Adsorption properties of bimetallic PdRu/Ru(0001) and Pt/Ru(0001) model catalyst surfaces

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1 Introduction

In this thesis I will present and discuss results of studies on the adsorption behaviour of two different bimetallic model catalysts. The first part deals with the adsorption of carbon monoxide on PdRu/Ru(0001) surface alloys, the second, more extensive part examines the adsorption and coadsorption behaviour of CO and hydrogen (deuterium) on well-defined submonolayer Pt–films on Ru(0001). Besides a fundamental interest in the functionality of bimetallic systems, these investigations are motivated by the importance of these and similar processes for heterogeneous catalysis in the chemical industry and for the operation of PEM fuel cells.

In the most general sense, a catalyst is a material that accelerates a process. The concept of a “catalysed process” was introduced for the first time in 1836 by Jöns Jacob Berzelius, after he realised that a large number of chemical reactions only occur when a certain compound is present, which is however not consumed by the reaction. In 1895 Wilhelm Ostwald defined a catalyst as “a substance which changes the rate of a reaction without itself being consumed in the process and without affecting the position of the equilibrium.”

It has to be emphasized that a catalyst only influences the rate of a reaction which would also occur without the catalyst (albeit extremely slowly). It does not facilitate reactions which otherwise would be thermodynamically impossible. This increase of the reaction rate is reached via establishing new reaction pathways under participation of the catalyst, which possess lower activation barriers than the uncatalysed reaction. In principle, the catalyst is neither consumed nor chemically altered in the process. Since the activation barrier is lowered for both directions in an equilibrium reaction, the position of the equilibrium remains unchanged. Besides affecting the reaction rate, a catalyst can also influence the selectivity of a reaction by catalysing only one of several possible reaction pathways.

About 90% of all chemical products pass through at least one catalysed stage during the production process, with heterogeneous catalysis being the most important type. In the case of heterogeneous catalysis, the catalyst is present in a different phase than the reactants, most often a solid catalyst is brought into contact with a gaseous or liquid mixture of reactants. Compared to homogeneous catalysis, where all reacting compounds are in the same phase, the separation of products from the catalyst is very simple, which makes it possible to run the reaction as a continuous process, an important advantage in industrial applications.
Heterogeneously catalysed reactions usually run via a complicated multi-step process, with adsorption of educts and desorption of products being the first and last steps, respectively. This makes not only the reaction itself interesting for scientific investigations, but the preceding adsorption and subsequent desorption processes as well. Catalysts employed in industrial processes often possess a rather complicated structure and composition; often they consist of metal particles deposited on an oxide substrate with a high specific surface area. The complicated structure makes it difficult to investigate the relationship between reactivity and electronic and structural properties of a catalyst. Additionally studies of catalysed reactions are complicated by the fact that most industrial processes run under pressure conditions which make the application of the majority of surface science methods impossible. In order to conduct surface science studies of catalytic processes it is therefore necessary to develop simplified model systems which possess well defined chemical and structural properties and which can be investigated under low pressure conditions. As a rule, model catalysts consist of metal single crystals or metal particles deposited on thin metal (oxide) films / oxide single crystals.

Investigations conducted on such model systems allowed the characterisation of many adsorbate systems in recent decades, advancing the understanding of surface processes encountered in heterogeneous catalysis. Yet, the employment of model systems also involves fundamental problems, which have to be considered when drawing conclusions from experimental results. Metal particles, which usually make up the active sites of a real catalyst, show a high number of differently oriented surface facets which can be reproduced only to a limited extent in studies on single crystals, the same is true for particle size effects and potential interactions between the metal particles and an oxide substrate. These disparities which present a fundamental difference between heterogeneous catalysis and surface science are known as the “material gap” [1‒3].

Further problems arise from the fact that most investigations on model systems are conducted under ultra–high vacuum (UHV) conditions, while most heterogeneously catalysed reactions run at above atmospheric pressure. The necessity for ultra–high vacuum conditions arises on the one hand from the fact that many surface analytical methods work only at lower pressures, on the other hand higher pressures would quickly lead to contamination of the surface with molecules from the residual gas. Working at UHV conditions leads to another problem; to achieve a high enough coverage at such low pressures, it is often necessary to cool the sample to cryogenic temperatures. At such low temperatures surface diffusion of the adsorbate
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species is often inhibited, therefore the structures assumed by the adsorbate layer can differ from the ones that occur in real catalysis at higher temperatures. Furthermore, activated reactions between adsorbate species will be kinetically hindered at low temperatures. This second fundamental break between real heterogeneous catalysis and model systems is known as the “pressure gap” [4–6].

Bimetallic catalysts attracted increasing interest over the last decades, due to the fact that often the chemical properties of bimetallic surfaces differ significantly from those of the respective individual components, often leading to superior catalytic performance compared to monometallic supported catalysts [7–10]. Additionally, a bimetallic catalyst offers the possibility to modify the reactivity by varying the composition and structure of the catalyst surface. The modified catalytic and general chemical surface properties are usually attributed to a number of different effects such as the electronic ligand effect, the geometric ensemble effect and the electronic strain effect [11–15]. The first describes the modifications of the electronic structure of a given surface atom arising from interactions with neighbouring surface atoms with differing electronic structures. A variation of this effect is the vertical ligand effect, which describes the electronic interactions between an overlayer and the underlying substrate. The second effect refers to the fact that for many reactions or the adsorption of certain molecules a particular number and configuration of atoms is required for active sites. Introduction of foreign atoms into such an ensemble can modify the activity towards certain reactions or completely suppress them [12,13,16]. The strain effect finally describes the modification of the electronic structure of a pseudomorphic overlayer (compared to the bulk surface) arising from a mismatch between the surface lattice geometries (lattice constants) of the substrate and the bulk form of the overlayer [14,15]. Since the composition and especially the distribution of the different atoms in the surface of a real catalyst are difficult to determine experimentally, the influence of these effects is difficult to verify directly and separately. The advantage of planar model catalysts is the possibility to prepare bimetallic surfaces with a well-known composition and distribution of individual surface components. Additionally, these more simple systems can be described by calculations based on the density functional theory (DFT). In recent years, these advantages have led to an increased understanding of bimetallic catalysis [15,17–24].

The first main part of this thesis presents the results of a series of TPD and IRAS experiments on the adsorption of CO on PdRu/Ru(0001) surface alloys. In particular, the effect of the formation of the surface alloy, as well as the influence of varying surface compositions on the
adsorption energy and geometry of CO are investigated and discussed. These results are complimentary to results obtained for deuterium adsorption on identical surfaces [25] and with those of previous studies on D₂ and CO adsorption on PtRu/Ru(0001) [26–31], and PdCu/Ru(0001) surface alloys [32]. The results of these studies are discussed with regard to the correlation between structural, electronic and chemical properties.

In the second, main part of the thesis, results of a systematic study focusing on the chemical properties of Ru(0001) surfaces covered to varying extents by large monolayer Pt islands are presented. The initial chapter concentrates on the separate adsorption of CO and hydrogen (deuterium) under UHV conditions, which was investigated via TPD and IRAS (for CO only), focusing on the influence of different Pt coverages on the adsorption energy and kinetics of the two adsorbates. The next chapter examines spill-over processes which occur after annealing a CO adlayer on a PtRu surface or after CO adsorption at higher temperatures. The results are discussed with regards to the CO_{ad} distribution on the bimetallic surface and the total coverage after adsorption at different temperatures. In the final chapter, the results of coadsorption experiments, which concentrate on the influence of different amounts of pre-adsorbed CO or deuterium on the adsorption and desorption behaviour of the respective other species, are presented and discussed. As additional points of interest, the resulting distribution of the coadsorbed species on the surface, blocking effects of pre-adsorbed molecules on the post-adsorbed species and possible displacement effects at different temperatures are discussed as well.
2 Experimental methods

2.1 Thermal desorption spectroscopy

Thermal desorption spectroscopy (TDS) also known as temperature programmed desorption (TPD) is a technique which is widely used to investigate adsorption and desorption processes that play an important role in heterogeneous catalysis. One of the advantages of TPD is the relatively simple experimental setup.

At the start of the experiment the surface of the sample, which is held at a constant temperature, is exposed to a gas (or a mixture of gases). After the exposure is completed the sample is heated at a constant rate, which leads to desorption of previously adsorbed molecules at certain temperatures. The desorbing molecules are usually detected by a mass spectrometer which allows the mass specific determination of the respective partial pressures as a function of temperature. Assuming a high enough pumping rate and a relatively low heating rate, the observed partial pressure is proportional to the desorption rate of the respective molecules [33,34].

The desorption rate $r_{\text{des}}$ is described as a function of temperature $T$ by the Polanyi–Wigner equation:

$$ r_{\text{des}} = -\frac{dN}{dT} = \frac{\nu}{\beta} N^n \cdot \exp \left( -\frac{E^*_{\text{des}}}{RT} \right) $$  \hspace{1cm} (2.1)

considering $N = N_0 \cdot \theta$ the equation can be written as:

$$ r_{\text{des}} = -\frac{d\theta}{dT} = \frac{\nu}{\beta} \theta^n \cdot \exp \left( -\frac{E^*_{\text{des}}}{RT} \right) $$  \hspace{1cm} (2.2)

- $\nu$ pre-exponential of the desorption reaction
- $\beta$ heating rate
- $N$ number of adsorbed molecules
- $N_0$ number of adsorption sites
- $\theta$ coverage
- $n$ reaction order
2 Experimental methods

\( E_{\text{des}} \) activation energy for desorption

\( T \) sample temperature

In the generic case the thermodynamic adsorption energy \( E_{\text{ad}} \) is the difference between the activation energies for desorption \( E_{\text{des}}^* \) and adsorption \( E_{\text{ad}}^* \): \( E_{\text{ad}} = E_{\text{des}}^* - E_{\text{ad}}^* \). In the case of non–activated adsorption \( (E_{\text{ad}} = 0) \) the adsorption energy is equal to the activation energy for desorption \( E_{\text{ad}} = E_{\text{des}}^* \).

Different features like peaks and shoulders in the TPD spectrum indicate the number of different adsorption states, which occur either due to the occupation of different adsorption sites or due to formation of coverage dependent, energetically different adsorbate structures. The position of these states on the temperature axis allows to calculate the adsorption energy or (in the case of activated adsorption) the activation energy for desorption respectively. Since the peak areas are proportional to the amount of adsorbed species in these states, it is possible (in the case of sufficiently resolved peaks) to determine the relative coverage of the respective species. Absolute coverage can be calculated via comparison with TPD spectra from samples with known coverage. It must be mentioned that TPD spectra only reflect the adsorption states at the respective desorption temperature, this allows only limited conclusions about conditions in the adsorbate layer at adsorption temperature.

A series of TPD experiments with different gas exposures and accordingly different initial adsorbate coverage can be used to determine the desorption order by evaluating the temperature shift of the desorption maximum of a state with varying initial coverage. Three fundamentally different cases can be distinguished:

1. For zero order desorption \( (n = 0) \) an increase of the initial coverage leads to a shift of the desorption maximum to higher temperature. The leading edges of the spectra coincide while the trailing edges rapidly drop off, once all molecules are desorbed. This kind of spectra is observed mostly for desorption from multi–layer films where desorption is independent of the adsorbate coverage until the first layer is reached.

2. In the case of first order desorption \( (n = 1) \) the temperature of the peak maximum is independent of the adsorbate coverage. The desorption states show a characteristic asymmetric form with the high temperature edge having a steeper slope than the low temperature edge. First order desorption is typical for non–dissociative adsorption (e.g. CO on Ru(0001)).
3. Second order desorption is usually observed for recombinative desorption of dissociated molecules (e.g. H₂). The position of the desorption maximum shifts to higher temperatures with increasing initial coverage. The desorption peaks have a symmetric form and a common trailing edge.

To illustrate the different characteristic features Figure 2.1 shows examples of desorption spectra of different reaction orders. The spectra were obtained from a numerical solution of the Polanyi–Wigner equation.

![Figure 2.1: Sample spectra for different desorption orders and initial coverages.](image)

The examples given above, however, only represent limiting cases for ideal systems without any interactions between the adsorbed species. The presence of attractive or repulsive interaction in real adsorbate systems often leads to apparent non–integer desorption orders and deviations from the typical spectrum shapes. The effective desorption order can be determined from the logarithmic form of the Polanyi–Wigner equation (2.2):

\[
\ln \left( -\frac{d\theta}{dT} \right) = n \cdot \ln \theta + \ln \left( \frac{\nu}{\beta} \right) - \frac{E_{\text{des}}^*}{RT}
\]  

(2.3)
2 Experimental methods

Assuming that the desorption energy and the pre-exponential are independent of coverage, the desorption order \( n \) can be determined from a logarithmic plot of desorption rate versus coverage.

Several different methods for evaluation of TPD spectra can be found in literature [33–37].

Redhead method

Redhead suggested a method to determine the activation energy for desorption \( E^*_{\text{des}} \) by evaluating the temperatures of the peak maxima. The desorption order \( n \) must be known and it is necessary to assume a value for the pre-exponential \( \nu \), additionally it is assumed that \( E^*_{\text{des}} \) and \( \nu \) are constants, which should be the case for small coverage. Since the derivative of the desorption rate with respect to temperature is zero at the peak maximum \( \left( \frac{d^2 N}{dT^2} = 0 \right) \) the following relations are obtained from the Polanyi–Wigner equation (2.2):

\[
\begin{align*}
\text{n} = 1 & \quad \frac{E^*_{\text{des}}}{RT^2_{\text{max}}} = \frac{\nu \beta}{\nu \exp \left( -\frac{E^*_{\text{des}}}{RT_{\text{max}}} \right)} \\
\text{n} = 2 & \quad \frac{E^*_{\text{des}}}{RT^2_{\text{max}}} = \frac{\theta_0 \nu \beta}{\nu \exp \left( -\frac{E^*_{\text{des}}}{RT_{\text{max}}} \right)}
\end{align*}
\]

\( \theta_0 \) initial coverage

\( T_{\text{max}} \) temperature of peak maximum

Equation (2.4) shows that \( E^*_{\text{des}} \) is independent from coverage and can be easily calculated from a measurement of \( T_{\text{max}} \). For \( 10^{13} > \frac{\nu}{\beta} > 10^8 \) the relation between \( E^*_{\text{des}} \) and of \( T_{\text{max}} \) can be approximated as:

\[
\frac{E^*_{\text{des}}}{RT_{\text{max}}} = \ln \left( \frac{\nu}{\beta} T_{\text{max}} \right) - 3.64
\]
For the case of second order desorption $E_{des}^*$ can be obtained from the slope of a plot of 
$\ln(T_{max}^2 \cdot \theta_0)$ versus $\left(\frac{1}{T_{max}}\right)$.

**Determination of the sticking coefficient**

The sticking coefficient $s$ corresponds to the probability for adsorption of a molecule 
impinging on the surface. It is obtained from the ratio of the number of adsorbed species $N_{ads}$ 
and the number of impinging molecules (or atoms) $N$. The number of adsorbed species is 
given by:

$$N_{ads} = \theta \cdot \sigma \cdot A$$  \hspace{1cm} (2.7)

$\sigma$  \hspace{0.5cm} surface atom density

$A$  \hspace{0.5cm} area of sample surface

From the kinetic theory of gases the impingement rate i.e. the number of atomic or molecular 
collisions with the surface per unit area per unit time is obtained as:

$$Z = \frac{p}{\sqrt{2 \cdot \pi \cdot m \cdot k \cdot T}}$$  \hspace{1cm} (2.8)

$p$  \hspace{0.5cm} gas pressure

$m$  \hspace{0.5cm} mass of gas atoms or molecules

$T$  \hspace{0.5cm} gas temperature

The total number of atoms or molecules impinging on the sample surface is given by the 
product of impingement rate $Z$ sample surface area $A$ and exposure time $t$:

$$N = Z \cdot A \cdot t$$  \hspace{1cm} (2.9)

For the sticking coefficient we obtain:

$$s = \frac{N_{ads} \cdot \sqrt{2 \cdot \pi \cdot m \cdot k \cdot T}}{p \cdot T}$$  \hspace{1cm} (2.10)
where \( p \cdot t \) is the gas exposure.

The initial sticking coefficient for an adsorbate free surface \( s_0 \) can be obtained by plotting \( s \) versus \( \theta \) and extrapolating to \( \theta = 0 \).

### 2.2 Infrared reflection absorption spectroscopy

Infrared spectroscopy is vibrational spectroscopy method based on excitation of molecular vibrations through absorption of infrared (IR) radiation. In the case of infrared reflection absorption spectroscopy (IRAS) IR radiation is reflected of the sample surface into a detector. A typical IR spectrum is recorded as absorption versus wavenumber [38–40].

