

Structure and complete chemical passivation of Pt(997)

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We report on scanning tunneling microscopy and infrared reflection absorption spectroscopy investigations of the stepped Pt(997) surface. The surface shows a regular terrace–step-structure with only moderate variations of the terrace widths with respect to the nominal structure. The adsorption of CO as well as the coadsorption of hydrogen and CO is studied. It is shown that covering the surface with a full monolayer of hydrogen at 165 K provides its complete passivation against adsorption from the residual gas atmosphere, without affecting the terrace–step-configuration. Thus the surface can be kept clean in UHV over months, a necessary precondition to serve as diffractive element in atom beam optics.

1. Introduction

Thermal energy atom scattering is one of the most sensitive means to examine the structure and dynamics of surfaces. Especially thermal helium atom scattering has become a powerful tool during the last 15 years due to the development of monochromatic He beam sources ($\Delta E/E = 0.02$) and high performance time-of-flight techniques (TOF) for energy resolved measurements such as surface phonon spectroscopy [1]. Nevertheless, substantial increase of energy resolution and/or transfer width is still needed in order to approach new physical problems. This requires further monochromatisation of the helium beam as well as an improvement of the energy analysis which can hardly be provided by the TOF technique for technical reasons and beam intensity problems. Therefore, we proposed recently [2] in analogy to the classical experiment of Estermann, Frisch and Stern [3] the use of surface diffraction as a dispersive device in a helium–surface triple axis spectrometer.

The vicinal Pt(997) surface (fig. 1), consisting of (111) terraces of 20.2 Å width separated by monoatomic steps of 2.27 Å height, is ideally suited as such a dispersive element. The nominal regular arrangement provides a stepped reflec-

tion grating for He-waves in analogy to the so-called Echelette-grating in classical optics. The close-packed (111) terraces act as mirrors for thermal helium atoms, reflecting more than 70% of the incoming intensity in the specular direction at $T_s = 150$ K [4]. If the scattering geometry is chosen suitably (the necessary condition for this is the coincidence of the specular direction of the terraces and a diffracted order of the macroscopic (997) plane), the reflected beam intensity can be concentrated in one single high-order diffraction peak [5]. So intensity losses are minimized when using the Pt(997) surface as a monochromator for the incoming He-beam as well as an analyser for the energy distribution of the atoms scattered by the sample surface. Its energy resolution is only limited by the finite divergence of the helium beam, smearing out the dispersive wavelength separation of the Echelette.

In this paper, we focus on two requirements which must be fulfilled for the vicinal platinum surface to serve as a dispersive device in atom optics:

(i) Irregularities in the strictly periodic terrace–step structure of the (997) surface would lead to a broadening of the diffraction peaks of the He-atoms scattered in a slightly nonspecular direction affecting the performance of the surface

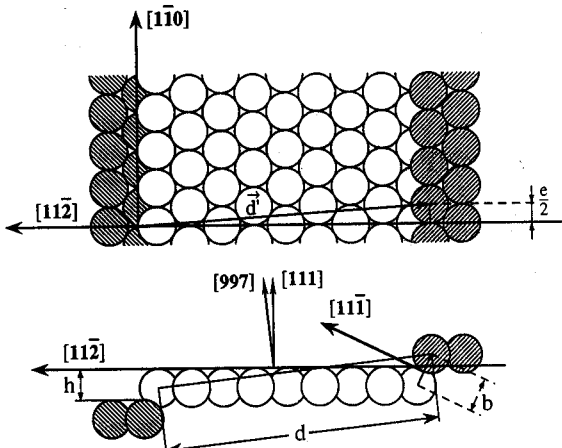


Fig. 1. Side and plane view of the Pt(997) surface; $d = 20.2 \text{ \AA}$, $h = 2.27 \text{ \AA}$.

as monochromator or analyser. We thus studied the microscopic structure of the real Pt(997) surface by scanning tunneling microscopy (STM) in order to verify that no coarse deviations from its nominal structure occur which would prevent its use for our purpose.

