

9. Adsorption of ethylene on Au(110)-(1×2)

Comparison of carbon monoxide and ethylene adsorption is particularly instructive since both molecules share common structural elements, e.g., π bonds, and have the same mass. They differ, when adsorbed on transition metal surfaces, in the type of the surface chemical bond. CO is known for its ability to form strong σ -donor bonds, in contrast to C_2H_4 , which forms weak π -donor bonds. Thus, major differences in the adsorption behaviour should be expected if the CO 5σ orbital is involved in the chemisorptive bond. However, it proves that both molecules possess strikingly similar desorption states and that ethylene is stronger bound to gold than CO. These observations support the idea that the CO 5σ orbital plays no important role in the CO-gold bond, an idea that was established in Chapter 8. Since both molecules form also π^* acceptor bonds ('back-bonding') with metal atoms on surfaces and in complexes, it is likely that these bonds are more important for the interaction with gold than the donor bonds, possibly because gold has no empty levels of sufficiently low energy for an effective molecule \rightarrow metal donor interaction.

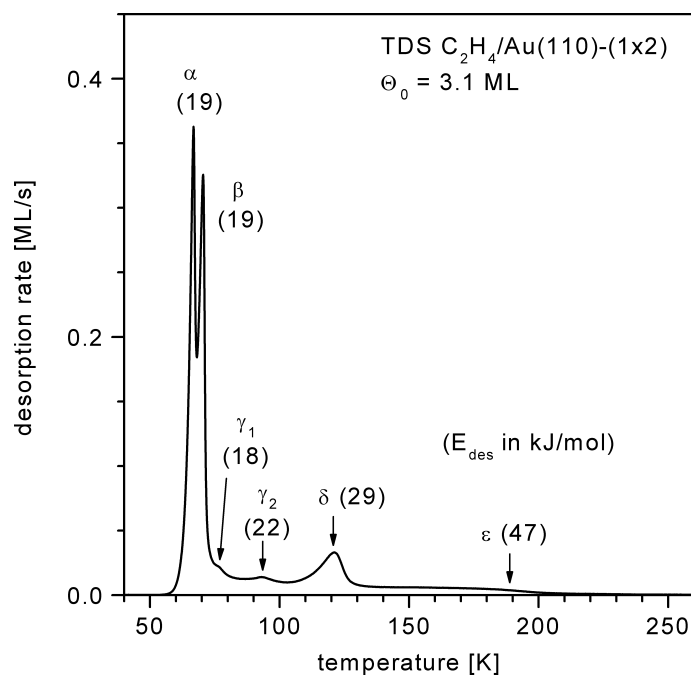


Fig. 9.1: Thermal desorption spectrum of 3.1 ML ethylene¹ on Au(110)-(1×2), taken with a heating rate of 1.00 K/s by detection of $C_2H_3^+$ ($m/z = 27$). Dosing pressure: 1×10^{-8} mbar. Desorption activation energies E_{des} (in kJ/mol) for the non-zero order peaks γ_1 - ϵ after Redhead [Re62] as indicated, using 1st-order frequency factors of $k_B T_{\text{max}}/h$ (with T_{max} marked by arrows). For α and β , E_{des} was obtained from a leading edge analysis [Ha84]. See Section 4.1.2 for the experimental details of the thermal desorption experiment and compare with the CO TD spectrum in Fig. 8.1.

¹ Ethylene gas 3.5, purity >99.95%, Messer Griesheim, Germany.

