On the adsorption site of ethylene at the Ni(110) surface: a combined experimental and theoretical study involving the unoccupied band structure


Lehrstuhl für Theoretische Chemie, Technische Universität München, 85747 Garching, Germany
Max-Planck-Institut für Plasmaphysik, Abteilung Oberflächenphysik, EURATOM-Association, 85748 Garching, Germany
Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Received 26 April 1995; accepted for publication 28 August 1995

Abstract

The adsorption of ethylene on Ni(110) was investigated by angle resolved inverse photoemission (ARIP) spectroscopy as well as by detailed density functional model cluster and slab model band structure calculations to clarify the preferred adsorption site. Cluster model calculations both at the local density as well as at the gradient corrected level of theory gave a slight preference for the di-σ over the π coordinated geometry on top of the ridges, but no or, at best, a very weak binding over the troughs. A dispersionless band in the ARIP spectra about 1.8 eV above $E_F$ is assigned to the band derived from the lowest unoccupied ethylene orbital, $1b_{2g}(\pi^*)$. The surface state feature of the clean Ni(110) surface connecting the image state at $\bar{\Gamma}$ and the $d_{yz}$ state $S_2$ at $\bar{Y}$ is lowered almost uniformly by 0.8 eV through the interaction with the adsorbate. For adsorption on top of the ridges in the so-called "half-bridge" position intermediate between the short bridge (di-σ) and the top site (π), the symmetry requirements imposed by the surface state band are ideally met by the second lowest unoccupied band of the adsorbate monolayer which changes its character from ethylene $4a_g$ at $\Gamma$ to $2b_{3u}$ at $\bar{Y}$. A similarly strong and uniform interaction is not possible when ethylene adsors above the troughs. Taking all experimental and theoretical evidence together, the adsorption site in the densely packed $c(2 \times 4)$ $C_2H_4$/Ni(110) adsorption system is identified as the half-bridge position on top of the ridges.

Keywords: Alkenes; Chemisorption; Density functional calculations; Inverse photoemission spectroscopy; Nickel; Single crystal surfaces; Solid–gas interfaces; Surface electronic phenomena

1. Introduction

It is one of the goals of surface science to provide a detailed understanding of catalytic reactions. This requires, among other things, a complete knowledge of the reaction intermediates, their adsorption sites and their bonding configurations. In addition, if the electronic structure of each of the relevant adsorption complexes is known, one can hope to finally approach a similar degree of understanding for surface reactions as it is rather common for gas phase reactions. However, despite considerable efforts for more than twenty years, such detailed information is not yet available for even the simplest reactions of heterogeneous catalysis.

In a few cases, though, substantial progress toward a more complete picture has been achieved. One of these model reactions is the dehydrogena-
tion of ethylene over a Ni surface. Demuth and Eastman [1], using photoemission, demonstrated in 1974 the dehydrogenation of ethylene to acetylene over Ni(111). The vibrational spectrum of the products was shown to correspond to co-adsorbed hydrogen and acetylene [2]. In recent photoelectron diffraction experiments Bradshaw and co-workers were able to determine the local adsorption geometry of both, ethylene before and acetylene after the reaction [3]. Little is known, however, about the electronic structure of the adsorption complex apart from a theoretical model study by Felter and Weinberg [4] devoted to the consequences of an adsorption-induced distortion on the photoemission spectrum based on calculations for an isolated molecule.

The adsorption of ethylene on Ni(110), too, has been the subject of numerous experimental and some theoretical investigations [5–10]. With respect to the electronic structure, the characterization of the system is more advanced than that of C2H4/Ni(111). According to the high-resolution electron-energy-loss spectroscopy (HREELS) study of Stroscio et al. [7] a strong rehybridization of the carbon atoms toward sp³ occurs when ethylene is adsorbed on Ni(110), suggesting a di-σ-type coordination of the adsorbate to the nickel surface. Similar electron-energy-loss spectra were reported by Anson et al. [6] and have been attributed to a di-σ coordinated adsorption species with its C–C axis aligned parallel to the (110) surface. On the other hand, the local symmetry of the adsorption complex was deduced [7] to be lower than C2v, from the occurrence of a dipole enhanced asymmetric CD2 stretch mode in specular direction for deuterated ethylene on Ni(110).

These results were in part confirmed by a recent detailed analysis of the adsorption geometry of ethylene adsorbed at monolayer saturation coverage \( \theta = 0.5 \) ML (ML = ethylene molecule per substrate atom) using low-energy electron diffraction (LEED) and angle-resolved ultraviolet photoemission spectroscopy (ARUPS) [10]. This investigation was supported by band structure calculations for slab models. Therein the C2H4 monolayer was found to arrange in a c(2 × 4) over structure with two ethylene molecules per unit cell, both aligned parallel to the ridges of the Ni(110) surface.

Furthermore, the relative displacement of the neighboring ethylene rows was determined to be half the Ni–Ni distance along [1\( \bar{1} \)0]. Finally, from the LEED pattern it was deduced that the two ethylene molecules in the c(2 × 4) unit cell are related to each other by a point group symmetry element compatible with the point group of the clean Ni(110) surface (see Fig. 1).

It is chemically intuitive to assume ethylene to adsorb on top of the Ni(110) ridges. Thus, a geometry of the adsorption complex was proposed with ethylene adsorbed there in a position intermediate between the short bridge and the top site, midway between \( \pi \) and di-σ coordination (Fig. 1c); this coordination will be referred to as "half-

Fig. 1. Various unit cells in real and in reciprocal space relevant to the adsorption system C2H4/Ni(110): (a) the clean Ni(110) surface, (b) the unsupported ethylene monolayer, and (c) the c(2 × 4) structure of the adsorption system C2H4/Ni(110) with the adsorbate on top of the ridges. The path \( \Gamma \rightarrow \bar{Y} \rightarrow \Gamma \) discussed in detail in the text is marked bold in the repeated zone schemes of the c(2 × 4) BZ (c). The dashed lines in (c) show paths in the repeated zone scheme that are equivalent to this path and indicate the corresponding paths in the SBZs of the repeated zone schemes of the subsystems (a) and (b). For the two subsystems, the maximally non-equivalent parts of these dashed paths are marked in bold to indicate those pieces along which the bands may interact to give the bands of the full adsorption system (c) on the path \( \Gamma \rightarrow \bar{Y} \rightarrow \Gamma \). Note that point \( \bar{D} \) marks the position halfway between \( \bar{S} \) and \( \bar{X} \) in the BZ of the clean (110) surface (a).
bridge. However, in principle, a geometry with all ethylene molecules translated in [001] direction by half a lattice constant is also compatible with the previously reported experimental and theoretical results [10]. In this alternative coordination, ethylene molecules would be sitting above the troughs of the (110) surface (cf. cluster III in Fig. 2).