The energy transfer from the incident IR photons which leads to the excitation of molecular vibrations occurs via the interaction between the E–field of the IR radiation and the dipole moment of a sample molecule. The general selection rule for vibrational transitions allows the excitation of vibrations only in cases where they lead to a change in the dipole moment \( \mu \) of the molecule.

\[
\left( \frac{d\mu}{dq} \right) \neq 0 \quad (2.11)
\]

\( q \) normal coordinate of the vibration mode

The quantity \( (d\mu / dq) \) is called the dynamic dipole moment. In the case of dipolar molecules adsorbed on metal surfaces interactions between the adsorbate dipole and metal electrons induce an image dipole in the metal surface. For a given orientation of molecule with respect to the surface the dipole moment can be separated into two components, normal and parallel to the surface respectively. Only the component normal to the surface can be excited by the E–field of incident light. The reason for this is made clear in Figure 2.2, while the image dipole of the normal component is oriented in the same direction, dipole and image dipole of the component parallel to the surface have an antiparallel orientation. In the former case the dipole moment is doubled, in the later dipole and image dipole cancel each other out [41].
In addition it has to be considered that the s-polarised component of the incident IR light experiences a 180° phase shift upon reflection from a metal surface, this causes the s-component of the E-field to cancel out via destructive interference, leaving no E-field component to interact with an adsorbate dipole parallel to the surface [39]. These observations lead to a new selection rule (surface selection rule) which states that IR radiation can excite only vibrational modes with a component of the dynamic dipole normal to the surface:

\[
\left( \frac{d\mu}{dq} \right)_\perp \neq 0
\]  

(2.12)

As a consequence of the formation of a surface–molecule bond, IR spectra of adsorbed molecules exhibit typical deviations compared to spectra of molecules in the gas phase. These allow to draw a number of conclusions about adsorption state, interadsorbate interactions and the type of bond between molecule and surface. The charge transfer induced by interactions between adsorbed molecules and surface atoms leads to a frequency shift of the molecular vibrational bands (chemical shift) compared to the gas phase spectrum. Intermolecular interactions within the adsorbate layer influence the strength of the adsorbate – metal bond, the formation of adsorbate islands or ordered structures can also lead to a frequency shift of vibrational bands. Additionally intensity and full width at half maximum of the spectral bands can provide information about the homogeneity of the adsorbate layer.
2 Experimental methods

Although various molecules have been investigated with vibrational spectroscopic methods carbon monoxide represents an ideal probe molecule for these experiments. The rather simple vibrational and electronic structure allows theoretical calculations and comparison to experimental results and facilitates the assignment of vibrational bands in multi component systems.

2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a widely used technique for surface analysis. It allows the determination of electronic structure and chemical composition of a sample and in many cases also of the oxidation or chemical state of surface atoms. As an experimental method photoelectron spectroscopy was developed by K. Siegbahn in 1960 as electron spectroscopy for chemical analysis (ESCA) [42]. The physical principle behind XPS is the photoelectric effect. The sample is exposed to electromagnetic radiation leading to emission of photoelectrons. The kinetic energy $E_{kin}$ of emitted electrons is a function of the energy $h \nu$ of the incident photons and the binding energy of electrons $E_B$.

$$E_{kin} = h \cdot \nu - E_B - \Phi_{spec} \quad (2.13)$$

$E_{kin}$ kinetic energy of emitted electrons  
$h \cdot \nu$ energy of incident photons  
$E_B$ binding energy of electrons in the solid  
$\Phi_{spec}$ work function of spectrometer

The binding energy is defined as the energy difference between the Fermi energy of the spectrometer $E_F$ and the energy of an electron in the solid, while the spectrometer work function $\Phi_{spec}$ corresponds to the difference between vacuum energy $E_{Vac}$ and the Fermi level of the spectrometer. Figure 2.3 serves to further illustrate the relationships between energy levels participating in the process.
In the course of an experiment the surface of a sample is irradiated by X-rays of a certain wavenumber. Interactions between the incident X-ray photons and valence or core electrons lead to emission of electrons from the sample surface, which are detected as a function of their kinetic energy. The wavelength of X-ray photons is known while the spectrometer work function can be determined via calibration measurements with reference samples; this allows calculating the binding energy of the original electron state from equation (2.13). The short mean free path of electrons in solids means that only outer atomic layers can be detected without loss of energy or intensity. In a typical XPS spectrum the number of detected photoelectrons is plotted versus the binding energy, Figure 2.4 shows the XPS spectrum of Ru(0001) as an example. Since the binding energies of core electrons are element specific it is possible to determine the elemental composition of a sample by evaluating the peak positions. The ratio of peak areas can be used to draw conclusions about the relative abundance of elements in the sample. A more detailed evaluation of the binding energies of individual states allows conclusions about the chemical state of the respective atoms. A higher oxidation number means a decreased electron charge of the concerned atoms, which in turn leads to an increased attraction between the atom core and the remaining electrons, resulting in a higher binding energy compared to a neutral atom. Conversely, a lower oxidation number leads to a
shift of the binding energy to lower values. This effect is known as the “chemical shift” and in many cases allows drawing conclusions about the binding states of surface atoms.

Figure 2.4: XPS spectrum of a clean Ru(0001) surface.

In order to evaluate XPS spectra it is often sufficient to apply an approximation known as Koopmans’ theorem. In this case it is assumed that the binding energy of an electron corresponds to the negative energy of the electron orbital since the energy levels of an atom are not altered during the ionisation process. This approximation neglects the rearrangement of the remaining electrons during the photoemission process which leads to a shift of the electronic energy levels and influences the energy state of the photoelectron.

Extensive treatments of theoretical and practical aspects of XPS can be found in literature [43–45].
3 Experimental section

3.1 Experimental setup

The experiments presented in this thesis were carried out in a UHV chamber with a base pressure \(< 10^{-10} \text{ mbar}\). UHV conditions are generated and maintained by a turbomolecular pump (Leybold–Heraeus, CV360, 345 l s\(^{-1}\)), an ion getter pump (Varian, Starcell, 400 l s\(^{-1}\)) and a Ti sublimation pump (VG, ST22).

The chamber is equipped with an Ar\(^+\) sputter gun for sample preparation and an electron beam evaporator (Omicron, EFM 3) which was used to prepare the bimetallic surfaces investigated in this thesis.

A quadrupole mass spectrometer (Pfeiffer Vacuum, Prisma QMS200) was used to record TPD spectra and for residual gas analysis. To prevent detection of gas molecules desorbing from the sample periphery or sample holder, the ion source is shielded by a Ta cap with a 4 mm aperture. During TPD experiments the sample was centered beneath the aperture at a distance of 0.5 mm.

To check for contaminations and to determine the composition of the bimetallic samples an XPS system is available consisting of an X–ray tube (VG, XR3E2) and a hemispherical analyzer (VG, CLAM 2). The X–ray tube contains two non–monochromatized anodes: Al K\(_\alpha\) (1486.6 eV) and Mg K\(_\alpha\) (1253.6 eV), XPS spectra were recorded with the Al K\(_\alpha\) anode. For survey measurements the pass energy was set to 50 eV, detail spectra to determine the composition of bimetallic surfaces were recorded with a pass energy of 20 eV.

IR spectroscopic measurements in this work were carried out with an FTIR spectrometer (Bruker, Tensor 27). The external beam of the spectrometer was directed and focused at the sample surface via a system of two mirrors. The reflected beam was additionally focused by a ZnSe lens into an LN\(_2\) cooled HgCdTe–(MCT)–detector (Judson, J15D14). The incident and emergent angles were 7\(^°\) with respect to the surface.

Dosing of gases for sample preparation (O\(_2\)) and TPD and IR experiments (CO, D\(_2\)) was done via leak valves. In order to achieve a higher local pressure a glass dosing tube (Ø 8 mm) was directed at the sample surface at a distance of 10 cm.
A Ru(0001) single crystal with a diameter of 8 mm and a thickness of 12 mm served as a substrate for all experiments. The temperature of the crystal is measured with a type C thermocouple (W5Re vs. W26Re), the thermocouple wires are fixed to the crystal via two boreholes through the crystal edge. Opposing sides of the crystal contain two slots which are used to clamp the crystal between two Ta wires (Ø 0.25 mm), which are spot welded between two Cu support rods. The support rods in turn are fixed to a hollow Cu block which can be cooled by liquid nitrogen, a Marcor® disc is placed between the Cu support roads and the Cu cooling reservoir in order to electrically isolate the sample from ground. This arrangement allows the sample to be cooled down to 90 K. The initial cool down from room temperature takes ca. 1 h, during TPD and IR experiments the sample can be cooled from 600 to 90 K in ca. 15 – 20 min.

Heating of the sample can be achieved by two different means. During TPD and IR experiments the sample was heated resistively via the Ta wires. A current of ca. 8 A results in a heating rate of 5 K s\(^{-1}\). In order to achieve temperatures of 1700 K which are necessary for sample preparation electron beam heating was used, for this purpose a thoriated tungsten filament (Ø 0.125 mm) is fixed 2 mm below the Ru crystal. A filament current of ca. 1.8 A and a voltage of ca. 1000 V allow the sample to be heated to 1700 K in ca. 60 s.

3.2 Sample preparation and characterization

A Ru(0001) crystal was used as the substrate for experiments presented in the following chapters. In order to deplete the upper layers of impurities which are always present in commercially available Ru, the crystal was initially annealed to 1300 K for ca. 45 hours in an oxygen atmosphere (10\(^{-8}\) mbar), in order to accelerate the diffusion of impurities to the surface the crystal was flash-terminated to 1600 K every 15 min. After this initial treatment the sample surface was sufficiently clean to perform TPD and IRAS experiments.

In order to prepare the sample before each experiment a standard procedure was applied which consisted of sputtering (p\(_{Ar}\) = 2×10\(^{-5}\) mbar, I\(_{ion}\) = 5 µA, U = 1.2 kV) for 15 min, followed by flash annealing to 1650 K in order to smooth the surface. Oxidizable impurities were removed from the surface by exposing the sample to 10×10\(^{-6}\) mbar\(\cdot\)s O\(_2\) at room temperature followed by flash annealing to 1700 K, three such oxygen cycles were usually
sufficient to obtain a clean surface. After the cleaning procedure was finished the sample was cooled down to 90 K with liquid nitrogen, concomitantly it was flash–annealed to 1700 K three times in order to remove remaining traces of adsorbed oxygen which would heavily influence the following experiments. In order to confirm the purity of the Ru(0001) surface, at the beginning of each series of measurements the TPD spectrum of a saturated CO adlayer at 90 K was recorded. The spectrum has a very characteristic form [46,47] as shown in Figure 3.1 which is very sensitive to surface impurities.

![TPD spectrum of a saturated CO adlayer on Ru(0001) at 90 K.](image)

**Figure 3.1:** TPD spectrum of a saturated CO adlayer on Ru(0001) at 90 K.

After the purity of the Ru(0001) surface was ascertained the PdRu/Ru(0001) or Pt/Ru(0001) model surfaces were prepared via physical vapor deposition with the help of an electron beam evaporator.

A detailed treatment on the formation of PdRu surface alloys on Ru(0001) and the statistics of the surface atom distribution can be found in Ref. [25]. In short, the surface alloys were prepared by depositing varying amounts of Pd at RT with a deposition rate of 0.1 ML min$^{-1}$, followed by annealing to 1150 K for 10 s. STM imaging revealed that alloying of the two components is confined to the first layer, while the loss of deposited Pd atoms into subsurface layers during the alloying procedure is negligible. Statistical evaluation of STM images showed that the system displays a clear preference for homometallic bonds, which results in phase separation and the formation of Pd islands in the first layer.
The formation and morphology of bimetallic PtRu surfaces has been extensively studied by STM [26,31,48,49]. Pt evaporation at 300 K results in the formation of Pt monolayer islands with a triangular dendritic shape on the Ru(0001) terraces, additionally similarly shaped Pt dendrites grow from Ru step edges. Both islands and dendrites occur with two different orientations, conforming to either fcc or hcp stacking with respect to the Ru(0001) substrate. Upon annealing to 600 – 700 K the Pt layer forms compact hexagonal islands on the terraces and smooth decorations of Ru steps. In contrast, deposition of Pt at higher sample temperatures (500 – 600 K) results in step–flow growth, with Pt atoms condensing exclusively along the Ru steps and no island formation, except at higher deposition rates or on very wide terraces [49].

Further annealing to 850 K leads to an increase in size of both islands and step decorations, concomitant with a decrease in island density via the Ostwald ripening process, where larger islands grow at the expense of smaller ones. Additionally the onset of surface alloy formation can be observed in the outer regions of islands and step decorations [48]. Finally annealing to 1300 K leads to the formation of a PtRu surface alloy in the outermost layer, with a random and homogeneous distribution of Pt and Ru atoms [31,48].

The platinum films investigated in the experiments presented in this work were prepared by depositing different amounts of platinum on the Ru(0001) substrate at 300 K sample temperature and a deposition rate of approximately 0.1 ML min⁻¹.

**Figure 3.2:** STM images of a Pt film on Ru(0001) with a Pt coverage of 0.45 ML (100 × 100 nm). a) after deposition at 300 K, b) after annealing to 700 K for 60 s. Results of A. Bergbreiter.
After deposition, the sample was annealed to 700 K for 60 s. Using these preparation parameters, STM measurements conducted in our institute by H. Hoster [50] and A. Bergbreiter [51] have shown that pseudomorphic monolayer Pt islands are formed on the Ru substrate, which coalesce at higher Pt coverages. STM images of a Pt film (0.45 ML Pt) after deposition at 300 K and after subsequent annealing are shown in Figure 3.2. After deposition of a monolayer–equivalent amount of Pt, the film covers ca. 90% of the ruthenium surface, while already some (second layer) Pt islands are formed on top of the monolayer film.

3.3 Data acquisition

Pt coverages given in this work were determined via XPS measurements carried out after the TPD and IR experiments, in order to prevent contamination of the surface. The Pt surface coverage as determined by STM measurements was used to establish an absolute calibration of the intensity ratio of the Pt(4f) and Ru(3d) states in XPS. The calibrated XPS intensities were used in this work to determine the amount of Pt on the surface, which is linearly related to the intensity ratio of the two peaks. As mentioned above, formation of a second Pt layer begins at a Pt coverage of approximately 0.9 ML with a part of the Ru(0001) substrate still uncovered. Pt coverages in this range therefore refer to monolayer–equivalents deposited on the surface, not necessary to the fraction of the Ru(0001) surface covered by Pt.

For TPD and IR experiments the sample surface was exposed to varying amounts of CO and/or deuterium. The dosing was carried out via backfilling of the chamber. The TPD experiments were carried out with a heating rate of 5 K·s$^{-1}$. Deuterium was used instead of H$_2$ in order to distinguish between adsorption from the background and the actual gas exposure and to minimize the contribution of the background to the TPD spectrum. Mass 28 was recorded during all experiments, including those carried out only with deuterium (i.e. no coadsorption) in order to monitor the CO$_{ad}$ coverage which can heavily influence D$_2$ TPD results. Integration of the CO signal showed the CO$_{ad}$ coverage resulting from adsorption from residual gas to be 0.005 – 0.01 ML. The IRAS measurements were carried out with a resolution of 4 cm$^{-1}$. In the case of experiments with pure CO (Section 4.2.4.2) 2000 scans (14 min) were collected for an IR spectrum, for coadsorption experiments (Section 4.4.4) the number of scans was reduced to 500 (3.5 min) in order to minimize possible desorption of D$_2$.
at 90 K. Reference spectra of the CO–free surfaces were recorded at temperatures sufficient to prevent CO adsorption from the residual gas.

3.4 Experimental problems

This section will deal with several problems which occurred with experimental equipment during the work on this thesis, leading to considerable delays in its completion. First of all, high deuterium exposures (> $100 \times 10^{-6}$ mbar·s) resulted in a decreasing intensity of the D$_2$ TPD spectra compared to spectra with lower exposures.

![Figure 3.3: D$_2$ TPD spectra from a surface with 0.75 ML Pt. D$_2$ exposures $\times 10^{-6}$ mbar·s: 40, 60 (solid lines), 100 (dashed line).](image)

This behaviour is illustrated in Figure 3.3. The decreasing intensity was mainly observed for samples with Pt coverages of 0.4 – 0.8 ML. Usually a clear loss of intensity was only observed for the high–temperature feature in the TPD spectra (dashed line in Figure 3.3), it cannot be excluded however, that the intensity of the low–temperature feature was reduced as well. For very high D$_2$ exposures where this effect occurred, it is expected that the high–temperature feature (related to desorption from Ru) is completely saturated, therefore all spectra above a certain D$_{ad}$ coverage should be identical in this temperature range and a
decrease in intensity is easily resolved. The low–temperature feature (related to desorption from Pt sites) on the other hand does not reach saturation even with very high D\textsubscript{2} exposures; it is therefore possible that a decreased intensity is masked by the continuous increase in intensity with increasing D\textsubscript{2} exposures.

