Ethylene adsorbed on Ni(110): An experimental and theoretical determination of the two-dimensional band structure

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We have investigated the saturated ethylene layer on Ni(110) by low-energy electron diffraction (LEED), angle-resolved ultraviolet photoemission spectroscopy (ARUPS), and near-edge x-ray-absorption fine structure (NEXAFS). This layer exhibits a c(2×4) LEED pattern that corresponds to a structure containing two adsorbates per primitive unit cell. The ethylene molecules are adsorbed with the molecular plane parallel to the surface and the C-C axis preferentially aligned along the [110] direction of the substrate, as is independently determined from the ARUPS and NEXAFS experiments. The two-dimensional (2D) adsorbate band structure is determined from the ARUPS spectra at various photon energies. Except for the π orbital, all ethylene-derived bands show significant dispersion (up to 2 eV), but no splitting as would be expected for a structure with two molecules per unit cell. Experimentally determined band structure is reproduced in all details by extended-Hückel-theory calculations for an unsupported ethylene layer. The structural model derived from LEED, ARUPS, and NEXAFS is confirmed both by force field and by the 2D band-structure calculations. This indicates that the adsorbate-adsorbate interactions are essentially decoupled from the adsorbate-substrate interaction, that is responsible for the chemisorption bond.

I. INTRODUCTION

So far the two-dimensional (2D) band structure of ordered adsorbate layers on metal surfaces has experimentally only been investigated for atomic adsorbates (rare gases, chalcogens), diatomic molecules [CO, NO, CO coadsorbed with K (Ref. 8)] and, very recently, to some extent for the more complex benzene molecule. While the majority of the studies for molecular adsorbates present experimental results only for the dispersion of one or several bands derived from the outer occupied molecular orbitals, there exist two extensive studies for CO/Co(001) (Ref. 5) and CO/Ni(110), where the experimentally observed 2D band structure of all outer valence levels is compared to that predicted from model calculations.

Ethylene adsorption on metal surfaces has received great interest in the past and is still a subject of numerous studies. On Ni(110) the adsorption has been studied in some detail by ultraviolet photoemission spectroscopy (UPS), temperature-programed desorption (TPD), low-energy electron diffraction (LEED), and high-resolution electron-energy-loss spectroscopy (HREELS). At low temperatures (below 170 K), ethylene adsorbs molecularly on Ni(110); the saturated ethylene layer is obtained for exposures above 3 L (1 L = 10⁻⁶ Torr s) and exhibits a c(2×4) LEED pattern. From HREELS measurements a di-σ-bonded ethylene species has been deduced that is adsorbed with the molecular plane essentially parallel to the surface, the symmetry of the adsorption complex being lower than C₂v. Depending on the initial ethylene coverage molecular desorption and/or dissociation of ethylene is observed upon heating; for low initial coverages ethylene decomposes upon heating as concluded from exclusive hydrogen desorption. At about half of the saturation coverage the desorption of hydrogen saturates and molecular ethylene desorption is observed.

We now have experimentally determined the 2D band structure and the azimuthal orientation of the ethylene molecules for the saturated ordered c(2×4) ethylene layer adsorbed on Ni(110) from very extensive angle-resolved ultraviolet photoemission spectroscopy (ARUPS) experiments at different photon energies by using linearly polarized synchrotron radiation. The orientation of the ethylene molecules is determined from the polarization, polar-angle, and azimuthal dependence of the emission from the various valence orbitals by applying simple symmetry selection rules. The experimentally determined band structure is compared to detailed band-structure calculations for various possible geometrical arrangements of the ethylene molecules on the Ni(110) surface. In addition, we also present the results from LEED and near-edge x-ray-absorption fine structure (NEXAFS) experiments to provide complementary information to the ARUPS results. Parallel to this study that deals with the structural and electronic properties of the saturated ethylene layer, where lateral interactions in the adsorbed layer play a dominant role, we have also investigated the interaction of ethylene at low coverages where lateral interactions are negligible and the "vertical" adsorbate-substrate interactions are dominant.
II. EXPERIMENT

All experiments have been performed in a two-chamber UHV system that has been described in detail elsewhere.\textsuperscript{3,10,12} Briefly, the system consists of a preparation chamber and an analyzer chamber. The preparation chamber is equipped with combined LEED and Auger optics, a quadrupole mass spectrometer for TPD (temperature-programmed desorption), and an ion sputter gun; the analyzer chamber contains the electron energy analyzer. The Ni(110) crystal was cooled down to 95 K by liquid nitrogen and could be resistively heated to 1300 K at linear heating rates between 0.1 and 20 K/s. The cleaning of the Ni(110) crystal was performed using standard procedures;\textsuperscript{92} the cleanliness was controlled by Auger electron spectroscopy (AES) and x-ray photoemission spectroscopy (XPS); surface order was checked by LEED. Ethylene of high purity was dosed onto the crystal via a multicapillary doser in order to produce uniform layers and keep the background pressure low. The base pressure in the system was in the mid-10^{-11}-mbar range and remained below 1\times10^{-10} mbar during the measurements.

