The adsorption of acetylene on Ni(110): An experimental and theoretical study

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The adsorption of acetylene on Ni(110) was investigated by temperature programmed desorption (TPD), low energy electron diffraction (LEED), angle resolved ultraviolet-photoelectron spectroscopy (ARUPS), and near edge x-ray absorption fine structure (NEXAFS) measurements, as well as by detailed model cluster calculations and slab model band structure calculations. By combining the experimental results and those of the cluster studies an orientation of the molecules is deduced with the C–C axis parallel to the surface and preferentially aligned along the substrate troughs ([110] azimuth) as well as with a highly coordinated adsorption site in the substrate troughs. A detailed analysis of the photoemission spectrum is given. The proposed adsorption geometry is corroborated by band structure calculations for various alternative sites and orientations that are shown to be very sensitive to the azimuthal orientation of the adsorbed molecules. © 1995 American Institute of Physics.

I. INTRODUCTION

The adsorption and decomposition of acetylene on metal surfaces has been investigated in great detail in the past and is still the subject of numerous studies.1–33 Most of these investigations have been performed on single-crystal surfaces using ultraviolet photoelectron spectroscopy (UPS), high resolution electron energy loss spectroscopy (HREELS), near edge x-ray absorption fine structure spectroscopy (NEXAFS), low energy electron diffraction (LEED), temperature programmed desorption (TPD), and more recently photoelectron diffraction (PED). Among these techniques, high resolution electron energy loss spectroscopy has been predominantly used to elucidate the chemical and geometric structure of the adsorbed molecules (for an overview see Ref. 1).

The bonding interaction of acetylene with the substrate is classified into two types characterized by two different sets of vibrational frequencies.1 The difference between these two types is associated with the bond order of the intramolecular C–C bond. Due to the interaction with the substrate the degree of hybridization of the C atoms is assumed to change from sp in the free molecule to sp$^2$ and beyond.1 Furthermore, different adsorption sites and different structures of the adsorption complex, such as bent, bent and twisted, as well as tilted acetylene molecules, have been proposed on various transition metal surfaces.1

The adsorption and thermal decomposition of acetylene on Ni(110) has previously been studied by several groups using UPS in combination with Hartree–Fock LCAO calculations of the ionization levels,4,5 HREELS, TPD, and LEED.3,2 At low temperatures ($T<180$ K) acetylene is molecularly adsorbed on Ni(110). From HREELS Bandy et al.3 deduce a di-$\sigma+\pi$ type interaction with the substrate with extensive rehybridization ($sp^{1.2}$) of the acetylene molecules.3 Stroscio et al.7 report a broadening of the C–H stretch mode and suggest a trans- or cis-bent acetylene species with different environments for the two C–H groups. Based on that conclusion they suggested a $\mu$-bridging adsorption site, i.e., an orientation of the C–C axis along the [001] azimuth, in accord with the earlier model proposed by Demuth.5 However, none of these studies contain direct information on the orientation and/or symmetry of the adsorption complex (as could be obtained e.g. by additional off-specular HREELS or angle resolved UPS) and thus, to a certain degree, these models have to be regarded as tentative.

We have performed a detailed angular resolved UV photoelectron spectroscopy (ARUPS) study on the adsorption of acetylene on Ni(110) using linearly polarized synchrotron radiation at different photon energies. The orientation of the acetylene molecules is determined from the polarization, polar angle, and azimuthal dependence of the emission from the various orbitals by applying simple symmetry selection rules. We also present results from TPD, LEED, and NEXAFS experiments to characterize the adsorbate layer, and to provide complementary information. The experimental results will be compared to results obtained from linear combination of Gaussian-type density functional (LCGTO-D) cluster calculations for various adsorption geometries. In addition, the experimentally determined band structure is compared to results of two-dimensional (2D) band structure calculations for various possible orientations of the acetylene molecules on the Ni(110) substrate. By combining all experimental and theoretical results a detailed description of the electronic structure and orientation of acetylene on Ni(110).
is derived, and the number of possible adsorption sites will be substantially restricted.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. Experiment

All experiments were carried out in a two chamber UHV system that has been described in detail before. The preparation of the acetylene layers as well as the TPD and LEED studies have been performed in the preparation chamber. The base pressure was in the low 10^{-11} mbar range and remained below 1 \times 10^{-10} during the measurements. The sample was cooled by liquid nitrogen to 95 K and could be resistively heated to 1300 K at linear heating rates between 0.1 and 20 K/s. The Ni(110) crystal was carefully aligned on the holder and cleaned in UHV using standard procedures. Surface cleanliness was verified by Auger electron spectroscopy (AES) or x-ray photoelectron spectroscopy (XPS), and surface order was controlled by LEED. The TPD spectra were collected using a software multiplexer that allowed the simultaneous survey of up to eight different masses. Acetylene of high purity was dosed onto the surface via a multicapillary array.

The ARUPS spectra were recorded at the Berlin Synchrotron facility BESSY using the TGM-1 monochromator. For these measurements the sample was transferred into the analyzer chamber through a gate valve. The electron energy analyzer is a homebuilt angle-multichannel instrument which allows simultaneous detection of electrons for polar angles between -10° and 90° at a fixed azimuth. The polar angle resolution of the detector is better than 2° with an azimuthal acceptance of 3°. For normal incidence (\(\alpha = 0°\)) different orientations of the electric field vector, E, with respect to the high symmetry directions of the Ni(110) substrate, [110] and [001], can be realized by rotating the sample around the surface normal. In addition, by rotating the analyzer, the plane of detection, D, can be aligned parallel (even or "allowed") geometry or perpendicular (odd or "forbidden") geometry to the field vector of the incoming radiation. For an incidence angle of \(\alpha = 45°\) measurements with an additional normal component of the electric field vector can be performed. The angle resolved spectra presented here have been integrated at \(\pm 5°\) around the nominal polar angle \(\phi\); for the determination of the 2D band structure a smaller integration range of \(\pm 1.5°\) was used.

The NEXAFS experiments were performed at the HETGM-2 monochromator at BESSY. Due to space restrictions and the specific design of our chamber only measurements at normal incidence were feasible. At the time of the measurements the monochromator showed no structure at the carbon edge, as concluded from CFS spectra of the clean sample.

B. Computational

Two different types of calculations have been performed. To investigate the adsorbate–substrate interaction the cluster approach has been used, while for studying the band structure two-dimensionally periodic slab models have been employed.

1. Cluster models

The cluster calculations were carried out using the linear combination of Gaussian-type orbitals density functional (LCGTO-DF) method 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. The exchange-correlation potential was approximated by the local density (LDA) Xa form with \(\alpha = 0.7\) to facilitate comparison with a previous study on the chemisorption system C2H2/Ni(110). In addition, based on the self-consistently determined LDA density gradient corrections (GC) to the exchange and correlation energy functional have been employed. The GC corrected energies were evaluated using a numerical integration scheme that has been slightly modified to efficiently deal 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. Further details on the LCGTO-DF cluster method have been described elsewhere.

The various basis sets used in the LCGTO-DF method, an orbital basis set as well as fitting basis sets for the charge density and the exchange-correlation potential, were taken from the previous study of C2H2/Ni(110). For Ni a (15s,11p,6d) molecular orbital basis set was contracted to (7s,6p,3d) using atomic LDA eigenfunctions. Similar, for C a (9s,5p,1d) basis contracted to (7s,4p,1d) and for H a (6s,1p) basis contracted to (4s,1p) was employed. The charge and exchange fitting basis sets have been generated by standard methods scaling the orbital exponents by 2 and 2.5, respectively. In addition both fitting basis sets have been augmented by \(p\) polarization functions with exponents 0.1, 0.25, 0.625, 1.562, 3, and 3.906 25 for each atom. Furthermore, the fitting basis sets for nickel have been contracted to [8s,3d(r²),5p] for the charge density fitting and to [9s,4d(r²),5p] for the exchange fitting basis.