Theoretically, this decrease in intensity of the QMS signal could be caused either by a lower D\textsubscript{ad} coverage on the sample surface or by a decrease of the magnification of the QMS (change in the partial pressure to ion current ratio), which leads to a lower signal intensity for the same D\textsubscript{ad} desorption rate. It was mentioned by Pfeiffer Vacuum, the manufacturer of the QMS 200, that high exposures of D\textsubscript{2} might have a reducing effect on the filament of the QMS ion source, leading to a lower ionisation probability for the analysed gases. Alternatively, it is possible that the long dosing times for very high D\textsubscript{2} exposures (~30 min for 150×10^{-6} mbar\textperiodcentered s D\textsubscript{2}) lead to a build–up of contaminants on the sample surface, which in turn leads to a reduced D\textsubscript{ad} coverage.

Experiments conducted to further investigate this problem resulted in the following observations:

a) Even after extremely high D\textsubscript{2} exposures (up to 10^{4}\times10^{-6} mbar\textperiodcentered s) of sample surfaces saturated with CO, no intensity decrease is observed for CO TPD spectra (see Figure 4.45).

b) Gas phase spectra recorded at the start and end of a D\textsubscript{2} exposure of 150×10^{-6} mbar\textperiodcentered s (at 10^{-7} mbar D\textsubscript{2}) showed no change in intensity of the deuterium related mass signals or the composition of the gas phase (Figure 3.4).

These observations indicate that the reason for the intensity decrease in D\textsubscript{2} TPD spectra after high D\textsubscript{2} exposures is most likely due to a reduced D\textsubscript{ad} coverage, while a modification of the QMS filament due to interactions with deuterium as the source of the problem appears unlikely. Experiments conducted to investigate the possible surface contaminants, however, failed to provide any conclusive information. XPS spectra recorded after a high D\textsubscript{2} exposure (Figure 3.5) showed only peaks which can be assigned to the Ru(0001) substrate and the deposited Pt. Unfortunately the it is nearly impossible to trace carbon contaminations by XPS, since the carbon 1s peak is superimposed by the much more intensive Ru 3d\textsubscript{3/2} peak.
Figure 3.4: Gas phase mass spectra recorded at the beginning (black) and end (red) of D2 exposure of $150 \times 10^{-6} \text{ mbar}\cdot\text{s}$.

Figure 3.5: XPS survey spectrum of a surface with 0.7 ML Pt after a TPD experiment with exposures up to $150 \times 10^{-6} \text{ mbar}\cdot\text{s}$.

However, detail spectra of the Ru 3d and Pt 4f regions recorded on the same Pt film immediately after preparation and subsequently after a high D$_2$ exposure do not show any
changes in intensity and line shape (Figure 3.6), indicating that changes in the concentration of carbon or other contaminants on the surface is below the XPS detection limit.

Figure 3.6: XPS spectra of the (a) Ru 3d and (b) Pt 4f regions after deposition of 0.5 ML Pt (black) and after a D₂ exposure series ending with $150 \times 10^{-6}$ mbar $\cdot$ s (red).

At the same time, mass spectra of the gas phase recorded during D₂ exposure do not indicate the presence of any species, which may to adsorb on the sample surface, in quantities significantly higher than at base pressure (Figure 3.7).

Figure 3.7: Gas phase mass spectra of the residual gas at base pressure (black) and at $1 \times 10^{-7}$ mbar D₂ (red).

Since the experimental equipment did not allow additional experiments in order to determine and eliminate the source of the problem, it was decided to limit the D₂ exposures to
≤ 100×10^{-6} \text{ mbar} \cdot \text{s}. This exposure was low enough not to cause the above mentioned problems, yet still high enough to saturate the clean Ru(0001) surface with D_{ad} and provide sufficient experimental data from bimetallic surfaces.

Other problems mainly manifested themselves as artefacts in the QMS signal during TPD measurements and gas dosing. One such artefact is illustrated in Figure 3.8; during CO dosing the QMS signal of mass 28 showed a continuous increase in intensity over time (in the range from 20 – 130 s in Figure 3.8), while the ion gauge indicated a constant pressure value. Interestingly this effect was not observed for mass 4 during the dosing of deuterium. This problem could be positively traced to the QMS 200 which was used to record the TPD spectra during all experiments described in this thesis. A second QMS (QMA 125) which was installed in the UHV chamber, showed a constant signal during CO dosing, in agreement with the ion gauge. This lead to the conclusion that the continuous increase in intensity observed for the mass 28 signal on the QMS 200 was an experimental artefact, while the CO pressure in fact remained constant. Charging effects within a layer of adsorbed contaminants on surfaces of the QMS ion source were mentioned by the manufacturer as a possible explanation for this problem.

![Figure 3.8: Mass 28 signal recorded during CO exposure. From 20 – 130 s the CO pressure remained constant at 1×10^{-7} \text{ mbar} (indicated by ion gauge).](image-url)
A different artefact was observed approximately at the same time, during residual gas measurements. Compared to earlier measurements, the residual gas spectrum displayed clearly abnormal intensities for masses 19, 35 and 37 (red spectrum in Figure 3.9).

![Figure 3.9: Residual gas spectra recorded at the same time with the QMS 200 (red) and QMA 125 (black). The signal intensity has been normalized to the signal of m/z = 28.](image)

In mass spectrometers with a grid ion source these masses are known to originate from so called EID (electron impact desorption) ions, which are desorbed via electron bombardment of compounds adsorbed on spectrometer surfaces during its operational history [52,53]. To make sure that these masses did not originate from actual contaminants in the residual gas, a QMA 125 was used to analyse the residual gas. The resulting spectrum did not display abnormal intensities for the concerning masses (black spectrum in Figure 3.9), leading to the conclusion that the QMS 200 at this point had accumulated an abnormal amount of adsorbates on the spectrometer surfaces. The QMS was sent to the manufacturer for cleaning, which eliminated both problems described above.

The third artefact was observed as an increase of intensity between the two main peaks and of the tail on the high temperature side of the TPD spectra of CO on Ru(0001). Usually, an increased intensity in this temperature range indicates an increased amount of surface defects. In this case however, the intensity was considerably higher than observed in any previous experiments. Similar to the artefact described above, this effect was not observed in D₂ TPD.
spectra. Therefore, an increase in the number of surface defects has not been considered as the source of this problem at first.

![Figure 3.10: CO TPD spectra on clean Ru(0001). (—) smooth surface, (---) surface with an increased number of defects, (···) artefact spectrum. Spectra are normalized to the same area.](image)

As can be seen from the blue spectrum in Figure 3.10 the signal does not drop back to the baseline at the end of the TPD run at 600 K, which made a background subtraction problematic. Since the area of the CO TPD spectrum on Ru(0001) was used to calculate the CO coverage for all other experiments, this would make any results questionable. As with the above mentioned problems a QMA 125 was used to further investigate the problem. The position and ion source of the QMA 125 were not optimal to conduct TPD experiments, however, a CO TPD spectrum on Ru(0001) recorded with this spectrometer clearly showed increased signal intensity between the main TPD peaks and on the high temperature side of the spectrum, identical to the spectra recorded with the QMS 200.

In order to investigate the smoothness of the crystal surface the crystal was transferred into a UHV chamber set up for STM measurements. While the quality of the obtained STM images (Figure 3.11) is limited, a rough estimate results in a rather narrow terrace width of 15 – 25 nm, indicating that the increased CO desorption in the concerned temperature ranges might result from increased CO amounts adsorbed at defect sites.
A first attempt to repolish the crystal surface by hand did not produce a satisfactory result and the crystal was sent to MaTeck GmbH for repolishing. After the crystal was returned, it was subjected to the cleaning procedure described in Section 3.2. Subsequent TPD experiments resulted in CO TPD spectra which again were identical to the spectrum shown in Figure 3.1.

After the sample crystal was repolished, D$_2$ TPD spectra recorded from sub–monolayer Pt films on the Ru(0001) surface showed some marked differences compared to spectra recorded on identically prepared surfaces before the beginning of the problems which necessitated the crystal to be repolished. These differences are illustrated in Figure 3.12. For the Ru related high–temperature desorption feature the changes mainly consist of an increased desorption on the low–temperature side of the main peak and decreased desorption on the high–temperature side. In the spectra recorded from 0.5 and 0.85 ML of Pt (Figure 3.12a and b) the older spectra (black solid lines) display a clear shoulder on the low–temperature side of the main Ru related peak, in the new spectra (red dashed lines), this feature is completely absent. The differences observed for Pt related desorption feature are even more pronounced, in the old spectra this feature consists of two poorly resolved peaks at ~115 and ~140 K, while the new spectra show only one desorption peak at 147 K. Additionally, the older spectra show a rather steep onset of desorption at 90 K in conjunction with the peak at 115 K, while desorption in the new spectra also starts at 90 K, but the initial onset is not as steep, followed by a marked increase at ~110 K. At the same time integration of the Pt and Ru regions of the spectra results in partial D$_{ad}$ coverages that are identical (within experimental accuracy) for both spectra.
Figure 3.12: D$_2$ TPD spectra recorded after an exposure of 100×10$^{-6}$ mbar D$_2$, before (….) and after (—) the Ru(0001) crystal was repolished. Pt coverages /ML: (a) 0.3, (b) 0.5, (c) (…) 0.85 (—) 0.9, (d) (…) 1.2 (—) 1.15.

The physical reason for the observed mismatch between the TPD spectra before and after the repolishing of the crystal is most likely related to the different amounts of surface defects or terrace widths. The increased desorption on the low-temperature side of the Ru peak in the spectra before repolishing can likely be attributed to the increased number of mixed adsorption ensembles along the border between the Ru steps and Pt step decorations, the same effect probably accounts for the decreased desorption on the high-temperature side of the Ru related TPD feature. On a smooth Ru(0001) substrate the number of such mixed ensembles is low compared to the number of pure Ru or Pt ensembles, however, considering the increased step density shown in Figure 3.11 the number of mixed PtRu ensembles is expected to increase proportionally to the step density. The adsorption of D$_2$ in this region can be compared to adsorption on PtRu surface alloys (see references [28,30,48]).
The discrepancies observed for the Pt related TPD feature are more difficult to explain. Of the two barely resolved features at ~115 and ~140 K, observed on Pt film surfaces with low to medium Pt coverage before repolishing, only the high temperature peak remains on surfaces with high Pt coverages (Figure 3.12c and d). On surfaces with high Pt coverages, this peak is found at roughly the same temperature as in TPD spectra recorded after the repolishing procedure. This feature can be assigned to D₂ desorbing from the inner parts of contiguous Pt areas (islands or step decorations). The origins of the other desorption feature at ~115 K on the other hand are not as clear. The very low desorption temperature indicates an adsorption energy that is lower than the adsorption energy of adsorption sites in contiguous Pt areas or on the edges of Pt islands and step decorations. These two kinds of adsorption sites, however, are the only ones that are observed in STM images of Pt film surfaces prepared on a smooth Ru(0001) surface [50,51]. Since no STM images were recorded of the Pt films before the crystal was repolished, it is difficult to relate the changes in the TPD spectra in this temperature range to specific changes in the morphology of the Pt films before and after repolishing.

In conclusion, it can be safely assumed that the morphology of the bimetallic surfaces after the repolishing procedure was identical to the morphology of the surfaces investigated in the STM experiments described in Section 3.2 (since these experiments were conducted on a smooth Ru(0001) crystal). The results of these STM experiments were therefore used to evaluate the TPD spectra presented in this thesis, all of which were recorded after the crystal was repolished.
4 Results and discussion

4.1 Chemical properties of structurally well-defined PdRu/Ru(0001) surface alloys – Interaction with CO

The content of the following section was published in reference [54] and is reproduced by permission of Elsevier. The style and numbering of references and figures has been modified in line with the layout of this thesis, the experimental section has been shortened for brevity. My contribution to this publication are the TPD and IRAS measurements, additionally I produced the first draft and was strongly involved in the creative process of the manuscript.

4.1.1 Abstract

The chemical properties of structurally well-defined PdRu/Ru(0001) monolayer surface alloys [25] and a Pd monolayer on Ru(0001) were studied by temperature programmed desorption and infrared reflection absorption spectroscopy using CO as probe molecule. IR experiments on the PdRu/Ru(0001) surface alloys demonstrate that CO adsorption on Ru sites resembles that on pure Ru(0001) (on–top adsorption), while adsorption on the Pd sites occurs on both multifold coordinated and on–top sites, similar to CO on Pd(111). A significant destabilization of CO adsorption on Pd sites for both, surface alloys and the Pd monolayer film, compared to pure Pd(111) surfaces is attributed to a combination of geometric strain and vertical electronic ligand effects; an additional variation in the CO adsorption bond strength in the surface alloys is attributed to changes in the neighboring surface atom shell (lateral ligand effects). The chemical modifications introduced by PdRu surface alloy formation are compared with findings for deuterium adsorption on the same surface alloys; effects of the two–dimensional (2D) distribution of surface atoms are illustrated by comparison with CO adsorption on PtRu/Ru(0001) surface alloys, where in contrast to the pronounced 2D phase segregation in PdRu/Ru(0001) the surface atoms are essentially randomly distributed.
4 Results and discussion

4.1.2 Introduction

The systematic modification of the physical and chemical properties of metals upon alloy formation is of considerable interest both from a fundamental point of view as well as for various applications. One of the earliest and still dominant applications is the use of bimetallic catalysts in heterogeneous catalysis, whose catalytic performance was found to be distinctly different from that of the individual components and often superior to that of monometallic supported catalysts [7,8,10]. The modified chemical and catalytic properties were explained by various structural and electronic effects such as electronic ligand effects, geometric ensemble effects and, more recently, electronic strain effects [11,12,14]. A more detailed introduction to these effects is given in a preceding paper [25]. Main problem in the unambiguous experimental identification and quantification of the different effects for supported bimetallic catalysts is the lack of structural information, in particular the missing knowledge of the exact concentration and even more of the two-dimensional (2D) distribution of the respective atomic species in the surface of the bimetallic nanoparticles. A basic understanding of the effects modifying the chemical/catalytic properties of bimetallic nanoparticle surfaces can be obtained, however, from model studies on bimetallic planar surfaces of massive solids with well-defined surface structure. Recently, we performed a number of studies on the chemical and electrochemical properties of PdAu/Au(111) [55], PdAu/Pd(111) [24], PdCu/Ru(0001) [20,32,56] and PtRu/Ru(0001) [26–31,57] monolayer surface alloys, where the surface composition and the 2D distribution of surface atoms was quantitatively determined by atomic resolution scanning tunnelling microscopy (STM). In combination with theoretical studies (density functional theory (DFT) calculations) [17,24,58–64], these studies allowed to clearly identify and distinguish between geometric ensemble effects, electronic ligand effects, and electronic strain effects, and even quantify the order of magnitude of the different contributions.

In the present paper, we report results of a similar type study on the correlation between surface structure and chemical properties on structurally well-defined PdRu/Ru(0001) monolayer surface alloys. Here, we focus on the interaction of CO with these surfaces, which was studied by temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS). This publication follows a preceding paper where we prepared a series of monolayer surface alloys with varying Pd content and characterized the atom distribution by STM and the deuterium adsorption behaviour by TPD [25]. This system turned out to be particularly interesting, since despite the rather similar chemical properties of the platinum...
group metals Pt and Pd the distribution of surface atoms is distinctly different for PtRu/Ru(0001) and PdRu/Ru(0001) monolayer surface alloys. While for PtRu/Ru(0001) the surface atoms are essentially randomly distributed [31], PdRu/Ru(0001) surface alloys tend to phase segregation and formation of 2D domains [25]. CO and deuterium adsorption complement each other in so far as CO is largely adsorbed in on-top sites, and hence is expected to be more sensitive to ligand effects, while deuterium, which is adsorbed in threefold hollow sites, is more sensitive to the elemental composition of the adsorption ensemble, i.e., to ensemble effects.

Previous studies of bimetallic PdRu surfaces were carried out on Ru(0001) substrates covered by Pd overlayers. Based on TPD, Auger electron spectroscopy (AES), and low energy electron diffraction (LEED) experiments, Park concluded that the growth of the first few monolayers proceeds via a layer–by–layer growth process with the first layer being pseudomorphic with respect to the Ru(0001) surface [65]. Furthermore, the CO$_{ad}$ saturation coverage for adsorption at room temperature was found to be significantly reduced compared to adsorption on the unmodified substrate. Campbell et al. came to similar results, and concluded that the change in adsorption properties of a Pd monolayer on Ru(0001) compared to pure Pd(111) is caused by transfer of electron density from Pd to Ru, leading to a greater fraction of empty states in the valence band of the Pd layer [66].

DFT calculations of CO adsorption on Ru(0001), Pd(111), and a Pd monolayer on Ru(0001) (Pd$_{ML}$/Ru(0001)) yielded identical CO adsorption geometries on Pd(111) and Pd$_{ML}$/Ru(0001) [62]. The adsorption energy, however, is significantly lower on the Pd monolayer compared to Pd(111), which was attributed to a shift of the d–band centre to lower energies. This conclusion is corroborated by DFT calculations on the interaction between a Pd monolayer and the Ru(0001) substrate, which indicate a depopulation of the d–states of Pd atoms and a charge transfer to the substrate [67,68].