The ARUPS experiments were carried out at the TGM-1 monochromator of the Berlin Synchrotron facility BESSY. The electron analyzer is a homebuilt angle multichannel instrument\textsuperscript{43} which allows simultaneous detection of electrons that are emitted under polar angles $\theta$ from $-10^\circ$ to $+90^\circ$ at a fixed azimuth. The polar-angle resolution is $2^\circ$ with an azimuthal acceptance of $3^\circ$. The specific design of the analyzer allows one to measure angular distributions of electrons, including normal emission ($\theta=0^\circ$) also at normal incidence ($\alpha=0^\circ$), which enables us to fully exploit symmetry selection rules and to map out the adsorbate Brillouin zone even at the $\Gamma$ point. In addition, the whole analyzer can be rotated around the surface normal of the sample to set the plane of detection either parallel or perpendicular to the electric-field vector. The combined resolution of electron analyzer and monochromator was set to 300 meV. The angle-resolved spectra given here have been obtained by averaging over a polar-angle range of $\pm5^\circ$; for the determination of the 2D band structure a smaller integration range of $\pm1.5^\circ$ was used.

The NEXAFS experiments were performed at the HETGM-2 monochromator at BESSY. Due to space restrictions at this beam line and the specific design of our chamber only measurements at normal incidence ($\alpha=0^\circ$) were feasible. At the time of the measurements the monochromator showed no structure in the intensity at the carbon edge, as concluded from the CFS spectra of the clean Ni substrate.

III. RESULTS AND DISCUSSION

A. LEED

For exposures larger than 3 L at a substrate temperature of 120 K the saturated ethylene layer is obtained, which exhibits a complex LEED pattern that is stable up to temperatures of 170 K. A photographic reproduction and a schematic drawing of the observed pattern is given in Fig. 1. All diffraction spots at positions ($\pm\frac{1}{2}(2n+1)$, $\pm\frac{1}{2}(2n+1)$) are elongated along the [001] direction of the substrate. In addition, the half order diffraction spots (0, $\pm\frac{1}{2}(2n+1)$) are missing for normal incidence of the electron beam in the energy range from 40 to 260 eV [Fig. 1(a)], but appear if the sample is tilted by some degrees along the [110] direction [Fig. 1(b)]. Based on this LEED pattern the observed structure is assigned to a c(2\times4) superstructure. These observations

![LEED patterns](image)

**FIG. 1.** LEED patterns of the saturated ethylene layer on Ni(110) obtained after a dose of 3 L; $U=200$ eV. (a) Normal incidence of the electron beam. (b) Sample tilted along [110] by $\approx10^\circ$. (c) Schematic drawing of the observed pattern: (○) substrate diffraction spots, (◼) adsorbate diffraction spots, (□) adsorbate diffraction spots only visible for non-normal incidence.
are in very good agreement with a recent study by Strosclair, Bare, and Hoo, who observed an identical complex LEED pattern for the saturated ethylene layer, which they did not analyze further.\textsuperscript{40}

Assuming one adsorbate molecule per primitive unit cell the c(2×4) structure would correspond to a coverage of 0.25 ML [where 1 ML (monolayer) is defined as one adsorbate molecule-substrate atom]. However, from detailed TPD studies we conclude that the C\textsubscript{2}H\textsubscript{4} saturation coverage is significantly larger than 0.25 ML.\textsuperscript{31} This indicates the existence of two ethylene molecules per unit cell and thus a coverage of 0.5 ML. Considering the van der Waals dimensions of (flat-lying) ethylene this suggests a fairly compressed saturated layer, which is indeed confirmed by the strong dispersions observed in the ARUPS measurements, and by the force-field calculations presented below.

B. ARUPS

The electronic structure of the saturated ethylene layer on Ni(110) has been studied by ARUPS using linearly polarized light at photon energies between 20 and 50 eV. For $\alpha=\theta^\circ$ (normal incidence, $E_x$ or $E_y$) the electric-field vector $E$ was aligned along the [001] or [110] high-symmetry direction of the substrate (by rotating the crystal) with the detection plane $D$ either parallel or perpendicular to $E$ (symbolically written as $D||E$ and $D\perp E$, respectively). For $\alpha=45^\circ$ ($E_x$ or $E_y$), ARUPS spectra have been collected for both azimuths with the detection plane parallel to $E$. For $D||E$, the so-called “allowed” geometry, only initial states that are even with respect to the plane defined by $E$ and $D$ are excited in the direction of the detector, whereas for $D\perp E$, the so-called “forbidden” geometry, only states that are odd with respect to the plane perpendicular to $E$ and parallel to $D$ can be excited in the direction of the detector.\textsuperscript{1,2}

Two series of ARUPS spectra collected at photon energies of 30 and 50 eV at the six different experimental geometries described above are depicted in Figs. 2 and 3, respectively. The emission from the various molecular peaks shows very distinct polarization, polar-angle, and azimuthal dependencies that indicate a well-defined adsorption geometry. In addition to the marked changes of intensity with emission angle the various peaks also show significant dispersion (changes in binding energy) with emission angle, indicative of the formation of a 2D adsorbate band structure (see below). In the following we will analyze the polarization and polar-angle dependence of the various molecular levels in detail to determine the orientation and the symmetry of the adsorbed ethylene molecules by comparison to the predictions from symmetry selection rules. For an overview of the spatial extension and the symmetry, the pertinent molecular orbitals of ethylene are depicted in Fig. 4.