According to the experimental findings (see below) and in the light of the structural data available on chemisorbed acetylene and on relevant transition metal olefin complexes the chemisorption cluster models have been constructed by assuming acetylene to adsorb with its C–C axis parallel to the [110] surface plane and aligned either parallel or perpendicular to the [110] rows of the surface. The four different potential adsorption complexes have been investigated (see Fig. 1). In three of them, acetylene was assumed to be located on top of the nickel rows, two of them \((\text{di}-\sigma\) and \(\pi\)) with the C–C axis parallel to the rows and the third \((\mu\)) with the C–C axis perpendicular to the rows. In a fourth geometry \((\tau\)) acetylene is chosen to lie in the troughs of the Ni(110) surface with its C–C axis parallel to the [110] rows. A partial geometry optimization of these four chemisorption complexes has been carried out conserving local C2v symmetry. The height of the C–C bond above the first crystal plane, the C–C bond length, and the wagging angle \(\gamma\) (the complement to 180° of the C–C–H angle) were allowed to vary. The C–H bond length was fixed at the value obtained in an optimization of the free acetylene molecule, 1.078 Å, the corresponding experimental value is 1.058 Å.
The substrate clusters were fixed at the ideal bulk geometry. For the di-σ and the μ bridging geometries, the Ni(110) surface is modeled by a Ni12(4,6,4) cluster. (The numbers in parentheses indicate the number of atoms in each crystal plane.) For the π geometry a Ni12(3,8,3) cluster was used. To describe the trough geometry the (3,8,3) cluster was extended by two more layers to yield a Ni24(8,3,4,3,8) cluster. In order to reduce the computational effort a second C2H2 molecule was placed at the "bottom" of every cluster to increase the overall symmetry of the model systems to D_{2h}. Since the two acetylene molecules are separated by more than 5 Å no direct interaction occurs as was confirmed by a test calculation of two free acetylene molecules at 5 Å distance. Similarly, the model clusters for the di-σ, μ and trough geometry were augmented by a second adsorbate molecule during the geometry optimization.

2. Slab models

The two-dimensional (2D) band structure calculations were performed with the help of an improved version of the FLM5S program package, a full-potential, all-electron LDA implementation for extended 2D periodic systems which utilizes expansions of Gaussian-type basis functions to represent the Bloch wave functions (orbital basis set) as well as the charge density and the exchange-correlation potential (fitting basis sets).

Band structure calculations were carried out for all four potential adsorption geometries (Fig. 1) with the Ni(110) substrate being fixed to the ideal crystal structure. The geometries of the adsorbed acetylene molecules were taken from the equilibrium geometry found for the corresponding cluster models. The periodic slab models were chosen according to the observed c(2×2) structure of the adsorbate overlayer. Thus each 2D unit cell contains one acetylene molecule and two nickel atoms per substrate layer. The corresponding reciprocal lattice is shown in Fig. 2. The k-space integration was performed using a two-dimensional analog of the tetrahedron method with 10 k points in the irreducible wedge of the surface Brillouin zone. To facilitate the integration, a rhombic unit cell equivalent to the common hexagonal Brillouin zone was used for this purpose (Fig. 2). Like in the cluster calculations the Xα approximation with α=0.7 was employed for the exchange correlation potential.

The orbital basis sets for Ni, C, and H were the same as in the cluster calculations, except that segmented contractions were utilized here instead of the generalized contraction scheme used in the cluster study. The procedure to construct the fitting basis sets differs from that followed in the cluster work. The exponents α_{n} of the s-type fitting basis sets were generated according to the expression

FIG. 2. Repeated Brillouin zone scheme for the c(2×2) overlayer of the adsorption system C_{2}H_{2}/Ni(110). The rhombic unit cell used for the k-space integration together with the irreducible k points (open circles) are also shown. The experimental k path along the [001] and the [110] directions is indicated by bold solid lines. The same k path is used for the representation of the calculated band structures (Fig. 10). The high-symmetry points Γ, S, and F of the reciprocal lattice are indicated by the filled circles.

![Temperature programmed desorption spectra for m/e=2 for various exposures of acetylene on Ni(110) at a surface temperature of 110 K; heating rate 4 K/s. The inset shows the C_{2}H_{2} coverage as a function of exposure.](image-url)
FIG. 4. Angle resolved UPS spectra for the saturated (θ = 0.5 ML) acetylene layer on Ni(110) for six different experimental geometries (see the text); photon energy 26 eV. Orbital positions and assignment are indicated in the form of a bar diagram. D indicates the plane of detection. E the orientation of the electric field vector.

\[
\alpha_n = \frac{\alpha_{\text{min}}(\alpha_{\text{max}} / \alpha_{\text{min}})^{n/N}}{q^{n(N-n)/[(2N-2)]}},
\]

with the ratio \( q = \lambda_1 / \lambda_N \) between the first and the last incremental factor \( \lambda_n = \alpha_n / \alpha_{n-1} \) being fixed at 0.5. In previous FILMS investigations, this procedure was found to provide balanced fitting basis sets. The most diffuse and tightest \( s \) exponents, \( \alpha_{\text{min}} \) and \( \alpha_{\text{max}} \), were obtained by scaling the corresponding orbital exponents. The exponents of the \( p \)-type polarization functions were chosen to be proportional to the \( s \)-type exponents and fixed such that the radial maximum position of the most diffuse polarization functions was located at the bond centers. The size of the fitting basis sets were (17s,5p) for Ni, (11s,3p) for C, and (8s,2p) for H.

In preliminary band structure calculations for acetylene adsorbed on top of the nickel rows based on a Ni(110) monolayer substrate model, the spin-polarization of the free Ni(110) monolayer was found to be completely quenched upon acetylene adsorption. Similarly, for a double-layer slab model with acetylene in di-\( \sigma \) geometry, the spin-polarization of the "surface" metal layer completely disappeared when acetylene was adsorbed. Furthermore, no significant differences, as compared to the corresponding spin-restricted calculation, could be detected in any of the bands which featured an acetylene population of more than 10%. Thus spin-restricted LDA calculations seem well suited to describe the band structure of acetylene adsorbed at the Ni(110) surface. Therefore, all further calculations were performed in spin-restricted fashion using a substrate consisting of two metal layers.

III. EXPERIMENTAL RESULTS

A. Thermal desorption

The adsorption/desorption behavior of acetylene on clean Ni(110) was investigated by TPD spectroscopy. Independent of coverage the only desorption product was \( H_2 \) (no desorption of \( C_2H_2 \)) indicative of complete dissociation of
Acetylene upon heating. A series of TPD spectra collected at a heating rate of 4 K/s for increasing acetylene exposures at temperatures below 120 K is depicted in Fig. 3. For low initial coverages two H₂ desorption peaks are observed at 320 K and at 380 K (curve a). With increasing exposure the rate maximum of the low-temperature peak shifts to 300 K while the peak at 380 K develops into a shoulder at the high temperature side (curves a–f). Upon further increasing exposures (>0.64 L, not corrected) a new peak starts to grow in at 240 K (curves g–k); simultaneously the high temperature shoulder develops into a broad peak at 360 K and an additional shoulder appears at temperatures between 400 K and 560 K, until saturation occurs at exposures above 2.6 L (curve l).

The thermal desorption of acetylene on Ni(110) was already the subject of a previous study by Strinos et al.2 Overall, the H₂ desorption spectra in Ref. 2 show the same qualitative behavior; only the spectra near saturation coverage differ somewhat from ours. In particular the peak at 360 K and the high temperature shoulder further increases in Ref. 2 at exposures above 2 L. We attribute this difference to an increase in background at higher exposures and not to additional hydrogen desorption from the sample (see coverage calibration). Furthermore, due to the higher adsorption temperature the desorption from acetylene multilayers was not observed in our study.