The heterogeneously catalysed oxidation of both CO and ethylene is of industrial importance. Ethylene epoxidation is usually performed on unsupported silver catalysts, but gold on an appropriate support might also be effective. The only effort in this direction, by Cant and Hall [Ca71], was not particularly promising, as several gold-based catalysts, e.g. gold sponge, Au/SiO₂, and Au/ α -Al₂O₃, proved to favour the total oxidation to CO₂ and H₂O. However, it is now well established that the preparation conditions play a decisive role especially in gold catalysis, which is one of the reasons why the gold-based catalysts have been regarded as unreliable for some time. Only recently, however, *propene* epoxidation has been achieved on supported gold clusters [Zw02], although the reaction of propene with chemisorbed oxygen on Au(111) and Au(100) produces only CO₂, CO, and H₂O [Da00]. In the only previous UHV single-crystal study of *ethylene* on gold, by Outka and Madix [Ou87b], the molecule was adsorbed on clean and oxygen-precovered Au(110)-(1×2) at temperatures above 110 K. However, no reaction with chemisorbed oxygen occurred.

Apart from catalysing oxidation reactions, supported gold catalysts proved also effective in the selective hydrogenation of acetylene to ethylene or ethane. In a study on Au/Al₂O₃ catalysts it was found that the product ratio depends strongly on temperature [Ji00]. Thus, a study of ethylene adsorption on gold should also be relevant for other fields of catalysis on gold.

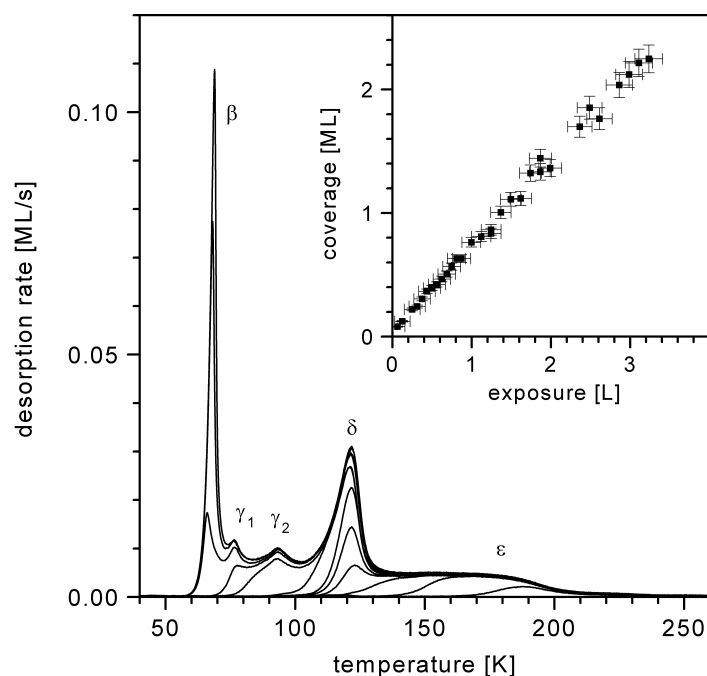


Fig. 9.2: TDS ethylene/ Au(110)-(1×2). Coverage series for low and medium coverages, taken with a heating rate of 2.35 K/s. The spectra correspond to the following initial coverages (in ML): 0.08; 0.22; 0.30; 0.39; 0.47; 0.57; 0.76; 0.84; 1.00; 1.12; 1.33; 1.37. Inset: Coverage (as evaluated by integration of the TD spectra) vs. exposure. Compare with Fig. 8.2.

9.1. Thermal desorption spectroscopy (TDS)

The ethylene thermal desorption spectra displayed in Figs. 9.1 - 9.3 allow direct comparison with the carbon monoxide spectra in Figs. 8.1 - 8.3. Already the overview C_2H_4 TD spectrum in Fig. 9.1 (3.1 ML, 4.25 L)², in which all 6 desorption states are populated, reveals the striking resemblance with the respective CO TDS in Fig. 8.1. In analogy to CO, the monolayer (ML) is associated with the peaks ϵ (between 130 K and 230 K), δ (121 K), γ_2 (93 K), and γ_1 (76 K), whereas β ($66 \text{ K} \leq T_{\text{max}} \leq 70 \text{ K}$) is attributed to the second layer and the non-saturating, zero-order α peak ($\geq 64 \text{ K}$) to condensed ethylene. As shown in the following sections, this assignment is supported by UPS and $\Delta\phi$. Except for the general high-temperature shift and the split γ peak in the case of C_2H_4 , the CO and C_2H_4 TD spectra show essentially the same features. The large low-temperature shift of the ϵ peak in Fig. 9.2 indicates again strong repulsive interactions between the adsorbed molecules. The extremely wide range of desorption temperatures for the monolayer range suggests that chemisorbed (ϵ) and physisorbed (δ , γ_1 , γ_2) species coexist in the first layer.

