$ and a $(\sqrt{3} \times \sqrt{3})$R30° periodicity. One molecule is adsorbed per surface cell; this means that a dimerization that could eventually be caused by the formation of weak S–H hydrogen bonding is excluded. To find the equilibrium configuration, we have used different starting geometries, with the S atom of the molecule initially placed above a substrate atom (top, t), into a bridge site (b), or into an fcc or hcp hollow (h) and with an initially tilted orientation of the C–S bond. The atomic coordinates in the two top layers of the substrate and of the molecule have been relaxed. The molecule was found to be weakly bound to the substrate (with an adsorption energy per molecule varying from about $-0.37$ eV on Ni(111) to $-0.75$ eV) in a strongly tilted, slightly asymmetric structure. Details are summarized in table 3.

5.1. Adsorption energy

The adsorption energy per CH$_3$SH molecule is given by

$$E_{\text{ads}} = E_{\text{tot}}(\text{CH}_3\text{SH} + \text{Metal}) - E_{\text{tot}}(\text{Metal}) - E_{\text{tot}}(\text{CH}_3\text{SH})$$

where $E_{\text{tot}}(\text{CH}_3\text{SH} + \text{Metal})$, $E_{\text{tot}}(\text{Metal})$ and $E_{\text{tot}}(\text{CH}_3\text{SH})$ are the total energies of the adsorbate/substrate complex, the clean substrate and of the gas-phase molecule, respectively. The values ranging between $-0.37$ eV on Ni and $-0.75$ eV on Pt indicate that the molecule is only physisorbed via weak polarization-induced forces. The site dependence of the adsorption energy is only rather modest, suggesting a rather high mobility of the adsorbed molecules on the surface. For example, the barrier for hopping between two bridge sites via a top site is only 0.04 eV on Ni and Pd surfaces. On Pt(111) surfaces the barrier for migration between two on-top sites via a hollow is slightly higher, about 0.15 eV. These small energy differences are in accordance with the experimental observation of a rather diffuse LEED pattern for the low-temperature molecularly adsorbed species [44].

5.2. Geometry

Due to the weak binding to the substrate and the low symmetry of the thiol molecule, relaxation to an equilibrium geometry is a rather tedious process. To make sure that the optimization explores all relevant regions of configuration space we used altogether eight different starting geometries, with the S atom placed above a high-symmetry site (on-top, bridge, fcc or hcp hollow) and with either an upright or a tilted orientation of the C–S bond. Relaxation of the two top layers of the substrate has been permitted. In all cases a tilted molecule was found to have a lower energy, but the S atom always moved slightly out of the high-symmetry position. In table 3 we have characterized each entry by the initial and final positions of the S atom and the direction of the tilt of the C–S bond. The final adsorption site was always slightly off-symmetry. We have used the distances from the three nearest substrate atoms to characterize the adsorption site: if one distance is distinctly shorter than the other two, the site was characterized as on-top (t), for two short distances as bridge (b) and for three approximately equal distances as hollow (h). However, for both bridge and hollow sites, the short distances may differ by up to $\sim 0.3$ Å. Sketches of the relaxed minimum-energy configurations are shown in figure 2.
Figure 2. Relaxed equilibrium configurations of a methane-thiol molecule on the (111) surfaces of (a) Ni (S atom bound to a bridge site, C–S axis tilted towards a neighboring Ni atom), (b) Pd (similar to on Ni, but with a shorter H–Pd distance) and (c) Pt (S bound on top of a Pt atom, C–S axis tilted along a bridge towards a Pt atom). Cf text.

On a Ni(111) surface, the relaxations starting from all four initial sites lead to different local minima differing by up to 0.1 eV in energy. The shorter metal (M)–S distances are around 2.3 ± 0.1 Å. The tilt angle varies between 42.2° and 32.0°, and increases with increasing distance from the surface (from hollow to top). The orientation of the methyl group is always such that the distance between the terminal H atoms and the metal atoms of the substrate is as large as possible to minimize Pauli repulsion. The shortest distance between the hydrogen atom of the thiol group and a surface atom is around 2.4 Å, allowing for the formation of a weak hydrogen bond. Adsorption of the molecule leads to activation of the S–H and C–S bonds. The S–H bond is slightly stretched from 1.35 Å in the gas-phase molecule to 1.37 Å and the C–S bond is elongated from 1.82 to 1.88 Å. The modest increase in the S–H bond length indicates only a weak activation for dehydrogenation. The formation of a dense thiol overlayer reduces the inward relaxation of the top Ni-layer, but a weak interlayer contraction is also calculated for the second and third layer.