From the H₂ desorption spectra the amount of adsorbed C₂H₂ as a function of exposure can be determined (see inset of Fig. 3). The desorption signal was calibrated by comparison to the well-known TPD spectra of a pure saturated H₂ layer on Ni(110),24 and yields an acetylene saturation coverage of 0.54±0.05 ML, where 1 ML is defined as 1 adsorbate molecule/substrate atom. This value is in good agreement with the value of 0.56±0.05 ML obtained by a comparison of the C-1s XPS-intensity of the saturated acetylene layer to the C-1s XPS-intensity of the saturated CO layer on Ni(110) with a well-known coverage.25

For acetylene coverages between 0.25 ML and saturation

![Figure 5](image_url)

**FIG. 5.** Angle resolved UPS spectra for the saturated (Θ=0.5 ML) acetylene layer on Ni(110) for six different experimental geometries (see the text); photon energy 50 eV. Orbital positions and assignment are indicated in the form of a bar diagram. D indicates the plane of detection, E the orientation of the electric field vector.
Unoccupied molecular orbitals of acetylene

1σ_g^* (p_z)

1σ_u (p_z)

Molecular orbitals of acetylene

1π_u (p_x)

1π_u (p_z)

3σ_g

2σ_u

2σ_g

FIG. 6. Molecular orbitals of the free acetylene molecule [after Jorgensen and Salem (Ref. 69)]. The symmetry labels correspond to the point group D_3h, of an unperturbed acetylene molecule.

coverage, a c(2×2) LEED pattern with diffuse half order spots is observed. Assuming one molecule per primitive unit cell, the c(2×2) structure corresponds to a coverage of 0.5 ML, in agreement with the saturation coverage derived from TPD and XPS. The fact that the c(2×2) pattern is already observed at intermediate coverages (Θ=0.5×Θ_{sat}) is indicative of island growth. This type of growth is also suggested from ARUPS measurements that reveal significant dispersion of the acetylene-derived peaks even for two dilute acetylene layers. The adsorbate induced spots (half order spots) are not as sharp as the substrate reflexes indicating that the sizes of the individual islands are smaller than the transfer width of the LEED optics (≈100 Å). Annealing of the adsorbed layers results in a sharpening of the c(2×2) pattern with a maximum around 230 K (onset of H_2 desorption) and a transfor-

mation into a sharp (2×1) pattern at temperatures above 550 K. These observations are in good agreement with the results obtained by Stroscio et al. 2

B. Angle resolved UPS

The electronic structure of the saturated acetylene layer has been studied by ARUPS using linear polarized light at photon energies of 26 eV, 30 eV, and 50 eV at six different experimental geometries. For normal incidence (α=0°, only x and y components of E) the electric field vector, E, has been aligned along the two high symmetry directions of the Ni(110) surface (E//110) or E//[001], and the detection plane, D, has been chosen either parallel (D//E) or perpendicular (D⊥E) to the electric field vector. This allows one to distinguish between states that are even or odd with respect to the detection plane. For α=45° (i.e., for an additional z-component of E) spectra have been recorded for both azimuths with the detection plane parallel to E.

In Figs. 4 and 5 the ARUPS spectra collected at photon energies of 26 eV and 50 eV, respectively, are depicted. Overall, the emission from the various acetylene derived levels shows distinct polarization, polar angle, and azimuthal dependencies that indicate a well defined adsorption geometry. In addition, the various peaks exhibit significant changes in binding energy with emission angle (i.e., dispersion), indicative of the formation of a 2D band structure. In the following we will assign the observed peaks to the molecular levels of acetylene and analyze their polar-angle and polarization dependence in detail to determine the orientation and symmetry of the adsorbed molecules by comparison to the predictions from symmetry selection rules. At this point we would like to mention that the emission of the acetylene derived levels is overall very weak for the used photon energy range as compared to C_2H_4/Ni(110). For an overview of the symmetry and the spatial extension, the pertinent molecular orbitals of acetylene are depicted in Fig. 6.

Detailed inspection of the spectra in Figs. 4 and 5 reveals six distinct photoemission peaks. By comparison to the gas phase spectrum of acetylene the three low lying peaks can be clearly identified as the 2σ_u, 2σ_g, and 3σ_g orbitals of molecular acetylene. The corresponding binding energies at the Γ-point (k=0) are 16.8, 11.2, and 9.0 eV, respectively. The assignment of the remaining three peaks cannot be derived simply from a comparison to the gas phase data since the spectrum of the free acetylene molecule contains only one more peak in that energy range, which is due to emission from the twofold degenerate 1π_u orbital. As described in detail below, this degeneracy is lifted by the adsorbate/substrate interaction which leads to a splitting of the 1π_u orbitals; due to additional adsorbate/adsorbate interaction the splitting depends on the parallel momentum, k_z, of the emitted electrons. The two peaks in the binding energy range between 6.0 and 7.5 eV are assigned to emission from these p_x and p_y derived 1π_u bands. (Here and in the following the y direction is taken along the C=C bond of acetylene and the z direction perpendicular to the surface.) Because of the observed dispersion and mixing of the various levels we are not able to simply separate differential shifts of the individual orbitals. By aligning the spectra at the binding energy values
(center of band) of the 2σg and 3σg orbitals with respect to the gas phase spectrum, we obtain a differential shift of the center of the 1πe derived bands by 2.4 eV to higher binding energies. Taking into account this shift and the combined width of the band (1.4 eV) one deduces that both the x and the z component of the 1πe level are shifted differentially with respect to the gas phase value. Assuming a similar relaxation for all valence orbitals, such shifts are usually attributed to a chemical bonding interaction. Since both levels are shifted, both orbitals have to contribute to the chemical bonding, indicating that acetylene is adsorbed on a highly coordinated adsorption site. The origin of the peak at 4.5 eV, which dominates the spectra in the odd geometry (DLE) for E[110] at photon energies of 26 and 30 eV (not shown) will be discussed below.

The orientation of the C–C axis with respect to the surface plane can be deduced from the normal emission behavior of totally symmetric orbitals at different incidence angles. This analysis reveals an orientation of the acetylene molecules with the C–C axis parallel to the surface: both totally symmetric orbitals, 2σg and 3σg, are not observed in normal emission (\( \theta=0^\circ \)) for normal incidence (\( \alpha=0^\circ \)), but show strong intensity for \( \alpha=45^\circ \), i.e., with a normal component of the electric field vector.

Information on the azimuthal orientation is usually derived from the emission behavior of the various orbitals in the symmetry planes of the substrate. The total symmetric 2σg and 3σg orbitals show very weak (if any) emission in the forbidden geometry (DLE). This fact provides a first indication that the acetylene molecules are azimuthally oriented, since for a flat lying acetylene molecule emission from totally symmetric orbitals is forbidden if the electric field vector is aligned along a substrate mirror plane. Further information on the azimuthal orientation can be obtained from the 2σg orbital which is antisymmetric under reflection at the \( \sigma_z \) plane. The 2σg orbital shows strong emission for E[110], but weak emission for E[001]. This indicates that the acetylene molecules are oriented with the C–C axis along the [110] azimuth, i.e., along the densely packed rows of the Ni(110) substrate. However, the alignment of the molecules along the [110] azimuth is not perfect because the emission of the 2σg orbital is weak, but does not vanish for E[001] (see below).

The emission characteristics of the 1πe derived bands can not be used to further check the proposed orientation because of the low cross section of these levels and due to the fact that in the same energy range emission from a Ni satellite is superimposed. Only at certain measurement geometries (e.g., for the spectra at 26 eV photon energy and \( \alpha=45^\circ \) in Fig. 4) two single peaks are clearly observed in the relevant binding energy range (\( E_B=6-8 \) eV) that are attributed to the \( 1\pi_e(p_x) \) and \( 1\pi_e(p_y) \) levels (see above). A clear assignment of the individual \( p_x \) and \( p_y \) components using symmetry selection rules is however difficult due to the dispersion and the mixing of these levels.