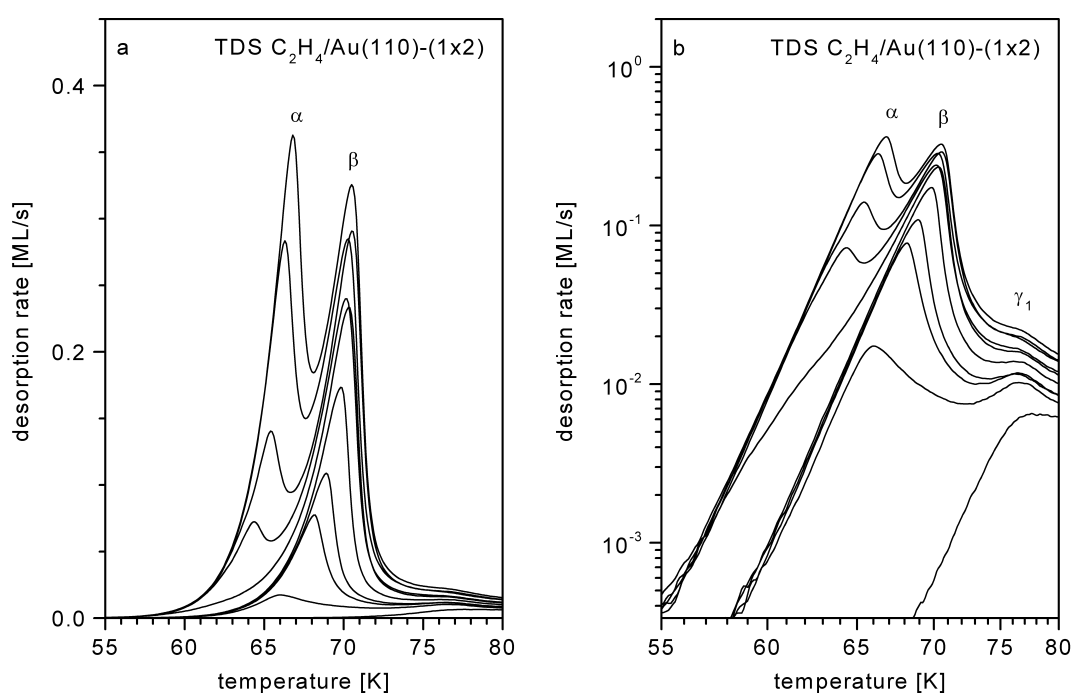


Fig. 9.3: TDS ethylene/Au(110)-(1×2). Low-temperature range of a series of high-coverage spectra (2.35 K/s). (a) Linear plot; (b) plot of $\log(\text{rate})$ vs. reciprocal temperature. Initial coverages (in ML): 1.00; 1.12; 1.33; 1.37; 1.70; 2.03; 2.25; 2.75; 2.99; 3.41.

² The pressure measurements – with an error of 20 % – were performed using a Bayard-Alpert type ionization gauge. The higher gauge sensitivity for C_2H_4 relative to N_2 was compensated by dividing the meter reading by a factor of 2.14.