To begin with, an orientation of the ethylene molecules with the molecular plane parallel to the surface is deduced by inspection of the emission from the $2a_1$ (Fig. 2) and $1b_{2u}$ (Figs. 2 and 3) orbitals which are totally symmetric with respect to the surface normal [$a_1$ (a) for a flat-lying ethylene molecule of $C_2\text{H}_4$ ($C_2\text{H}_4$) point-group symmetry; see Table I]. Both orbitals are not observed in

![C_2H_4 / Ni(110)](image)

**FIG. 2.** Angle-resolved UPS spectra for the saturated (0.5 ML) ethylene layer on Ni(110) for six different experimental geometries (see text); photon energy: 30 eV. The orbital positions of the isolated molecule on Ni(110) (Ref. 41) are indicated in the form of a bar diagram.
normal emission ($\vartheta = 0^\circ$) for $\alpha = 0^\circ$ (only $E_x$ or $E_y$) but show strong intensity for $\alpha = 45^\circ$, i.e., with a nonvanishing $z$ component of the electric-field vector $E$. The behavior of the $3a_g$ orbital, which is also totally symmetric, is more difficult to assess since at certain angles (in particular at normal emission) it is energetically degenerate with the $1b_3u$ orbital due to the strong dispersion of the latter (see below).

Information on the azimuthal orientation is usually determined from the emission behavior from the various orbitals in the symmetry planes of the substrate. For densely packed well-ordered layers, where the adsorbate-derived bands exhibit significant dispersion, the symmetry of the adsorption complex may have to be described by including neighboring adsorbates. As will be shown below, for ethylene on Ni(110) the site symmetry is $C_1$. For $C_1$ symmetry, however, no conclusions on the azimuthal orientation of an adsorbed molecule can be derived, since this point group does not contain mirror planes.

To simplify matters, we will at first ignore the forma-

**TABLE I.** Symmetry selection rules for several molecular symmetries of ethylene at various experimental geometries. $E_x$, $E_y$, and $E_z$ are the Cartesian components of the electric-field vector of the incoming light with respect to the surface plane and a flat-lying ethylene molecule ($x$ defines the direction of the C-C axis for the $C_{2h}$ and $C_{s}$ representations); $D_x$ and $D_y$ characterize the alignment of the detection plane. $N$ indicates that a band is allowed in normal emission and at all other angles, "+" and "−" indicate that emission in the detection plane is allowed or forbidden, respectively.

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FIG. 3. Angle-resolved UPS spectra for the saturated ($\Theta = 0.5$ ML) ethylene layer on Ni(110) for six different experimental geometries (see text); photon energy: 50 eV. The orbital positions of the isolated molecule on Ni(110) (Ref. 41) are indicated in the form of a bar diagram.
Molecular Orbitals of C₄H₄
Symmetry: D₄h (C₄ᵥ)

1b₂u (a₁)
1b₂g (a₂)
3a₁g (a₁)
1b₃u (b₂)
2b₁u (b₁)

H=C=CH

FIG. 4. Molecular orbitals of free ethylene. The labels correspond to the D₄h point group of the free molecule, the labels in parentheses to that of a flat-lying molecule of C₄ᵥ symmetry.

tion of the 2D band structure in the following and we will try to determine the azimuthal orientation by comparing the observed emission behavior from the various orbitals to the predictions for C₄ᵥ symmetry of an isolated flat-lying ethylene molecule on Ni(110). The most characteristic azimuthal dependence is observed for the 2b₁u (b₁) for C₄ᵥ symmetry) orbital. Emission from this orbital is particularly strong for E aligned along the [110] direction of the substrate, but only weak for E[001]. This behavior indicates a preferential orientation of the ethylene molecules with the C-C axis along the [110] direction, i.e., parallel to the troughs of the Ni(110) surface. The same conclusion is derived from the opposite behavior of the 1b₃u (b₂ for C₄ᵥ) orbital that is strong for E[001] and weak for E[110]; it should be noted that the analysis for the 1b₃u (b₂) orbital is not as straightforward due to the above-mentioned degeneracy with the 3a₁g orbital in certain spectra, i.e., at certain points in k space. Further evidence for a well-defined azimuthal orientation stems from the fact that the totally symmetric 2a₂ and 1b₂u orbitals have only very weak intensity in the so-called forbidden geometries. This is expected from symmetry selection rules when the detector is placed in a mirror plane of the system. Finally, we have to analyze the behavior of the 1b₂g (a₂ for C₄ᵥ) orbital. This orbital is observed in all geometries (in particular, also in normal emission) independent of the polarization, with the emission somewhat stronger for D1E as expected for a molecule that is azimuthally oriented along a substrate high-symmetry direction. The nonvanishing normal emission intensity of the 1b₂g (a₂) orbital is not compatible with C₄ᵥ, C₂, or C₂ᵥ symmetry and thus indicates that the symmetry of the adsorption complex is even lower, namely C₁. These results are in good agreement with the conclusions derived from HREELS measurements by Stroscio, Bare, and Ho, who conclude that the ethylene molecules in the saturated c(2×4) layer on Ni(110) are adsorbed with their molecule plane parallel to the surface, exhibiting a symmetry lower than C₂ᵥ.⁴⁰