Finally, we analyze the origin of the emission at 4.5 eV binding energy which cannot be explained by the emission of a former occupied acetylene derived level. A substrate induced feature can also be ruled out because the ARUPS spectra of the clean sample show no feature in the relevant binding energy range. Since our XPS and also the HREELS experiments show no indication for dissociation of the acetylene molecules upon heating to 180 K, the assignment of this peak to a decomposition product at adsorption temperatures of 110 K can also be ruled out. Thus we have to attribute the emission at 4.5 eV to an acetylene derived state. Indeed, the cluster calculations (described below) indicate a significant contribution of the \( p_z \) component of the unoccupied twofold degenerate \( 1\pi_e \) level to metal derived states at the bottom of the Ni d band. This assignment to a \( 1\pi_e(p_z) \) derived state is confirmed by the analysis of the polarization and polar-angle dependence of the various acetylene derived levels: Overall, the emission behavior of this peak is similar to that of the 2σg orbital, i.e., strong emission for E[110], but no emission for E[001] which implies a similar symmetry character. This symmetry is in agreement with the symmetry of the \( p_z \) component of the former occupied \( 1\pi_e \) orbital. From energetic arguments (i.e., aligning the spectrum of C2H4/Ni(110) with respect to the gas phase spectrum) one could also assign the peak at 4.5 eV to the (not differentially shifted) \( p_z \) component of the occupied \( 1\pi_e \) level. However, this would lead to several discrepancies. First of all, the \( 1\pi_e(p_z) \) orbital is antisymmetric with respect to the C–C axis and the observed emission characteristic thus would imply a molecule with the C–C axis perpendicular to the substrate rows, which is in contradiction (1) to the orientation derived from the symmetry analysis above, (2) to the NEXAFS results (see below), and (3) to the results of the band structure calculations (see below). Secondly, with this assignment one of the two peaks between 6 and 7.5 eV could not be explained. Therefore we are led to the conclusion that the emission at 4.5 eV cannot be assigned to the \( x \) component of the occupied \( 1\pi_e \) orbital, but is indeed due to a metal derived state of appropriate symmetry which is energetically lowered due to the mixing with the unoccupied acetylene \( 1\pi_e \) orbital. The symmetry of this state is necessarily that of the interacting \( p_z \) component and for a flat lying acetylene...
molecule corresponds to the symmetry of the $2\sigma_u$ orbital, i.e., it is antisymmetric with respect to reflection at the $\sigma_z$ plane.

In conclusion, the ARUPS spectra of acetylene on Ni(110) show distinct polarization, polar angle, and azimuthal dependencies which are characteristic for a well defined adsorption geometry. The given assignment of the spectra is consistent with acetylene molecules adsorbed with the C–C axis essentially parallel to the surface and aligned along the [110] azimuth. However the detailed analysis considering the behavior of all molecular orbitals indicates that the azimuthal alignment of the C–C axis is not perfect. The fact that both components of the $1\pi_g$ orbital are involved in the bonding suggests that the molecules are adsorbed in a highly coordinated adsorption site. Taking into account the derived orientation of the molecules we therefore propose that acetylene is adsorbed in the troughs of the Ni(110) substrate. This adsorption site is further supported by the cluster and the band structure calculations as will be discussed below.

C. NEXAFS

To independently check the proposed orientation of acetylene on Ni(110) we have also performed NEXAFS experiments at normal incidence ($\alpha = 0^\circ$). The power of this technique is certainly limited by restricting the measurements to this geometry. Nevertheless, some conclusions on the azimuthal orientation of the adsorbed acetylene molecules can be derived.

The NEXAFS spectra were measured with the electric-field vector aligned either along the [110] or the [001] azimuth (Fig. 7). They have been collected in the Auger electron yield mode with a CFS energy of 264 eV and were normalized to the spectrum of the clean sample. The spectra show three characteristic features at photon energies of 285.5, 290, and 297 eV. The first peak is attributed to the C=C $\pi^*$ resonance. As is evident in the spectrum for E[110], the $\pi^*$ resonance exhibits a shoulder at the low energy side, indicating that this transition consists of two components. A similar splitting of the $\pi^*$ resonance for normal incidence has been reported for acetylene adsorbed on Pt(111) (Ref. 23) where the molecule is also believed to lie flat on the surface. For normal incidence and a flat lying, undistorted acetylene molecule transitions are allowed only into the component of the $1\pi_g(p_x)$ orbital that lies parallel to the surface, transitions to the $1\pi_u(p_y)$ component are symmetry forbidden. However, if the $1\pi_u(p_y)$ component mixes with metal states, as is suggested by the ARUPS results and the cluster calculations, and if therefore the C–H groups are bent upward, the shape of the unoccupied $1\pi_u(p_y)$ derived orbital will be altered, exhibiting an admixture of $p_z$ character (of $\sigma$-type symmetry). Therefore this transition can be observed even for normal incidence, but this resonance should be broadened due to the interaction with the substrate.

For acetylene adsorbed with the C–C axis oriented along a high symmetry direction of the substrate we thus expect a strong transition into the $p_z$ component if the electric-field vector is aligned perpendicular to the molecular axis and a weak transition into the $p_x$ derived component for E aligned along the C–C axis. The fact that the $\pi^*$ resonance is stronger for E[001] confirms that the molecules are oriented with the C–C axis along the [110] direction. Again, this alignment should not be perfect, since the molecule is also believed to lie flat on the surface. In [110] direction clearly consists of two components.

The second peak at 297 eV is attributed to the C–C $\sigma^*$ resonance. Overall, the strength of the $\sigma^*$ resonance is consistent with the molecules lying flat on the surface. This transition does not exhibit an azimuthal dependence that one would expect for an azimuthal oriented molecule, since transitions to $\sigma^*$ type orbitals are allowed only with the electric-field vector aligned along the C–C axis. However, for acetylene the existence of multielectron peaks with noticeable intensity above the ionization potential are well known. These shake-up excitations are broad and overlap with the $\sigma^*$ resonance which is shifted due to the adsorption induced change of the C–C bond length. In particular, a peak at 295 eV is attributed to two-electron excitations with a final state of the type $(1s^{-1})[(1\pi^{-1})$ of (Ref. 61) and is thus proportional to the $\pi^*$ transition intensity. Therefore, the observed intensity at the position of the $\sigma^*$ resonance is not necessarily due to a rotation of the C–C axis out of the [110] azimuth, but may be caused by multielectron excitations, related to the intensity of the $\pi^*$ transition. Finally, we discuss the broad feature around 290 eV. CMS-Xα calculations for the free acetylene molecule by Wurth and Stöhr reveal two states of $\pi$ and $\sigma$ symmetry of similar oscillator strength beyond the ionization potential. Thus a definite assignment cannot be given. However, the polarization dependence is
consistent with a transition into a state of $\pi$ symmetry.

The comparison to the NEXAFS spectrum of the free molecule reveals that the energetic position of the C–C $\alpha^*$ resonance is moved from about 310.7 eV for the free molecule\textsuperscript{24} to lower energies at about 297 eV for acetylene adsorbed on Ni(110). From this shift the bond length may be estimated to be 1.43±0.05 Å by applying the “bond length with a ruler” relationship.\textsuperscript{25,63} Because quantitative predictions based on this scheme are not beyond criticism,\textsuperscript{25} this value should be taken as a qualitative indication only. A similar value of 1.45 Å has been obtained for acetylene adsorbed on Ni(111) (Ref. 24) and Pt(111);\textsuperscript{21} the value is also in good agreement with the results of the cluster calculations for acetylene adsorbed in the troughs of the Ni(110) substrate (see below).