(ii) Adsorption of residual gas molecules reduces the He-reflectivity of the terraces due to diffuse scattering. Therefore it is necessary that

the surface can be made inert to the ambient residual atmosphere (10^{-10} mbar) in order to ensure a maintenance-free operation for several hours or even days. By combined STM and reflection absorption infrared spectroscopy (RAIRS) studies a method for a complete long-term passivation of Pt(997) was developed.

2. Experimental

The experiments were carried out in a two-chamber stainless-steel UHV system with a base pressure of 1×10^{-10} mbar (fig. 2). The preparation chamber is equipped with the usual techniques for sample preparation and control, like ion gun, quadrupole mass analyser, LEED and AES. By a long travel manipulator, the sample can be transferred to the analysis chamber where surface infrared spectroscopy and scanning tunneling microscopy experiments are performed. Two nitrogen-purged plexiglass chambers contain the infrared optics and the spectrometer (Mattson Galaxy 6020) and are linked to the UHV chamber by KBr windows. The infrared beam taken from the spectrometer passes through a

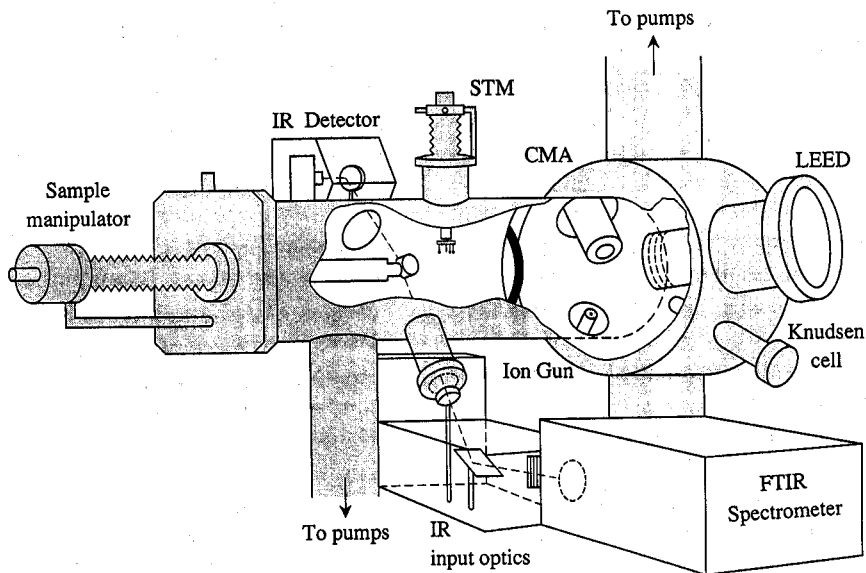


Fig. 2. Schematic view of the UHV system: on the right-hand side, the sample preparation chamber; on the left-hand side, the STM/RAIRS chamber.

polarizer and is focused through one of the windows onto the sample at an angle of $85^\circ \pm 1^\circ$. The reflected IR-light leaves the UHV chamber through a second window and is collected by a mercury-cadmium-telluride detector.

Both chambers can be separated by a gate valve in order to perform STM or RAIRS experiments under "real" pressure conditions (mbar range).

By turning the crystal in a horizontal position, a STM of the beetle type [6] can be positioned onto the sample holder. The holder is directly mounted to a liquid helium cryostat, allowing the crystal to be cooled down to 20 K, by means of electron bombardment it can be heated up to 1400 K. The temperature range for tunneling experiments, however, is currently restricted to about 150–550 K, limited by vibrations due to the liquid helium flow and the piezo tube depolarisation temperature.

The crystal was oriented, cut by spark erosion and polished to the desired orientation to within 0.1° . It was cleaned by repeated cycles of bombardment with 800 eV Ar^+ -ions at 900 K resulting in layer-by-layer sputtering as checked by STM, heating in 2×10^{-6} mbar oxygen at 900 K and annealing at 900 K. Surface order and cleanliness was routinely verified by STM, LEED and AES.