Relative coverages were evaluated by numerical integration of TD spectra, *absolute* coverages as described in Section 4.1.6. As in the case of CO, the ethylene monolayer (ML) coverage is defined as the maximum number of molecules which have direct contact to the metal surface. This is assumed to be the case for the desorption states $\gamma_1 - \epsilon$. Accordingly, a relative coverage of $\Theta_{\text{C}_2\text{H}_4} = 1.0$ ML corresponds to an absolute coverage of $\sigma_{\text{C}_2\text{H}_4} = (5.2 \pm 1.0) \times 10^{18} \text{ m}^{-2}$ or to 1.2 ± 0.2 molecules in the surface unit cell ($2.89 \text{ \AA} \times 8.16 \text{ \AA}$).

The first-layer desorption energies, which are displayed in Fig. 9.1, were estimated using the Redhead formula, Eq. 4.12 [Re62]. The frequency factor ν_1 was approximated by $k_B T_{\text{max}}/h$. The desorption energies for α and β were obtained from a leading edge analysis [Ha84] as explained Section 4.1.3.

The high-coverage TD spectra for initial coverages between 1.00 ML and 3.41 ML, displayed in Fig. 9.3, exhibit clearly separated signals for desorption from the second layer (β) and from condensed ethylene multilayers (α). The common leading edges in the case of α indicate zero-order desorption, a result that is confirmed by the order plot (see Section 4.1.3) in Fig. 9.4, from which $n_\alpha = 0.01 \pm 0.03$ is obtained. Despite the high-temperature shift of β , which suggests $n_\beta \ll 1$, the desorption order is $n_\beta = 0.93 \pm 0.20$.

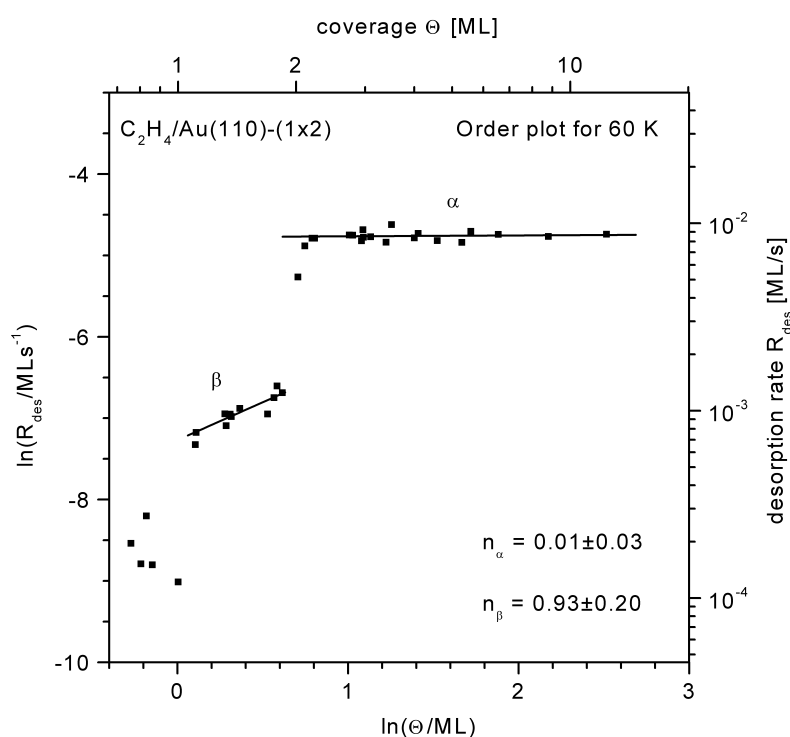


Fig. 9.4: TDS ethylene/Au(110)-(1×2). Representative order plot for $T = 60 \text{ K}$.

COMPARISON WITH LITERATURE DATA – In the only previous C₂H₄/Au study, by Outka and Madix [Ou87b], the authors observed in TDS, starting at 110 K, a broad, ill defined signal stretched over the whole spectrum (between 110 K and 375 K). The maximum position (at \approx 150 K) is too close to the starting temperature to be reliable, if we take the enormous heating rate of 11 K/s into account.