The fact that the intensity of the various peaks in the ARUPS spectra does not completely vanish for certain geometries, as predicted from symmetry selection rules for C₂ᵥ symmetry, could be attributed to the lower site symmetry of the ordered ethylene layer. On the other hand, this could also indicate that the C-C axis of the ethylene molecules is not perfectly aligned along the [110] direction. At this point it is useful to note that the polarization, polar-angle, and azimuthal dependences of the emission from the various orbitals of the saturated ethylene layer are overall very similar to those observed for a dilute ethylene layer⁴¹ where no dispersion is observed for the different molecular levels. This indicates an essentially identical orientation of the ethylene molecules in the dilute layer and in the saturated layer. Based on this similarity we further conclude that the intensities observed for the saturated layer are mainly dominated by the intensity expected from an isolated molecule. Thus, at the next level of approximation, formation of a 2D band structure leads "only" to the dispersion of the various levels. This justifies to some extent the analysis of the ARUPS spectra by symmetry selection rules in terms of the isolated adsorption complex ethylene/Ni(110), as performed above.

In summary, we conclude that ethylene is adsorbed on Ni(110) with the molecular plane parallel to the surface and the C-C axis preferentially oriented along the [110] direction of the substrate (this orientation is independently verified by NEXAFS; see below). The symmetry of the adsorption complex is C₁, which is probably due to a low-symmetry adsorption site and/or a twisting of the CH₂ groups with respect to the molecular axis upon adsorption. Nevertheless, in the following structural model and for the band-structure calculations (see below) we will treat ethylene as being adsorbed with local C₂ᵥ symmetry to simplify matters (see also Sec. IV).

C. NEXAFS

To independently check the proposed orientation of the adsorbed ethylene molecules on the Ni(110) surface we have also performed NEXAFS experiments at normal incidence (α=0°). Measurements in this geometry alone certainly do not allow one to apply the full potential of this method; nevertheless, we believe that definitive conclusions on the orientation of ethylene on the Ni(110) substrate can be drawn. The experiments should allow us to determine whether the ethylene molecules are adsorbed flat on the surface, and to determine the azimuthal orientation.

We have therefore performed NEXAFS experiments for the saturated ethylene layer with the electric-field vector aligned either along the [001] or the [110] azimuth. The spectra (see Fig. 5) have been collected in the Auger
electron yield mode with a CFS energy of 260 eV and were normalized to the spectrum of the clean sample at the same CFS energy.

The spectra show essentially four characteristic features that exhibit distinct polarization dependences for the two azimuths. The first steplike feature at a photon energy of 285.0 eV is at the energetic position of the C=C C $\pi^*$ resonance. It should be noted that a strong $\pi^*$ resonance is expected even for a di-$\sigma$-bonded ethylene molecule. The second peak at 288.8 eV is attributed to excitations into a C-H* orbital [2b$_{3u}$ molecular orbital (MO); see Ref. 45] and a Rydberg orbital. The third peak at 292.0 eV is due to two-electron excitations and the fourth peak at 297.0 eV is attributed to the C-C $\sigma^*$ shape resonance. The small steplike intensity at the energetic position of the $\pi^*$ resonance (which can at least partly be attributed to adsorbate-derived final states just above the Fermi edge of substrate) as well as the pronounced C-C $\sigma^*$ resonance for E $||$[110] show that the ethylene molecule essentially lies down on the surface. The fact that the C-C $\sigma^*$ resonance is much stronger for E $||$[110] than for E $||$[001] indicates that the molecule is preferentially oriented with the C-C axis along the [110] direction, i.e., along the troughs of the Ni(110) substrate. This conclusion is further corroborated by the behavior of the peak at 288.3 eV that is dominated by the excitation to the C-H* orbital (the contribution from the Rydberg-derived state is expected to be negligible due to its “out-of-plane” character). For this C-H* state one expects the opposite azimuthal polarization dependence than that of the $\sigma^*$ resonance which is indeed observed in Fig. 5. The peak at 291.5 eV shows essentially no polarization dependence as is expected for a multielectron excitation.

The comparison to the NEXAFS spectrum of the free molecule reveals that the energetic position of the C-C $\sigma^*$ shape resonance is moved to lower energies from about 300 eV for the free molecule to 297.0 eV for ethylene chemisorbed on Ni(110). From this shift the C-C bond length is determined to $1.45 \pm 0.04 \text{ Å}$ by applying the well-established “bond lengths with a ruler” analysis. This value is identical within $\pm 0.02 \text{ Å}$ to those determined by NEXAFS for ethylene adsorbed on Ni(100) (Ref. 23) and Ni(111) (Ref. 53) and in good agreement with the value of 1.40 Å obtained from linear-combination-of-Gaussian-type-orbitals (LCGTO-LDF) (where LDF represents local-density functional) cluster calculations of the isolated ethylene molecule on Ni(110).