On a Pd(111) surface the situation is similar; all initial adsorption sites lead to local energy minima differing by at most 0.06 eV and shortest M–S distances between 2.3 and 2.4 Å. The slightly increased height above the surface correlates with a larger tilt angle. The energetically most stable configuration in a bridge position, tilted towards a surface atom, differs from the three local minima in top or hollow sites by a rather short M–H distance of only 1.84 Å and a more strongly stretched S–H bond length of 1.42 Å. We have cross-checked this result by repeating the relaxation with slightly different initial configurations, but the final relaxation configuration was always the same. On the other hand, we could not find configurations with similar short M–H distances starting from other initial sites. The elongation of the C–S bond is smaller than for adsorption on a Ni surface. Even the clean Pd(111) surface shows a weak expansion of the first and a small contraction of the second interlayer distance. The formation of a thiol-layer enhances the expansion of the first interlayer distance to more than 1%, while the contraction of the second layer spacing is reduced.

In contrast to Ni and Pd surfaces, on Pt(111) the preferred adsorption site is on top of a substrate atom, with a very large tilt angle of 60°. In this configuration, the length of the C–S bond remains unchanged, only the S–H bond is stretched to 1.36 Å. On Pt, a position of the molecule in one of the threefold hollows is unstable. From the fcc hollow, the molecule relaxes to a top position differing from the equilibrium configuration in terms of tilt angle and shortest M–H distance. This result indicates that the multidimensional potential energy surface has multiple minima—in principle this would suggest an exploration using dynamical simulated annealing strategies. However, we have not done this because of the high computational effort. From the hcp hollow, the molecule relaxes to a bridge position with a strong tilt of the C–S bond representing another local potential energy minimum. The relaxation of the Pt substrate is similar to that observed for Pd, but the outward relaxation of the top layer is now even more pronounced.