9.2. UV photoemission measurements

The ethylene/Au(110) UP spectra as displayed in Figs. 9.5 and 9.6 are difficult to interpret because they contain more signals due to the lower molecular symmetry of C₂H₄ (compared to CO). Even if we assume a rigid shift of all orbitals by 1.0 -1.5 eV due to the

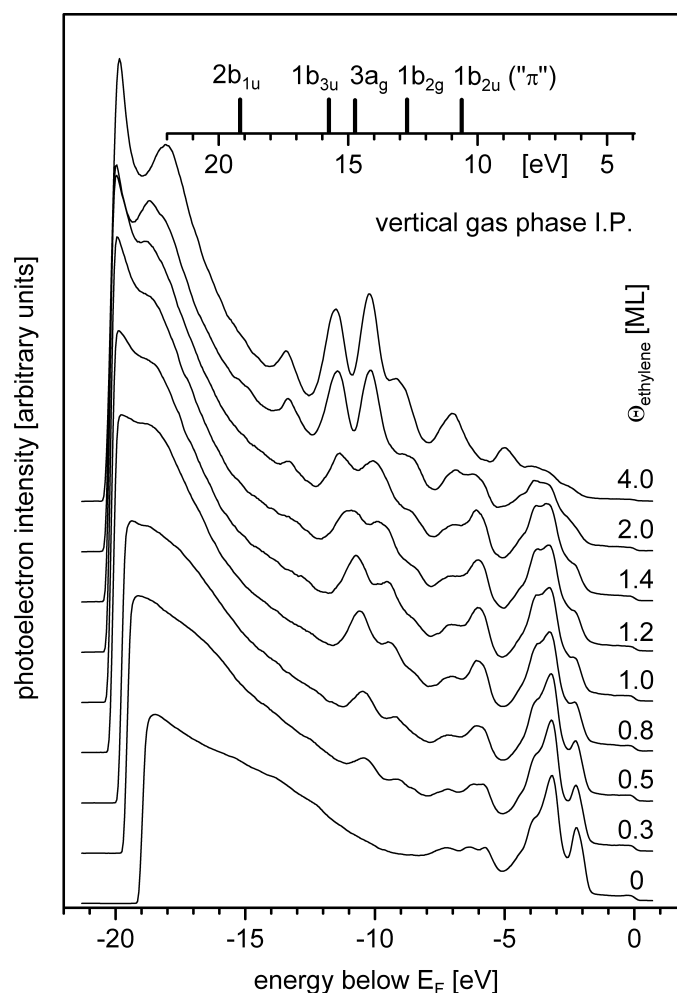


Fig. 9.5: UP spectra ($h\nu = 24$ eV) of C₂H₄/Au(110)-(1×2) for several C₂H₄ coverages. Sample temperature 28 K, M polarization, normal emission. For the alignment of the energy scales in Figs. 9.5 and 9.6, the gas phase spectrum was shifted by $\varphi + \Delta\varphi$ with $\varphi = 5.37$ eV (Ref. [Hü96] in agreement with our measurements) and $\Delta\varphi = 1.43$ eV according to Section 9.4. Gas phase values after [Tu70]. Details of the UPS experiment can be found in Section 4.2.

extra-molecular relaxation energy as in the case of CO, the assignment of the multilayer emissions to the gas phase signals is not straight-forward. Unfortunately, it is not even possible to clearly identify the $1b_{1u}$ emission from the " π " orbital, which is the most important occupied orbital for bonding to the surface as well as for a comparison with CO. The emission around 7.0 eV (at 4.0 ML) is unlikely because this would require a *positive* extra-molecular relaxation energy, and the peak at 6.0 eV (at 4.0 ML) occurs also in the case of CO and stems probably from the Au 5d band. Thus, the only remaining emission is that around 5.0 eV (in the 4.0 ML spectrum), which is, in the interesting sub-monolayer range, certainly shifted to even lower binding energies and thus completely obscured by the gold 5d band. Therefore, comparison of the CO and C₂H₄ UP spectra is much less instructive than the comparison of the respective TD spectra was.