3. STM investigations of the clean Pt(997) surface

It is by no means evident that a high Miller-indexed metal surface shows its nominal structure. Of the vicinal surfaces studied up to now by STM only a few are strictly regular at room temperature, possibly with slight variations of the terrace widths, namely Ni(771) [7], Cu(117) [8], and Cu(1,1,11) [9]. The ordered superlattice of equally spaced monoatomic steps is stabilized by the repulsive step-step interaction between two neighbouring steps. Besides the fact that topologically steps cannot intersect each other, this interaction has its origin in elastic as well as in electrostatic forces. At elevated temperatures thermal disorder through generation of kinks com-

petes with the order established by the repulsive step-step interaction. This thermal kink proliferation eventually results in a roughening transition of the vicinal surface [10]. The Au(332) and Au(755) surfaces [11] are indeed found to be kink-rich with extremely varying terrace widths even at 300 K. The step-step interaction is repulsive on a short- and long-range scale, but might become attractive at intermediate distances. The terrace width distribution of Cu(1,1,19) has been found to be asymmetric and broad with an additional maximum at low values, which was attributed to this attractive part in the interaction potential [8]. Some vicinal metal surfaces show even more complex phenomena like step height and terrace width doubling (Au(1,1,11) [11]) or microfacetting (Pt(210) [12]).

Fig. 3 displays a $600 \text{ \AA} \times 600 \text{ \AA}$ STM image of the Pt(997) surface. After careful preparation, it shows a terrace-step arrangement close to its nominal structure, with terrace widths varying moderately around their nominal width of 20.2 \AA . Measurements of the step heights revealed that only monoatomic steps occur at the surface. However, it was found that in the presence of

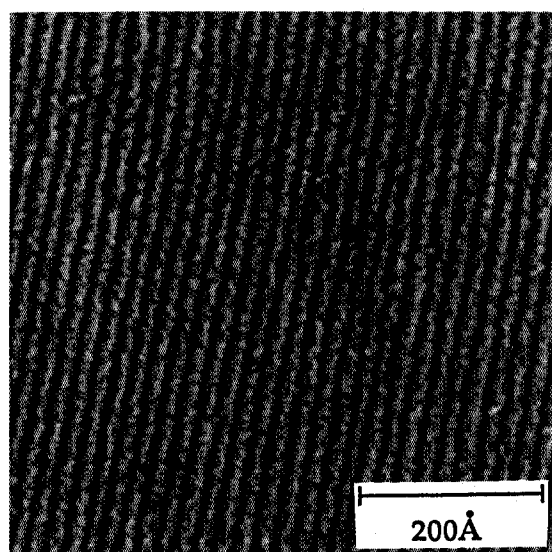


Fig. 3. $600 \text{ \AA} \times 600 \text{ \AA}$ STM image of Pt(997) at 300 K (the derivatives of the lines of constant current were recorded, tunneling bias 0.2 V, tunneling current 1 nA). The dark lines represent the monoatomic steps running in the $[1\bar{1}0]$ direction.

even very small amounts of impurities the steps are pinned during the annealing, affecting the regular surface structure in a quite large area around the contamination. Fig. 4 shows the presence of kinks on the surface, changing their position on a time-scale much faster than the time needed to record a complete STM image. Therefore, each subsequent picture of the same sample area appears different. In view of a more quantitative statement, we calculated a step separation distribution, analysing 1000 individual linescans from 12 tunneling images (fig. 5). We find a gaussian distribution centered around the nominal width of 8.5 atom spacings, corresponding to 20.2 Å. The standard deviation of the distribution is 3 Å. As shown by numerical simulations in our earlier paper [2], this value for the step irregularity is far below a limit which would prevent the performance of the Pt(997) surface as a microscopic "Echelette grating" for He-wave monochromatisation.