It is the purpose of this work to aid in deciding between these two main geometrical arrangements. Two strategies have been pursued toward this goal. On the one hand, the previous cluster model calculations [9] were supplemented by comparing models for both coordination alternatives with ethylene sitting on top of the ridge and over the trough. Furthermore, these density functional (DF) calculations were extended by using a non-local gradient corrected (GC) approximation to the exchange–correlation (XC) energy functional in addition to the more common local density approximation (LDA). On the other hand, further information about the bonding of ethylene on Ni(110) was acquired by angle-resolved inverse photoemission spectroscopy (ARIPS). The experimentally measured unoccupied band structure was then compared to the results of various LDA slab model calculations.

2. Technical details

2.1. Cluster model calculations

The cluster model calculations were carried out using the linear combination of Gaussian-type orbitals density functional (LCGTO-DF) method [11] to solve the effective one-electron equations which result in the Kohn–Sham approach to density functional theory. A spin-polarized version of the method was employed. In the calculations mentioned above [9] the XC potential was approximated by the Xa potential. Here, the more common Vosko–Wilk–Nusair (VWN) parametrization of electron gas results [12] was used in the local spin density (LSD) approximation to the XC potential.

Moreover, based on the self-consistent electron density determined from the LSD calculations, gradient corrections to the exchange energy functional [13] and to the correlation energy functional [14] were evaluated to examine the influence of a non-local density functional approximation on the various observables of the adsorption system; this XC functional will be referred to as BLYP. The post-hoc procedure to account for nonlocal contributions to the XC functional is quite economic and has been found to yield results of adequate accuracy [15,16]. The gradient corrected energies were evaluated using a numerical integration scheme [17,18] that has been modified to deal efficiently with a large number of transition metal atoms. To determine the cluster Fermi energy a fractional occupation number formalism was used which is based on a formal Gaussian broadening (by 0.3 eV) of the cluster level spectrum [19]. Further details on the LCGTO-DF cluster method have been described elsewhere [11,20].

The different basis sets used in the LCGTO-DF method, an orbital basis set as well as fitting basis sets for the charge density and the XC potential, were taken from a previous study of C₃H₄/Ni(110) [9]. For Ni a (15s,11p,6d) molecular orbital (MO) basis set was contracted to [7s,6p,3d] using atomic LSD eigenfunctions. Similarly, for C a (9s,5p,1d) basis contracted to [7s,4p,1d] and for H a (6s,1p) basis contracted to [4s,1p] were employed. The charge and exchange fitting basis sets have been generated by standard methods [21], scaling the orbital exponents by 2 and 2/3, respectively. In addition, both fitting basis sets have been augmented by p polarization functions with exponents 0.1, 0.25, 0.625, 1.5625 and 3.90625 for each atom. Furthermore, the fitting basis sets for Ni have been

Fig. 2. Cluster models for ethylene adsorbed on various sites of the Ni(110) surface: π (I), di-σ (II), and the trough position (III). The surrounding polygons mark the size of the cluster models, (3,8) for π, (4,6) for di-σ, and (6,4) for the trough position.
contracted to \([8s,5p,3d(r^2)]\) for the charge density fit and to \([9s,5p,4d(r^2)]\) for the XC potential fit.

2.2. Slab model calculations

The band structure calculations for the slab models were performed with an improved version of the FILMS program package \([22–24]\), a full-potential, all-electron LSD implementation for extended, 2D-periodic systems, which – like the LCGTO-DF program – utilizes expansions of Gaussian-type basis functions to represent the wave functions (orbital basis) as well as the charge density and the XC potential (fitting bases).

It has been shown previously that the experimentally determined occupied bands of \(C_2H_4\) on Ni(110) are reproduced very well in band structure calculations for an unsupported monolayer of \(C_2H_4\) \([10]\). This is due to the fact that the \(C_2H_4\) bands in question lie in an energy gap of the Ni band structure. For the unoccupied band structure as derived from ARipe spectroscopy significant hybridization between substrate and adsorbate bands has to be expected and a realistic model for the adsorption complex requires the Ni substrate to be included. The unit cell of the full chemisorption system \(c(2\times4)\) \(C_2H_4/Ni(110)\) contains two adsorbate molecules and four Ni atoms per crystal layer (Fig. 1) and thus presents a sizeable challenge to an accurate self-consistent LCGTO treatment.

Therefore, the analysis of the interaction in the adsorbate system was largely based on band structure calculations for the two subsystems: the nickel substrate was modeled by a Ni(110) five-layer slab (nearest neighbor distance: 2.49 Å \([25]\)) and the adsorbate overlayer by an ethylene monolayer slab. Both subsystems were calculated using the same orbital basis functions as in the cluster model investigations. With the number of contractions identical to the cluster calculations, a segmented contraction scheme was employed, however, which is better suited for the structure of the FILMS program. The fitting bases have been generated following a strategy similar to the well-tempered expansions \([26]\); details of this scheme have been described elsewhere \([24]\). The basis sets used, both for the charge density and the XC potential fit, were of type \((17s,5p)\) for Ni, \((11s,3p)\) for C, and \((8s,2p)\) for H. To keep the computational effort for the full adsorption system manageable, the substrate had to be restricted to the first crystal layer only and smaller basis sets had to be used. This monolayer slab model for the Ni(110) surface consists of tightly packed Ni rows with an atom spacing of 2.49 Å along the rows (x direction) and one lattice constant (3.52 Å) perpendicular to the rows (y direction, Fig. 1). The orbital basis sets for the full adsorption models were of valence double-zeta plus polarization quality \([27,28]\): a \((15s,9p,4d)\) MO basis contracted to \([5s,4p,2d]\) for Ni, a \((10s,6p,1d)\) MO basis contracted to \([3s,2p,1d]\) for C, and a \((5s,1p)\) MO basis contracted to \([2s,1p]\) for H. The fitting basis sets were of type \((15s,3p)\) for Ni, \((10s,2p)\) for C, and \((5s,1p)\) for H.