5.3. Electronic properties

The electronic properties of this weakly interacting adsorbate/substrate complex are dominated by the interaction between the molecular eigenstates of the methane-thiol molecule falling into the energy range covered by the d-band of the metal. Figure 3 shows as an example the electronic density of states for CH₃SH adsorbed in bridge sites of Pd(111). The overall picture is the same for the other two substrates, considering their slightly higher (Pt) or lower (Ni) d-band widths and the weak spin-polarization of Ni. According to the
Table 4. Adsorption energies and geometrical data for CH₃S chemisorbed on the (111) surface of Ni, Pd and Pt at a Θ = 1/3 coverage.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Site</th>
<th>Eₜ₆₅</th>
<th>hₛ₅₆</th>
<th>dₛ₅₆</th>
<th>dₛ₅₃</th>
<th>Tilt angle</th>
<th>Δdₛ₅₃/Δdₛ₅₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni perp.</td>
<td>t–t</td>
<td>−1.35</td>
<td>2.03</td>
<td>3.18</td>
<td>2.12, 2.13, 2.17</td>
<td>1.84</td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>b–h/b</td>
<td>−2.77</td>
<td>1.69</td>
<td>2.34, 2.18, 2.18</td>
<td>1.85</td>
<td>31.87</td>
<td>0.2/−0.1</td>
</tr>
<tr>
<td>fcc–h</td>
<td>−2.70</td>
<td>1.58</td>
<td>2.16, 2.16, 2.16</td>
<td>1.85</td>
<td>0.</td>
<td>+0.3/+0.2</td>
<td></td>
</tr>
<tr>
<td>hcp–h</td>
<td>−2.68</td>
<td>1.60</td>
<td>2.17, 2.17, 2.17</td>
<td>1.85</td>
<td>0.</td>
<td>+0.3/+0.3</td>
<td></td>
</tr>
<tr>
<td>Ni tilted</td>
<td>t</td>
<td>Unstable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>b–h/t</td>
<td>−2.75</td>
<td>1.68</td>
<td>2.20, 2.21, 2.16</td>
<td>1.86</td>
<td>35.1</td>
<td>+0.3/+0.2</td>
</tr>
<tr>
<td>fcc–h/t</td>
<td>−2.77</td>
<td>1.67</td>
<td>2.21, 2.21, 2.21</td>
<td>1.86</td>
<td>34.8</td>
<td>−0.3/−0.2</td>
<td></td>
</tr>
<tr>
<td>hcp–h/t</td>
<td>−2.71</td>
<td>1.67</td>
<td>2.22, 2.22, 2.20</td>
<td>1.86</td>
<td>32.7</td>
<td>−0.1/−0.3</td>
<td></td>
</tr>
<tr>
<td>Pd perp.</td>
<td>t–h/t</td>
<td>−2.59</td>
<td>1.69</td>
<td>2.35, 2.33, 2.35</td>
<td>1.87</td>
<td>37.1</td>
<td>+1.1/−0.0</td>
</tr>
<tr>
<td></td>
<td>b–h/b</td>
<td>−2.72</td>
<td>1.74</td>
<td>2.61, 2.30, 2.30</td>
<td>1.85</td>
<td>41.37</td>
<td>+0.7/+0.0</td>
</tr>
<tr>
<td>fcc–h</td>
<td>−2.62</td>
<td>1.51</td>
<td>2.27, 2.27, 2.27</td>
<td>1.84</td>
<td>0.</td>
<td>+0.6/+0.2</td>
<td></td>
</tr>
<tr>
<td>hcp–h</td>
<td>−2.53</td>
<td>1.59</td>
<td>2.29, 2.29, 2.29</td>
<td>1.85</td>
<td>0.</td>
<td>+1.3/+0.4</td>
<td></td>
</tr>
<tr>
<td>Pd tilted</td>
<td>t–h/t</td>
<td>−2.60</td>
<td>1.69</td>
<td>2.35, 2.33, 2.35</td>
<td>1.87</td>
<td>37.1</td>
<td>+1.1/−0.1</td>
</tr>
<tr>
<td></td>
<td>b–h/b</td>
<td>−2.73</td>
<td>1.78</td>
<td>2.70, 2.30, 2.30</td>
<td>1.85</td>
<td>34.0</td>
<td>+1.2/+0.5</td>
</tr>
<tr>
<td>fcc–h/t</td>
<td>−2.67</td>
<td>1.66</td>
<td>2.34, 2.35, 2.33</td>
<td>1.86</td>
<td>37.0</td>
<td>−0.2/−0.2</td>
<td></td>
</tr>
<tr>
<td>hcp–h/t</td>
<td>−2.60</td>
<td>1.69</td>
<td>2.35, 2.35, 2.33</td>
<td>1.87</td>
<td>37.6</td>
<td>−1.0/−0.2</td>
<td></td>
</tr>
<tr>
<td>Pt perp.</td>
<td>t–h/h</td>
<td>−2.70</td>
<td>1.90</td>
<td>3.07, 2.32, 2.32</td>
<td>1.84</td>
<td>53.8</td>
<td>−1.2/−0.8</td>
</tr>
<tr>
<td></td>
<td>b–h/b</td>
<td>−2.73</td>
<td>1.86</td>
<td>2.96, 2.32, 2.32</td>
<td>1.86</td>
<td>48.9</td>
<td>−1.2/−0.7</td>
</tr>
<tr>
<td>fcc–h</td>
<td>−2.50</td>
<td>1.45</td>
<td>2.27, 2.27, 2.27</td>
<td>1.84</td>
<td>0.</td>
<td>+0.9/+0.1</td>
<td></td>
</tr>
<tr>
<td>hcp–h</td>
<td>−2.28</td>
<td>1.60</td>
<td>2.31, 2.31, 2.31</td>
<td>1.86</td>
<td>0.</td>
<td>+1.6/−0.4</td>
<td></td>
</tr>
<tr>
<td>Pt tilted</td>
<td>t–h/h</td>
<td>−2.73</td>
<td>1.86</td>
<td>2.32, 2.32, 2.97</td>
<td>1.84</td>
<td>49.0</td>
<td>+1.3/−0.7</td>
</tr>
<tr>
<td></td>
<td>b–h/b</td>
<td>−2.78</td>
<td>1.67</td>
<td>2.96, 2.32, 2.32</td>
<td>1.86</td>
<td>49.2</td>
<td>+1.8/−0.1</td>
</tr>
<tr>
<td>fcc–h/t</td>
<td>−2.48</td>
<td>1.67</td>
<td>2.38, 2.34, 2.38</td>
<td>1.87</td>
<td>34.8</td>
<td>+1.1/−0.3</td>
<td></td>
</tr>
<tr>
<td>hcp–h/t</td>
<td>−2.37</td>
<td>1.75</td>
<td>2.42, 2.43, 2.34</td>
<td>1.88</td>
<td>36.5</td>
<td>+1.8/−0.4</td>
<td></td>
</tr>
</tbody>
</table>

* We use the following nomenclature to characterize the adsorption geometry: initial position of the S atom (top; t; bridge; b; fcc hollow; fcc; hcp hollow; hcp); final position of the S atom/C–S bond tilted towards t, b or h site.

Figure 3. Electronic density of states of the Pd atoms in the surface layer (green—gray) and on the S atom (red—dark) for methane-thiol adsorbed on Pd(111). For comparison, the vertical bars mark the molecular eigenstates of the free molecule. Energies are given relative to the Fermi level. (See text.)