### D. Experimental determination of the 2D band structure

As already mentioned, dispersion is observed in the ARUPS spectra of Figs. 4 and 5 for several molecular levels of acetylene. The 2D band structure has been determined along the two high-symmetry directions of the substrate and is depicted in Fig. 8. The extended adsorbate Brillouin zone that is deduced from the ($2\times2$) LEED pattern is given in Fig. 2. The symmetry points of this structure which are used to label the band structure in Figs. 8 and 10 are also indicated. For the $3\pi_g$ and $2\sigma_g$ as well as the $1\pi_g$ derived bands the data obtained at photon energies of 26, 30, and 50 eV fall right on top of each other within the error margin of ±0.15 eV. Since the emission of the $1\pi_g$ orbital is weak and thus

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**TABLE I.** Comparison of the chemisorption geometry (distances $d$ and $180^\circ$ complement $\gamma$ of the C–C–H angle), and binding energy $E_b$ calculated for the Ni$_4$(C$_2$H$_2$)$_2$ and Ni$_4$(C$_2$H$_3$)$_2$ cluster models, respectively, and the experimental data of various nickel olefine complexes. All values are reported (separated by commas) for cases where different experimental geometries exist for a specified binding type (coordination).

<table>
<thead>
<tr>
<th>System</th>
<th>Coordination</th>
<th>$d$(Ni–C) (Å)</th>
<th>$d$(C–C) (Å)</th>
<th>$\gamma$(CH) (°)</th>
<th>$E_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_4$(C$_2$H$_2$)$_2$</td>
<td>$\pi$</td>
<td>1.85</td>
<td>1.29</td>
<td>47</td>
<td>2.1</td>
</tr>
<tr>
<td>Ni$_4$(C$_2$H$_3$)$_2$</td>
<td>$\text{di-}\sigma$</td>
<td>1.83</td>
<td>1.31</td>
<td>47</td>
<td>2.7</td>
</tr>
<tr>
<td>Ni$_4$(C$_2$H$_3$)$_2$</td>
<td>$\mu$</td>
<td>1.89</td>
<td>1.35</td>
<td>36</td>
<td>3.0</td>
</tr>
<tr>
<td>Ni$_4$(C$_2$H$_3$)$_2$</td>
<td>trough</td>
<td>1.96, 2.05$^a$</td>
<td>1.42</td>
<td>55</td>
<td>3.3</td>
</tr>
<tr>
<td><strong>Experiment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_2$/Ni(111) (exp)$^b$</td>
<td></td>
<td>1.98</td>
<td>1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni (olefine 1)$^c$</td>
<td>threefold</td>
<td>1.94, 2.21</td>
<td>1.28, 1.33</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Ni (olefine 2)$^d$</td>
<td>threefold</td>
<td>1.90, 2.00</td>
<td>1.43</td>
<td>53.3</td>
<td></td>
</tr>
<tr>
<td>Ni (olefine 3)$^e$</td>
<td>$\mu$</td>
<td>1.927</td>
<td>1.386</td>
<td>39.4</td>
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</tr>
<tr>
<td>Pt (olefine 4)$^f$</td>
<td>$\pi$</td>
<td>2.025</td>
<td>1.280</td>
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<td></td>
</tr>
<tr>
<td>Pt (olefine 5)$^g$</td>
<td>$\pi$</td>
<td>2.01</td>
<td>1.26</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Co (olefine 6)$^h$</td>
<td>$\mu$</td>
<td>2.10</td>
<td>1.36</td>
<td>48</td>
<td>60</td>
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<tr>
<td><strong>Gas phase</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_2$ (exp)$^i$</td>
<td></td>
<td></td>
<td>1.208</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_2$ (calc)</td>
<td></td>
<td></td>
<td>1.208</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Distance of the carbon atom from first and second row nickel atom, respectively.

$^b$Reference 66.

$^c$Ni(CO)$_2$(CF$_3$C$_2$F)$_2$, Ref. 70.

$^d$Ni$_4$(CO)$_2$(CF$_3$C$_2$F)$_2$, Ref. 70.

$^e$Reference 45.

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**TABLE II.** Comparison of the geometry and the binding energy $E_b$ calculated for the Ni$_4$(C$_2$H$_2$)$_2$ and the Ni$_4$(C$_2$H$_3$)$_2$ cluster models at the local density (LDA) and the gradient correction (GC) level of theory. The clusters used for the various binding types (coordination) are the same as in Table I.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$d$(Ni–C) (Å)</th>
<th>$d$(C–C) (Å)</th>
<th>$\gamma$(CH) (°)</th>
<th>$E_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi$</td>
<td>1.85</td>
<td>1.96</td>
<td>1.29</td>
<td>2.08</td>
</tr>
<tr>
<td>$\text{di-}\sigma$</td>
<td>1.83</td>
<td>1.92</td>
<td>1.31</td>
<td>2.68</td>
</tr>
<tr>
<td>$\mu$</td>
<td>1.89</td>
<td>1.97</td>
<td>1.35</td>
<td>2.98</td>
</tr>
<tr>
<td>trough</td>
<td>1.96$^i$</td>
<td>2.02$^i$</td>
<td>1.42</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>2.05$^i$</td>
<td>2.19$^i$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^i$Distance from first row nickel atom.

$^j$Distance from second row nickel atom.

obscured by emission of the Ni-satellite, the 1πg bands are not well resolved and the apparent dispersion might therefore also be caused by angle dependent intensity mixing. However, at the Y points of the surface Brillouin zone a splitting of the 1πg derived bands of 1.5 eV is clearly resolved. At this high-symmetry point the bands belong to different representations and thus no mixing or degeneracy of the bands is expected. The strongest dispersion of 0.6 eV is observed for the 2πg band along the [110] direction with a very characteristic minimum between the Y point and the Γ point. Along the [001] direction this band shows essentially no dispersion. The 3σg derived bands exhibit a dispersion of about 0.3 eV magnitude along the [001] direction whereas the 2σg band shows hardly any dispersion as expected from its localized character. A detailed analysis of the band structure will be given in Sec. IV B.

IV. THEORETICAL RESULTS
A. Cluster calculations

The results of the geometry optimization of the four different adsorption sites are summarized in Table I together with experimentally determined structures of various transition metal complexes with acetylene as a ligand. The acetylene structures of the π and the di-σ geometry are calculated to be very similar, a finding which is reminiscent of the situation for ethylene adsorbed on Ni(110). In both cases the C–C bond length increases strongly, by about 0.1 Å, compared to the value of the free molecule, reaching 1.29 and 1.31 Å for π and di-σ geometry, respectively. The other two sites examined exhibit rather different equilibrium geometries. In the case of the μ adsorption site the C–C distance, 1.35 Å, is longer than the calculated value for the C–C double bond in the free ethylene molecule, 1.33 Å. For the adsorption site in the trough, the C–C bond is elongated even further, to 1.42 Å; this value is essentially identical to the one calculated for ethylene adsorbed on the top rows of the nickel (110) surface. The elongation of the C–C distance is accompanied by an out-of-plane bending of the hydrogen atoms of 47° for the π and di-σ structure and of 55° for the trough geometry. Thus in the trough geometry the tilting angle almost reaches the value of 59° which corresponds to the H–C–C angle calculated for the free ethylene molecule. Taken together, these results indicate a rehybridization of the carbon configuration from sp to acetylene and sp² and beyond. For ethylene adsorbed on Ni(110) an analogous rehybridization from sp² towards sp³ has been observed. Only the μ geometry exhibits a different behavior, a longer C–C bond than the π and the di-σ geometries, yet a smaller tilting angle of the H–H bond, 35°.