The \(k\)-space integration was performed using a 2D analogue of the tetrahedron method \([29]\). Triangles of equal size were employed to cover the various surface Brillouin zones (SBZ) (Fig. 1) resulting in 25 \(k\)-points in the irreducible wedge of the substrate Brillouin zone and of the SBZ of the ethylene monolayer, and 15 \(k\)-points for the \(c(2\times4)\) SBZ of the complete adsorption system. Further details of the geometries on the various slab and cluster models used in the present investigation will be given below.

2.3. ARipe spectroscopy

The experiments were carried out in a stainless steel UHV chamber with a base pressure of \(10^{-8}\) Pa. The experimental set-up for the ARipe spectroscopy has been previously described in detail \([30]\). The sample was cleaned by repeated Ar ion bombardment and annealing cycles \([30]\) until the surface states characteristic of the clean Ni(110) surface were fully recovered in the IPE spectra \([31]\). The adsorption of ethylene was monitored via the workfunction change \((\Delta\phi_{\text{sat}} = -0.51\ \text{eV})\) as measured by means of the diode method. In addition, thermal desorption spectra were recorded which agreed well with those reported previously \([9]\). The structure of the saturated \(C_2H_4\) layer was characterized by LEED. The LEED unit featured a double-stage multichannel-plate image intensifier which allowed recording the
LEED pattern with a sample current of less than $10^{-9}$ A. As it turned out during the ARIPe experiments, the saturated $C_2H_4$ layer is extremely radiation sensitive, even at electron energies below 30 eV. For this reason the surface had to be cleaned and reexposed several times in order to accumulate the series of ARIPe spectra shown below.

3. Results and discussion

3.1. Cluster model study of the structure of the adsorption complex

According to the experimental results mentioned above [6,10] the chemisorption cluster models for $C_2H_4/Ni(110)$ have been constructed by assuming the ethylene to adsorb with its C–C axis parallel to the [110] rows of the substrate. Models for adsorption both on the ridges as well as above the troughs were taken into account. To reduce the computational effort for the geometry optimization only chemisorption models with local $C_{2v}$ symmetry were considered, just as in the previous study [9]. This choice is an idealization of the experimental findings [7,10], but we do not expect any major influence on the calculated bond lengths since previous cluster investigations [9] gave quite similar results for the di-$\sigma$ and the $\pi$ coordination, both for the adsorbate geometry and for the electronic structure of the model clusters. These findings were confirmed by the computational results of the present investigation.

Three structure models for the adsorption system $C_2H_4/Ni(110)$ were studied in detail, one for an adsorption site above the troughs of the Ni(110) surface, and two for sites on top of the ridges. At the chosen adsorption site above the troughs, ethylene is di-$\sigma$ coordinated with respect to the second Ni layer, whereas on top of the ridges, di-$\sigma$ as well as $\pi$ coordinated adsorbate geometries were considered (Fig. 2). The Ni(110) surface was modelled by the clusters $Ni_{11}(3,8)$, $Ni_{10}(4,6)$, and $Ni_{10}(6,4)$ for the $\pi$, the di-$\sigma$, and the trough geometry, respectively. (The numbers in parentheses refer to the substrate atoms in the first and in the second crystal plane that were taken into account in the cluster model.) The shape of these clusters is indi-
cated in Fig. 2 by the polygons surrounding the ethylene molecules in the corresponding adsorption sites.

In Table 1 we summarize the geometry parameters and the adsorbate binding energy of the various cluster models obtained for the different approximations to the exchange–correlation energy functional employed. It should be noted that the $X\alpha$ results taken from a previous study [9] refer to slightly different model clusters, as indicated in the first column of Table 1. For comparison, the experimentally and the theoretically determined structure of gas phase ethylene, and some experimental data on nickel olefin complexes are also given. As can be seen from this table, the geometry of the adsorbed molecule remains almost unaffected by the different approximations to the XC functional. This finding is in agreement with the results of a recent cluster and slab model investigation on the adsorption of acetylene on Ni(110) [16], where no significant influence of the XC approximation on the internal structure of the adsorbate has been found, too. In agreement with previous calculations [9], the C–C bond is found to be elongated by about 0.1 Å compared to the free molecule, and the H–C–H plane is bent upward from the crystal plane by 22–28° when ethylene adsorbs on the ridges of the Ni(110) surface. These geometrical changes indicate a significant rehybridization of the carbon atoms from $sp^2$ toward $sp^3$, in particular in the di-$\sigma$ coordination. Such a rehybridization is compatible with the expectation [10] that in $C_2H_4/Ni(110)$ a reasonably strong chemisorption interaction takes place and with the conclusions drawn from HREELS measurements [7].

The metal–adsorbate interaction is more sensitive to the XC approximation than the adsorbate geometry. With the change from LSD (VWN) to the gradient-corrected BLYP functional the Ni–C bond length increases by 0.12 and 0.15 Å for the di-$\sigma$ and the $\pi$ geometry, respectively. For the trough position the LSD approximation gives a rather weak binding energy of only 0.43 eV and concomitantly a very long Ni–C distance. At the BLYP level of theory no adsorbate–substrate binding is found, the repulsive energy declines from $E_b = -1.05$ eV at $d(Ni-C) = 2.7$ Å down to $E_b =$
Table 1

Comparison of the adsorption geometry and the binding energy $E_b$ calculated by cluster models for various adsorption sites using different approximations to the exchange–correlation (XC) energy functional; also shown are structural data obtained from experiment; the structures are characterized by various bond distances $d$, the angle $\angle$(HCH) and the out-of-plane bending angle $\gamma$ of the CH$_2$ groups