DFT calculations, the HOMO–LUMO gap of the free molecule is 4.52 eV, i.e. of the same order of magnitude as the d-band width of the substrate metals. If the energy scales of the density of states of the substrate and of the molecular eigenstates are aligned at the Fermi level, the position of the HOMO corresponds roughly to the center of the d-band, while the next molecular eigenstates formed by C–S and S–H bonding states at a binding energy of −4.80 eV fall at the lower edge of the d-band of Ni and Pd and about 2 eV above the band edge of Pt. The LUMO is located within the empty s–p band of Pt. The incipient occupation of these antibonding states is responsible for the increased S–H bond lengths. The molecular eigenstates located at the edge of the metal band are also shifted to higher binding energies and mix with the metal d-states.

The formation of a dense thiol overlayer also leads to a reduction of the work function to 4.88 eV (Δφ = −0.24 eV) for Ni, 5.10 eV (Δφ = −0.20 eV) for Pd and 5.57 eV (Δφ = −0.21 eV) for Pt.

6. Formation of a dense methane-thiolate overlayer

Our results for the formation of a close-packed methane-thiolate overlayer with a coverage of Θ = 1/3 and a (√3 × √3)R30° periodicity are summarized in table 4. In view of the difficulty of finding the most stable geometry of the adsorbate/substrate complex (as documented by the
conflicting results reported in the literature), we have used eight different starting geometries, with the sulfur atom in one of the four high-symmetry sites (t, b, fcc-h, hcp-h) and either a perpendicular or a tilted C–S bond. The initial tilt angle relative to the surface normal was always 45°, the direction of the tilt was towards a neighboring bridge site for the S atom on top of a metal atom and towards a neighboring substrate atom for the molecule in a bridge or hollow position.

6.1. Adsorption energies

The adsorption energy for CH₃S adsorbed in a tilted configuration with the S atom close to an fcc hollow site of the Ni(111) surface is about −2.77 eV/molecule. On the Pd(111) surface we find a similar adsorption geometry with a slightly larger tilt of the molecular axis (details see below) and an adsorption energy of −2.73 eV/molecule. On a Pt(111) surface the stable adsorption site is halfway between an fcc hollow and a neighboring bridge position and the adsorption energy is −2.78 eV. Only a few previous DFT results are available for comparison. All use a plane-wave code and gradient-corrected exchange–correlation functionals—Jiao et al [31] used the STATE code [85], Majumder [32] used the VASP code and Ghiringhelli et al [26] used the CPMD code [86]. Jiao et al [31] report adsorption energies for methane-thiolate in fcc hollows of Ni(111) and Pd(111) of −3.07 eV/molecule and −3.11 eV/molecule, respectively, but only of −2.65 eV on Pt(111). The calculations refer to a coverage of 1/6, using a (3 × 2) surface cell. Only upright adsorption in the hollow was considered. Majumder [32] studied the adsorption of isolated CH₃S on Pt(111) in the low-coverage limit (using a (5 × 5) surface cell) and found an adsorption of −3.03 eV/molecule for a bridge-adsorbed species. The higher adsorption in comparison to our result is a consequence of the lower coverage. For Pt(111), Ghiringhelli et al [26] reported for the same coverage as in our work a lower adsorption energy of −2.42 eV/molecule in a hollow position. For the other two metals, results have been reported only for a lower coverage of 1/4 ML. The fcc hollow is the stable adsorption site on all three substrates, with adsorption energies decreasing from −2.93 on Ni to −2.67 eV/molecule on Pt. All their results refer to an upright position of the CH₃S radical. For the equilibrium geometries, however, we note appreciable differences between our results and those from earlier investigations.

6.2. Adsorption geometry

Our results displayed in table 4 emphasize the importance of choosing a starting geometry which does not bias the final result. Adsorption of CH₃S in a perpendicular geometry on a top or a hollow site of an fcc (111) surface leads to an adsorbate/substrate complex which could, in principle, have full C₃ᵥ symmetry if the Jahn–Teller distortion of the free radical is lifted. In these cases the perpendicular configuration may be at least locally stable, as we found for the on-top site on Ni(111) and for both hollows on the surfaces of all three metals. Only for adsorption in a bridge site is the threefold symmetry broken already in the ideal starting geometry, and in all cases we find that the relaxation leads immediately to the stable adsorption geometry consisting of a tilted molecule with the S atom bound to an fcc hollow (Ni) or in a position between bridge and hollow (Pd and Pt).

On Ni(111) the stable adsorption site is in the center of an fcc hollow, with the C–S axis tilted by 32° with respect to the surface normal. A perpendicular position of the molecule allows for a slightly shorter distance of the S atom from the surface, but is 0.07 eV/molecule higher in energy. A location in a hcp hollow is disfavored by 0.06 eV for a tilted and 0.02 eV for a perpendicular geometry. A relaxation starting from a bridge position (upright or tilted) leads to the same final state, except for a slightly off-symmetry location of the S atom. This minor difference could only be eliminated by using a very strict criterion for the residual forces.