After a brief description of the experimental procedures and setup, we will first report results of CO TPD measurements on PdRu/Ru(0001) surface alloys of different composition, complemented by similar measurements on bare Ru(0001) and on Pd$_{ML}$/Ru(0001). In Section 4.1.4.2, we present results of IRAS measurements, performed after increasing adsorption of CO at 100 K. In the last section (discussion), we compare the present results with those obtained for deuterium adsorption on similar surfaces [25] and with those of previous studies on deuterium and CO adsorption on PtRu/Ru(0001) [26–31,57], and
4 Results and discussion

PdCu/Ru(0001) [32] surface alloys, and finally summarize the complementary results of these studies on the correlation between structural, electronic and chemical properties.

4.1.3 Experimental

The experiments described in this section were carried out on the UHV system described in detail in Section 3.1. For sample preparation procedures and details on data acquisition, I refer to Sections 3.2 and 3.3, respectively.

4.1.4 Results

4.1.4.1 Interaction of CO with PdRu/Ru(0001) surface alloys – TPD results

For comparison, we start with CO TPD spectra of the unmodified Ru(0001) surface, which are displayed in Figure 4.1a. For small CO exposures, only a single peak (α_1 peak) at 487 K is observed. With increasing coverage it shifts to lower temperatures and is centered at 460 K for 0.33 ML CO. At CO coverages above 0.33 ML, a second peak develops with the maximum at 402 K (α_2 peak). The spectra are identical to those reported previously [26,29,46,69]. The α_1 state is associated with the formation of a (√3 × √3)R30° structure, with CO molecules linearly adsorbed in an on–top configuration on Ru atoms, while the α_2 peak is formed at higher coverage [69]. Using the value for the preexponential factor for desorption of 10^16 s\(^{-1}\), which was reported previously by Pfnür et al. [46,69] for small CO\(_{\text{ad}}\) coverages on Ru(0001), a Redhead analysis yields an activation energy for desorption of 155 kJ mol\(^{-1}\) for the α_1 peak. Sets of desorption spectra from PdRu/Ru(0001) surface alloys with varying Pd concentrations and from a closed Pd monolayer on the Ru(0001) substrate (Pd\(_{\text{ML}}\)/Ru(0001)) are collected in Figure 4.1b–h. The respective CO TPD spectra at saturation coverage are additionally compiled in Figure 4.2 to illustrate the changes of the CO adsorption behavior more clearly. The TPD sets of PdRu/Ru(0001) surface alloys with Pd contents below 64% (Figure 4.1b–f) show for small CO exposures a single desorption peak β_1, which shifts from 491 K at 9% Pd to 459 K at 64% Pd. Since its position is almost identical to that of the α_1 peak on Ru(0001), it is assigned to desorption from Ru sites of the surface alloy. For CO saturation, the desorption maximum of the β_1 peak shifts only little with
increasing Pd content to low temperatures, from 460 K at 9% Pd to 454 K at 64% Pd (Figure 4.2). At the same time, also the trailing edge of this peak shifts to lower temperatures with increasing Pd content, and this shift is more pronounced than that of the peak maximum. As one would expect from the diminishing Ru fraction in the topmost layer, the $\beta_1$ peak decreases in intensity with increasing Pd concentration, and is finally (for a surface alloy with 87% Pd) only visible as a small high temperature shoulder to the desorption states related to Pd.

In the TPD spectra of surface alloys with smaller Pd concentrations (up to 15%), a further desorption peak (denoted $\beta_2$ in the following) is observed around 390 K, which can be traced back to the $\alpha_2$ peak of the unmodified Ru(0001) surface. Similar to the $\beta_1$ peak, also the $\beta_2$ desorption state loses intensity with increasing Pd content. At the same time, the clear separation between these two peaks, which is observed for the unmodified Ru(0001) surface, is reduced for the bimetallic surfaces. For a surface alloy with 31% Pd, the $\beta_2$ state is only visible as a very weak peak between desorption from Pd sites at lower temperatures and the $\beta_1$ peak at higher temperature.

In TPD spectra of the bimetallic surfaces with Pd concentrations below 15%, a third peak appears as a shoulder at considerably lower temperature. This $\beta_3$ state is attributed to desorption from Pd sites on the surface, as its intensity steadily grows with increasing Pd concentration, from a shoulder at 15% Pd into a well-pronounced peak centered at 322 K at 31% Pd. Additionally, a fourth desorption state denoted as $\beta_4$ state emerges at even lower temperature (around 220 K) and remains visible for all surface alloys with higher Pd concentration. Eventually, for surface alloys with very high Pd contents (beginning at 64% Pd), the formation of a fifth desorption state $\beta_5$ is observed at even lower temperature (around 160 K).

The CO TPD spectra of a Pd$_{\text{ML}}$/Ru(0001) surface are depicted in Figure 4.1h. A closed Pd monolayer on the Ru(0001) substrate constitutes the theoretical upper limit for the Pd concentration of a PdRu/Ru(0001) monolayer surface alloy. After CO saturation, the spectrum is composed of three peaks, which were also observed in previous TPD studies of CO desorption from similarly prepared Pd monolayers on Ru(0001) [32,66] and were denoted as $\gamma_1 – \gamma_3$ states. After CO saturation, they are located at 327 K ($\gamma_1$), 237 K ($\gamma_2$), and 175 K ($\gamma_3$), respectively. In the room temperature study by Park [65], only CO desorption from Ru sites is detected, while Pd sites cannot be populated under these conditions.
Figure 4.1: CO TPD spectra of (a) unmodified Ru(0001), (b)-(g) different Pd$_{1-x}$/Ru(0001) surface alloys with varying Pd contents (alloy compositions given in each panel), and (h) Pd$_{0.09}$/Ru(0001) (1.06 ML Pd on Ru(0001) after CO exposure at 100 K. CO exposures ×10$^{-6}$ mbar·s: 0.25, 0.5, 1, 1.5, 2, 2.5, 5, 10 and 50.

A comparison of the desorption spectra of the PdRu/Ru(0001) surface alloys with the Pd$_{0.09}$/Ru(0001) shows that the desorption states $\beta_3 - \beta_5$ of the surface alloys are essentially identical with the desorption states $\gamma_1 - \gamma_3$ of the Pd monolayer film (cf. Figure 4.2), demonstrating again that the desorption states $\beta_3 - \beta_5$ are due to CO desorption from Pd sites of the surface alloys. Compared to CO desorption from Pd(111) single crystal surfaces [70–74], the desorption maximum is shifted to lower temperatures by about 150 K on surface
alloys with high Pd contents. For the Pd monolayer, the desorption energy in the main desorption peak ($\gamma_1$ peak) is estimated to $\sim$100 kJ mol$^{-1}$, which is $\sim$40 – 50 kJ mol$^{-1}$ lower than that reported for Pd(111) (main peak) [70,75]. It agrees well, however, with the value of 95 kJ mol$^{-1}$ calculated by DFT techniques by Gonzalez and Illas [62] for a low coverage CO adlayer (0.11 ML) on a Pd monolayer on Ru(0001).

![Figure 4.2: CO TPD spectra of the unmodified Ru(0001) surface, various PdRu/Ru(0001) surface alloys and the Pd$_{ML}$/Ru(0001) surface after CO saturation.](image)

The saturation coverages of CO on surface alloys with different Pd contents derived from the above TPD spectra are presented in Figure 4.3a. It first increases slightly from 0.68 ML on Ru(0001) to 0.78 ML on a surface with 15% Pd. For higher Pd concentrations, the value
decreases again to 0.66 ML (87% Pd) and then remains constant up to 1.06 ML Pd, in good agreement with results of Hager et al. [32] for a Pd monolayer film on Ru(0001) ($\theta_{\text{CO(Sat)}} = 0.68$ ML).

![Graph showing CO saturation coverage and initial CO sticking coefficient](image)

**Figure 4.3:** (a) CO saturation coverage on PdRu/Ru(0001) surface alloys with varying Pd content. (b) Initial CO sticking coefficient on PdRu/Ru(0001) surface alloys with varying Pd content.

The subtle increase of the saturation coverage for surface alloys with 10 – 30% Pd was reproducibly obtained in a number of measurements, always comparing CO TPD spectra after saturation of the Ru(0001) substrate and of the PdRu/Ru(0001) surface alloys. For a more detailed discussion of possible origins of the increase of the CO$_{\text{ad}}$ coverage in this range of Pd contents, however, additional measurements are needed.
Results and discussion

Figure 4.4 shows the sticking coefficients $s(\theta)$ for pure Ru(0001) and PdRu alloy surfaces with 64% and 87% Pd as a function of CO coverage. On all three surfaces, the sticking coefficient shows only a slight decrease for increasing CO coverage up to 0.5 ML. At higher CO coverages, the sticking coefficient decreases rapidly to zero for the saturated CO adlayer. This dependence of the sticking coefficient is identical to the behavior reported by Pfnür and Menzel [47] for CO adsorption on the Ru(0001) surface. A similar $s(\theta)$ dependence was reported also for CO adsorption on Pd(111) [76] and on PtRu/Ru(0001) surface alloys and Pt monolayer films on Ru(0001) [29].

![Figure 4.4: Sticking coefficient as a function of CO coverage on Ru(0001) (■) and PdRu/Ru(0001) surface alloys with different Pd contents (64% Pd (▼) and 87% Pd (●)). Fitted values are represented by dashed lines (cf. Eq. (4.1)).](image)

The variation of the sticking coefficient with CO coverage differs from that of simple first-order Langmuir adsorption kinetics. This difference was explained by the presence of a precursor state in the adsorption process [77]. The experimentally observed dependence of the sticking coefficient on CO coverage was fitted to the equation proposed by Kisliuk for adsorption via a precursor state [77]:

$$s = s_0 \left(1 + \frac{\Theta K}{1-\Theta}\right)^{-1}$$  \hspace{1cm} (4.1)
where \( K = \frac{p_d'}{p_a + p_d'} \) (\( p_d' \) is the probability for desorption from the precursor state over an occupied site, and \( p_a \) and \( p_d \) are the probability for chemisorption and desorption from the precursor state over an empty site). The experimental data can be fitted for all Pd contents by calculated curves (dashed lines) with \( K = 0.1 \) (Figure 4.4), indicating that a precursor state exists not only on the pure Ru and Pd surfaces and sites, but also on the PdRu/Ru(0001) surface alloys. Similar findings were reported for CO adsorption on PtRu/Ru(0001) surface alloys [29].

The initial sticking coefficients \( s_0 \) for surface alloys with varying Pd concentrations are depicted in Figure 4.3b. The well–known initial sticking coefficient for CO adsorption on the unmodified Ru(0001) surface of 0.7 [29,47] was used for calibrating the flow in front of the doser. The formation of the PdRu/Ru(0001) surface alloys first leads to an increase of the initial sticking coefficient to \( s_0 \approx 0.9 \), which remains constant for Pd contents up to 64% Pd. Beyond this coverage, it decreases back to 0.71 for the Pd monolayer. This latter value for the Pd_{ML}/Ru(0001) agrees again fully with previous findings [32]. For comparison, for PtRu/Ru(0001) surface alloys, the initial sticking decreases when going from CO adsorption on the pure Ru(0001) substrate to CO adsorption on the surface alloys [29].

### 4.1.4.2 Adsorption of CO on PdRu/Ru(0001) surface alloys – IR measurements

For the IR measurements, we also start with CO adsorption on unmodified Ru(0001) and on Pd_{ML}/Ru(0001), respectively. Figure 4.5a displays IR spectra obtained from Ru(0001) after increasing CO exposure. In these spectra only a single absorption band is observed, which shifts with increasing exposure from 1994 cm\(^{-1}\) (0.5×10\(^{-6}\) mbar·s, ~0.02 ML CO) to 2060 cm\(^{-1}\) (50×10\(^{-6}\) mbar·s, CO\(_{ad}\) saturation). Both, the peak position and the shift with increasing CO coverage, are fully in line with results reported by Pfnür et al. [78]. These authors assigned this band to the C–O stretch vibration of CO adsorbed on–top of Ru atoms; the shift was attributed to a combination of increasing dipole – dipole coupling and chemical effects due to intermolecular repulsion.
Figure 4.5: Infrared spectra at 100 K after CO exposure on (a) Ru(0001) and (b) Pd$_{ML}$/Ru(0001) (1.10 ML Pd on Ru(0001)). CO exposures $\times 10^{-6}$ mbar·s: (a) on Ru(0001) 0.2, 0.5, 1, 2, 5 and 20; and (b) on Pd$_{ML}$/Ru(0001) 1, 2, 5 and 20.

The IR spectra recorded on a 1.1 ML Pd/Ru(0001) surface (Figure 4.5b) show the development of different IR bands with increasing CO coverage, indicative of a coverage–dependent change of the preferential adsorption site of CO. After smaller exposures (below $5\times10^{-6}$ mbar·s, ~0.15 ML CO), only a single broad band between 1860 and 1895 cm$^{-1}$ is observed. After larger exposures ($10\times10^{-6}$ mbar·s, ~0.58 ML CO), this band is replaced by two bands at 1943 and 2093 cm$^{-1}$, which remain at their positions also after CO$_{ad}$ saturation. Almost identical IR spectra were reported for a similarly prepared Pd$_{ML}$/Ru(0001) surface in a previous study of CO adsorption on Pd$_X$Cu$_{1-X}$/Ru(0001) surface alloys [32]. The single band after lower exposure is assigned to CO adsorption on threefold hollow sites, while the two
features at 1943 and 2093 cm\(^{-1}\) after larger CO exposures are attributed to CO on bridge and on–top sites.

The results for a Pd\(_{\text{ML}}\)/Ru(0001) surface can be compared also to those of previous vibrational spectroscopic studies of CO adsorption on Pd(111) [39,79–83], which largely showed a similar behavior, with initial occupation of threefold hollow sites for smaller CO\(_{\text{ad}}\) coverages (up to 0.33 ML) and change to bridge sites at higher coverages (above 0.50 ML). In contrast to Pd\(_{\text{ML}}\)/Ru(0001), the IR spectrum after CO\(_{\text{ad}}\) saturation on Pd(111) shows features at 2110 cm\(^{-1}\) (on–top) and at 1895 cm\(^{-1}\) (threefold sites). The subtle differences, occupation of on–top and bridges sites on Pd\(_{\text{ML}}\)/Ru(0001) rather than of on–top and threefold sites (Pd(111)) at high CO coverages, may be explained either by changes of the electronic properties of the Pd\(_{\text{ML}}\)/Ru(0001) surface compared to Pd(111) or by differences in the CO adlayer density [39].

A change of the adsorption site occupation was observed before also for Pt\(_{\text{ML}}\)/Ru(0001), with exclusive adsorption on on–top sites at CO\(_{\text{ad}}\) saturation [23,84], while both on–top and bridge sites are occupied on Pt(111) [85,86].

Finally, it should be noted that at low CO\(_{\text{ad}}\) coverages the bands related to CO on threefold sites on Pd\(_{\text{ML}}\)/Ru(0001) are shifted by ~40 cm\(^{-1}\) to higher wave numbers compared to Pd(111), while at CO\(_{\text{ad}}\) saturation the bands for CO on linear sites are shifted by ~20 cm\(^{-1}\) to lower wave numbers. This will be discussed in more detail later (section 4.1.4.3).

Next, we present IR data recorded on six different PdRu/Ru(0001) surface alloys with Pd contents of 12%, 22%, 42%, 58%, 75%, and 90%, respectively. Figure 4.6a and b show IR spectra obtained from surface alloys with 12% and 22% Pd after exposure to increasing CO doses at 100 K. For both alloy surfaces, a single absorption band is observed, which shifts with increasing CO exposure from ~1990 to ~2065 cm\(^{-1}\). Considering the peak shape and the pronounced up–shift of the peak position with increasing CO coverage, the spectra largely resemble those of CO\(_{\text{ad}}\) on pure Ru(0001). We did not detect additional features related to CO adsorbed on Pd sites. Compared to the spectra of pure Ru(0001), the main difference is a small down–shift of the vibrational band by ~5 cm\(^{-1}\) at low COad coverages, turning into an up–shift by ~5 cm\(^{-1}\) at saturation. Hence, the up–shift with increasing COad coverage is more pronounced for adsorption on the Ru sites of these surface alloys compared to pure Ru(0001).

At a Pd surface content of 42% (Figure 4.6c), the IR spectra show at lower COad coverages again only the band of CO adsorbed on–top of Ru sites, which is down–shifted by ~8 cm\(^{-1}\) compared to Ru(0001) and is located at 1986 cm\(^{-1}\). At saturation coverage, the peak position
is identical to that on Ru(0001). In addition, a small IR signal appears at 2097 cm$^{-1}$, which is related to CO$_{ad}$ on on–top Pd sites. Furthermore, a broad IR feature with low intensity develops between 1940 and 1980 cm$^{-1}$, indicating the onset of the occupation of bridge adsorption sites on the Pd surface atoms. These signals grow with increasing Pd content and become more significant in the IR spectra of the surface alloy with 58% Pd (Figure 4.6d).