<table>
<thead>
<tr>
<th>System</th>
<th>Adsorption site</th>
<th>$d$(Ni–C) (Å)</th>
<th>$d$(C–C) (Å)</th>
<th>$\gamma$ (deg)</th>
<th>$\angle$(HCH) (deg)</th>
<th>$E_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{14}$(C$_2$H$_4$)$_2$</td>
<td>di-$\sigma$</td>
<td>Xx</td>
<td>2.06</td>
<td>1.41</td>
<td>23</td>
<td>117.6$^a$</td>
</tr>
<tr>
<td>Ni$_{10}$(C$_2$H$_4$)</td>
<td>di-$\sigma$</td>
<td>VWN$^b$</td>
<td>1.95</td>
<td>1.41</td>
<td>22$^c$</td>
<td>117.6$^a$</td>
</tr>
<tr>
<td>Ni$_{10}$(C$_2$H$_4$)</td>
<td>di-$\sigma$</td>
<td>BLYP$^d$</td>
<td>2.07</td>
<td>1.43</td>
<td>28</td>
<td>115.8</td>
</tr>
<tr>
<td>Ni$_{14}$(C$_2$H$_4$)$_2$</td>
<td>$\pi$</td>
<td>Xx</td>
<td>2.01</td>
<td>1.42</td>
<td>23</td>
<td>117.6$^a$</td>
</tr>
<tr>
<td>Ni$_{11}$(C$_2$H$_4$)</td>
<td>$\pi$</td>
<td>VWN$^b$</td>
<td>1.99</td>
<td>1.42</td>
<td>22$^c$</td>
<td>117.6$^a$</td>
</tr>
<tr>
<td>Ni$_{11}$(C$_2$H$_4$)</td>
<td>$\pi$</td>
<td>BLYP$^d$</td>
<td>2.14</td>
<td>1.41</td>
<td>24</td>
<td>116.1</td>
</tr>
<tr>
<td>Ni$_{10}$(C$_2$H$_4$)</td>
<td>Trough</td>
<td>VWN$^b$</td>
<td>3.03</td>
<td>1.34$^a$</td>
<td>5$^a$</td>
<td>117.6$^a$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>Xx</td>
<td></td>
<td>1.53</td>
<td></td>
<td>0</td>
<td>117.6$^a$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>BLYP$^d$</td>
<td></td>
<td>1.33</td>
<td></td>
<td>0</td>
<td>116.9</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>Exp.</td>
<td></td>
<td>1.330</td>
<td></td>
<td>0</td>
<td>117.6</td>
</tr>
<tr>
<td>Ni(olefin-1)$^f$</td>
<td>Exp.</td>
<td></td>
<td>2.025</td>
<td></td>
<td>1.385</td>
<td></td>
</tr>
<tr>
<td>Ni(olefin-2)$^a$</td>
<td>Exp.</td>
<td></td>
<td>2.063</td>
<td></td>
<td>1.403</td>
<td></td>
</tr>
<tr>
<td>Ni(111)/C$_2$H$_4$$^h$</td>
<td>Exp.</td>
<td></td>
<td>1.90</td>
<td></td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>Ni(111)/C$_2$H$_4$$^h$</td>
<td></td>
<td></td>
<td>$\pm$0.02</td>
<td></td>
<td>$\pm$0.18</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. [9].  
$^b$ LSD approximation [12].  
$^c$ Not optimized.  
$^d$ XC energy calculated with post-hoc gradient corrections [13,14] based on the self-consistent density determined with the LSD approximation.  
$^e$ Ref [40].  
$^f$ Olefin-1: all-trans-1,5,9-cyclododecatriene [34].  
$^g$ Olefin 2: bicyclo[2.2.1]-heptene [35].  
$^h$ Ref. [3].

$-0.09$ eV at $d$(Ni–C) = 3.7 Å. Thus, the results of the present cluster models render adsorption above the troughs rather unlikely. However, one should keep in mind that it is quite difficult to accurately calculate the adsorbate binding energy in a cluster model [32,33]. In particular, for cluster sizes as used in the present study, the resulting values can only be taken as an estimate. Therefore, a weak binding of ethylene over the troughs cannot be completely ruled out by the present results.

For the di-$\sigma$ position, the bond lengths obtained with the Xx functional (and with slightly different cluster models) are close to the BLYP results, for the $\pi$ position, they are similar to the LSD result. Unfortunately, no experimental metal–carbon distances seem to be known for ethylene adsorbed on the Ni(110) surface. However, we may resort to a recent result for the Ni(111) surface [3] and to olefin $\pi$ complexes of zero-valent nickel [34,35] (see Table 1). With one exception (the $\pi$ adsorption site with the BLYP functional), all calculated values for the Ni–C distance at the adsorption sites on top of the ridges fall within the range spanned by the experimentally determined values for tris(bicyclo[2.2.1]-heptene)nickel(0) [35] and for C$_2$H$_4$/Ni(111) [3].

The Xx binding energy gave a slight preference to the $\pi$ coordination [9]. This trend has not been confirmed by the calculations with the XC functionals VWN and BLYP where the di-$\sigma$ geometry is favored by about 0.1 eV. For both adsorption sites on top of the ridges, the BLYP binding energy is calculated at about 0.5 eV, i.e. 1.4 eV below the VWN results. Thus the BLYP binding energies lie considerably below 1 eV, a value typical for a strongly interacting chemisorption system. Similar low binding energies have also been found for the chemisorption system C$_2$H$_4$/Ni(110) [16].
Calculations for the molecular cluster Ni(C₂H₄) [36,37] show a comparable lowering of the dissociation energy with the introduction of gradient corrections to the exchange-correlation functional, namely by 1.12 eV relative to the VWN energy of 3.05 eV. Experimental data on the adsorption energy in C₂H₄/Ni(110) and C₂H₂/Ni(110) would be helpful to clarify this issue. Although cluster models represent the limit of low adsorbate coverage, some implications may be extracted for the case of a densely packed ethylene overlayer. First, the internal geometry parameters of ethylene are not expected to be affected strongly by the nonbonding interactions between neighboring ethylene molecules, but small additional distortion may occur since the packing in the dense c(2×4) overlayer is somewhat higher than in a situation where only the van der Waals interaction would be present [10]. Second, the profound difference in the metal–adsorbate interaction found in the present calculations excludes the trough position also for the densely packed adsorbate. Moreover, the calculated values for the binding energy make it plausible that ethylene molecules may glide relatively freely along the ridges. These findings support the viability of using a force field method [10] to find the optimal relative position of the two ethylene molecules inside one c(2×4) unit cell. These similar values for the binding energy in the di-σ and the π position are consistent with the proposed half-bridge position on the ridges.

3.2. The unoccupied band structure

3.2.1. ARIPE spectra

Fig. 3 shows a set of ARIPE spectra for the clean [31] and the ethylene covered Ni(110) surface. The angle θ of electron incidence was varied in the ΓY azimuth. Just above the Fermi energy, E_F, the spectra of the clean surface show transitions into the empty Ni d band (Fig. 3a). At around 2.5 eV, inside the Y band gap, there is a very intense transition into the p_d derived surface state S_1 [38]. Additionally, at normal incidence, a weak emission is seen due to transitions into the image state 4.1 eV above the Fermi level. The image state feature on Ni(110) is very weak because it is degenerate with the bulk continuum. For off-normal incidence, this feature at first nearly disappears, but upon entering the Y band gap the surface state band S_2 reappears at the corresponding energy.