On Pd(111) an initial configuration with an upright molecule in a hollow is conserved upon relaxation, but disfavored by 0.11 eV/molecule and 0.20 eV/molecule for the fcc and hcp hollows, respectively. The most stable configuration is reached from an initial state with a perpendicular or tilted molecule in a bridge position. In the final relaxed configuration the S atom is located about halfway between bridge and fcc hollow and the C–S axis is tilted by 44° across the bridge position towards a Pd atom (see figure 4(a)). Relaxations starting from either on-top or hollow positions relax to a state with the S atom almost in the center of a hollow, but as the direction of the tilt is towards a nearest-neighbor Pd atom the tilt angle is only about 37° (see figure 4(b)). These configurations are higher in energy by 0.06–0.14 eV/molecule.

On a Pt(111) surface the stable geometry of the adsorbate is similar to that on Pd(111), but with a larger tilt angle. Relaxation starting from bridge site leads to a configuration with a S atom even slightly more displaced from the center of the fcc hollow and a larger tilt angle of 49°. In this case a configuration very close to the absolute minimum can also be reached starting from an on-top site. Small variations in the displacement from the center, of the height of the S molecule above the surface and of the tilt angle result in only modest variations of the potential energy (an increased height allows for a larger tilt angle; larger displacement from the hollow leads to increased height etc).

The strong chemisorptive bond between adsorbate and substrate also leads to a modification of the substrate geometry. On Ni(111) this effect is confined to a reduced inward relaxation of the top layers, but on Pd(111) and Pt(111) the binding of the CH₃S layer induces an outward relaxation of the top layer. On Pd the outward relaxation even extends to the second interlayer spacing. The interatomic distances of the molecule are only slightly affected—only the C–S distance is stretched from 1.79 to 1.85 Å on Ni and Pd and to 1.84 Å on Pt.

Detailed information on the adsorption geometry is only available in the work of Ghiringhelli et al [26]: Jiao et al [31] seem to have considered only upright molecules located in an fcc hollow. Ghiringhelli et al report at a coverage of θ = 1/3 an upright adsorption not only on Pt, but also on Ag and Au. At a coverage of θ = 1/4 very modest tilt angles of 9.3°–11.7° are reported for the equilibrium geometries of...
CH₃S adsorbed on the surfaces of Ni, Pd, Pt and Ag; only on a Au(111) surface has a somewhat larger tilt angle of 21.2° been reported. The striking contrast to our results evidently asks for an explanation. We have already mentioned that for Ag(111) and Au(111) surfaces the results of Ghiringhelli et al are also at variance with a number of other studies (although there are also reports favoring an upright geometry). A very detailed investigation of the variation of the adsorption energy of CH₃S on Au(111) with the angle of the C–S tilt and with the exact position of the S atom has been presented by Yourdshahyan and Rappe [19]. If the position of the S atom is fixed in an fcc hollow, the variation of the energy with the tilt angle shows three minima of increasing depth at about 5°, 15° and 34°, separated by barriers of about 0.05 eV. A two-dimensional potential energy surface as a function of the angle and the displacement of the S atom along a straight line from top to fcc, bridge and hcp hollow also shows multiple minima. In the high-coverage limit the deepest minimum corresponds to a position between bridge and fcc hollow and a strong tilt of 43.2°. A C–S bond tilted by ~50° relative to the surface normal resulting from ab initio DFT calculations has also been reported by Maksymyvch et al [23]. These authors also calculated contrast images for scanned tunneling microscopy (STM). Best agreement with the experimental STM images was found for a bridge-adsorbed CH₃S species (slightly displaced towards the hollow site) and a tilt angle of about 50°.

Figure 4. Relaxed equilibrium configurations of a methane-thiolate radical molecule on Pd(111): (a) stable configuration with the S atom in an fcc hollow, slightly displaced towards a bridge site and the C–S axis tilted by 44° across the bridge; (b) metastable configuration with the S atom in the center of an fcc hollow and the C–S axis tilted by 37.6° towards a Pd atom (\(\Delta E = 0.13\) eV/molecule). (See text.)

The result of Ghiringhelli et al for this coverage corresponds to a local minimum at the fcc hollow with zero tilt. Our results confirm the existence of such a local minimum also for adsorption on a Pt(111) surface. For this metastable configuration the height of the S atom above the surface (1.52 Å) and the S–metal distances (2.30 Å) reported by Ghiringhelli et al are in good agreement with our results (cf table 4). Hence there is evidence that the upright adsorption geometries for methane-thiolate on the Ni-group metals reported by these authors and by Jiao et al [31] represent only local energy minima.