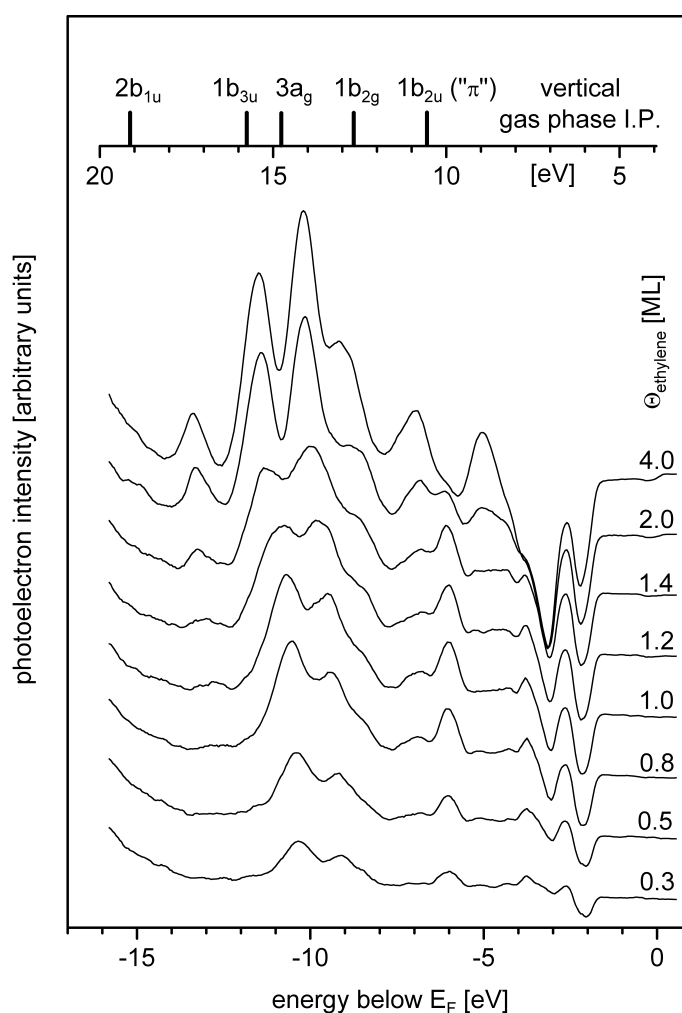


Fig. 9.6: UP difference spectra ($h\nu = 24$ eV) of C₂H₄/Au(110)-(1×2) for the spectra in Fig. 9.5, obtained by subtraction of a spectrum of the clean surface. Sample temperature 28 K, M polarization, normal emission.

As in the case of CO, the chemisorbed species ϵ and the first-layer physisorbed species δ , γ_1 , and γ_2 lead to different signals in the UP spectra. This is especially visible for the most intense peaks around 9 eV and 10.3 eV (in the 0.3 ML spectrum).

Polarization resolved ethylene UP spectra are displayed in Fig. 9.7. The only significant polarization-dependent change is that of the signal around 10.3 eV, which loses intensity as the polarization changes from Z to X. If we assume that the ethylene molecule is adsorbed with the molecular plane parallel to the surface (which is most likely), then only the levels $3a_g$ and $1b_{2u}$ (π) should, according to the dipole selection rules, show such a behaviour³. The assignment of the 10.3 eV signal to $3a_g$ is reasonable, as comparison with the gas phase emission shows. It would imply a shift of 0.5 eV towards lower binding energies relative to the gas phase, which could be explained by the image charge screening due to the substrate. However, this peak assignment remains somewhat uncertain (because it implies a signal shift to higher binding energies upon adsorption) and therefore we refrain from further analysing the spectra.