Adsorption of ethylene (Fig. 3b) completely suppresses the surface state S_2. Apart from the transitions into the Ni d band just above E_F, the dominating feature on the adsorbate covered surface is a band labeled A which disperses from 3.3 eV at Γ up to about 5 eV at Υ. A broad, weakly dispersing band is also noted at around 1.8 eV.

The observed transitions on the clean and on the adsorbate covered surface are summarized in an E(k_z) diagram (Fig. 4). Within a large part of the SBZ, in particular along the line ΓY, one observes three bands on the adsorbate covered...
Fig. 4. Projected bulk band structure of Ni(110) together with the ethylene induced bands as measured by inverse photoemission. Points and crosses denote measurements with different photon detection geometry. The solid lines show the measured surface state energies of the clean Ni(110) surface. The escape energies $E_{\text{esc}} = E_{\text{vac}} + \hbar^2 k^2 / 2m$ of the clean and the ethylene saturated surface are marked by short and long dashed lines, respectively.

The lowest band just at $E_F$ differs only in intensity from the spectral structure already seen on the clean Ni surface; it is due to residual transitions into the empty Ni d band. The next higher band at about 1.8 eV shows little dispersion. It has no counterpart on the clean surface and thus must be due to an adsorbate induced band originating from weakly overlapping orbitals. The third band, labeled A, exhibits a surprising similarity to the image state band and the $S_2$ surface state band on the clean surface. In fact, it is tempting to associate the appearance of band A simply with the downshift of the surface states caused by the workfunction reduction. This explanation, however, does not hold if examined in closer detail: the workfunction drops by 0.51 eV upon ethylene adsorption, while the surface state band is downshifted by about 0.80 eV. Thus, the binding energy of band A with respect to $E_{\text{vac}}$ amounts to approximately 1.0 eV at $\Gamma$, which is beyond the theoretical limit for the image state binding energy. Moreover, within the framework of image state theory adsorption of a molecular layer may be modeled by introduction of a dielectric sheet on the metal surface. This should result in a reduction of the image state binding energy rather than in an increase as it is observed here. Thus one is led to conclude that the downshift of the surface state band is, at least in part, due to a bonding interaction with MOs of the adsorbate. This conclusion is supported by the observed increase in intensity, which indicates that band A contains considerable contributions from electronic states within the adsorbate layer.

3.2.2. The Ni(110) surface

We start the interpretation of the unoccupied band structure of the adsorbate covered substrate with a discussion of the band structures of the two subsystems, the clean Ni(110) substrate and the unsupported adsorbate layer. It is informative to compare the calculated band structure of a five-layer (5L) slab model (see Fig. 5) to the projected bulk and the surface bands of a semi-infinite surface.

Fig. 5. Band structure of a Ni(110) five-layer slab model. For the sake of clarity, only minority spin bands are shown. Solid and dashed lines represent even and odd bands with respect to the mirror plane through the central crystal layer. The labels $s, p_x, d_{xz},$ etc. indicate the symmetry of the dominant orbital contribution of the surface atoms to the band edge and to the surface bands (the latter indicated by shading) at $\bar{X}$ and at $\bar{Y}$. 
Ni(110) substrate (Fig. 4). For the sake of clarity only the minority spin bands are shown in Fig. 5; for all bands above $-4$ eV the exchange splitting is below 0.2 eV.

Quite surprisingly, since a 5 L slab model is still rather thin (4.98 Å), the general features of the projected bulk bands as well as the band gaps at $\bar{X}$ and $\bar{Y}$ are already discernible in the band structure of this 5 L model slab (and, as matter of fact, even for a substrate monolayer, see below). In a qualitative fashion this holds also for the character of the various wave functions. At $\bar{Y}$, the lower edge of the band gap (at about $-4$ eV) originates from Ni orbitals of $p_z$ character, as is also the case in the surface band structure of Ni(110) [38]. At $\bar{X}$, crystal orbitals with $p_x$-type character are found at the lower gap edge (around $-2$ eV), just like at the semi-infinite Ni(110) surface [38]. Other interesting features are connected to the formation of surface states in the gaps around $\bar{X}$ and $\bar{Y}$, as was verified by inspection of the various Bloch wave functions. Due to the slab geometry, each of these features arises twice and the splitting of the corresponding bands (marked by shaded areas in Fig. 5) provides a measure for the interaction of the two surfaces, an artifact of the slab model. Both at $\bar{X}$ and $\bar{Y}$ this splitting is about 0.5 eV for the lower and about 1.1 eV for the higher lying surface state features. The character of these surface state features, too, is quite similar to that of the corresponding surface band structure of Ni(110) [38]. For example, the lower lying “surface state” within the region of the projected $\bar{Y}$ band gap has strong $p_z$ character, while the higher one exhibits essentially $d_{yz}$ character with a $p_y$ contribution (Fig. 5).

When comparing the energies of the calculated bands to experiment one has to keep in mind two model aspects that affect the band structure in opposite direction. In general, band gaps, if calculated as differences of the corresponding Kohn–Sham one-electron energies, turn out too small [39]. On the other hand, the orbital basis sets, while optimized for the description of occupied states, should be able to reproduce the lower lying sp-type bands, but will place bands connected to the more oscillatory or extended surface wave functions at too high energies. Inspection of Figs. 4 and 5 shows that the latter effect is significantly stronger. Comparison with experiment shows that, at the lower edges of the gaps and for the lower lying surface feature at $\bar{Y}$, the calculated energies are too high by 0.5 eV with respect to $E_F$. For the two surface states at $\bar{Y}$ and $\bar{X}$ with energies of about 6 eV above $E_F$ the discrepancy increases to 1.5–2 eV and the upper edge of the gap at $\bar{X}$ is calculated about 3 eV too high [38]. In the 5 L band structure the band which corresponds most closely to the image state at $\bar{F}$ and to the $S_2$ surface state of the semi-infinite substrate appears 2.5 eV higher in energy than the experimentally determined image state. This additional upward displacement of the theoretical band by about 0.5 eV, compared to the shift of the other calculated features in this energy range, is due to the fact that the LD approximation yields an unrealistic vacuum barrier which falls off much faster than the true image barrier.

For the analysis of the ARIF band structure of the adsorbate layer to be given below it is important to note that the experimental band $S_2$ can be identified with the $d_{yz}(p_y)$ derived surface state. In other words, this state has a nodal plane perpendicular to the (110) surface and aligned along the atom rows. At $\bar{F}$, the corresponding surface state band may be identified with the lowest image state. Accordingly, at $\bar{F}$ it exhibits a totally symmetric plane wave character with wavefronts parallel to the surface. There is no nodal plane perpendicular to the surface.