Our predicted adsorption geometries also agree favorably with experiment. For CH₃S/Ni(111) we even find quantitative agreement with the experimental values of Mullins et al [6] for the S–Ni distance of 2.20 ± 0.2 Å (2.21 Å), the tilt angle of ~35° (34.8°) and the C–S bond length of 1.85 ± 0.02 Å (1.86 Å) (theoretical results in parentheses). The value for the S–Ni distance is also in good agreement with the value of 2.25 ± 0.04 Å measured by Fernandez et al [38] using EXAFS. For CH₃S/Pt(111) Koestner et al [13] estimated a tilt angle of about 45° from combined EXAFS and HREELS studies, to be compared with our prediction of 49°. Lee et al [45] discussed interpretations of their NIXSW data in terms of different adsorbate geometries and concluded that CH₃S is adsorbed in a tilted ‘off-top’ position with Pt–S distances in the range between 2.3 and 2.4 Å, in good agreement with our calculated Pt–S distances of 2.32 Å.

6.3. Electronic analysis

Some information is required about the stability of the low-symmetry adsorption complexes of methane-thiolate. Figure 5 shows the local electronic DOS for the Pd surface layer and on the S atom for the stable configuration of CH₃S/Pd(111). Compared to a thiol-covered surface we note only small changes around the Fermi level, as also reflected in the work functions which are even slightly enhanced for the thiolate covered surfaces compared to those with thiol monolayers (by

Figure 5. Electronic density of states of the Pd atoms in the surface layer (green—gray) and on the S atom (red—dark) for methane-thiolate adsorbed on Pd(111). For comparison, the vertical bars mark the molecular eigenstates of the free CH₃S radical. Energies are given relative to the Fermi level. (See text.)
Figure 6. Difference electron density distribution for CH$_3$S/Ni(111) with the S atom bound in an fcc hollow and the C–S axis tilted across a Ni–Ni bridge (a) and CH$_3$S/Pt(111) with the S atom bound in a bridge site and the C–S axis tilted over a neighboring hollow (b). Larger green and yellow balls show the metal atoms of the substrate and the S atom, respectively, the methyl group is marked by the dark blue ball representing the C atoms and the bonding hydrogen atoms shown in red. Violet and light blue surfaces show the isodensity surfaces for electron accumulation (violet) and depletion (light blue), at values of ±0.02 electrons Å$^{-3}$. For both configurations a front (left) and a side view (right) is presented. (See text.)

0.02/0.04/0.06 eV on Ni/Pd/Pt surfaces). Significant changes are found at higher binding energies. The HOMO, HOMO-1 and HOMO-2 states of the radical fall within the energy range covered by the d-band of the substrate. All three S p states hybridize strongly with d states of the substrate, producing a strong bonding/antibonding splitting leading to a shift of all molecular eigenstates by about 2 eV to larger binding energies. The HOMO-2 state composed of bonding states located on the methyl group is located at the lower edge of the Pd d-band, it also undergoes a weak interaction with the metal d states leading to polarization of the electron distribution in the methyl group. This effect increases in the sequence Ni–Pd–Pt, following the increased width of the d-band. The strong covalent interaction between adsorbate and substrate, however, is entirely dominated by the S p–Pd d interaction: donation of electrons from the occupied p$_\sigma$ state (HOMO-1) to the metal d-band (leading a weaker C–S p$_\sigma$ bond) and back-donation to the partially occupied S p$_\pi$ states (HOMO). The degeneracy of the S p$_\pi$ states perpendicular to the C–S axis is broken, and the S p states parallel to the surface and perpendicular to the tilted C–S axis interact with the substrate in a different way.

The formation of the covalent adsorbate–substrate bond and the influence of the adsorbate geometry is most directly seen in the difference electron density distributions defined as

$$
\Delta \rho(\vec{r}) = \rho(\vec{r})_{\text{CH}_3\text{S}–\text{metal}} - \rho(\vec{r})_{\text{metal}} - \rho(\vec{r})_{\text{CH}_3\text{S}},
$$

where $\rho(\vec{r})_{\text{CH}_3\text{S}–\text{metal}}$, $\rho(\vec{r})_{\text{CH}_3\text{S}}$ and $\rho(\vec{r})_{\text{metal}}$ are the charge densities of the adsorbate/substrate complex, the free thiolate radical and the clean substrate, respectively. Figure 6(a) shows the difference electron density for CH$_3$S/Ni(111) where the adsorption occurs in the center of an fcc hollow and figure 6(b) displays the same information for CH$_3$S/Pt(111) where the S atom is located almost at a bridge site, only slightly displaced towards the hollow.