D. Structural model

Based on the observed c(2×4) structure containing two molecules per unit cell and the well-defined azimuthal orientation we deduce a real-space structure for ethylene on Ni(110). The molecules are adsorbed with the molecular plane parallel to the surface and the C-C axis aligned along the [110] direction of the substrate; the ideal coverage corresponds to 0.5 ML. This suggests the following structural model as depicted in Fig. 6(a): The molecules are adsorbed in dense rows along the [110] direction with every second substrate site occupied. Neighboring adsorbate rows are shifted relative to each other by half a lattice vector along [110]. As a consequence (translationally) equivalent adsorption sites are occupied only every second row entailing a primitive unit cell containing two molecules for the c(2×4) structure. The adsorbate unit cell is an oblique unit cell which leads to the existence of two different domains that are schematically depicted in Fig. 6(b).

With each of the [110] rows occupied by ethylene mol-

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**FIG. 5.** NEXAFS spectra of the saturated ethylene layer on Ni(110) collected at normal incidence and a CFS energy of 260 eV.

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**FIG. 6.** Structural model for the c(2×4) ethylene layer on Ni(110) as determined from LEED, ARUPS, and NEXAFS: (a) single domain; (b) domain structure including both possible domains and the corresponding domain walls (see text).
molecules, the adsorbate overlayer is obviously quite densely packed. Interadsorbate distances are comparable to van der Waals distances and, therefore, lateral nonbonding interactions will play an important role in determining the registry of neighboring adsorbates rows. Their effect may be even more pronounced as essentially no site specificity has been found for the ethylene-substrate bonding (short-bridge chemisorption or di-σ bonding versus on-top chemisorption or π bonding) in model cluster investigations.  

To quantify this lateral interadsorbate interaction, a “molecular modeling” technique has been used, details of which are given elsewhere. In summary, force fields were used to describe the van der Waals-type interactions between adsorbates. The substrate was not explicitly taken into account, but merely set the intermolecular spacing for a hypothetical overlayer. Calculations were made for an isolated two-dimensional molecular array containing three adjacent [110] rows of ethylene molecules with distances appropriate for the c(2×4) overlayer on a Ni(110) surface. The molecules were oriented parallel to the [110] direction as suggested by the ARUPS results. The nonbonding interaction (per adsorbate) was calculated as the middle row of molecules was displaced relative to two rows bordering it.

A definite energy minimum was found for a displacement of half a lattice vector (1.25 Å) along the [110] direction, confirming the model structure postulated above (see Fig. 7). The location of this energy minimum turned out to be insensitive to geometrical details of the adsorbate, although the energy barrier between adjacent sites along the [110] direction changed substantially when the CH₂ units were bent upward by 17° as found in Zeise's anion. A further lowering of the barrier, but again no change of the location, resulted when the CH₂ units of one adsorbate were twisted with respect to the molecular axis by 10° each, confirming that the lateral registry is largely determined by nonbonding interactions, preferentially between hydrogen atoms.

At this point we should come back to the observed LEED structure with the partially elongated and partially missing diffraction spots. The elongation of the (±π/3(2n + 1), ±π/2(2n + 1)) diffraction spots along the [001] direction indicates that the size of the domains in that direction is significantly smaller than the coherence length of the instrument. The fact that the integer order diffraction spots and the (±π/3(2n + 1), ±m) diffraction spots are not elongated, suggests that the origins of the different domains are separated by even integer multiples of the substrate lattice distance along [001] [see Fig. 6(b)]. The extinction of the (0, ±π/3(2n + 1)) diffraction spots for normal incidence indicates that the structure contains pairs of molecules that are translationally inequivalent, but are related by a point transformation. We thus propose that the adsorption site of ethylene on Ni(110) has to be a site centered between the on-top site and the short bridge site (see Fig. 6). For this site the two molecules contained in the unit cell are related by a C₂ point transformation. As a consequence, the contributions of the two molecules in the unit cell (see Fig. 6) to the scattered amplitude cancel for the (0, ±π/3(2n + 1)) diffraction spots at normal incidence. All scattering processes involving one scattering event at the adsorbate will also yield no contribution; only scattering paths where the electron is scattered at least twice in the adsorbate layer could contribute some intensity, which indicates that the intensity of the (0, ±π/3(2n + 1)) diffraction spots at normal incidence is not exactly zero, but very weak. Alternatively, the absence of the (0, ±π/3(2n + 1)) diffraction spots at normal incidence could indicate the existence of a glide plane in the adsorbed structure as suggested in Ref. 40. However, the structural model depicted in Fig. 6 does not contain a glide plane.