3.2.3. The unsupported ethylene monolayer

For the band structure calculation of the ethylene monolayer, the second subsystem of our adsorption model, we used an average geometry for the ethylene molecule obtained from the various LDA cluster models: $d(C–C)=1.41$ Å, out of plane bending angle $\gamma$ of the $\text{CH}_2$ groups $=22^\circ$, $\angle (\text{HCH})=119^\circ$ and $d(C–H)=1.09$ Å. The unit cell for the unsupported ethylene monolayer has half the size of the unit cell for the full adsorption system, as shown in Fig. 1b. Although the main interest of the present investigation are the unoccupied bands of the adsorption system, it is worth noting that the occupied band structure calculated for this model is essentially identical to the one
previously calculated by a tight-binding method [10].

In the discussion of the band structure of the ethylene monolayer we will focus on the unoccupied bands along the path \( \Gamma' \rightarrow Y' \) in [001] (y) direction (Fig. 1b). The corresponding part of the \( \text{C}_2\text{H}_4 \) monolayer band structure is shown in Fig. 6. Here and in the following the high symmetry points of the adsorbate monolayer alone will be indicated by primed symbols without overbar, like \( \Gamma' \). To facilitate the discussion, we present in Fig. 7 sketches of pertinent unoccupied MOs of ethylene; also given are their energies as calculated for the molecule in its gas phase geometry. In order to identify the contributions of the different MOs to the Bloch wave functions of the periodic system we have applied a symmetry transformation to the orbital basis in such a way that the resulting molecular building blocks may be classified according to the irreducible representations of the point group of the free molecule, \( \text{D}_{2h} \). The results of this analysis are indicated in Fig. 6 where the first label refers to the dominant MO contribution as obtained from a Mulliken analysis, while the second label, where given, indicates a less important, but still significant contribution of another orbital.

At \( \Gamma' \) the lowest unoccupied band (Fig. 6) derives from the C–C anti-bonding \( 1b_{3g}(\pi^*) \) orbital (Fig. 7). This orbital is expected to interact significantly with the substrate, but the overlap within the molecular layer is small. Accordingly, the band shows essentially no dispersion. Its energy is about 1 eV lower than that of the MO in the free molecule. This lowering is due to the adsorbate-like geometry assumed in the present slab model as can be seen by comparison with the MO energies of a distorted ethylene molecule; the adsorbate–substrate interaction is missing in this model. At \( \Gamma' \) the next two higher lying bands derive, as expected, from the next two unoccupied MOs above the \( \pi^* \) level, \( 4a_g \) and \( 2b_{3g} \). Inspection of Fig. 7 in combination with the lateral arrangement

Fig. 6. Unoccupied band structure of an unsupported monolayer of ethylene molecules in a distorted geometry modeling the adsorption interaction, laterally arranged according to the \( c(2 \times 4) \) over layer of the \( \text{C}_2\text{H}_4/\text{Ni}(110) \) adsorption system (see Fig. 1). The labels refer to MOs whose contributions dominate at the high-symmetry points. The dashed lines illustrate an avoided crossing of bands originating from the \( 4a_g \) and \( 2b_{3g} \) molecular orbitals. The \( k \)-space symmetry labels of the unsupported monolayer are indicated at the bottom of the figure by primed symbols without bars.

Fig. 7. Sketches of the \( \pi \) and various unoccupied orbitals of free ethylene. Orbital energies from an LCGTO-LDF calculation.
(Fig. 1) shows that both interact significantly across the rows in [001] direction, in particular through their hydrogen contacts. This interaction is bonding for MO $4a_g$, but antibonding for MO $2b_{3u}$. Consequently, the resulting bands, taken individually, disperse in opposite direction along the path $\Gamma \rightarrow Y'$ shown in Fig. 6; the lower band bends upward in energy at $\Gamma'$, the upper one downward. Since the two bands may interact along this path, an avoided band crossing results as indicated by the dashed lines in Fig. 6. As a result, the band above the $\pi^*$ level disperses upward only weakly and changes its character from predominantly $4a_g$ at $\Gamma'$ to predominantly $2b_{3u}$ at $Y'$. This band will play an important role in rationalizing the structure of the unoccupied bands in the full adsorption system.

3.2.4. The adsorption system

After having considered the subsystems in some detail we now proceed to the discussion of the full adsorption system. Band structures of two different slab models were calculated. One was taken to represent adsorption at the asymmetric bridge position on top of the ridges (Fig. 1) as proposed previously [10]. In the other slab model, with the adsorption layer displaced by half a lattice constant in [001], an adsorption site above the troughs was investigated. The same internal geometry of the ethylene molecule was used as in the monolayer calculation discussed above. In the asymmetric bridge coordination there are two non-equivalent Ni–C nearest-neighbor distances. Since one may expect the band structure to be determined to a large extent by the lateral arrangement of the adsorption system, we made the simplifying assumption of a non-tilted adsorbate above the top crystal plane, taking an average height from the cluster LDA calculations with the ethylene molecules on top of the ridges. For adsorption on the ridges, this line of reasoning translates into Ni–C bond lengths of $d_1$(Ni–C) = 1.99 Å and $d_2$(Ni–C) = 2.30 Å, respectively. For adsorption above the troughs, where the cluster calculations did not yield a bound adsorbate, the smallest Ni–C distance was chosen to be 2.36 Å. This is about halfway between the smallest distance in the di-σ coordination and the distance resulting from a horizontal shift of the ethylene molecule from the ridge to the trough position (2.66 Å). The substrate was modeled by a Ni monolayer and the smaller contracted basis sets were used to reduce the computational effort (see Section 2.2).

The resulting band structures for the two different models are shown in Figs. 8c and 8d. The analysis of calculated bands is difficult for several reasons. Due to the c(2×4) unit cell, the SBZ is four times smaller than that of the clean surface. Accordingly, several umklapp processes are possible. For instance, at $\bar{\Gamma}$ (combined SBZ) substrate states from $\bar{\Gamma}$, $\bar{Y}$ and $\bar{D}$ may interact with ethylene states both from $\bar{\Gamma}$ and $\bar{Y}'$ (Fig. 1). The umklapp processes cause several avoided band crossings in the calculated band structure. In contrast, umklapp processes are usually weak in photoemission or inverse photoemission. Thus the experimental bands reflect the periodicity of the substrate or the one of the adsorbate rather than the total adsorption system. This was already noted in the photoemission study of the present system [10]. Accordingly, many of the back-folded bands appearing in the calculated band structure are not visible in the k-resolved spectroscopies. Furthermore, a detailed consideration reveals that Ni states from $\bar{\Gamma}'$ interact predominantly with the ethylene states from $\bar{\Gamma}$; similarly, substrate states at $\bar{Y}$ interact mainly with adsorbate states at $\bar{Y}'$.