For the methane-thiolate adsorbed in a hollow on Ni(111) we find that electron density is withdrawn from the S p$_\sigma$ states extending along the C–S axis (hence weakening the C–S p$_\sigma$ bond) and from the S p$_\pi$ states extending parallel to the surface. The electron density is increased in the bonding regions between the S atoms and all three Ni atoms surrounding the hollow. Regions of electron accumulation and electron depletion are also found around the Ni atoms, suggesting that adsorbate–substrate bonding is based on a re-hybridization of both Ni and S orbitals and involves no substantial electron transfer. The electron density on the methyl group is not affected by the adsorption.

For adsorption close to a bridge position on Pt(111) the picture looks rather different: now only the two Pt atoms forming the bridge are involved in the covalent bonds with the S atoms. On these Pt atoms the re-hybridization mostly affects the d$_{z^2}$ states extending perpendicular to the surface which are strongly polarized towards the atoms. On the S atom, bonding
involve mostly the p states perpendicular to the C–S axis. In contrast to Ni, we find that adsorption on Pt also leads to a weak electronic polarization of the methyl group.

Given the rather small energy differences, it is difficult to assess the reasons why on the heavier metals the less symmetric sites with a lower metal coordination are the preferred adsorption sites. Evidently tilt angle and adsorption site are correlated. For the formation of a tilted configuration at high-coverage steric reasons (minimization of the Pauli repulsion between the methyl groups) have also been invoked [18, 19]. Here we find that the adsorption-induced polarization of the methyl group could also play a role. The small positive charge on the methyl group in figure 6(b) is polarization of the methyl group could also play a role. The adsorption site are correlated. For the formation of a tilted configuration at high-coverage steric reasons (minimization of the Pauli repulsion between the methyl groups) have also been invoked [18, 19]. Here we find that the adsorption-induced polarization of the methyl group could also play a role. The small positive charge on the methyl group in figure 6(b) is oriented towards the negative charge created by the depletion of the ppσ states around the S atom. This interaction stabilizes configurations displaced towards the bridge site and more strongly tilted away from the surface normal.

7. Dissociation of adsorbed methane-thiol

In the gas-phase the dissociation of methane-thiol into a methane-thiolate radical and molecular hydrogen is a strongly endothermic process, but experiments show that on noble- and transition-metal surfaces dissociation is favored by the strong interaction of the thiolate radical with the support. We have investigated the dissociation of the molecularly adsorbed thiol into co-adsorbed thiolate and atomic hydrogen. The initial state is the stable configuration of the adsorbed thiol as described above, the final (product) state consists of a thiolate and a H-atom co-adsorbed within a (3√3 × 3√3)R30° cell. Both co-adsorbates occupy an fcc hollow (see figure 7, although for the Pd(111) surface the thiolate is displaced towards a bridge site). In this configuration, each substrate atom binds both to the S atom of the thiolate and to the H atom. Hence the co-adsorption reduces the binding of the thiolate and the height of the S atom above the metal surface is also increased by 0.06 Å. On a Cu surface, this also leads to a slightly increased tilt angle (which remains unchanged on Pd and Pt surfaces). The co-adsorption energies are −2.88/−2.87/−2.80 eV on Ni/Pd/Pt surfaces. The adsorption energy of an isolated hydrogen atom (relative to molecular hydrogen in the gas phase) calculated using the same surface cell is −0.56/−0.59/−0.48 eV on the same surface. Combined with the adsorption energies for thiolate from table 4 we find that the co-adsorption energies are less favorable by 0.45/0.45/0.43 eV than the sum of the adsorption energies for isolated thiolate radicals and H atoms on these three surfaces.

The heat of reaction for the dissociation (CH₃SH(a) → CH₃S(α) + H(a)) is −0.85/−0.52/−0.42 eV on Ni/Pd/Pt surfaces (i.e. dissociation is exothermic even in this high-coverage limit. On Ni(111) a transition state search using the dimer method [55] did not find a saddle point on the potential energy profile for this reaction. The potential energy decreases monotonously along the reaction path and dissociation is not activated. On Pd(111) we have identified a transition state with a small activation barrier of +0.18 eV. In the transition state the S–H bond is stretched to 1.73 Å and both the thiolate and the H-atom occupy bridge positions (see figure 8). The molecule is only slightly rotated around the C–S axis. The nature of the transition state has also been verified by the analysis of the vibrational eigenmodes. All eigenstates except the S–H stretching mode have real eigenvalues, confirming that this configuration represents a first-order saddle point.