**Figure 4.6:** Infrared spectra at 100 K after CO exposure on various PdRu/Ru(0001) surface alloys (alloy composition given in each panel). CO exposures for all surface alloys ×10$^{-6}$ mbar·s: 0.2, 0.5, 1, 2, 5 and 20.
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After small exposures, the band related to on–top adsorbed CO on Ru sites is still the only observable feature. Compared to Ru(0001), it shows a down–shift of ~12 cm\(^{-1}\) at low CO coverages.

After larger CO exposures, additional signals at 1930 – 1970 cm\(^{-1}\) (bridge adsorption on Pd) and a band at 2093 cm\(^{-1}\) (on–top adsorption on Pd) reflect adsorption on Pd sites. For a surface alloy with 75% Pd (Figure 4.6e), the band attributed to CO adsorbed on Ru sites is again the only feature after CO exposures up to \(2.5 \times 10^{-6}\) mbar\(\cdot\)s (up to 0.15 ML CO). In this CO\(_{ad}\) coverage range, the IR band is at the same position as for the 58% Pd containing surface (Figure 4.6d). After a larger CO exposure (\(5 \times 10^{-6}\) mbar\(\cdot\)s, 0.27 ML CO), this band is considerably broadened – the peak width increases from 26 to 31 cm\(^{-1}\) – and a broad shoulder has grown in on the low frequency side of the peak. At CO\(_{ad}\) saturation (0.70 ML CO), the intensity of the band related to CO\(_{ad}\) on Ru sites has lost a significant part of its intensity. Instead, bands related to CO\(_{ad}\) on Pd sites (on–top adsorbed CO at 2092 cm\(^{-1}\), bridge adsorbed CO at 1956 cm\(^{-1}\)) appear, which gain intensity compared to CO adsorption on the 58% Pd surface alloy. Even at a Pd surface content of 90%, the band assigned to CO adsorbed on Ru atoms is still the first detectable feature in the spectra after low CO exposures. Also for this surface alloy, the peak broadens significantly with increasing CO coverage. The overall up–shift of its position with increasing CO\(_{ad}\) coverage is considerably reduced compared to the pure Ru(0001) surface or to the surface alloys with lower Pd content. At higher CO\(_{ad}\) coverages, the intensity of the Ru related CO\(_{ad}\) band decreases strongly. At CO\(_{ad}\) saturation, it is only present as a broad feature between 1990 and 2060 cm\(^{-1}\). CO adsorption on Pd sites of the surface is identified after larger CO exposures (\(5 \times 10^{-6}\) mbar\(\cdot\)s, 0.20 ML CO). It is reflected by a band at 1880 cm\(^{-1}\), corresponding to CO\(_{ad}\) bound on Pd threefold hollow sites. The intensity of the latter peak again increases compared to surface alloys with lower Pd contents. Analogously to CO\(_{ad}\) on the Pd\(_{ML}/\)Ru(0001) surface, this band is replaced by two bands (on–top and bridge bonded CO at 2093 and 1956 cm\(^{-1}\)) after further increasing CO exposures. The band for the bridge bonded CO\(_{ad}\) is significantly broader compared to CO\(_{ad}\) on the Pd monolayer, for on–top bonded CO\(_{ad}\), the broadening of the band is less pronounced.

The IR spectra of the different PdRu/Ru(0001) surface alloys show close similarities in the occupation of different adsorption sites by CO: (i) linear (on–top) adsorption on the Ru component of the surface alloy, as reported before for unmodified Ru(0001) [39,87]; (ii) adsorption on threefold hollow sites provided by Pd surface atoms at lower local CO\(_{ad}\) densities; and (iii) a change from threefold hollow sites to a mixture of linear and bridge sites.
at higher (local) coverage on the Pd surface atoms, similar to CO adsorption on Pd$_{\text{ML}}$/Ru(0001) [32]. The order in which the IR bands appear with increasing CO$_{\text{ad}}$ coverage, first CO$_{\text{ad}}$ on Ru sites and then CO$_{\text{ad}}$ on Pd sites, agrees with the population of surface sites derived from the TPD spectra. The minimum Pd content for the appearance of features related to CO adsorption on Pd surface atoms, however, is significantly higher than expected from the surface composition [25] and from the TPD spectra. Possible explanations for this discrepancy will be discussed in the next section.

4.1.4.3 Discussion

The modification of the energetics of deuterium adsorption on Pd monolayer films on Ru(0001) and on monolayer PdRu/Ru(0001) surface alloys, as compared to adsorption on unmodified Ru(0001) and on Pd(111), and the underlying physical effects were discussed in detail in a reference [25], using the d–band model introduced by Hammer and Nørskov [88,89] as basis. According to this model, the strength of the adsorption bond on metal surfaces is related to the position of the d–band center. Shifts of the d–band center induce a change of the adsorption properties, with a down–shift (up–shift) leading to a weakening (strengthening) of the adsorption bond [88,89]. For bimetallic systems, the center of the d–band is influenced by different effects. The main contributions relevant for adsorption on bimetallic PdRu surfaces are valid also for CO adsorption on these surfaces and shall therefore only be summarized briefly in the following:

(1) For monometallic pseudomorphic metal films, strain effects due to a change of the lattice size of the deposit compared to its natural bulk lattice constant result in a down–shift (upshift) of the d–band center for compressive (tensile) strain, and hence in a weakening (strengthening) of the adsorption bond on that monolayer compared to adsorption on a surface of the respective bulk material (‘strain effect’) [14,15,58,90]. For adsorption on a pseudomorphic Pd monolayer film on Ru(0001), where the Pd atoms are compressed by 1.8% relative to Pd(111), this results in a down–shift of the d–band center and a concomitant destabilization of the adsorption bond compared to adsorption on Pd(111).

(2) Additionally, adsorption on the Pd monolayer film is weakened by the strong electronic interaction of the Pd layer with the underlying Ru(0001) substrate (‘vertical
ligand effect’). Previously, the CO adsorption strength was found to increase again when going from a pseudomorphic Pt monolayer film deposited on a Ru(0001) substrate to bi– and multilayer (pseudomorphic) Pt films. This effect was attributed to a stronger interaction between Pt and Ru compared to Pt and Pt [23], leading to a pronounced weakening of the adsorption bond on the monolayer Pt film compared to Pt(111). With increasing thickness of the pseudomorphic film, the influence of the vertical ligand effect decreases very quickly and has largely vanished for a trilayer Pt film [23]. In contrast, the strain effect should be independent of the film thickness and stay constant, as long as the film is pseudomorphic. From these data and calculations, the strain effect was estimated to be responsible for 40% of the destabilization. For Pd/Ru(0001), this question has not been investigated in such a systematic way, but Campbell et al. [66] reported an up–shift of the CO desorption peak temperature from 340 to 420 K and finally to 480 K when going from a monolayer to a bilayer and finally to an eight layer thick Pd film on Ru(0001) demonstrating the influence of the vertical ligand effect for Pd/Ru(0001). The combination of these two effects is responsible for a down–shift of the center of the d–band and a concomitant destabilization of adsorption on a Pd monolayer on Ru(0001). In earlier DFT calculations, a down–shift of the center of the d–band by −0.47 eV compared to Pd(111) was found [58].

(3) For monolayer surface alloys, the adsorption bond on Ru or Pd surface atoms (on–top adsorption) is modified by strain effects, vertical ligand effects, and lateral ligand effects (within the surface layer). This is evident already by the result of the above DFT calculations, where the shift of the d–band center for an isolated Pd impurity in a Ru(0001) surface compared to Pd in a Pd(111) surface (−0.82 eV) was much more pronounced than that obtained for a Pd monolayer film (−0.47 eV) [58]. With increasing Pd content in the surface layer, the two effects work in opposite directions, both for adsorption on Pd and Ru surface atoms. Strain effects lead to an increasing destabilization with increasing Pd content in the pseudomorphic surface layer, due to the increasing number of larger Pd atoms surrounding a given Pd or Ru surface atom. In contrast, lateral ligand effects tend to stabilize the adsorption bond on these surface atoms with increasing Pd content, because of the weaker interaction between Pd and Pd (or Ru and Pd for adsorption on Ru sites) compared to Pd and Ru (or Ru and Ru for adsorption on Ru sites). Experimentally, however, these effects cannot be separated (see below).
(4) For deuterium adsorption (adsorption on threefold sites), ensemble effects were predicted to play a major role, influencing the adsorption bond by the composition of the adsorption trimer (mixed adsorption ensembles). In analogy to deuterium adsorption on PtRu/Ru(0001) surface alloys [30,91], the adsorption bond strength was proposed to decrease in the order Ru\textsubscript{3} > Ru\textsubscript{2}Pd > RuPd\textsubscript{2} > Pd\textsubscript{3} [25]. While for on–top adsorption of CO variations in the adsorption bond with varying Pd surface content can be explained by ligand effects, such kind of ensemble effects can be used for a formal description of the CO adsorbed on bridge and multifold sites.

The CO TPD spectra demonstrate that desorption from the Pd sites is shifted to considerably lower temperatures compared to CO\textsubscript{ad} desorption from unmodified Ru(0001) [26,29,46,69] or Pd(111) [70,72–74,92], reflecting a pronounced weakening of CO adsorption on these sites. For Pd\textsubscript{ML}/Ru(0001), the desorption maximum of the $\gamma_1$ peak is shifted by approximately 150 K to lower temperatures compared to the main CO desorption peak on Pd(111), which is centred at ~480 K [70,72–74,92]. Using the Redhead method and a preexponential factor of $10^{15}$ s\textsuperscript{-1}, the CO desorption energy is estimated to be ~100 kJ mol\textsuperscript{-1} for the Pd monolayer, which is ~40 – 50 kJ mol\textsuperscript{-1} lower than for CO adsorption on Pd(111) [73–75,92]. The estimated desorption energy agrees well, however, with the value of 95 kJ mol\textsuperscript{-1} calculated by DFT techniques by Gonzalez and Illas [62] for CO adsorbed on a Pd monolayer on Ru(0001) and with the findings of earlier experimental studies [32,66].

The modification of the electronic properties of the Pd monolayer on Ru(0001) by a combination of ligand and strain effects leads also to changes of the peak positions of the CO stretch vibrations in the IR spectra compared to unmodified Pd(111). Since the peak positions at higher CO\textsubscript{ad} coverages are influenced also significantly by other effects (dynamic dipole coupling and chemical shifts due to CO\textsubscript{ad} – CO\textsubscript{ad} interaction), it is difficult to derive meaningful conclusions under these conditions. Therefore, we will mainly concentrate on the peak position after small CO exposure. Comparing CO adsorption on Pd\textsubscript{ML}/Ru(0001) and Pd(111), a considerable shift to higher wave numbers is evident for adsorption on the bimetallic surface. While the CO signal appears at ~1825 cm\textsuperscript{-1} for small CO coverages on Pd(111) [72,93], it is located at ~1865 cm\textsuperscript{-1} for Pd\textsubscript{ML}/Ru(0001). The up–shift in frequency at lower CO\textsubscript{ad} coverages agrees with expectations based on the Blyholder model [94] and the d–band model [88–90], respectively. According to those models, the down–shift of the center of the d–band in the Pd\textsubscript{ML}/Ru(0001) surface compared to Pd(111) should lead to less electron
transfer into the antibonding $2\pi^*$ orbital of the CO molecules, and hence to an up–shift of the vibrational frequency, as observed experimentally.

For CO$_{ad}$ saturation, the shift of the linearly bonded CO$_{ad}$ species is in the opposite direction, it is down–shifted by $\sim$20 cm$^{-1}$ to lower wave numbers compared to CO adsorption on Pd(111). Most likely, this discrepancy can be explained by differences in the CO$_{ad}$ coverage and in the CO$_{ad}$ – CO$_{ad}$ interactions. Additionally, it has been shown for Pd(111) that the CO adlayer structure at saturation and the corresponding IR spectrum depend also on the exposure conditions [72,83].

Similar trends of a decreasing adsorption energy were observed also for deuterium adsorption on a Pd$_{ML}$/Ru(0001) surface, where the initial adsorption energy (activation energy for desorption) decreases from $\sim$100 kJ mol$^{-1}$ on the unmodified Ru(0001) surface to $\sim$60 kJ mol$^{-1}$ for PdRu/Ru(0001) surface alloys with Pd concentrations approaching 100% or for the Pd$_{ML}$/Ru(0001) surface [25]. The latter value is significantly lower than that on the unmodified Pd(111) surface ($\sim$90 kJ mol$^{-1}$) [95]. An even more pronounced shift was derived in DFT calculations by Pallassana et al. [96], with calculated H binding energies of $\sim$257 and $\sim$221 kJ mol$^{-1}$ for H adsorption on Pd(111) and Pd$_{ML}$/Ru(0001), equivalent to a decrease of the adsorption energy from 78 kJ mol$^{-1}$ for Pd(111) to only 6 kJ mol$^{-1}$ for Pd$_{ML}$/Ru(0001). For comparison with TPD experiments it is important to note that deuterium adsorption on Pd$_{ML}$/Ru(0001) is activated by $\sim$15 kJ mol$^{-1}$ [97], which increases the activation energy for desorption correspondingly.

Finally, it should be mentioned that in addition to substrate–adsorbate interactions also adsorbate–adsorbate interactions will be active. For CO adsorption on Pd$_{ML}$/Ru(0001), these can be clearly separated from effects induced by substrate–adsorbate interactions, since the latter should be constant for the whole surface. They are responsible for the width and peak structure of the desorption peak. For the surface alloys, in contrast, the peak broadening due to ligand and strain effects can hardly be separated from CO$_{ad}$ coverage–dependent changes in the adsorption energy due to adsorbate – adsorbate interactions.

Comparison with CO adsorption on Pt$_{ML}$/Ru(0001) shows a rather similar behavior [29]. First of all, CO adsorption on the Pt sites/ensembles of these surfaces is also destabilized by $\sim$40 – 50 kJ mol$^{-1}$ compared to Pt(111), the desorption energy decreases from $\sim$140 kJ mol$^{-1}$ for unmodified Pt(111) [98,99] to $\sim$90 kJ mol$^{-1}$ for Pt$_{ML}$/Ru(0001) [29,23,84]. The main CO desorption peaks are at 327 K ($>\theta_{CO}$) for Pd$_{ML}$/Ru(0001) (CO/Pd(111): $\sim$510 K ($<\theta_{CO}$) –
480 K ($>\theta_{\text{CO}}$) [70,72–74,92]) compared to 303 K ($>\theta_{\text{CO}}$) for Pt$_{\text{ML}}$/Ru(0001) [29] (CO/Pt(111): ~450 K ($<\theta_{\text{CO}}$) – 400 K ($>\theta_{\text{CO}}$) [98,99]). The similar (relative) magnitude of bond weakening for both deposit films is surprising, since due to the larger size mismatch between Pt and Ru atoms of 2.8% (compared to 1.8% in the case of PdRu) stronger strain effects are expected for PtRu/Ru(0001). Possibly, these stronger strain effects in the PtRu surface alloy layers are compensated by weaker electronic ligand effects compared to the PdRu/Ru(0001) surface alloy. This assumption seems to be reasonable, because of the better overlap of Ru and Pd states compared to that of Ru and Pt. Here, it is important to keep in mind that for Pt$_{\text{ML}}$/Ru(0001) vertical ligand effects are responsible for 60% of the total weakening of CO adsorption [23]. It may be assumed therefore that on PdRu/Ru(0001) surfaces the contribution of vertical ligand effects is even larger. It should also be noted that the destabilization does not only depend on the substrate, but also on the adsorbate. In contrast to CO adsorption, the adsorbed deuterium is more strongly destabilized on Pt$_{\text{ML}}$/Ru(0001) (relative to Pt(111)) than on Pd$_{\text{ML}}$/Ru(0001) (relative to Pd(111)). Finally, comparing the vibrational characteristics of CO adsorbed on Pd and Pt monolayer films, we find an unexpected down–shift for CO vibrational frequency on Pt$_{\text{ML}}$/Ru(0001) (relative to CO adsorption on Pt(111)) for both low and higher CO$_{\text{ad}}$ coverages [29].

For the PdRu/Ru(0001) surface alloys, additional effects arise from the interplay of strain and lateral ligand effects, leading to shifts of the CO desorption peaks with varying Pd content. For CO adsorption on Ru sites, ensemble effects can be excluded due to the exclusive adsorption of CO on on–top sites. Strain effects due to incorporation of Pd atoms in the surface layer will lead to a destabilization of CO adsorption on neighboring Ru atoms, while electronic ligand effects should stabilize the CO adsorption on the Pd sites upon alloy formation (see point 3 above). CO TPD spectra show a continuous down–shift of the trailing edge of the $\beta_1$ peak, which is assigned to desorption from the Ru sites. In the present case, the increasing destabilization by strain effects with increasing Pd content seems to overcompensate the (stabilizing) lateral ligand effects.