Besides the clean Pt(997) surface with nominal step structure, two additional structural phases can be prepared [13,14]: dosed with oxygen at temperatures between 500 and 800 K, terraces

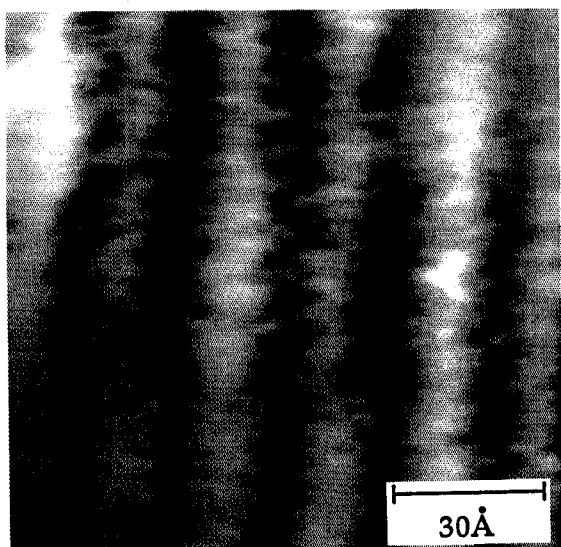


Fig. 4. Absolute height STM image ($150 \text{ \AA} \times 150 \text{ \AA}$) of Pt(997) at 300 K (tunneling bias 0.5 V, tunneling current 8 nA). The widths of the steps (dark regions) are overestimated by multiple atom tip effects.

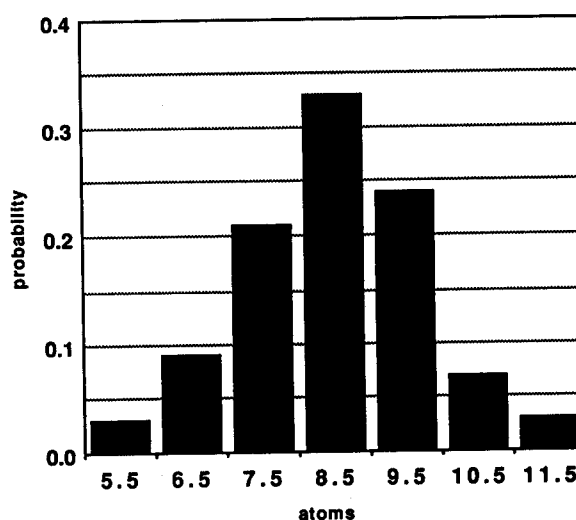


Fig. 5. Terrace width distribution on Pt(997) in units of atoms. In the histogram the data within ± 0.5 atom about the possible lattice distances of 7, 8 or 9 atoms, etc., are assembled.

with double widths and double height steps are observed. Heating the crystal to temperatures above 1000 K leads to partial faceting of the surface. Especially the latter phenomenon was extensively studied by STM and will be published in a forthcoming paper [15].

4. Chemical passivation of the Pt(997) surface

As mentioned before, a long-time use of the Pt(997) surface for quantitative measurements in a He-spectrometer requires its passivation against adsorption of molecules from the residual gas atmosphere, consisting mainly of H_2 , CO, CO_2 , H_2O and hydrocarbons to a less extent. Upon adsorption of 0.05 ML of CO, for instance, the specular He-reflectivity of the (111) terraces is reduced by 50% [16] due to the large diffusive scattering cross section of the CO-molecules. Adsorption of H_2O or CO_2 leads to a comparable effect, but they stick onto the Pt surface only at temperatures below 150 K [17,18]. On the other hand, a Pt(111) surface covered by a full monolayer of hydrogen, which is by far the largest component of the residual gas, has a He-reflectiv-