The structural data available for transition metal acetylene complexes (Table I) are similar to the ones calculated in the present study of chemisorption model clusters. The experimental values for the C–C bond length fall in the range of 1.26–1.46 Å, the tilting angles vary from 27° to 60°. Ranging from 1.83 to 2.05 Å the LDA values for the Ni–C distances are in general somewhat shorter than the corresponding experimental data (Table I). However, the optimized Ni–C bond length significantly depends on the form of the exchange-correlation potential employed. As can be seen from Table II, the Ni–C bond length changes remarkably when gradient corrected exchange-correlation potentials are used. The tendency of the LDA results to overestimate the strength of the transition metal-to-ligand bond is reduced by the gradient corrections; for all four geometries, the Ni–C distance increases by about 0.1 Å. On the other hand, the influence of gradient corrections on the relaxed acetylene geometry is quite small. Similar results were found calculating the free acetylene molecule. There the C–C bond remains essentially unchanged when gradient corrections are applied.

The influence of the gradient corrections on the adsorbate binding energy is quite noticeable. Overall the GC binding energies are lower by about 2 eV than the corresponding LDA results. At the LDA level of theory, the trough geometry seems favored by about 0.3 eV, but GC binding energies favor the μ site by about 0.3 eV (Table II). However, it is well known that the binding energy converges rather slowly with cluster size and the observed energy differences among the various sites are certainly of the order of fluctuations accompanied by a change in the model cluster size. Therefore, no definitive conclusion concerning the adsorption site can be drawn from the calculated values of binding energy alone. On the other hand, the μ geometry has been excluded in the analysis of the ARUPS results (see above).
Recent experiments by Bao et al. show that on Ni(111) acetylene prefers the adsorption site of highest coordination. Assuming the same preference on the Ni(110) surface, the trough geometry should be the favorite adsorption site. As will be discussed in detail below, this adsorption site is supported by the band structure calculations.

The one-electron level spectra of the C$_2$H$_2$/Ni(110) model clusters for the four different geometries are compared in Fig. 9. The orbitals of the free acetylene molecule are labeled according to the irreducible representations of the symmetry group $D_{2h}$. The four spectra are aligned at the Fermi level to facilitate a comparison and only spin-averaged orbital energies are displayed; the spin splitting is rather small, less than 0.5 eV for all given orbitals (the largest splitting is observed for levels within the nickel 3d band). For levels below the Ni 3d manifold (indicated by the shaded areas) the splitting is even less than 0.2 eV. Thus any spin splitting will be neglected during the following discussion.

As expected, the influence of interaction between cluster and adsorbate on the low-lying, acetylene $\sigma$ derived orbitals is very weak. Except for the trough geometry the adsorbate population in each of these orbitals amounts to more than 90% (Fig. 9). In the case of the trough geometry, the acetylene molecule is surrounded by four nickel atoms in the neighboring rows of the (110) surface. Correspondingly the substrate population in the $\sigma$ derived acetylene orbitals is somewhat higher (about 10%). This slight increase of the substrate population, however, might be just a consequence of the well-known ambiguities of a Mulliken population analysis.

The differences in the orbital energies of the $\sigma$ derived acetylene orbitals between the various adsorption geometries are mainly due to the geometrical changes of the adsorbate and the concomitant rehybridization. This has been verified by test calculations on isolated molecules in the equilibrium geometry of the corresponding adsorption complexes where qualitatively the same energetic shifts of the $\sigma$ orbitals were found. Especially the profound downward shift of the $2\alpha_3$ orbital for the trough geometry can clearly be attributed to the strong elongation of the C=C bond in this adsorption complex (Table I).

If one invokes a simple two-level model for the interaction of the highest occupied molecular orbital (HOMO) of the acetylene molecule (1$\pi_1$) with substrate orbitals of energy close to the lower end of the Ni 3d manifold, one expects a pair of adsorbate–substrate bonding orbitals below the 3d manifold and a corresponding pair of antibonding orbitals with significant adsorbate character somewhere in the upper region of the 3d band. The first two orbitals are the 1$\pi_1$(p$_z$) and 1$\pi_1$(p$_x$) orbitals mentioned previously. Similarly, the lowest unoccupied molecular orbital (LUMO) of acetylene, 1$\pi_1^*$, interacts with orbitals of the Ni 3d manifold leading to the formation of a pair of antibonding orbitals at higher energies and several backbonding orbitals with high acetylene population within the 3d manifold. For simplicity, the latter orbitals will be denoted as 1$\pi_1$(p$_z$) and 1$\pi_1$(p$_x$), or simply as $p_{x,z}^\pi$ and $p_{x,z}^\pi$. The same notation will be adopted to label the various energy bands of the calculated band structures (see below). However, one should keep in mind that these orbitals of the adsorption complex are in general dominated by substrate character. As already discussed they may be identified with the feature around 4.5 eV in the
ARUPS spectra (see Sec. III B). Of course, the actual situation in an adsorption cluster is more complex, but nevertheless some features of the simple two-level interaction model can be identified in the one-electron spectra shown in Fig. 9. In this spirit, the high-lying orbitals with significant adsorbate character are connected by solid and dashed lines for \( p_z \)-type and \( p_x \)-type orbitals, respectively (Fig. 9).

For the HOMO as well as for the LUMO a strong interaction between the metal and the acetylene \( p_z \) orbitals is found, resulting in a profound downward shift of the 1\( \pi_e(p_z) \) and 1\( \pi_m(p_z) \) levels as compared to the corresponding orbital energies of the free acetylene molecule (about 3.5 eV for \( p_z \) and up to 8 eV for \( p_x^* \)). This shift is largest for the trough geometry, as can be rationalized by the unique high coordination of the adsorbed acetylene molecule in this model. Furthermore it should be pointed out that the energy of the lowest lying level with \( p_x^* \) population is far below the Fermi level in each of the four adsorption models. Hence a strong back donation from the surface to the adsorbate takes place via these occupied orbitals, consistent with the calculated elongation of the C–C bond.

Another interesting aspect of the level spectra shown in Fig. 9 is the energy of the \( p_x \) partner of the 1\( \pi_m \) and 1\( \pi_e \) levels, respectively, compared to that of the corresponding \( p_z \) orbitals. For the \( \delta-\sigma \) and the \( \pi \) geometries where the adsorbate is located relatively high above the Ni(110) rows (see Tables I and II) and thus only a poor overlap between the \( p_z \)-type orbitals and the substrate occurs, the energy shifts of these orbitals are much smaller than those of the \( p_x \)-type orbitals. On the other hand, in the case of the trough and the \( \mu \) geometry where the adsorbate is located significantly closer to the substrate, the \( p_x \)-type orbitals, too, may overlap with the appropriate substrate orbitals. As a consequence one finds a \( p_x \) orbital above the lowest lying \( p_z \) orbital instead of a second \( p_z \) orbital as is the case for the \( \delta-\sigma \) and the \( \pi \) geometry (Fig. 9). The same holds for the 1\( \pi_m \) levels. There is even an occupied orbital with 1\( \pi_m(p_z) \) admixture which therefore participates in the back donation from the substrate to the antibonding states of the adsorbed acetylene. For the \( \delta-\sigma \) and the \( \pi \) geometry, the levels of this type remain above the Fermi energy by about 3 eV. Again, this fact correlates with the calculated elongation of the C–C bond which is more pronounced (by 0.04–0.11 Å) for the \( \mu \) and trough geometry than for the \( \delta-\sigma \) and the \( \pi \) geometry (Table I).

**B. Band structure calculations**

The cluster models did not provide unambiguous evidence on the geometry of the acetylene adsorption complex at the Ni(110) surface. Hence, similar to the successful strategy used for the chemisorption system C\(_2\)H\(_2\)/Ni(110) (Ref. 34) the band structures of the various models have been calculated and will be compared to the experimentally determined ARUPS band structure to clarify the structure of the adsorption complex. However, to corroborate the significance of these calculations, the dispersion of the adsorbate derived energy bands and the characteristic differences between the various structure models will be analyzed in some detail first.

The band structures for the four geometries, \( \delta-\sigma \), \( \pi \), trough, and \( \mu \), have been calculated using a double layer model of the Ni(110) substrate (Fig. 10). Bands with Bloch wave functions exhibiting significant acetylene characteristics (more than 30% for the \( 1\pi_m \) bands and at least 50% for all other bands) are emphasized in Fig. 10. For the sake of simplicity, these bands will be denoted as acetylene bands in the following discussion.