Another problem in comparing calculated and experimental bands arises from the energy offsets of the calculated unoccupied bands discussed already above for the clean substrate surface. In the following we concentrate our discussion on the $\Gamma' \rightarrow \bar{Y}' \rightarrow \Gamma'$ line in the [001] direction.

In the experimental band structure (Fig. 4) there appears a weakly dispersing adsorbate induced band at about 1.8 eV above the Fermi level. By comparison with the calculated band structure shown in inserts c and d of Fig. 8, it seems quite natural to associate this feature with the $1b_{3g}(\pi^*)$ band localized mainly on the ethylene adlayer. By comparison with the ethylene band energy obtained in the same basis (see Fig. 8b) one notes a lowering by 1.4 eV through the interaction with the substrate sp bands. This downward shift is somewhat smaller than that calculated for the occupied $1b_{2u}(\pi)$ derived band, about 2.2 eV, in
observed adsorbate induced band, labeled A in Fig. 4, to the Ni(110) image state at \( \bar{\Gamma} \) and to the \( d_{yz} \) derived surface state \( S_2 \) at \( \bar{\Upsilon} \). However, the downshift upon ethylene adsorption exceeds the lowering of the workfunction. Consequently, it has to be due in part to a bonding interaction with higher lying ethylene bands as discussed.

Ethylene orbitals may interact with the image state band at \( \bar{\Gamma} \) only if the corresponding orbitals are totally symmetric (see Fig. 9). This is true irrespective of the ethylene adsorption site. Of course, for energetic reasons one will foremost consider an interaction with unoccupied adsorbate molecular orbitals. Of these, only MO \( 4a_g \) fulfills the symmetry and energy requirement. More interesting are the symmetry conditions for the interaction with the surface state \( S_2 \) at \( \bar{\Upsilon} \), where it has \( d_{yz} \) character (with small \( p_y \) admixture). As described above, this surface state has an \( xz \) nodal plane at the ridges. If ethylene molecules are adsorbed on top of the ridges with their C–C axis in [1\( \bar{\Gamma} \)] direction, only those MOs can interact with the \( d_{yz}(p_y) \) surface state, which have an odd parity with respect to reflection at this nodal plane. Thus the interaction is restricted to orbitals of \( b_{3u} \) symmetry (see Fig. 7). In Fig. 9 the situation is illustrated for MO \( 2b_{3u} \). An interaction with \( b_{2g} \) orbitals is excluded at \( \bar{\Upsilon} \) because these orbitals transform antisymmetrically with respect to reflection at the \( yz \) mirror plane in contrast to the \( d_{yz}(p_y) \) surface state. Alternatively, if the molecules are adsorbed above the troughs, an interaction with the \( S_2 \) surface state at \( \bar{\Upsilon} \) is only possible for totally symmetric, \( a_g \), MOs as inspection of the Fig. 9 reveals. There is no individual adsorbate band which has \( a_g \) symmetry both at \( \bar{\Gamma} \) and \( \bar{\Upsilon} \) (see Fig. 6). For ethylene molecules adsorbed above the troughs the interaction with the image state at \( \bar{\Gamma} \) and the interaction with \( S_2 \) at \( \bar{\Upsilon} \) must therefore involve different ethylene bands. This is difficult to conceive in view of the rather uniform adsorbate induced downward shift of the resulting adsorbate surface feature A throughout the whole SBZ (Fig. 4). In particular, the \( 4a_g \) derived band lies rather high in energy at \( \bar{\Upsilon} \) (Fig. 6).

The situation is entirely different for ethylene molecules adsorbed above the ridges. Here, in order to interact with the Ni \( S_2 \) surface state band,
the adsorbate band has a similar dispersion as the surface state band on the clean Ni surface. Both bands disperse upward by 1–2 eV when going from \( \bar{\Gamma} \) to \( \bar{\Upsilon} \) and from \( \Gamma' \) to \( \Upsilon' \), respectively. The required change in symmetry is brought about by the avoided band crossing. The interaction of this adlayer band with the Ni surface state band is schematically illustrated in Fig. 9 for both, the \( \bar{\Gamma} \) and the \( \bar{\Upsilon} \) point of the SBZ.

The band which represents the adsorbate-induced feature A in the ARIPE is not easy to discover in the band structures of the two slab models (Fig. 8) because it is obscured by several avoided crossings along the path \( \Gamma' \rightarrow \Upsilon' \rightarrow \Gamma' \). In inserts (c) and (d) of Fig. 8 substrate features of the appropriate symmetry behavior have been connected by a shaded band to indicate its shape. On the one hand, for the adsorption model with ethylene on the ridges (insert (c)), the surface state feature of the clean Ni(110) (indicated in bold in insert (a)) is lowered in energy at \( \bar{\Gamma} \) and disperses upward by about 1.8 eV. On the other hand, for ethylene above the troughs (insert (d)), the surface state feature occurs at much higher energies, in particular at \( \bar{\Upsilon} \), and its dispersion is accordingly larger, 3 eV. However, close inspection of the wave functions of the various bands reveals that the interaction does not occur with the ethylene monolayer as described above, but with two higher lying bands (at about 4 eV, see Fig. 8b). This is a consequence of the fact that, as analyzed in detail in Section 3.1 for the 5 L substrate band structure, all relevant substrate bands are calculated too high in energy. On the other hand, the ethylene bands occur at too low energies since the LD approximation underestimates the band gaps, in particular for more localized states like those composed of the ethylene orbitals. This energy mismatch is especially apparent for the model slabs representing the adsorption system where only one substrate layer and a smaller contracted basis set had to be used (Figs. 8a and 8b).