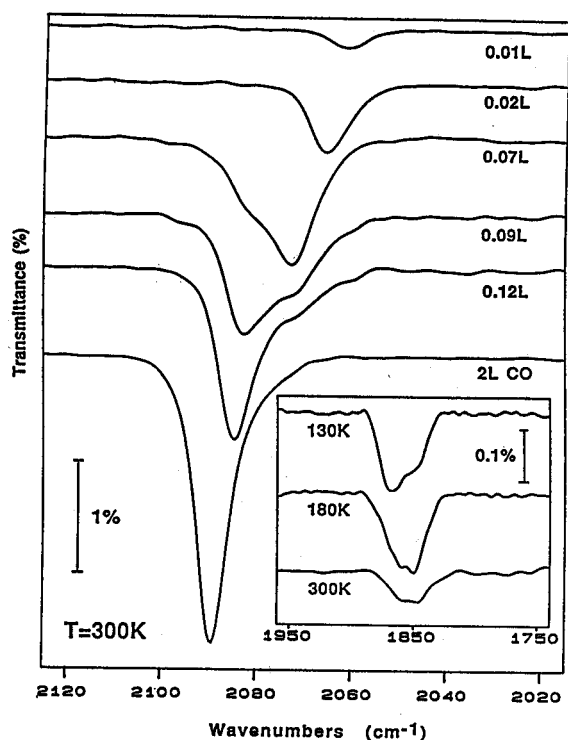


Fig. 6. Infrared spectra of CO on clean Pt(997) versus exposure at 300 K. The inlay shows the absorption bands in the bridging region at saturation coverage as a function of temperature. All spectra shown are taken at 2 cm^{-1} resolution and are corrected for the baseline.

ity of about 80% of clean Pt(111) [19] (hydrogen forms a (1×1) structure on Pt(111)).

We will show here by IRAS measurements that in addition, a hydrogen-covered Pt(997) surface is highly inert with respect to ambient gases. Because of the mentioned particular role of CO, we concentrate on a quantitative analysis of the CO/H-coadsorption on Pt(997).

4.1. CO on clean Pt(997)

As a first step, we have investigated the adsorption of CO on clean Pt(997) in the temperature range of 100–350 K with RAIRS and LEED. Fig. 6 shows as an example the RAIRS results at 300 K. Initial adsorption leads to the formation of an infrared absorption band at 2061 cm^{-1} , shifting to 2072 cm^{-1} with increasing coverage. A higher frequency band appears at intermediate coverage at 2082 cm^{-1} , shifting to 2090 cm^{-1} at

saturation, while the lower frequency band disappears. At lower temperatures, no substantial change is observed except a slight shift of both bands to higher frequencies (2101 cm^{-1} at saturation and 100 K). The appearance of these two bands resembles those observed in the adsorption of CO on Pt(335) [20,21], where the first band is assigned to CO-molecules on step edge sites, whereas the second band indicates the occupation of terrace-on-top-sites. A strong dipole-dipole coupling between the two modes close in frequency leads to the observation of only one single line at saturation. In the higher coverage regime, we observe in addition a broad absorption band in the bridging region around 1850 cm^{-1} (fig. 6a, inlay). At lower temperatures, the band becomes more intense and also more structured, indicating that several contributions are involved, as already known for Pt(111) [22]. At temperatures above 300 K the band further weakens in intensity and disappears at around 350 K. No absolute CO-coverage calibration has been made, but we estimate the saturation coverage to be located near the values of $\theta = 0.63$ for the (335) plane [23] and $\theta = 0.68$ for the (111) plane [24].

By LEED we observe on Pt(997) a sharp $c(4 \times 2)$ structure at higher CO-exposures of about 0.5 L together with a diffuse background, the pattern being very sensitive to the electron beam of the LEED gun. The best ordered structure is observed at around 250 K, while at higher temperatures the spots decrease in intensity and disappear at around 350 K. A higher exposure to CO leads only to an increase of the diffuse background. The LEED measurements indicate that on Pt(997) the close packed terraces are already large enough to permit the formation of $c(4 \times 2)$ islands, which is the dominant structure of CO on the flat (111) plane at higher coverages [24]. In contrast, on Pt(112) [25] and Pt(335) [21] no, or different ordered structures were observed due to the lower terrace width.