**E. Experimental determination of the 2D band structure**

As already mentioned, significant dispersion is observed in the ARUPS spectra of Figs. 2 and 3 for several molecular levels. From the variation of the binding energy (kinetic energy) with the emission angle the two-dimensional band structure of the saturated ethylene layer can be evaluated using the free-electron dispersion relation for the final state of the electron:

\[ k_{\perp} = \left[ \frac{(2m/\hbar^2)}{E_{\text{kin}}} \right]^{1/2} \sin \theta. \]

The 2D band structure has been determined along the two high-symmetry directions ([110] and [001]) of the substrate and is depicted in Fig. 8. The substrate high-symmetry directions (mirror planes) are no mirror planes of the adsorbate Brillouin zone; however, they are the...
FIG. 8. 2D band structure of the saturated ethylene layer as determined from ARUPS spectra at different photon energies: (+) $h\omega=26$ eV, (II) $h\omega=30$ eV, (O) $h\omega=50$ eV. Also shown is the calculated band structure for geometry II (solid line; see text). The labels correspond to the high-symmetry points of the Brillouin zone as deduced from the c(2×4) LEED pattern (see Fig. 9, top left).

only ones that are experimentally meaningful since they represent equivalent directions of the adsorbate Brillouin zones of the two possible domains and thus allow unequivocal conclusions about the 2D adsorbate band structure. The data obtained from angle-resolved UPS spectra at $h\omega=26$, 30, and 50 eV fall right on top of each other within the margin of error of $\pm 0.15$ eV. The highest-lying $1b_{2u}$-derived band shows essentially no dispersion, as expected from its out-of-plane ($\pi$) character. The $1b_{2g}$ and the $2b_{1u}$ band exhibit no dispersion along the [001] direction, but significant dispersion along the [1$\bar{1}$0] direction. The $3a_g$ and $1b_{3u}$ bands show dispersion along both azimuths. At the $\Gamma$' points ($k_{\|}=0 \text{ Å}^{-1}$ and $k_{\perp}=1.8 \text{ Å}^{-1}$ along [001]) these bands are energetically degenerate, with the binding energy of the $1b_{3u}$ band being even somewhat smaller than that of the $3a_g$ band (8.4 versus 8.6 eV). The magnitude of the dispersion differs for the various bands; the highest value of 2 eV is observed for the $1b_{3u}$ band. In Fig. 9 the extended adsorbate Brillouin zone that is deduced from the observed c(2×4) LEED pattern is depicted. The various symmetry points of this structure which are used to label the band structure in Fig. 8 are also indicated. As evident from Fig. 8, the 2D adsorbate band structure does not reflect the symmetry of the adsorbate Brillouin zone as deduced from LEED. Furthermore, the detailed analysis of the spectra reveals no splitting of any of the adsorbate bands as one would expect from the existence of two molecules per unit cell. This leads us to the conclusion (also based on the band-structure calculations presented below) that the 2D surface Brillouin zone that is derived from the LEED pattern is not appropriate to describe the experimentally observed band structure.

F. Band-structure calculations

Band-structure calculations on ethylene overlayers adsorbed on Ni(110) were undertaken with a twofold goal in mind. First, we attempted to rationalize the energies and dispersions of the experimentally determined adsorbate-derived bands as described in the preceding section. Furthermore, by unraveling the complex information contained in these bands, we also tried to understand whether this band structure is sufficiently specific to the geometry of the overlay that further evidence for the structural model proposed in Sec. III D may be obtained. To check the structural sensitivity of the adsorbate-derived bands and, at the same time, the qualitative reasoning put forth in understanding these bands, we also investigated two further idealized structures which are at variance with our force-field results.

The band-structure calculations were performed in a
tight-binding approximation at the extended-Hückel-theory level. Standard parameters were used to describe the adsorbate. Slater-type orbitals with exponents \( \xi(2s) = \xi(2p) = 1.63 \) are employed for the carbon valence orbitals, the corresponding diagonal Hamiltonian matrix elements being \( h_{2s}(2s) = -18.2 \text{ eV} \) and \( h_{2p}(2p) = -9.5 \text{ eV} \); for hydrogen the standard extended-Hückel-theory parameters are \( \xi(1s) = 1.30 \) and \( h_{1s}(1s) = -13.6 \text{ eV} \). For the substrate, parameters were taken from previous chemisorption studies on Ni surfaces. \( \xi(4s) = \xi(4p) = 2.10, \ h_{2s}(4s) = -7.8 \text{ eV}, \ h_{2p}(4p) = -3.7 \text{ eV}, \xi(3d) = 5.75 \) and \( 2.00 \) with contraction coefficients 0.5683 and 0.6293, respectively, \( h_{2d}(3d) = -9.9 \text{ eV} \). To facilitate the comparison with the experimental band structure, we adjusted the adsorbate Hamiltonian by a correction which is diagonal in the representation of the free-ethylene molecular orbitals and which has the effect that the correct photoelectron spectrum of free ethylene is obtained in a molecular calculation. The Hamiltonian matrix elements describing the lateral interaction between the various adsorbates are not affected by this correction term. Furthermore, this term was held constant during the variation of the geometry of the adsorbate layer (see below). The geometry of the adsorbed ethylene was taken as determined in recent LCGTO-LDF cluster calculations. There, a C-C bond length of 1.40 Å and an upward bending of the CH₃ units by about 20° was found. This geometry is similar to the one determined by x-ray and neutron diffraction for the organometallic complex \([\text{Cl}_3\text{Pt(C}_2\text{H}_4)]^{2-}\), Zeise's anion. As a first result, we noted by comparison with an unsupported ethylene layer that the ethylene-derived energy bands exhibit rather little influence of the substrate. Of the five highest-lying bands only the \( \sigma \)-derived band undergoes a significant energy shift by 0.75 eV, but shows essentially no dispersion. In agreement with the cluster calculations, hardly any difference is expected between the various adsorption sites. The calculated bands are consistent with the fact that the experimental band structure does not exhibit any splitting of the bands at the edge of the adsorbate surface Brillouin zone as one might expect for the \( \bar{Y} \) points of the \( c(2 \times 4) \) “LEED” geometry, reflecting the geometry with two ethylene molecules per unit cell (see below). However, the first unoccupied ethylene band, derived from the \( \pi^* \) band orbital, strongly interacts with the substrate bands. Inverse photoemission might be able to detect a splitting of the corresponding bands. Since only negligible influence of the nickel substrate on the ethylene bands was observed in the present investigation, all further calculations were performed on unsupported ethylene layers.