Focusing now on CO adsorption on Pd sites, we also find small shifts of the peaks related to desorption from Pd sites ($\beta_3–\beta_5$) to higher temperature with increasing Pd surface contents. They are most obvious for the $\beta_4$ and $\beta_5$ peaks at higher Pd concentrations, but are also detected for the $\beta_3$ peak with a shift from 320 K (45% Pd) to 325 K (87% Pd). This shift (and the stabilization of CO adsorption on the Pd sites with increasing Pd concentration) can be explained in a similar way as discussed before, by a combination of strain and ligand effects.
Here, this result seems to indicate that for CO adsorption on Pd sites the weakening of adsorption due to strain effects is overcompensated by stabilization due to ligand effects. Additionally, it has to be noted that an ensemble effect is in operation with a change from on–top to energetically more favorable threefold CO adsorption sites. It is impossible to decide on the basis of the TPD experiments, which of these two possibilities is responsible for the observed concentration–dependent stabilization of CO adsorption on the Pd part of the surface alloys.

Similar coverage–dependent shifts of the CO desorption peaks were observed also in TPD experiments with PtRu/Ru(0001) surface alloys and were explained in the same framework with counteracting strain and ligand effects [29]. Ensemble effects can be neglected in this case, since CO is exclusively adsorbed in linear on–top sites on this surface alloy system for all Pt contents. The magnitude of the peak shift was significantly larger for those surface alloys with a value of ~0.5 K per percent Pt in the surface [29] than for the present PdRu/Ru(0001) surface alloys (~0.1 K per percent Pd). This may, at least partly, be explained by the less efficient intermixing in the PdRu/Ru(0001) surface alloy (tendency for segregation [25]) compared to the statistic distribution in PtRu/Ru(0001) [31]. In general, however, the influence of the different ordering behavior in these two surface alloys on the CO desorption is relatively small and difficult to be resolved from the TPD spectra without additional input. The latter could be provided, e.g., from DFT calculations of the adsorption energy of CO on adsorption sites with different ligand environments, which could be used as basis for subsequent simulations of the TPD spectra.

The results of the IR measurements demonstrate the occupation of on–top adsorption sites on the Ru atoms of the surface alloys, similar to CO adsorption on the unmodified Ru(0001) surface [78,87]. For surface alloys with smaller Pd contents (up to at least 22% Pd), no extra features due to CO adsorption on Pd sites are detected in the IR spectra, although the formation of the β3 adsorption state in the CO TPD spectra is clear evidence for the occupation of these sites. Assuming a sufficiently fast equilibration of COad on the surface alloys, one would expect that due to the lower CO adsorption energy on the Pd sites they are occupied only after the available Ru sites are filled. For surface alloys with small Pd concentrations, this implies that adsorption on Pd sites starts at high COad coverages close to saturation, where coupling effects between neighboring CO molecules can influence the IR spectra considerably [100]. Therefore, the absence of an IR signal due to on–top adsorbed CO on Pd atoms (at ~2090 cm−1 for PdML/Ru(0001) and surface alloys with higher Pd contents)
may be most simply explained by dynamic coupling of these molecules to CO adsorbed linearly on Ru surface atoms (typically at ~2060 cm$^{-1}$ after CO saturation) leading to a joint feature. The absence of IR features related to CO$_{ad}$ on bridge or threefold Pd sites cannot be explained in the same way, since vibrational coupling effects should be negligible in this case due to the large difference of the vibrational frequencies. Therefore, it seems that for surface alloys with smaller Pd contents CO is exclusively adsorbed on on–top sites. The absence of CO adsorption on threefold hollow sites for surface alloys with smaller Pd content cannot be explained by the lack of Pd$_3$ ensembles on these surfaces, since already at rather small Pd contents such ensembles are formed due to the tendency for 2D segregation (at ~20% Pd: ~5% of all trimers are pure Pd$_3$ ensembles [25]). Instead, this effect is possibly explained by simple geometric considerations. For small Pd ensembles, which are predominantly formed at lower Pd contents, the surrounding CO$_{ad}$ molecules, which are bound in an on–top configuration on the Ru atoms, may force the CO$_{ad}$ molecules on the Pd ensemble in an on–top configuration. The energy gain of the system, which could be reached by occupying bridge or threefold sites on the Pd ensemble, would obviously be overcompensated by the resulting energy loss due to increased CO$_{ad}$–CO$_{ad}$ repulsions or due to a lateral shift of the surrounding CO$_{ad}$ molecules adsorbed on Ru sites. In contrast, for CO adsorption on PdAu surface alloys, where CO does not adsorb on the (surrounding) Au surface atoms at 100 K, even individual Pd$_2$ dimers and Pd$_3$ trimers were sufficient to favor CO adsorption in bridge and threefold hollow configurations [24]. Similar results were obtained also for CO adsorption on PdCu monolayer surface alloys on a Ru(0001) substrate, where threefold hollow Pd sites are populated as soon as the required Pd$_3$ ensembles are present [32]. Furthermore, although CO adsorption on Cu sites is possible, it turned out that occupation of mixed threefold adsorption ensembles does not occur and that for bimetallic layers with Pd atoms diluted in a Cu layer CO adsorption on–top on Pd monomers is the most stable adsorption site [32].

For PdRu/Ru(0001) surface alloys, it is difficult to clearly determine the influence of the Pd content on the CO peak position for adsorption on Pd sites, since the Pd sites are only filled after larger CO exposures. CO adsorption on the Ru sites, on the other hand, exhibits a distinct shift to lower wave number with increasing Pd content, with the peak position shifting from 1991 cm$^{-1}$ for unmodified Ru(0001) to 1987 and 1982 cm$^{-1}$ for surface alloys with 42% and 90% Pd, respectively. As already pointed out in the discussion of the IR results on Pd$_{ML}$/Ru(0001), according to the Blyholder formalism such a shift would point to a
stabilization of CO adsorption on the surface, while experimentally a small destabilization is observed in the TPD experiments. The origin of this discrepancy is not yet solved.

Here, it is again interesting to compare with the results of IR experiments on PtRu/Ru(0001) surface alloys [29]. In that case, the peak position after small exposures shifts continuously to higher wave numbers for CO adsorption on the Ru surface atoms with increasing Pt concentration, from 1991 cm\(^{-1}\) for unmodified Ru(0001) to ~2030 cm\(^{-1}\) for a surface alloy with 46% Pt. For larger Pt surface concentrations it remains at this position. The smaller peak shift observed for CO\(_{ad}\) on the PdRu/Ru(0001) surface alloys (Ru sites) compared to PtRu/Ru(0001) may be explained most easily by the different ordering behavior of the two surface alloys: for PtRu surface alloys, the complete intermixing of the components (statistical distribution) enhances the influence of the strain and ligand effects introduced by alloy formation. In contrast, for PdRu/Ru(0001) surface alloys, the tendency for 2D segregation weakens the influence of these effects on the IR peak positions (see also the above discussion of the down–shift of the trailing edge of the \(\beta_1\) peak with increasing Pd or Pt content).

Finally, we compare the influence of ensemble, ligand, and strain effects on the adsorption behavior of deuterium [25] and CO on PdRu/Ru(0001) surface alloys. We assume that deuterium is adsorbed on threefold hollow sites for both components of the surface alloy similar to the situation on unmodified Ru(0001) [101,102] and Pd(111) [103]. Therefore, the occupation of mixed adsorption ensembles is possible for deuterium adsorption. In contrast, CO is exclusively adsorbed on on–top sites for the Ru surface atoms, while for the Pd surface atoms the preferred adsorption site changes from on–top at smaller Pd contents to threefold hollow at higher Pd contents. The occupation of mixed adsorption ensembles seems improbable for CO adsorption due to the preference of linear adsorption on Ru sites. Therefore, the composition of the adsorption ensemble (compact trimer) will be very important for the binding energy of adsorbed deuterium, while ligand effects (i.e., the composition of the neighboring atoms around a central atom) will be dominant for CO adsorption, if the relatively small ensemble effect arising for Pd ensembles by a change from on–top to threefold hollow adsorption with increasing Pd content is neglected. For recombinative deuterium desorption we had suggested that the composition of a compact pentamer, which provides adsorption sites for two adjacent D adatoms, will determine the measured adsorption energy or activation energy for desorption [25]. Because of the large number (20) of different adsorption ensembles for deuterium adsorption, an increasing Pd surface content leads to a continuous broadening and simultaneous down–shift of the D\(_2\)
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For CO adsorption, the binding strength is dominated by the identity of the bonding surface atom or the adsorption ensemble, either a Ru surface atom or a Pd atom/Pd₃ ensemble. Ligand effects, determined by the nature of the shell of atoms surrounding the central atom, have a smaller influence. Compared to deuterium adsorption, however, CO adsorption is affected much stronger by repulsive adsorbate–adsorbate interactions. The sum of these effects leads to the observed continuous broadening and down–shift of the CO desorption spectra with increasing Pd content.

Overall, the adsorption of the two probe molecules CO and D₂ leads to similar conclusions on the modification of the adsorption properties of a Ru(0001) surface upon PdRu surface alloy formation or upon deposition of a Pd monolayer film. On a qualitative scale, the changes in the adsorption behavior with increasing Pd content can be well–described in terms of the d–band model, and the existing DFT calculations show good agreement also on a semi–quantitative scale. Further work is required, however, to fully understand the vibrational behavior of the CO adlayer, in particular the rather high Pd content required to detect Pd–CO species in the IR spectra.

4.1.4.4 Summary

We have investigated the interaction of structurally well–defined pseudomorphic monolayer PdRu surface alloys on Ru(0001) with CO by TPD and IRAS experiments. The modification of CO adsorption upon PdRu surface alloy formation was compared with findings for deuterium adsorption on the same surface alloys [25]. This comparison allows to differentiate between ligand and ensemble effects, since different adsorption sites/ensembles are occupied by these two species. Effects of the 2D distribution of metal surface atoms are illustrated by comparison with CO adsorption on PtRu/Ru(0001) surface alloys, where in contrast to the pronounced 2D phase segregation in PdRu/Ru(0001) the surface atoms are essentially randomly distributed. Comparison with CO adsorption on PdCu/Ru(0001) surface alloys, which have a preference for unlike neighborhoods, finally gave insight into the CO adsorption behavior on Pd adsorption ensembles without interference with CO ad on neighboring Cu sites. The main results can be summarized as follows:
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(1) Adsorption of CO on Pd monolayers and on the Pd sites of PdRu/Ru(0001) surface alloys is significantly weakened (by 30–40%) in comparison to adsorption on Pd(111) surfaces, which is attributed to a combination of strain effects and the interaction of Pd with the underlying Ru(0001) substrate (‘vertical ligand effects’). Similar effects were also observed for deuterium adsorption on the same monolayer films.

(2) CO adsorption occurs in rather similar configurations on both surfaces, Pd$_{\text{ML}}$/Ru(0001) and Pd(111), with threefold sites being populated at low coverages, while at saturation CO$_{\text{ad}}$ is adsorbed on on–top and bridge sites on the Pd monolayer films and on on–top and threefold sites on Pd(111). The up–shift of the vibrational frequency from CO$_{\text{ad}}$ on Pd$_{\text{ML}}$/Ru(0001) compared to Pd(111) observed at low CO$_{\text{ad}}$ coverages (+40 cm$^{-1}$, threefold sites) agrees with expectations based on Blyholder model and d–band model. This is different for CO$_{\text{ad}}$ saturation, where instead of the expected up–shift a down–shift (−20 cm$^{-1}$, on–top sites) is observed. This discrepancy is tentatively explained by differences in the CO$_{\text{ad}}$ saturation coverage and the CO adlayer structure.

(3) Trend and magnitude of the (relative) decrease in CO adsorption energy resemble that on Pt$_{\text{ML}}$/Ru(0001), despite the much larger compressive strain (2.8% vs. 1.8%) in the latter film. This is tentatively explained by a (relatively) stronger interaction between surface layer and Ru(0001) substrate (stronger vertical ligand effects on Pd$_{\text{ML}}$/Ru(0001)), which compensates the smaller contribution from the strain effect.

(4) CO adsorption on PdRu/Ru(0001) surface alloys is dominated by the chemical nature of the substrate atom or ensemble of substrate atoms. Nevertheless, it differs distinctly from that on the unmodified Ru(0001) substrate or on the Pd$_{\text{ML}}$/Ru(0001) surface.

i. On Ru surface atoms, CO adsorbs on on–top sites both on the surface alloy and on the Ru(0001) substrate. It is increasingly destabilized with increasing Pd content (down–shift of the trailing edge of the high temperature desorption peak), which can be explained by a combination of strain effects and lateral ligand effects (destabilization by larger and less strongly interacting Pd ligands). In contrast to expectations, however, the CO frequency exhibits a down–shift with increasing Pd surface content.

ii. CO adsorption on Pd surface atoms varies with Pd content. At lower Pd contents (< 20%), IR spectra do not resolve CO$_{\text{ad}}$ on Pd, although TPD spectra clearly demonstrate the population of Pd related sites. This discrepancy is
explained by on–top adsorption on Pd atoms, due to steric reasons, and dynamic coupling with the neighboring CO_{ad} species. At medium Pd contents (40 – 50%), CO_{ad} adsorbs on on–top sites at lower local CO_{ad} coverages (on the Pd surface atoms) and on on–top and bridge sites at high local CO_{ad} coverages. The difference compared to CO on Pd(111) can be explained by ligand effects and/or steric effects connected to the pronounced preference for on–top adsorption on Ru surface atoms. At medium Pd contents (40 – 50%), eventually adsorption on Pd sites is detected after CO saturation. A small signal due to CO_{ad} on on–top Pd sites and a broad feature due to CO_{ad} on bridge Pd sites are observed. This resembles the behavior on Pd(111), with the exception of bridge site occupation instead of threefold hollow sites on Pd(111).

iii. CO adsorption on mixed sites (PdRu dimers or Pd_{3–n}Ru_{n} trimers) is unlikely due to the energetic preference for on–top adsorption on Ru surface atoms.

(5) The different distribution of the surface atoms in PdRu compared to PtRu monolayer surface alloys on Ru(0001) has little effect on the CO adsorption energetics because of the dominant effect of the chemical nature of the adsorption atom/ensemble. This is different from deuterium adsorption, where adsorption on mixed adsorption ensembles results in intermediate adsorption energies.

(6) In contrast to the energetics and CO_{ad} site population, the adsorption kinetics and the saturation coverage on the different surface alloys and on the unmodified Ru(0001) substrate or the Pd modified Pd_{ML}/Ru(0001) differ only little. On all surfaces and similar to adsorption on the related PtRu/Ru(0001) surface alloys, CO adsorption proceeds via a precursor state. These results differ significantly from deuterium adsorption on the same surfaces, where the weak interaction of D_{ad} with the Pd or Pt surface atoms results in an activation barrier for deuterium adsorption on Pd_{ML}/Ru(0001) and Pt_{ML}/Ru(0001) and thus in a significant decrease in the (initial) sticking coefficient.
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4.2 Interaction of CO and deuterium with bimetallic monolayer Pt island/film covered Ru(0001) surfaces

The content of the following section was published in reference [104] and is reproduced by permission of the PCCP Owner Societies. The style and numbering of references and figures has been modified in line with the layout of this thesis, the experimental section has been shortened for brevity. The computer calculations for the simulations of D$_2$ TPD spectra in Section 4.2.5 as well as Figure 4.18 and Table 1 were produced by T. Diemant from the Institute of Surface Chemistry and Catalysis, Ulm University. My contribution to the publication are the TPD and IRAS measurements, additionally I produced the first draft and was strongly involved in the creative process of the manuscript.

4.2.1 Abstract

The adsorption properties of structurally well-defined bimetallic Pt/Ru(0001) surfaces, consisting of a Ru(0001) substrate partly or fully covered by monolayer Pt islands or a monolayer Pt film, were studied by temperature programmed desorption (TPD) using CO and deuterium as probe molecules. Additionally, the adsorption of CO was investigated by infrared reflection absorption spectroscopy (IRAS). The presence of the pseudomorphic platinum islands or monolayer film leads to considerable modifications of the adsorption properties for both adsorbates, both on the Pt part of the surface and, to a smaller extent, also on the Ru part of the surfaces. In addition to distinct weakly bound adspecies, which are adsorbed on the monolayer Pt islands, we find unique contributions from island edge desorption, from spill-over processes during the desorption run, and a general down-shift of the peak related to desorption from Pt-free Ru(0001) areas with increasing Pt coverage. These effects, which we consider as characteristic for adsorption on bimetallic surfaces with large contiguous areas of the respective types, are discussed in detail.