Qualitatively, the three low-lying acetylene \( \sigma \) bands show the same \( k \)-dependence for all three geometries with acetylene aligned parallel to the Ni(110) rows. From the original \( \Gamma \) point to the first repeated \( \Gamma \) point in the [110] direction the 2\( \sigma_\pi \) and 3\( \sigma_\pi \) bands exhibit a topology with two local minima or maxima, respectively, while the dispersion along the [001] direction is significantly weaker (Fig. 10). The 2\( \sigma_\pi \) band, on the other hand, shows only weak dispersion. Since the acetylene population in these Bloch states amounts to about 90% the dispersion of the \( \sigma \) bands is mainly due to the direct lateral interadsorbate interaction. This rationalization has been verified by a comparison with the bands of an unsupported acetylene monolayer. Nevertheless some influence of the substrate is discernible in the band structures. The dispersion found for the trough geometry is noticeably larger than that of the \( \delta-\sigma \) and the \( \pi \) geometries, reflecting the higher substrate coordination of the adsorbate.

The band dispersions found for the \( \mu \) geometry with the acetylene C–C axis perpendicular to the nickel rows are quite different. A single maximum and minimum in the \( k \)-dependence of the 2\( \sigma_\pi \) and 3\( \sigma_\pi \) bands along the [110] direction and an equally profound dispersion of these bands along the [001] direction. Both features can be explained within a simple molecular orbital picture of a free acetylene monolayer using nearest-neighbor interaction. Based on the shape of the free acetylene molecular orbitals (Fig. 6), the \( k \)-dependent lateral interaction of those orbitals may be sketched (see Fig. 11). In the case of the \( \delta-\sigma \), the \( \pi \), and the trough geometry the nearest neighbors to an adsorbed acetylene are those along the nickel rows in the [110] direction. The phase of these neighboring molecules is unaffected by the different \( k \)-points along [001], the \( \Sigma \) line (Fig. 11 panel a and b), and thus the corresponding bands should not exhibit any dispersion; this is indeed confirmed by the calculated band structures (Fig. 10). In the case of the \( \mu \) geometry, the nearest acetylene neighbors are those on the nearest nickel row, i.e., in the [112] direction. For the \( \sigma_\pi \) bands (panel a) the phase between nearest-neighbor adsorbates alters from a binding character at the \( \Gamma \) point to an antibonding behavior at the \( \Gamma \) point while the \( \sigma_\pi \) band (panel b) is governed by an antibonding character at the \( \Gamma \) point and a bonding overlap between nearest-neighbor acetylene molecules at the \( \Gamma \) point (Fig. 11). As a consequence, the \( \sigma_\pi \) bands exhibit an upward dispersion from \( \Gamma \) to \( \Gamma \) and the \( \sigma_\pi \) band a downward dispersion as can be seen in the calculated band structures of Fig. 10. Similar arguments may be invoked to rationalize the dispersion along the [110] direction (the \( \Delta \) line). For the \( \mu \) geometry the overlap with the nearest neighbors in the [112]
direction is changing its character when going from the \( \vec{Y} \) point to the \( \vec{Y} \) point, resulting in a dispersion with a single maximum or minimum, respectively, at the \( \vec{Y} \) point (Fig. 10). For the other three geometries with acetylene aligned parallel to the Ni(110) rows, the overlap toward the next-neighbor adsorbates on the same nickel row is equal at the \( \vec{Y} \) and the \( \vec{Y} \) point while it has opposite character somewhere in between. Consequently the dispersion of these bands should exhibit two separate local maxima or minima on the path from the original \( \vec{Y} \) point to the first repeated \( \vec{Y} \) point along [110], just as found in the calculated band structures (Fig. 10).

Concerning the acetylene \( \pi \) derived bands, the strong interaction between the substrate and the HOMO \( 1\pi_p(p) \) states of the adsorbed acetylene molecule which has already been observed in the cluster models can be seen in the band structures of the four structure models as well. It leads to an energetically isolated \( p_2 \) band well below the 3\( d \) band complex of the substrate (Fig. 10). Compared to the 3\( \sigma_g \) band, the dispersion of the 1\( \pi_p(p) \) band is much too strong to be rationalized by direct lateral acetylene interaction. Note that the acetylene 1\( \pi_p(p) \) orbital is mainly localized at the C–C bond while the 3\( \sigma_g \) orbital is spread out over the whole molecule including the terminating hydrogen atoms (Fig. 6). Indirect (through bond) interaction via the nickel orbitals has to be taken into account. We will refrain from a detailed discussion of the influence of these substrate admixtures in the topology of the \( \pi \) bands, but point out that a consistent explanation of the dispersion of the \( \pi \) bands may be obtained by including the substrate orbitals into the overlap arguments invoked above. In the case of the 1\( \pi_p(p) \) band of the di-\( \sigma \) and the \( \pi \) geometry, for example, the dispersion is mainly due to the \( k \)-dependence of an admixture of Ni 4\( s \) character at the bottom of the 3\( d \) manifold. Thus the local minimum at the \( \vec{Y} \) point along the [110] direction is a consequence of the doubling of the substrate unit cell in the (2\( \times \)2) overlayer and the concomitant doubling of the Ni 4\( s \) band.

In agreement with the findings of the cluster investigation, one of the most obvious differences between the di-\( \sigma \) and the \( \pi \) geometry and the two remaining geometries is the interaction of the acetylene HOMO \( p_2 \) states with the substrate. As already mentioned, the distance of the adsorbed acetylene molecule to the Ni(110) surface atoms is sufficiently small to allow for a significant overlap between the flat-lying acetylene \( p_2 \) and appropriate substrate orbitals in the case of the trough and the \( \mu \) geometry. This results in the separate 1\( \pi_p(p) \) band well below the \( d \)-band manifold as discernible in the calculated band structures (Fig. 10). Depending on the orientation of the adsorbate and the \( k \)-direction, two possibilities occur. In one case, two acetylene HOMO bands (\( p_2 \) and \( p_3 \)) exhibit differing symmetry character with respect to the mirror plane parallel to the \( k \) direction and thus the corresponding bands are allowed to cross (along [110] for the trough geometry and along [001] for the \( \mu \) geometry). Alternatively, there is no symmetry operation to distinguish between those two states and band crossings are forbidden, along [001] for the trough geometry and along [110] for the \( \mu \) geometry. Nevertheless, since the two \( \vec{Y} \) points along the [110] and the [001] direction are equivalent, the chemical character of these bands has to change even in the case of a forbidden crossing as is indicated in Fig. 10 by the separate labels inside the band structure panel.

In the case of the di-\( \sigma \) and the \( \pi \) geometries where acetylene is located relatively high above the Ni(110) rows (Table I) in addition to the 1\( \pi_p(p) \) band two more bands with significant adsorbate \( \pi \) population in the corresponding Bloch wave functions can be found in the lower energy region of the 3\( d \) band complex (Fig. 10). Employing a detailed population analysis these states have been identified as bonding linear combinations between substrate orbitals and the acetylene HOMO 1\( \pi_p(p) \) and the LUMO 1\( \pi_s(p) \), respectively. As already seen in the one-electron level spectra obtained by the model cluster calculations, the overlap of the acetylene LUMO 1\( \pi_p(p) \) with the substrate is too weak to result in an occupied bonding 1\( \pi_s(p) \) state. In the trough and the \( \mu \) geometries, however, altogether four bands with significant acetylene 1\( \pi \) admixtures (the two \( l \)\( \sigma \) bands already discussed and two further bands attributed to \( l \pi \) adsorbate admixtures) may be found in the vicinity of the bottom of the 3\( d \) band complex (Fig. 10). For the high coordinated trough geometry the 1\( \pi_p(p) \) band even separates from the 3\( d \) manifold. This high lateral coordination of the adsorbate which is unique to this structure model is also reflected in the noticeably stronger dispersion of the 1\( \pi_s \) bands compared to the other structure models.