4.2. H-adsorption on a CO-precovered surface

The coadsorption of hydrogen and CO on Pt(111) has been extensively studied by various

techniques. Both TEAS [26] and RAIRS [27] experiments reveal that repulsive interactions in the mixed adlayer lead to the formation of pure CO-islands of higher local coverage than the average CO-coverage. At coverages even below 0.1 ML of CO, islands with local coverages up to $\theta = 0.5$ were observed, indicated by the formation of a $c(4 \times 2)$ LEED superstructure. The size of the islands was largest around 150 K. In the presence of higher H_2 -pressures in the 0.001 to 0.1 mbar range the hydrogen induced desorption of preadsorbed CO is observed [28,29]. The repulsive H-CO interaction (6–8 kcal/mol in a nearest neighbour model) reduces the desorption activation energy of CO (31 kcal/mol at low coverage) to a value smaller than the heat of adsorption of hydrogen (19 kcal/mol). Two or three hydrogen atoms are assumed to mediate the displacement of each CO-molecule. The weaker bound CO in the compressed adlayer at $\theta > 0.5$ begins to desorb at 130 K, whereas the $c(4 \times 2)$ adlayer at $\theta = 0.5$ is more stable and is displaced only above 300 K.

On Pt(997), we observe the nearly complete removal of CO in the presence of a hydrogen atmosphere already at temperatures above 150 K. We exposed the surface, which was predosed to CO at 165 K, to 5×10^{-5} mbar hydrogen at the same temperature. During the hydrogen exposure, the CO absorption band decreases continuously in intensity and shifts to lower frequency. After an extended hydrogen treatment (100 000 L), only a weak band at 2069 cm^{-1} remains, corresponding to a small amount of CO adsorbed at step sites (less than 0.03 ML, as roughly estimated by a comparison of the integrated intensities of the step peak). From the absence of an absorption band in the bridging region which would indicate the formation of CO-islands, we conclude that the CO is removed due to the adsorption of hydrogen.

The differences to the Pt(111) case, that is the considerably lower H_2 -pressure required to desorb the CO and the lower desorption temperature, can be related to the details of the adsorption mechanism of hydrogen on Pt(111). It is well known that the adsorption of H_2 on Pt(111) is dominated by steps as dissociation sites [30], at

least at low temperatures. This cannot be counteracted by decorating the steps with CO [31]. As the step density on Pt(997) is two orders of magnitude higher than on a well-prepared Pt(111) surface, the sticking probability of hydrogen is substantially enhanced and lower hydrogen pressures are sufficient to remove the CO. In addition, the desorption activation energy E_d for terrace-bound CO on stepped platinum surfaces (27.4 kcal/mol at low coverage to 23.3 kcal/mol at saturation on Pt(335) [23], 28.5–22.5 kcal/mol on Pt(112) [32], 27–24 kcal/mol on Pt(S)[6(111) \times (100)] [33]) is lower than E_d of the more strongly bound CO on Pt(111) (32 kcal/mol at low coverage to 28 kcal/mol at $\theta = 0.5$ [24]). These reduced values of the stepped surfaces which are closer to E_d of the CO in the compressed adlayer on Pt(111) (< 23 kcal/mol [24]) may explain the removal of the terrace CO at lower temperatures. The studies in refs. [23,32,33] found also that CO is up to 8 kcal/mol more tightly bound to the step sites than to the terrace sites. This difference cannot be completed by the increased heat of adsorption of hydrogen on steps (3 kcal/mol) [34], and the removal of the step CO remains incomplete.

4.3. CO-adsorption on a H-precovered surface

On Pt(111), adsorbed H reduces not only the CO saturation coverage but also the sticking coefficient even at low CO coverages [35]. A full monolayer of H ($\theta_H = 1$) prevents the subsequent adsorption of CO even after extended exposure, as revealed by TEAS [31]. Fig. 7 displays the IR spectra of a CO-saturation coverage adsorbed on Pt(997) predosed to hydrogen at 165 K. For comparison, the absorption peak of CO on clean Pt(997) at this temperature is shown. Upon pre-exposure of the surface to 10 000 L H_2 , the saturation coverage of CO is markedly reduced. The higher CO-exposure needed for saturation indicates the lowering of the sticking coefficient by preadsorbed hydrogen. Increasing the hydrogen predose leads to a further weakening and broadening of the CO-absorption-band, which shifts also to lower frequencies. After saturation with 60 000 L H_2 only a broad, weak band cen-