In Sec. III D, a geometry of the ethylene overlayer was deduced from the LEED analysis and from force-field calculations where neighboring rows of adsorbate molecules are shifted with respect to each other by half a lattice distance along the [110] direction. This geometry leads to an oblique lattice for the unsupported ethylene layer which, in contrast to the full \( c(2 \times 4) \) structure, contains only one adsorbate molecule per unit cell; note that this structure of the unsupported layer is obtained by simply neglecting the underlying Ni(110) substrate in Fig. 6(a). Besides this structure (geometry II), we also investigated geometry I with no relative shift of neighboring rows and geometry III obtained shifting the rows by a full lattice vector. The relative positions of the ethylene molecules and the resulting unit cells are displayed in the upper part of Fig. 10 together with the underlying nickel layer.

As explained in Sec. III E, the energy bands were experimentally observed along directions in \( k \) space that correspond to high-symmetry directions of the Ni(110) surface. Unfortunately, these directions are, in general, no high-symmetry directions in the \( k \) space of the ethylene layer. This can be seen in detail in Fig. 9 where the experimental path in \( k \) space is shown in the repeated Brillouin-zone scheme of all three lattices. In addition, the situation for a \( c(2 \times 4) \) structure (LEED geometry), taken in a straightforward manner, is also shown. A comparison with geometry II shows no similarity due to the different shapes of the unit cell. Together with the absent splitting of bands, this provides an important tool for the interpretation of the measured band structure. The experimental path in \( k \) space goes through four \( \bar{T} \) points of the LEED structure that correspond to two pairs of \( \bar{T} \) and \( \bar{Y} \) points of geometry II. Therefore, the LEED structure is ruled out by the observed bands which lack the necessary degeneracies. However, we would like to point out that the measured bands in Fig. 8 have been labeled according to the apparent \( c(2 \times 4) \) structure.

We now compare the band structures for the geometries I–III in some detail. They are shown in Fig. 10 for the experimentally relevant energy range. Obviously, differing dispersions are found for the three geometries, allowing conclusions concerning the geometries of the ethylene overlayers. The experimental \( k \) points in the [110] direction trace a rather unusual path through the repeated zone scheme which corresponds to a simple, a two- and fourfold path in the first Brillouin zone of the corresponding scheme (see Fig. 9), implying a different number of high-symmetry points in each case. Thus, the energy bands along this direction are difficult to compare. On the other hand, the [001] direction from the \( \bar{Y} \) to the \( \bar{Y} \) and back to the \( \bar{Y} \) point, although not a high-symmetry direction for geometry II, is identical for all three structures. We shall therefore focus on this part of the band structure.

Along the [001] directions, three of the ethylene bands, associated with the orbitals \( 1b_{3u}, 3d_{2g}, \) and \( 1b_{2u} \), are quite unaffected by the structural change. This may be rationalized by nearest-neighbor interactions taking the shape of the corresponding orbitals into account (see Fig. 4). On the other hand, the remaining two bands, \( 2b_{1u} \) and \( 1b_{2g} \), are quite different for the three geometries. Again, their dispersion is easily understood by reference to the shape of the corresponding ethylene orbitals. As an example, we will compare the overlap of the \( 1b_{2g} \) orbital between neighboring rows (see Fig. 11). For geometry I, the interaction is obviously antibonding, resulting in a band that slopes downward when going away from the \( \bar{Y} \) point. In geometry III, this band displays the opposite dispersion in agreement with the bonding overlap toward the neighboring rows. Finally, in geometry II, this lateral
FIG. 10. Calculated band structure for the saturated (unsupported) ethylene layer with different lateral arrangements of the molecules. The top labels correspond to the symmetry points for the adsorbate Brillouin zone derived from the c(2×4) LEED pattern; the bottom labels correspond to the Brillouin zone for the calculated geometries. In each case the relative position of neighboring ethylene molecules is shown at the top of the figure together with the unit cell of the corresponding lattice.

FIG. 11. Schematic representation of the 1b2g Bloch wave function at the Γ' point of ethylene molecules placed on neighboring nickel rows in the various geometries.

overlap is nonbonding, leading to a dispersionless band just as found experimentally.