On Pt(111) the thiol molecule is initially physisorbed close to a top position. In the transition state the molecule moves to a bridge position and the molecular axis rotates such that the thiol-hydrogen atom can connect to a Pt atom across a hollow. The activation energy in the transition state is 0.61 eV/molecule and the S–H hydrogen bond is stretched only to 1.46 Å. To reach the final co-adsorption state the hydrogen atom moves via an on-top position first to a neighboring bridge site, while the thiolate is only slightly displaced from the bridge site towards the hollow position. In this configuration the potential energy is essentially stationary, a small additional energy gain of 0.03 eV can be achieved by moving the hydrogen into a hollow and shifting the thiolate by about 0.1 Å closer to the hollow. The reaction scenario and the potential energy profile are shown in figure 9. It is remarkable that the transition states for the dissociation on Pd and Pt
surfaces have a quite different character. On the Pd surface, the S–H bond is strongly stretched; in this ‘late’ transition state the sulfur–hydrogen bond is already broken. On Pt in contrast we find an ‘early’ transition state where the sulfur–hydrogen bond undergoes only a modest elongation. The calculated activation energy for the dehydrogenation of methane-thiol on Pt(111) is in very good agreement with the experiments of Rufael et al [8] who reported an apparent activation energy of 18 kcal mol$^{-1}$ (or 0.78 eV/molecule).

However, we must also emphasize that as the investigation of the stable adsorption geometries of the absorbed thiol and thiolate have demonstrated that the potential energy surface is characterized by multiple local minima, the same has to be expected for the saddle point structure. Our simulations have identified one possible, but probably not the only, transition state for the dehydrogenation of methane-thiol.

8. Discussion and conclusions

Molecular and dissociative adsorption of methane-thiol on the (111) surfaces of the Ni-group metals have been studied in the high-coverage limit using density functional theory. Molecular adsorption is found to be promoted by weak polarization-induced forces, leading to adsorption energies increasing from $-0.37$ eV/molecule on Ni(111) to $-0.75$ eV/molecule on Pt(111). In the fully relaxed equilibrium configurations, the S atom is located close to a bridge site on Ni and Pd, but close to an on-top site on Pt. In all cases the C–S axis is strongly tilted relative to the surface normal, the tilt angle and the height of the S atom above the surface increasing in the sequence Ni $\rightarrow$ Pd $\rightarrow$ Pt. Adsorption leads to a modest elongation of the C–S and S–H bond lengths, promoted by a modest back-donation of electrons from the metal d-band to the LUMO orbital of the thiol molecule.

Bonding of methane-thiolate is, in contrast, promoted by a strong covalent bond between the S p states and the metal d band, leading to adsorption energies reaching about $-2.8$ eV/molecule on all three surfaces. The determination of the stable adsorbate geometry is hampered by the existence of multiple local minima on the potential energy surface as a function of lateral position and height of the S atom and tilt of the C–S axis. We have demonstrated that, as for alkane-thiolates on noble-metal surfaces, a strongly tilted configuration with the S atom in an off-symmetry position between bridge and fcc hollow is preferred. On Ni(111) the stable position is almost exactly in the center of the hollow, while on Pd(111) and Pt(111) it is gradually shifted towards the bridge site. The increasing lateral displacement is correlated to an increasing height above the surface and a tilt angle increasing from $32^\circ$ to $49^\circ$. These results emphasize the similarity with thiolate adsorbed on noble metal surfaces and contradict earlier studies reporting, due to insufficient relaxation, an adsorption in the center of an fcc hollow and no tilt in the high-coverage limit.

The preference for a tilted adsorption geometry has been shown to be associated with the electronic structure of the thiolate radical. Bonding is promoted by electron donation from the occupied bonding pp $\sigma$ states on the S atom to the substrate and back-donation to the partially occupied non-bonding pp $\pi$ states whose degeneracy is broken in the adsorbed configuration.

In our calculations dispersion forces have been neglected. Dispersion corrections are likely to increase the low energies for the molecular adsorption of methane-thiol by a contribution of the order of 0.1 eV/molecule. The correction could also favor a higher S–metal coordination, but a tilted structure will remain favored. The corrections for the strongly adsorbed thiolate are expected to be less important.

We have also investigated the dissociation of the adsorbed thiol leading to the formation of co-adsorbed methane-thiolate and atomic hydrogen. This process is predicted to be exothermic and not activated on Ni(111), but activated on Pd(111) and Pt(111). The reduced exothermic heat of reaction correlates with an increased activation energy for dissociation. For Pt(111) the calculated activation energy is in very good agreement with experiment.
Experimental information on adsorption geometries is rather scarce. For the best-studied system CH$_3$S/Ni(111) we find quantitative agreement between theory and experiment. More experimental information is available from vibrational spectroscopy. A companion paper will present a detailed comparison of experimental and theoretical spectroscopies.

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