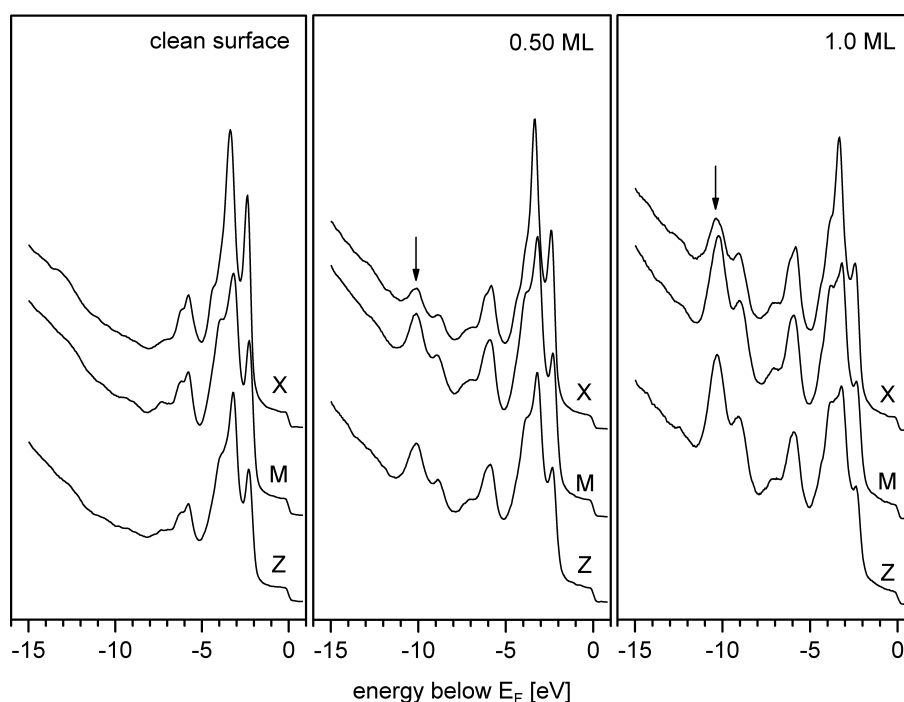


Fig. 9.7: Normal-emission polarization-resolved UP spectra ($h\nu = 24$ eV) for $C_2H_4/Au(110)-(1\times 2)$. Variation of the incidence angle of the linearly polarized UV light in the $(00\bar{1})$ mirror plane (with the polarization vector parallel to that plane). The geometric details of the experiment and the meaning of X, M, and Z polarization were explained in Section 4.2.2. Sample bias -10 V.

³ A detailed analysis of the symmetry selection rules in an ethylene-adsorption ARUPS experiment is given in Ref. [We92].

9.3. LEED

No ordered C₂H₄ overlayers could be observed with LEED in the whole temperature (≤ 28 K) and coverage range. This result shows that the lack of adsorbate long-range order on Au(110) in the presence of repulsive interactions is not unique to CO, even in the case of increased adsorbate-substrate interactions. The same explanations as given in Section 8.3 may apply.

9.4. Work function ($\Delta\phi$) measurements

Adsorption of C₂H₄ on Au(110)-(1×2) causes an even larger work function reduction than CO adsorption, but the $\Delta\phi$ curve, which is displayed in Fig. 9.8, shows less structure. Similar to CO, occupation of the high-temperature desorption states, $\Theta_{\text{C}_2\text{H}_4} < 0.4$ ML, leads to an almost linear decrease of approximately -1 eV. With the same arguments as given in Section 8.4, this linearity is in agreement with the repulsive interactions seen in TDS. In contrast to CO adsorption, the δ -C₂H₄ state causes no plateau, but the curve is significantly flattened, which shows the operation of depolarisation effects.