4.2.2 Introduction

The interaction of simple molecules such as H$_2$, CO, O$_2$ or methanol with bimetallic PtRu surfaces has been investigated extensively, driven by the application of bimetallic supported
PtRu nanoparticle catalysts as anode material in low temperature fuel cells [105,106]. Therefore, these surfaces can also be considered as model systems for the investigation of the interaction of small molecules with structurally well-defined bimetallic surfaces. For example, concepts developed in heterogeneous catalysis such as the electronic ligand effect and the geometric ensemble effect [12,13,16], together with the electronic strain effect introduced later [14,15], were investigated and quantified using the adsorption of CO and hydrogen as well as the coadsorption of these species on bimetallic PtRu/Ru(0001) monolayer surface alloys [29,30,48,107]. The latter experiments were performed using mixed bimetallic PtRu/Ru(0001) surfaces with quantitatively well-defined atomic neighborhoods, which were prepared by deposition of submonolayer amounts of Pt at room temperature and subsequent flash annealing to 1300 K. This leads to surface confined intermixing in the topmost layer, where the distribution of the different atoms in these surfaces is quantitatively known from high resolution scanning tunneling microscopy (STM) studies [31]. Electronic strain and vertical ligand effects were investigated in studies of the chemical properties of Ru(0001) surfaces covered by mono- and multilayers of Pt [23,26,27,84,108].

In the present paper, we report results of a systematic study focusing on the chemical properties of Ru(0001) surfaces covered to varying extents by large monolayer Pt islands, using the adsorption of CO and hydrogen (deuterium), respectively, as example. These islands are sufficiently large that island edge effects should only play a minor role. On these surfaces, the variety of different types of sites is between that of surfaces covered by homogeneous mono- or multilayer films and that of surface alloys. In addition to energetic effects, however, also transport effects caused by limited surface diffusion may play a role because of the significant distances between Pt and Ru areas, while such effects can largely be neglected for the bimetallic PtRu surface alloys. For instance, Jakob and coworkers reported that CO molecules adsorbed on extended Pt islands on the Ru(0001) substrate are frozen below ~90 K and can only diffuse to the energetically more favorable adsorption sites on the Ru area at a higher temperature (~140 K) [108]. Selected results on the adsorption of these species on monolayer Pt islands covered Ru(0001) were reported already earlier [26,28]. The influence of the Pt coverage on the overall chemical properties of these surfaces, however, has not been studied systematically so far. We are specifically interested in the question, whether adsorption is purely additive, i.e., whether adsorption can be described to a first approximation as a simple superposition of adsorption on the Pt and Ru surface areas, or whether additional effects have to be considered as well. First results on these aspects,
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demonstrating pronounced CO$_{\text{ad}}$ spill-over from Pt monolayer covered areas to Pt–free Ru(0001) areas during the TPD measurements, were published recently [109].

The morphology of bimetallic PtRu surfaces has been extensively studied by STM [26,31,48,49]. Pt deposition at 300 K with deposition rates around 0.05 ML min$^{-1}$ results in the formation of triangular dendritic islands on the terraces of the substrate with two different orientations, associated with either hcp or fcc stacking with respect to the Ru(0001) substrate. Similarly oriented dendrites also grow from Ru step edges. Upon annealing this surface to temperatures between 600 and 700 K, the dendritic islands collapse to compact hexagonally shaped islands and smooth decorations of Ru steps [26,31,48,49]. Further annealing to 850 K leads to a decrease in island density, most likely via an Ostwald ripening process, where the larger islands grow at the expense of smaller ones [48,49]. Additionally, intermixing (surface alloy formation) starts at temperatures above 750 K, although the intermixing of Pt and Ru atoms is still confined to the edges of Pt islands and step decorations at this temperature [48]. Annealing of the surface to 1300 K finally leads to the formation of a two–dimensional PtRu alloy with Pt and Ru atoms distributed statistically and homogeneously in the outermost surface layer [31,48]. Deposition of platinum at temperatures above 517 K results in step flow growth, starting at ascending Ru steps; at these temperatures, Pt island formation occurs only for higher deposition rates or on very large terraces [31].

Following a brief description of the experimental setup and procedures (Section 4.2.3), we will first describe the results of temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) measurements on the adsorption and desorption of CO on surfaces covered by different amounts of Pt monolayer islands (Section 4.2.4.1 and 4.2.4.2). Next, we report D$_2$ TPD measurements on similar surfaces (Section 4.2.4.3). Finally, the results are discussed in a comprehensive picture (Section 4.2.5).

4.2.3 Experimental

The experiments described in this section were carried out on the UHV system described in detail in Section 3.1. For sample preparation procedures and details on data acquisition, I refer to Sections 3.2 and 3.3, respectively.
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4.2.4 Results

4.2.4.1 Interaction of CO with Pt/Ru(0001) – TPD results

Series of TPD measurements were performed on Ru surfaces covered with different amounts of Pt (0.1, 0.2, 0.3, 0.55, 0.7, 0.9 ML) and compared to spectra recorded on a clean Ru(0001) surface and on a surface covered by a Pt monolayer film (1.1 ML Pt). The respective TPD series after increasing CO exposures are displayed in Figure 4.7. For a better illustration of the changes in the desorption behaviour with increasing Pt coverage, the spectra obtained for CO_{ad} saturation coverage are additionally collected in Figure 4.8. For these measurements, the CO exposure was carried out at a sample temperature of 90 K. Figure 4.7a shows desorption from an unmodified Ru(0001) surface with the characteristic $\alpha_1$ and $\alpha_2$ peaks at 461 and 404 K, and the onset of desorption at 298 K, in good agreement with literature data [26,29,69]. The CO TPD spectra recorded from a surface with 1.1 ML Pt are depicted in Figure 4.7h. After CO_{ad} saturation, the spectrum exhibits several characteristic features, the most prominent ones are two distinct peaks at 290 K ($\beta_1$) and 220 K ($\beta_3$) and a small shoulder at 245 K ($\beta_2$). These features are attributed to CO_{ad} desorption from the Pt monolayer covered areas [26,29]. The rather broad feature between 350 and 530 K is associated with CO_{ad} desorption from defects in the Pt monolayer, which include Pt free Ru(0001) surface areas and Pt islands in the second layer (see discussion).

After characterization of CO_{ad} desorption from the pure Ru(0001) surface and from a surface covered by an almost closed Pt monolayer, we now turn to the results obtained from surfaces partially covered by Pt monolayer islands. Figure 4.7b–g show TPD spectra recorded from Pt$_x$/Ru(0001) surfaces with increasing amounts of Pt ($x = 0.1 – 0.9$ ML). For the lowest CO exposure ($\varepsilon_{CO} = 0.15 \times 10^{-6}$ mbar·s), all spectra show a single desorption peak with approximately similar desorption intensity, equivalent to similar CO_{ad} coverage. Based on the desorption temperature, this peak is attributed to CO_{ad} desorption from the Pt–free Ru areas ($\alpha_1$ peak). Compared to the Pt–free Ru(0001) surface, the peak shifts successively to lower temperature with increasing Pt content. This shift is illustrated in Figure 4.9a, showing the down–shift of the CO_{ad} desorption peak maximum and of the positions of the leading and trailing edges of this peak with increasing Pt content. The edge positions were evaluated by linear extrapolation of the two desorption peak edges at half maximum to zero.
Figure 4.7: CO TPD spectra recorded on (a) unmodified Ru(0001), (b) – (g) different Ptₓ/Ru(0001) surfaces covered partly by Pt monolayer islands (Pt coverage given in each panel), and (h) Pt monolayer film (1.1 ML Pt on Ru(0001)) after CO exposure at 90 K (heating rate β = 5 K s⁻¹). CO exposures ×10⁻⁶ mbar s⁻¹: 0.15, 0.3, 0.6, 0.9, 1.2, 1.5, 2.1, 3, 6, 15, 30.

The shift is relatively small for low to intermediate Pt coverages (up to ~0.3 ML), e.g., from 492 K for pure Ru(0001) to 480 K for θ_{Pt} = 0.3 ML (peak maximum). A further increase of the Pt content results in a more significant shift. Eventually, the peak maximum appears at 409 K for θ_{Pt} = 0.7 ML. At even higher Pt coverages, the peak position remains about constant. For
example, for a surface with $\theta_{\text{Pt}} = 0.9$ ML, the peak maximum is located in the same temperature range. For the latter surface, CO$_{\text{ad}}$ desorption from the Pt layer (most probably second layer desorption) is superimposed on the $\alpha_1$ peak, which makes a quantitative evaluation difficult. Therefore, this surface was not included in Figure 4.9a. Comparison of the positions of the leading and trailing edges shows a broadening of the CO desorption peak with increasing Pt coverage, from 70 K for unmodified Ru(0001) to ~100 K for the surface with $\theta_{\text{Pt}} = 0.7$ ML. Possible reasons for the observed down-shift of the Ru related desorption features will be discussed later.

Similar to the pure Ru(0001) surface, the $\alpha_1$ CO desorption peak shifts to lower temperatures with increasing CO exposure also for the bimetallic surfaces, which is attributed to increasing repulsive interactions in the adsorbate layer. In addition, the $\alpha_1$ peak maximum after CO saturation also shifts to lower temperatures with increasing Pt coverage (see Figure 4.9a). This shift at first parallels the one found after the smallest CO exposure. For surfaces with high Pt content ($\theta_{\text{Pt}} = 0.7$ ML), however, the difference between peak maxima at low CO$_{\text{ad}}$ coverage and CO$_{\text{ad}}$ saturation decreases to only 3 K. This development simply reflects the fact that with decreasing Pt–free Ru(0001) areas, thermally activated spill–over of CO$_{\text{ad}}$ (see below) will lead to higher local CO$_{\text{ad}}$ coverages and hence increasing interactions between CO$_{\text{ad}}$ on these areas even after low CO exposures ($0.15 \times 10^{-6}$ mbar·s). After the filling of the $\alpha_1$ peak, another feature forms on the bimetallic surfaces with small to intermediate Pt content, which is labelled $\alpha_2$ analogous to pure Ru(0001). It remains as a distinct feature up to a Pt coverage of 0.55 ML. As one would expect, the desorption intensity from these two peaks, which reflect desorption from the Pt–free Ru areas of the bimetallic surfaces, decreases in intensity with increasing Pt coverage.

Coming to CO$_{\text{ad}}$ desorption from the Pt covered part of the surface, an additional shoulder develops on the low–temperature side of the Ru(0001) related desorption features on a surface with 0.1 ML Pt (Figure 4.7b), and CO$_{\text{ad}}$ desorption starts already at ~260 K. Since the position of this feature corresponds to that of the $\beta_1$ peak on a closed Pt monolayer film, it is assigned to CO$_{\text{ad}}$ desorption from Pt monolayer islands. At a Pt coverage of 0.2 ML (Figure 4.7c), this feature appears as a distinct peak with a maximum at 295 K, and desorption starts at ~230 K. With increasing Pt coverage ($\theta_{\text{Pt}} = 0.55$ ML, Figure 4.7e), the onset of desorption shifts to ~200 K and two additional features are formed on the low–temperature side of the $\beta_1$ peak, a shoulder at around 245 K and a sharp peak at 225 K (termed $\beta_2$ and $\beta_3$ peaks, respectively),
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while the maximum of the $\beta_1$ peak shifts to 290 K. Beyond this Pt coverage, the position of the main $\beta_1$ peak and the onset of desorption are not affected by a further increase in Pt coverage, while the maximum of the $\beta_3$ peak down-shifts to 220 K at 0.7 ML Pt, where it remains constant for higher Pt coverages. For a better overview, the temperature dependence of the characteristic features of CO$_{ad}$ desorption from the Pt part of the bimetallic surfaces, the peak maxima of the $\beta_1$ and $\beta_3$ peaks and the leading edge, is illustrated in Figure 4.9b. The edges were evaluated again by linear extrapolation of the peak edges at half maximum to zero.

The variation of the CO$_{ad}$ saturation coverage with increasing Pt coverage, obtained after exposing the surface to $30 \times 10^{-6}$ mbar·s CO at 90 K, is presented in the inset of Figure 4.8. The CO$_{ad}$ coverage was calculated by integrating the spectra and normalization to the well-known value of 0.68 ML for the CO$_{ad}$ saturation coverage on Ru(0001) at 100 K reported by Pfün r et al. [47]. The CO$_{ad}$ saturation coverage stays at 0.68 ML for surfaces with small Pt contents up to 0.1 ML, it then starts to decrease for surfaces with higher Pt content and levels off at $\sim 0.55 \pm 0.05$ ML CO for surfaces with more than 0.5 ML Pt. To exclude the possibility that the CO exposure is not sufficient to reach the saturation coverage on the bimetallic surfaces, also higher CO exposures up to $120 \times 10^{-6}$ mbar·s were dosed on these surfaces at 90 K, without leading to an increase in the amount of adsorbed CO.

The CO$_{ad}$ saturation coverage determined on the Pt monolayer covered surface is almost double as high as the value of 0.3 ML reported by Jakob and Schlapka [84]. Considering the fact that at low temperatures surface diffusion of CO$_{ad}$ is increasingly hindered and at 80 K essentially inhibited [108], this discrepancy is tentatively attributed to the somewhat higher adsorption temperature in the present measurements. The temperature difference may be sufficient to allow ordering in a more densely packed adlayer at the higher temperature.

It is interesting to note that the characteristic desorption features eventually found on the Pt monolayer film are fully present only on samples with a Pt coverage above 0.5 ML. This is surprising, since on an atomic scale rather large, contiguous Pt islands are formed already for relatively low Pt coverage.
Figure 4.8: CO TPD spectra recorded on the unmodified Ru(0001) surface, various Pt/Ru(0001) surfaces, and 1.1 ML Pt on Ru(0001) after CO saturation. Inset: CO saturation coverages on these surfaces.

For instance, for 0.2 ML Pt, the Pt islands reach already a diameter of ~10 – 20 nm; and at 0.5 ML Pt, they start to coalesce. Therefore, contributions of edge atoms should play an important role only for very low Pt coverage. Neglecting these, the TPD spectra obtained after CO saturation should be a summation of the contributions from the Ru part (α₁ and α₂ peak) and the Pt part (β₁ – β₃ peaks). Experimentally, the β₃ peak is only observed on surfaces with higher Pt coverage (θ_{Pt} ≥ 0.55 ML). We have shown in a preceding publication [109], that this apparent discrepancy can be explained by a partial spill–over of CO_{ad} molecules from the Pt islands to the Pt–free Ru(0001) areas while recording the TPD spectrum.
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Figure 4.9: Temperature shifts of the prominent CO TPD features from (a) the Ru part and (b) the Pt monolayer islands/Ru(0001). (a) Ru part: leading edge (▲), peak maximum (●) and trailing edge (▼) after the smallest CO exposure ($e_{CO} = 0.15 \times 10^{-6}$ mbar·s); and $\alpha_1$ peak maximum after CO$_{ad}$ saturation (○). (b) Pt monolayer islands/Ru(0001): leading edge (▲), $\beta_1$ (●) and $\beta_3$ (○) peak maximum after CO$_{ad}$ saturation.

CO$_{ad}$ surface diffusion on the Pt islands is too slow at low temperature (90 K) and sets in between 100 and 150 K [84]. This leads to depopulation of the least stable $\beta_3$ peak related to CO$_{ad}$ desorption from the Pt islands and a shift of the CO$_{ad}$ desorption onset to higher temperature. This transfer of CO$_{ad}$ molecules is most pronounced for bimetallic surfaces with low Pt content, where the additional uptake capability of the Pt–free Ru(0001) areas is rather large. It decreases steadily with increasing Pt surface content. For surfaces with Pt coverages beyond 0.5 ML, this CO$_{ad}$ transfer is relatively small, and TPD spectra exhibit all CO$_{ad}$
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desorption features characteristic for desorption from a Pt monolayer film covered surface. Interestingly, CO$_{ad}$ uptake on the Pt–free Ru(0001) areas is possible even for the CO$_{ad}$ saturated surface (under UHV conditions) [109].

The CO$_{ad}$ TPD features from the Pt part of the surfaces are fully populated upon CO exposure at higher temperature, e.g., upon dosing at 150 K [109]. In this case, CO$_{ad}$ molecules initially adsorbed on the Pt islands, which then diffused to the Pt–free Ru(0001) areas, can be replenished by further CO uptake. As an example, the result of such an experiment on a surface with 0.3 ML Pt is shown in Figure 4.10. For comparison, the TPD trace obtained after CO adsorption at 90 K is included as well (dashed line). The higher adsorption temperature leads to an appreciable increase of the CO$_{ad}$ coverage already for a dose of $30\times10^{-6}$ mbar·s CO. After a dose of $120\times10^{-6}$ mbar·s, the onset of CO$_{ad}$ desorption from this surface is at ~200 K, exactly the same temperature as on the closed Pt monolayer. Simultaneously, the $\beta_3$ feature is populated in the TPD spectrum, which is observed for CO exposure at 90 K only at much higher Pt coverages (> 0.5 ML).