Only an adsorbate energy band of similar or higher energy than the substrate band \( S_2 \) connecting the image state at \( \bar{\Gamma} \) and the \( d_{yz} \) state at \( \bar{\Upsilon} \) may lead to a lowering of \( S_2 \) resulting in the observed band A (Fig. 4). Experimentally the image state at \( \bar{\Gamma} \) is found 4.1 eV above \( E_F \). One may estimate the

Fig. 9. Sketch illustrating the interaction of the ethylene 4a_s orbital (at \( \Gamma' \)) and the Ni image state at \( \bar{\Gamma} \) (upper panel) as well as the interaction of the 2b_2g orbital (at \( \Upsilon' \)) and the Ni S_2 surface state at \( \bar{\Upsilon} \). The wave functions are shown in the [110] \( (yz) \) plane perpendicular to the Ni rows. The first and second substrate layer atoms are indicated by open and filled circles, respectively, the carbon atoms are marked by crossed circles. Different phases of the wave functions are indicated by light and dark shading.

a single adlayer band of the proper symmetry requirements at \( \Gamma' \) and \( \Upsilon' \) is available:

It is the band just above the non-dispersing \( \pi^* \) band (Fig. 6). A rather uniform interaction throughout the whole SBZ may be expected since
energy position of the ethylene $4a_g$–$2b_{3u}$ band relative to the substrate Fermi energy by taking the energy of the $\pi^*$ band at 1.8 eV above $E_F$ as reference. According to the adsorption slab model, this band is lowered by 1.4 eV due to the interaction with the substrate. Furthermore, at $\Gamma''$ the $4a_g$–$2b_{3u}$ band of the ethylene monolayer is calculated 1.0 eV above the $\pi^*$ band (Fig. 6). Thus, this band should be positioned about 4.2 eV above the Fermi energy of the adsorption system before the interaction with the substrate is turned on. It should therefore be ideally suited for the interaction with the substrate surface feature band in question, both by energy and by symmetry. One should keep in mind though, that the higher lying virtual adsorbate states, although conveniently discussed in the MO and/or band picture, are to be taken as representatives for molecular continuum states and thus exhibit the character of a resonance featuring a certain energy width. To some extent this is reflected in the LCGTO representation by virtual molecular orbitals (or Bloch wave functions) of the same symmetry, but higher lying in energy, in particular when a rich GTO basis set is used. This effect is seen in the calculated band structure of the adsorption model slabs where an adsorbate band of higher energy is found to interact with the substrate surface band.

A brief look onto the bands in the $x$ direction ($\tilde{\Gamma} \rightarrow \tilde{X} \rightarrow \tilde{\Gamma}$) might conclude this discussion (Fig. 4). Clearly, strong interactions are observed for all surface states in the $\tilde{X}$ band gap. This indicates the absence of selection rules restricting such interactions. Consequently, this finding supports the assumption of an adsorption site with low symmetry regarding the $x$ direction, i.e. a half-bridge rather than a true bridge or on-top adsorption site.

4. Summary and conclusions

A combined experimental and theoretical investigation has been undertaken to clarify the adsorption site of ethylene in a densely packed $c(2 \times 4)$ overlayer on Ni(110). Previous study based on ARUPS measurement, cluster model and band structure calculations for the occupied adsorbate bands [9,10] had provided rather detailed information on the adsorption geometry and the relative position of the two adsorbate molecules in the unit cell. However, this investigation was not able to decide between the two major alternatives, adsorption on top of the ridges and over the troughs of the (110) surface. This open question has been answered by the present combined experimental and theoretical study in favor of the chemically intuitive adsorption on top of the ridges.

Using the LCGTO-DF method, cluster models have been studied both in the local density approximation and with a gradient corrected exchange-correlation functional. Geometry optimization confirmed previous results for the internal degrees of freedom of the adsorbate obtained with the local density $X\alpha$ functional [9] as well as the adsorption on top of the ridges. Coordination above the troughs was unbound or, at best, weakly bound at the local density level of theory. The $\text{di-}\sigma$ coordination was found to be slightly preferred by energy over the $\pi$ coordination. In both cases, the internal geometry of the adsorbate is very similar: the C–C bond is elongated to about 1.42 Å and the CH$_2$ units bent away from the surface by about 28° and 24° for $\text{di-}\sigma$ and $\pi$ coordination, respectively. With the gradient corrected energy functional the Ni–C bond distances are calculated to 2.07 and 2.14 Å, respectively, and adsorbate–substrate bonding is strongly reduced (by about 1.4 eV) to about 0.6 and 0.5 eV, respectively. The $\text{di-}\sigma$ and $\pi$ geometry show similar binding energies in the cluster models, in agreement with the fact that the most likely position for high coverage is the half-bridge position.

Angular resolved inverse photoemission spectra were measured for the adsorption system C$_2$H$_4$/Ni(110) and compared to the spectra of the clean Ni(110) surface. To assist in the interpretation of these spectra, band structure calculations were carried out for slab models of both subsystems, the Ni(110) surface and an ethylene monolayer, as well as for the adsorption system with the help of the FILMS program. This program system allows density functional calculations for 2D-periodic slab systems in close analogy to the LCGTO-DF cluster method. A dispersionless band 1.8 eV above the Fermi energy was identified as the band derived from the ethylene $\pi^*$ orbital.
A symmetry analysis of the band structures of the unsupported ethylene monolayer representing the adsorbate and of a Ni five-layer slab representing the substrate yields a detailed picture of the interactions in the total adsorption system which is fully compatible with the experimental data obtained by inverse photoemission. In particular, the analysis of the interaction between the image state and a d_{xz} derived surface state band on the one hand with an adsorbate bond on the other hand strongly supports an adsorption geometry of the ethylene molecules on top of the atom rows of the Ni(110) surface. It is, to our knowledge, the first example where the interaction of molecular orbitals with substrate surface states has been identified and analyzed in such detail.

The exploitation of the nodal structure of a surface state and its consequences for the interaction with an adsorbate derived band should have a more general applicability for the determination of adsorption sites. This strategy, exemplified in the present work, may benefit from the fact that, for many metals, various surface states with differing nodal structures exist in gaps of the projected bulk band structure. However, the slab model calculations also illustrate the difficulties, if not pitfalls, an interpretation of such complex systems may have to meet, in particular since such complicated adsorbate structures necessarily involve approximations, which might affect the substrate and the adsorbate in a rather different way. In the present case it proved to be indispensable to consider the individual subsystems and to characterize their interaction in a semi-quantitative way in order to critically evaluate the results of the calculation for the full adsorption system.

Acknowledgements

We are grateful to Professor H.-P. Steinrück for valuable discussions and to P. Ulbricht for assistance with the cluster calculations. E.B. and J.C. wish to thank Professor Dose for continuous support. This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) via SFB 338 (EB and NR), by the Fonds der Chemischen Industrie (NR), and by the United States Department of Energy (JCB).

References