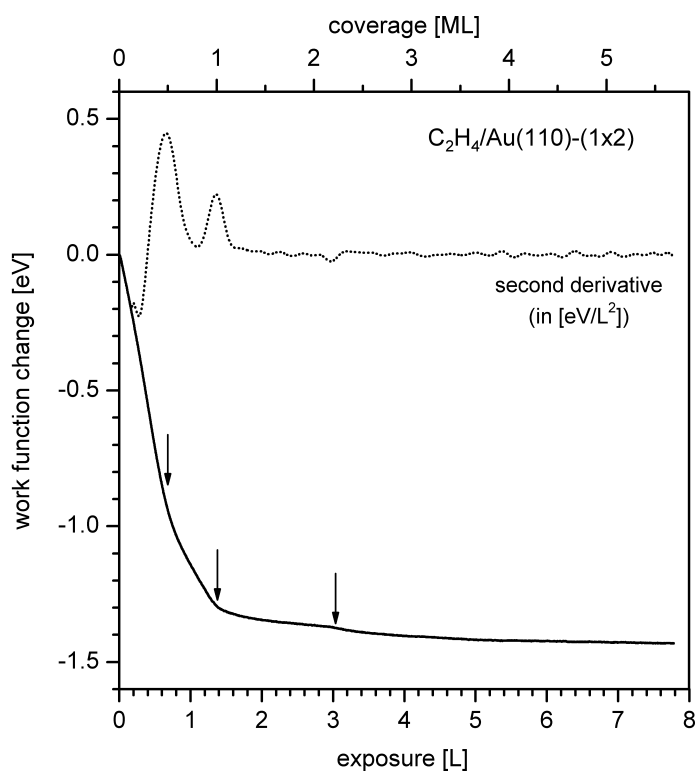


Fig. 9.8: Work function change due to C₂H₄ adsorption on Au(110)-(1×2) at 28 K (solid line). Dosing pressure $p_{\text{C}_2\text{H}_4} = 1 \times 10^{-8}$ mbar. The maxima in the second derivative (dotted line, smoothed) indicate the exact positions of the bends in the $\Delta\phi$ curve.

In the linear region of the $\Delta\phi$ curve, the initial dipole moment of the individual adsorption complex, μ_0 , can be determined by means of the Helmholtz equation (Eq. 4.48). Using the absolute coverage values as evaluated in Section 9.1, we obtained $|\mu_0| = (0.98 \pm 0.20)$ D. Within the margins of error, this value is equal to that of CO/Au(110) (0.93 ± 0.20 D).

Occupation of the γ states (above ≈ 0.75 ML) does not lead to substantial effects in the $\Delta\phi$ curve. This result is consistent with our interpretation of the work function change in the respective coverage range of CO, which was attributed to the *molecular* dipole moment of CO (cf. Section 8.4). The completion of the first layer coincides with a sharp bend at $\Theta_{\text{C}_2\text{H}_4} = 1.0$ ML, and another bend is visible above 2 ML. Higher coverages leave ϕ unchanged. The lack of a minimum-maximum structure as observed in the case of CO suggests that this feature in the CO $\Delta\phi$ curve is indeed related to the dipole moment of the CO molecule.

9.5. Conclusions

At 28 K, C_2H_4 adsorbs non-dissociatively with high sticking probability on gold and appears to be weakly chemisorbed. Thermal desorption spectra show six desorption states with desorption energies below 47 kJ/mol and indicate the coexistence of chemisorbed and physisorbed species at monolayer (ML) coverage. The desorption peaks associated with sub-monolayer coverages below 0.4 ML show substantial shifts to lower temperatures as coverage increases, thus indicating repulsive interactions between the ethylene molecules. Adsorbed C_2H_4 lowers the work function of the gold surface by 1.30 eV at 1 ML, but the $\Delta\phi(\Theta)$ curve is less complex as in the case of CO, which is explained by the lack of a molecular dipole moment. The initial dipole moment of the ethylene-gold complex, 0.98 D, is close to that of CO (0.93 D). UP spectra show different signals for chemisorbed and physisorbed ethylene within the first layer. The remarkable correspondence of TDS and $\Delta\phi$ results for carbon monoxide and ethylene adsorption on gold suggests a similar bonding to the surface, probably involving the π and π^* orbitals of the molecules (rather than the 5σ orbital in the case of CO).

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