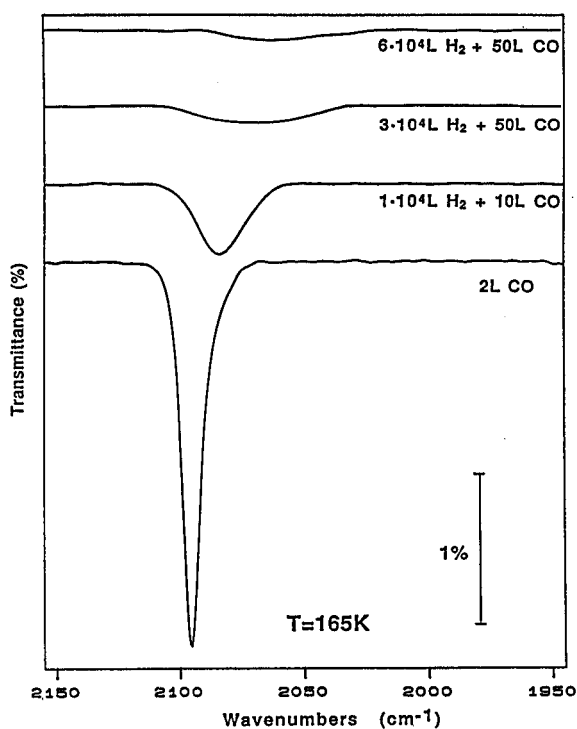


Fig. 7. Infrared spectra of CO at saturation coverage as a function of predosing of the surface to hydrogen at 165 K. The spectra shown are taken at 2 cm^{-1} resolution and are corrected for the baseline.

tered around 2060 cm^{-1} upon CO-exposure is observed, corresponding to less than 0.02 ML of CO supposed to be mainly adsorbed at step sites. Considering that the residual gas atmosphere in a standard UHV system contains about 1×10^{-11} mbar CO, it would last more than 50 days until the indicated amount of 2% of CO is adsorbed and would lead to a noticeable reduction of the helium diffraction intensity.

5. Structure of the H/Pt(997) surface and conclusions

The coadsorption experiments reveal that covering the Pt(997) surface with a full monolayer of hydrogen provides a long-term passivation against CO-adsorption. The crystal has to be held at a temperature around 165 K to minimize H-desorption [19] and to prevent that H_2O formed upon adsorption, or reaction with adsorbing

residual oxygen sticks to the surface (the desorption temperature of H_2O from Pt(111) is 150 K [17]). To conserve the complete hydrogen monolayer, the crystal must therefore be exposed permanently to an atmosphere of 10^{-9} to 10^{-8} mbar of hydrogen. We did not perform a quantitative analysis concerning the adsorption of hydrocarbons, being present to a certain amount in the residual gas. However, no evidence of C-H species on the surface was observed in the infrared spectra even after long-time exposure of the passivated surface to the residual gas. It is indeed well known from previous hydrogen/ethylene coadsorption studies on Pt(111) [36], that already a precoverage of 0.9 ML hydrogen reduces the sticking coefficient for ethylene by an order of magnitude. Also the amount of hydrogenate products decreases sharply at high H-precoverages. We can thus conclude that the fully hydrogen-saturated Pt(997) surface is completely passivated against residual-gas-adsorption.

This would of course be meaningless if the surface underwent a structural change upon hydrogen exposure. As indicated by a sharp (1×1) LEED pattern, hydrogen forms a (1×1) structure on the terraces as expected from the Pt(111) data. We performed STM measurements of the hydrogen-passivated Pt(997) surface at 165 K, showing that neither the average terrace width nor the terrace width distribution is influenced by the hydrogen overlayer. This is also consistent with a former TEAS study of H/Pt(997) [34], where a complete hydrogen monolayer did not change the positions and the widths of the diffraction peaks of the clean surface. Only the intensities of the higher order peaks have been found to be reduced to about 60%.

As summary, we emphasize that our structural investigations and the available method of chemical passivation confirm that the Pt(997) surface is suitable to serve as a diffractive element in atom beam optics.

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