V. COMPARISON BETWEEN EXPERIMENT AND THEORY

In the last section various profound differences have been uncovered between the calculated band structures of the different structure models in the energy range relevant for a comparison to the experimentally determined band structure of acetylene adsorbed on the Ni(110) surface (Fig. 10). A partial exception is provided by the di-\( \sigma \) and the \( \pi \) geometry whose band structures only differ in the magnitude of the band separation between the 2\( \sigma \) and 3\( \sigma \) as well as between 1\( \pi_p(p) \) and the bottom of the 3\( d \) manifold. The characteristic dispersion features of the various bands that are sensitive to the structure of the adsorption complex should enable one to identify the geometry of the adsorption system \((2\times2)\) \( C_2H_2/Ni(110) \). This comparison cannot be expected to yield quantitative agreement with the measured band structure since LDF one-particle energies are not directly related to electronic binding energies. However, recently a similar strategy has been successfully employed in order to clarify the geometrical structure of the periodic adsorption system \((2\times2)\) \( C_2H_2/Ni(110) \) on the basis of semiempirical band structure calculations. In that case the densely packed adsorbate overlayer led to characteristic geometry-dependent band dispersions of the various bands associated with the ethylene \( \sigma \) molecular orbitals. Here, bands generated by both acetylene \( \sigma \) and \( \pi \) levels have to be taken into account.
binding energies at both of these k points are discernible. Thus the μ geometry with the C–C axis of acetylene aligned perpendicular to the Ni(110) rows can immediately be excluded, in agreement with the results from the analysis of the angle dependence of the ARUPS results (see above). Another characteristic feature of the experimental band structure is the band at 6 eV which does not exhibit any significant dispersion. Near the Γ points along the [001] and the [110] directions this band is accompanied by partial satellite bands with an energy of about 7.5 eV which do not show any dispersion either. Both aspects of the experimental band structure are reproduced most satisfactorily by the calculated band structure for the trough geometry (see Fig. 8), which is the only one of the remaining structure models, di-σ, π and trough, with both energetically split 1πT bands separated from the 3d manifold (Fig. 10).

A strong argument favoring the trough geometry would be the observation of an allowed band crossing of the 1πT(pπ) and 1πT(pπ) band along the [110] direction. The experimental data are compatible with such a crossing although a clear identification is certainly not possible. This interpretation relies on the assignment of the downward branch at 7 eV which is discernible around 2 Å⁻¹ in the right panel of the experimental band structure (Fig. 8). However, the position of this feature does not exactly match one of the theoretically determined bands. Together with the indication gleaned from the ARUPS results that the acetylene 1πT(pπ) orbital is strongly involved in the adsorbate–substrate interaction (see above), the trough geometry is the most likely candidate for the structure of the adsorption system. Further support for this interpretation is connected to the third band discernible in the ARUPS data which matches very nicely the almost separated 1πT(pπ) band calculated just below the 3d band complex of the substrate (Fig. 8). Moreover the computed gap of 1.3–2.0 eV between the 2πu and the 3σg band agrees quite well with the experimental value which amounts to about 2 eV, if one take into account that the LDF one-particle energies are compared to experimental ionization energies. Furthermore, since relaxation effects are not included in the computed one-particle energies, the calculated and experimental band structures are aligned by a global shift of 2.4 eV. Overall the agreement between the experimental and theoretical band structure for the trough geometry is very satisfactory.

VI. SUMMARY

We have investigated the adsorption of acetylene on Ni(110) by various experimental and theoretical methods. The experimental studies include temperature programmed desorption (TPD), low energy electron diffraction (LEED), angle resolved ultraviolet photoelectron spectroscopy (ARUPS) using linearly polarized synchrotron radiation, and near edge X-ray absorption fine structure (NEXAFS); from the theoretical side LCGTO-DF calculations have been applied both at the local density level and employing a gradient corrected (GC) exchange-correlation energy functional; furthermore two-dimensional band structure calculations were performed using an improved version of the FILMS program package.

Acetylene is molecularly adsorbed on Ni(110) at 100 K with a saturation coverage of ~0.5 ML (1 ML = 1 molecule/surface atom); starting at ~50% of saturation, a c(2×2) LEED pattern is observed up to saturation coverage indicative of the formation of two-dimensional islands. Upon heating complete decomposition of acetylene occurs. From the ARUPS and the NEXAFS spectra an orientation of the C–C axis parallel to the surface is deduced with a preferential alignment of the C–C axis along the substrate troughs ([110] azimuth). From the differential shifts of both the pπ and pπ components of the 1πT orbital to higher binding energies on the order of 1.5–2.5 eV a highly coordinated adsorption site in the substrate troughs is deduced. Furthermore, an additional peak in the UPS spectrum of acetylene on Ni(110) that has no counterpart in the spectrum of the free molecule is attributed to the pπ-component of the formerly unoccupied 1πT orbital that is lowered below the substrate d-manifold by the chemical interaction with the substrate.

The latter assignment as well as the acetylene adsorption site in the troughs of the Ni(110) surface have been determined in conjunction with theoretical cluster and slab model studies that have been performed for various possible adsorption sites. These include di-σ and π adsorption geometries with the C–C axis along [110] and the molecule adsorbed on the rows, an adsorption site in the troughs of the Ni(110) surface with the C–C axis along [110], and a μ-bonding site with the molecule adsorbed on the short bridge of the rows and the C–C axis perpendicular to the troughs, i.e., along [001]. While the equilibrium geometry of the adsorbed acetylene molecule is essentially unaffected by the use of gradient corrections to the exchange-correlation potential, the adsorbate–substrate distance is substantially increased, by about 0.1 Å. This elongation is accompanied by a profound weakening of the adsorbate–substrate bond by roughly 2 eV. According to the binding energies, the trough geometry seems favored by about 0.3 eV for the LDA calculations, while applying gradient corrections, the adsorbate is most strongly bound (by about 0.3 eV) in the μ geometry. However, since the energetic differences between the various structure models are rather small, no conclusive statement concerning the adsorption geometry can be deduced from the binding energies alone. Comparing the one-particle spectra of the various cluster models and the band structure of the corresponding slab models, the formerly unoccupied 1πT(pπ) orbital below the substrate d-band is only reproduced for the trough geometry. At the G2 level of theory the optimized geometry parameter for the latter geometry are 2.02 and 2.19 Å for the distance of the carbon atom to the first and second row nickel atoms, respectively, 1.42 Å for the C–C distance and 56° for the CH bending angle with respect to the substrate plane. The relatively long C–C bond length (that is in good agreement with the value determined from NEXAFS, 1.43±0.05 Å) and the large bending angle indicate a strong degree of hybridization of the C atom of sp² or beyond.

Further information of the interaction of acetylene with Ni(110) as well as on lateral interactions in the adsorbed layer is obtained from the dispersion of the various levels in the ARUPS spectra. The experimentally determined adsor-
bated band structure shows significant and distinct dispersion of the various molecular levels. By comparison to the 2D band structure calculation, the orientation and adsorption site of acetylene is verified. These calculations, too, have been performed for acetylene adsorbed in the dis-σ, π, trough, and μ geometry. The k dependence of the various bands, in particular the 2σ bands along the [001] and [110] directions, allow one to determine the rule out an adsorption geometry with the C–C axis perpendicular to the substrate rows. For the other three geometries the best agreement with the experimental spectra are obtained for adsorption in the substrate troughs.

Finally we want to point out that for a complicated adsorption system such as acetylene on Ni(110), detailed conclusions on the orientation, adsorption site, bonding interaction, and adsorbate band structure can only be obtained by the combination of different experimental methods along with state-of-the-art model calculations.

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