Excellent agreement between the measured and calculated bands is found for geometry II, essentially along the complete experimental path in k space. This can clearly be seen from Fig. 8, where both band structures are displayed. Since the experimental bands are measured relative to the Fermi energy, the energy scales of the two band structures had to be shifted relative to each other: a minimum average deviation of the four low-lying bands at the Γ' point was chosen for this purpose. The complete measured energy dispersion is very well reproduced for all calculated bands. Only the 3a1g band shows some discrepancies; but they are less than 0.5 eV, indicating the limits of the approximate band-structure method. Furthermore, the σ-derived band (1b2g) lacks the substrate-induced shift (about 0.75 eV). This overall very satisfactory result provides further strong evidence that geometry II, where ethylene molecules of neighboring rows are displaced along the [110] direction by half a lattice vector, is realized in a saturated ethylene layer on Ni(110).

IV. CONCLUSIONS

The experimentally determined band structure (Fig. 8) cannot be ascribed to the Brillouin zone that is deduced from the c(2×4) structure with a primitive unit cell con-
taining two nonequivalent ethylene molecules. The existence of two adsorbates per unit cell should result in a splitting of the adsorbate-derived bands; only, at certain high-symmetry points of the adsorbate Brillouin zone some of the bands would be degenerate. The ARUPS spectra collected at different photon energies (which rules out cross-sectional effects) and over a fairly wide range in k space do not, however, provide evidence for a splitting of any of the bands. Such a splitting has been observed in the ARUPS spectra for the molecular level of the saturated CO layer on Ni(110), where the molecules are adsorbed in a p2mg structure. In this structure the CO molecules that are adsorbed along the rows (|1|00) are alternatively tilted with respect to the surface by ~20° along the [00|1] and [00|1] azimuth, which leads to a unit cell containing two nonequivalent CO molecules.\(^7,62-64\) As a consequence, all adsorbate-derived occupied\(^7\) (and also unoccupied\(^6|0\) bands are significantly split in the experiment as well as in the calculated band structure.

The band-structure calculations for the unsupported ethylene layer show almost perfect agreement with the experimental results for the c(2×4) ethylene layer on Ni(110). This means that the 2D adsorbate band structure is determined by the adsorbate-adsorbate interactions only. The "vertical" adsorbate-substrate interactions, which are responsible for the bonding of the mole- cule to the surface, are essentially decoupled from the lateral interactions. This conclusion is strengthened by the fact that the out-of-plane (π) orbital (1b\(_{2u}\)) that is mainly responsible for the bonding shows only minor dispersion in the experiment and in the calculation. We further con- clude that the two molecules in the unit cell must be effectively equivalent with respect to the lateral arrangement and that they must have an identical orientation with respect to the substrate.

We have recently made a similar observation for CO adsorbed on Ni(111) where the experimentally determined band structure for the c(4×2) and the (\(√7/2×√7/2\))R19.1° overlayers also show no evidence for splitting, although the unit cells of the adsorbate structures contain two and four molecules, respectively.\(^9\) In both structures the molecules occupy nonequivalent adsorption sites, but have identical orientation (perpendic-ular to the surface). The absence of a splitting of the various bands for these systems further confirms that the 2D band structure for identically oriented molecules is determined only by the relative positions of the molecules with respect to the neighboring molecules and that the details of bonding to the substrate are not important (at least at the present level of accuracy). The major role of the substrate is to act as a template for fixing the distance between neighboring adsorbate molecules.\(^54,55\) It is noted at this point that both CO/Ni(111) and C\(_2\)H\(_4\)/Ni(110) represent strong chemisorption systems with chemical binding energies of the order of 1 eV.

The band-structure calculations show dramatic differences between various lateral arrangements of ethylene in the adsorbed layer. This sensitivity to changes in the lateral arrangement allows one to discriminate between different models for the structure of the adsorbed overlayer. In the present study the structural model derived independently from the force-field calculations and the 2D band-structure calculations not only confirms the absolute value of 0.5 ML for the saturation coverage, but also is in perfect agreement with the structure deduced from LEED. Due to the high sensitivity of the 2D band structure to the nearest-neighbor interactions the relatively small size of the domains does not influence the results.

The good agreement between the experimentally determined band structure and the calculated band structure suggests that the band structure is less sensitive than symmetry selection rules to the details of the adsorption geometry: Even though the detailed analysis of the ARUPS data indicates a C\(_1\) symmetry of the adsorbed molecule, the experimental band structure is very well reproduced by calculations for an unsupported ethylene layer with a "perfectly" oriented, flat-lying ethylene mol- ecule. However, while the band-structure calculation is very sensitive to the relative position (distance) of the neighboring molecules, it is not as sensitive to details of the adsorption geometry of the single molecule. In retrospect, this justifies the treatment based on a local C\(_{2v}\) adsorption geometry.

Finally, we want to comment on the conclusions on the chemical structure of ethylene adsorbed on various metal surfaces which have, in many cases, been derived from the binding energies of the various valence levels as determined from UPS.\(^17,18\) Most of these measurements have been obtained for saturated layers in the angle-integrated mode or at certain angles only. The fact that the various molecular levels in a densely packed ethylene layer show significant dispersion [up to 2 eV for Ni(110)] indicates that one has to treat the determined energies with some reservations and that it might be necessary to reconsider some of the conclusions derived from those values. Furthermore, the very strong lateral interactions in a densely packed layer, as evident from the dispersion of the 2D band structure, might also be of some importance in the interpretation of HREELS spectra.

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