Figure 4.10: CO TPD spectra of a surface with $\theta_{Pt} = 0.3$ ML. CO exposures $\times10^{-6}$ mbar·s: 30 at 90 K (dashed line) and 30 at 150 K, 60 at 150 K, 90 at 150 K, 120 at 150 K. Inset: CO saturation coverages after $30\times10^{-6}$ mbar·s at 90 K (▲) and $120\times10^{-6}$ mbar·s at 150 K (○).

In the next step, we evaluated the adsorption kinetics for CO adsorption at 90 K on surfaces with increasing Pt coverage. The initial sticking coefficients $s_0$, obtained from the initial slope
of the CO uptake curves (CO coverage versus CO exposure), are depicted in Figure 4.11. The value for CO adsorption on Ru(0001) was used to calibrate the CO exposure by comparison with the known value of $s_0 = 0.7$ [47]. Deposition of Pt on the Ru(0001) surface does not have a significant influence on $s_0$, it remains at around 0.7 up to a closed Pt monolayer. This result agrees well with the conclusion of approximately equal sticking probabilities on the Pt–free Ru(0001) area and on Pt monolayer Ru(0001) islands (~0.5 ML Pt, adsorption at 80 K) reported by Jakob et al. [84]. The independence of $s_0$ from the Pt coverage is also in line with results for CO adsorption on PtRu/Ru(0001) surface alloys of varying composition [110]. The invariance of the CO sticking probability with varying Pt coverage indicates that the change of the CO binding strength, which is evidenced by the TPD results, has no measurable influence on the adsorption kinetics.

In the main graph, Figure 4.11 shows the coverage dependence of the sticking coefficient $s(\theta)$ for surfaces with Pt coverages of 0.2, 0.55, 0.9 and 1.1 ML.

![Figure 4.11](image)

**Figure 4.11**: Sticking coefficient as a function of CO coverage on 0.2 ML Pt (●), 0.55 ML Pt (■), 0.9 ML Pt (▲) and 1.1 ML Pt (♦). Lines represent fitted values (cf. eq (4.2)). Inset: Initial sticking coefficient $s_0$(CO) with varying Pt content after CO exposure at 90 K.

For these surfaces, which cover the whole range of Pt coverages up to completion of a monolayer Pt film, the sticking coefficient shows only a slight reduction with increasing CO$_{\text{ad}}$ coverage up to about 0.4 ML CO. For higher CO$_{\text{ad}}$ coverage, it rapidly decreases and reaches
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zero for the saturated CO adlayer. An identical dependence was observed in our experiments on the non–modified Ru(0001) surface (not shown for the sake of brevity) and was also reported before for CO adsorption on pure Ru(0001) [47] and Pt(111) [98,99,111]. It was observed also for CO adsorption on PdRu/Ru(0001) [54] and PtRu/Ru(0001) [29,110] surface alloys.

This coverage dependence of $s(\theta)$, which deviates considerably from simple first order Langmuir adsorption kinetics, is typical for adsorption via a precursor state. A fit of the experimental data to the relation derived by Kisliuk for precursor adsorption [77]:

$$s(\theta) = s_0 \left(1 + K \cdot \frac{\theta}{1 - \theta}\right)^{-1}$$  \hspace{1cm} (4.2)

where $K = \frac{p_d'}{p_a + p_d'}$ ($p_d'$: probability for desorption from the precursor state over an occupied site, $p_a$ and $p_d$: probability for chemisorption and desorption from the precursor state over an empty site respectively, $\theta = 1$ for saturation coverage), is indicated by the different lines in Figure 4.11. For the non–modified Ru(0001) surface [54] and the surface with 0.2 ML Pt, the fit yields a value of $K=0.1$. For surfaces with higher Pt coverage, this value decreases successively; to 0.07 ($\theta_{Pt} = 0.55$ ML), 0.05 ($\theta_{Pt} = 0.9$ ML) and finally 0.03 for a surface with 1.1 ML Pt. Formally, this behaviour indicates a higher probability for adsorption from a precursor state over an already occupied adsorption site on the Pt monolayer covered areas compared to adsorption on Pt–free Ru(0001) areas. Considering, however, the complex adsorption process including spill–over of CO$_{ad}$ and the varying saturation coverages despite similar number of adsorption sites, a detailed discussion on a microscopic scale seems to be out of reach at this point.

4.2.4.2 Interaction of CO with Pt/Ru(0001) – IRAS

Here, we start with spectra from non–modified Ru(0001) and a surface with an almost closed Pt layer ($\theta_{Pt} = 1.1$ ML) again. Figure 4.12a displays a set of IR spectra recorded on a Pt–free Ru(0001) surface after increasing CO exposure at 90 K (exposures see figure). The spectra show only a single band, which shifts from 1991 cm$^{-1}$ after the lowest CO exposure to 2060 cm$^{-1}$ at CO$_{ad}$ saturation. Both the peak position and the observed shift with increasing
CO\textsubscript{ad} coverage agree fully with results reported by Pfnür et al. for CO\textsubscript{ad} on Ru(0001) \cite{78}. The band was assigned to the C–O stretch vibration of CO\textsubscript{ad} in a linear configuration; the blue–shift with increasing CO\textsubscript{ad} coverage was explained by a combination of dipole–dipole coupling and a chemical shift due to increasing intermolecular repulsion between adsorbed CO molecules \cite{78}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_12.png}
\caption{Infrared spectra at 90 K after CO exposure to (a) Ru(0001) and (b) 1.1 ML Pt on Ru(0001). CO exposures ×10\textsuperscript{-6} mbar s are given in each panel.}
\end{figure}

A similar set of IR spectra recorded on a 1.1 ML Pt/Ru(0001) surface (Figure 4.12b) also features a single IR band. With increasing CO\textsubscript{ad} coverage, the band position is almost invariant; with 2084 cm\textsuperscript{-1} at low coverage and 2090 cm\textsuperscript{-1} at saturation. This signal is attributed to CO adsorbed in a linear (on–top) configuration on the Pt monolayer film. At higher CO\textsubscript{ad} coverage, an additional small shoulder develops at 2105 cm\textsuperscript{-1}, which is assigned
to CO adsorption on second Pt layer islands [23]. These data and assignments are in excellent agreement with results of an earlier IR study on CO adsorption on mono- and multilayer Pt modified Ru(0001) surfaces by Jakob and Schlapka [84], and almost identical IR spectra were reported before for a similarly prepared PtML/Ru(0001) surface, which we used as reference material in a study of CO adsorption on PtRu/Ru(0001) surface alloys [29]. Compared to CO adsorption on Pt(111), the IR spectra of CO_ad on a closed Pt monolayer show two major differences: (i) the band for linearly adsorbed CO_ad is shifted by about \( \sim 15 \text{ cm}^{-1} \) to lower wave numbers at CO_ad saturation [85], and (ii) there is no evidence for bridge–bonded CO_ad species, which are found on non–modified Pt(111) at higher CO_ad coverage (band at \( \sim 1850 \text{ cm}^{-1} \)) [85,111]. Also the latter observation agrees perfectly with previous reports [84].

In Figure 4.13, we present sets of spectra recorded on Pt/Ru(0001) surfaces with Pt coverages of \( \theta_{\text{Pt}} = 0.1, 0.3, 0.4, 0.6 \) and 0.9 ML upon adsorption at 90 K. The IR spectra of the surface with 0.1 ML Pt (Figure 4.13a) mainly show a single band, which shifts from 1994 cm\(^{-1}\) at low CO_ad coverage to 2062 cm\(^{-1}\) at CO_ad saturation. Based on the band position, it must originate from CO adsorbed on the Pt–free parts of the Ru(0001) surface (CO_ad(Ru)). At higher CO_ad coverage, a second feature with much lower intensity appears at around 2085 cm\(^{-1}\), which therefore is assigned to CO adsorbed on the Pt islands. Increasing the Pt coverage from 0.1 to 0.3 ML (Figure 4.13b) has a pronounced effect on the IR spectra. In addition to the main CO_ad(Ru) band, which starts at 1995 cm\(^{-1}\) after the smallest CO exposure, a second feature appears already at low CO_ad coverage at 2060 cm\(^{-1}\). Despite the significantly lower wave number compared to the band at 2085 cm\(^{-1}\) mentioned above, we assign this band to CO_ad species on Pt islands as well. It was proposed before by Schlapka et al. [108], that the coordination of the Pt atom on which a CO molecule is adsorbed has a significant influence on the position of the corresponding IR band. By comparison with CO adsorption on flat and stepped Pt single crystal surfaces, Schlapka et al. attributed features at 2041 and 2047 cm\(^{-1}\) to CO adsorbed on kink or step sites at the edges of Pt islands, respectively [108]. Adsorption inside the Pt islands was associated with a feature at 2085 cm\(^{-1}\) (for low CO_ad coverage) [108], in agreement with our findings for CO adsorption on a closed PtML/Ru(0001) surface. Therefore, we relate the feature at 2060 cm\(^{-1}\) to adsorption at the edges of the Pt islands, while the higher wave number band results from CO_ad adsorbed on the inner part of the Pt monolayer islands. With increasing CO_ad coverage, this latter band shifts to higher wave number and appears at 2090 cm\(^{-1}\) at CO_ad saturation coverage. At the same time, due to dynamical coupling, the band at 2060 cm\(^{-1}\) loses intensity and eventually disappears. Parallel
4 Results and discussion

to these modifications, also the $\text{CO}_{\text{ad}}(\text{Ru})$ band shifts to higher wave number and appears at 2060 cm$^{-1}$ at CO saturation.

The spectra recorded on the surface with 0.4 ML Pt (Figure 4.13c) are rather similar. Again only the feature related to CO adsorption on Ru sites at around 1994 cm$^{-1}$ is observed at the lowest CO$_{\text{ad}}$ coverage. Increasing the CO$_{\text{ad}}$ coverage leads to the formation of a rather broad band at 2055 – 2085 cm$^{-1}$, which narrows at higher CO$_{\text{ad}}$ coverage and is located at 2085 cm$^{-1}$ after CO$_{\text{ad}}$ saturation. Concomitantly, the CO$_{\text{ad}}$(Ru) band shifts to 2058 cm$^{-1}$ on the CO$_{\text{ad}}$ saturated surface. The IR spectra recorded for a surface with 0.6 ML (Figure 4.13d) mainly show the band of CO$_{\text{ad}}$ on Pt, starting out at 2081 cm$^{-1}$ at the lowest CO coverage and gradually shifting to 2089 cm$^{-1}$ with increasing CO coverage. The band of CO$_{\text{ad}}$(Ru), on the other hand, is present only as a broad feature with a very low intensity starting at 2007 cm$^{-1}$ for low CO coverage and shifting to 2052 cm$^{-1}$ at CO saturation. Finally, in the spectra on the surface with 0.9 ML Pt (Figure 4.13e), no feature related to CO adsorption on Ru sites is visible any more, leaving only the Pt related CO$_{\text{ad}}$ band, which shifts with increasing CO coverage from around 2085 cm$^{-1}$ to 2090 cm$^{-1}$.

In agreement with findings for the unmodified Ru(0001) surface [78,87], the IR data demonstrate that only on–top adsorption sites are occupied on the Pt–free Ru(0001) surface areas. On the Pt islands, the IR spectra also show only bands related to CO adsorbed in an on–top configuration. Analogous findings were reported before by the group of Jakob for differently prepared Pt/Ru(0001) samples for Pt coverages up to 1 ML [84,108]. Additionally, those authors detected a very weak IR band related to CO adsorption in bridge sites, which they related to adsorption on defect sites of the Pt films [84].

The peak positions of the two main features in the IR spectra, which are attributed to CO adsorbed on the Pt–free Ru(0001) substrate and in the inner parts of the Pt islands, respectively, remain almost constant on surfaces with different Pt content. For Pt coverages up to 0.4 ML, the band related to CO adsorbed on Ru sites is detected at ~1995 cm$^{-1}$ after a CO exposure of $0.3 \times 10^{-6}$ mbar-s and shifts to ~2060 cm$^{-1}$ at CO$_{\text{ad}}$ saturation. Similarly, the Pt band after CO$_{\text{ad}}$ saturation exhibits only a slight shift from 2088 cm$^{-1}$ on a surface with 0.2 ML Pt to 2090 cm$^{-1}$ on a closed Pt layer. It should be noted that CO$_{\text{ad}}$ – CO$_{\text{ad}}$ interactions and dynamic coupling effects can significantly influence the band position at higher CO$_{\text{ad}}$ coverage.
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**Figure 4.13:** Infrared spectra at 90 K after CO exposure to various Pt$_x$/Ru(0001) surfaces (Pt coverage given in each panel). CO exposures $\times 10^{-6}$ mbar·s are given next to each spectrum.
As expected, an increasing Pt coverage leads to an increasing intensity of the CO<sub>ad</sub>(Pt) band and a decrease of the CO<sub>ad</sub>(Ru) band intensity at CO<sub>ad</sub> saturation, where both areas are populated. However, starting with the surface with 0.3 ML Pt, the relative intensities of the CO<sub>ad</sub>(Pt) and CO<sub>ad</sub>(Ru) bands after CO saturation do not correspond to the relative amounts of Pt and Ru atoms in the surface, or to the relative amounts of CO adsorbed on the different adsorption sites as evaluated from the TPD spectra. This is especially obvious for the surface with 0.6 ML Pt, where the CO<sub>ad</sub>(Ru) band is already rather weak, while according to the TPD measurements at least 30% of the CO<sub>ad</sub> molecules (at saturation) come from Ru sites. Such effects are generally explained by the well–known phenomenon of intensity transfer from the lower frequency (CO<sub>ad</sub>(Ru)) to the higher frequency band (CO<sub>ad</sub>(Pt)) due to dynamic coupling effects [112]. Intensity transfer effects were in fact also invoked to explain the development of the IR spectra after CO adsorption on PtRu/Ru(0001) surface alloys with varying surface composition [29]. In the present system, where large areas of the two types of surfaces, Pt–free Ru(0001) and Pt monolayer covered Ru(0001) areas, coexist on the surface, these coupling effects should be much weaker and limited to the interface region. Furthermore, the IR spectra show a too low intensity of the CO<sub>ad</sub>(Ru) band even for low CO<sub>ad</sub> coverages, where the larger intermolecular distances should lead only to weak dipole–dipole coupling between CO<sub>ad</sub> molecules [84]. Therefore, the physical origin of this effect remains unclear in the moment.

Comparing these results with spectra previously reported by Jakob and Schlapka for CO adsorption on submonolayer Pt covered Ru(0001) surfaces [84], the general trends in both studies closely resemble each other. Those authors, however, found a much more pronounced band at 2060 cm<sup>-1</sup> (at CO<sub>ad</sub> saturation) related to CO adsorbed on the Pt–free Ru(0001) on a surface covered by a 0.55 ML Pt film. In fact, they could detect the CO<sub>ad</sub>(Ru) related band at CO<sub>ad</sub> saturation for all surfaces up to a (nominal) Pt coverage of 1.1 monolayers. It can only be speculated that the different morphology of the Pt films in the two cases is the origin for the different outcome of the IR measurements. While Jakob and Schlapka deposited Pt under step–flow growth conditions (deposition at 600 K, very low deposition rate), which can produce second layer Pt already at Pt coverages well below 1 ML due to differing terrace widths, our films are characterized by monolayer Pt islands on the Ru(0001) terraces up to rather high Pt coverages. This leaves a smaller fraction of Pt–free Ru(0001) areas at nominally identical Pt coverages in our experiments, at least in the higher submonolayer coverage regime. In fact, our spectrum after CO<sub>ad</sub> saturation recorded at 0.6 ML Pt closer resembles the spectrum which Jakob and Schlapka reported for 0.85 ML Pt.
It is also informative to compare these results with previous findings for PtRu/Ru(0001) surface alloys [29]. In that case, a random distribution of Pt and Ru atoms in the surface layer was produced by annealing to 1300 K after Pt deposition [29,31]. On these surface alloys, marked shifts of the IR peak positions were observed for CO adsorption on both Ru and Pt sites. For the CO\textsubscript{ad}(Ru) species, the peak obtained after small CO exposures shifts from \(\sim 1990 \text{ cm}^{-1}\) for non–modified Ru(0001) to \(\sim 2030 \text{ cm}^{-1}\) for surface alloys with a Pt concentration beyond 40%. After CO\textsubscript{ad} saturation, which is necessary to populate the weakly binding sites, the peak related to CO\textsubscript{ad}(Pt) species shifts simultaneously from \(\sim 2070\) to \(\sim 2090 \text{ cm}^{-1}\) for surface alloys with 22% and 46% Pt, respectively. These shifts reflect the strong modification of the electronic properties of the surface atoms upon surface alloy formation, which also influences the chemical properties of the surface alloys reflected by a gradual change of the CO adsorption strength on the sites of the surface alloys with varying surface composition.

In the present system with contiguous larger Pt islands on the Ru(0001) substrate, the lack of major peak shifts of both the Ru– and Pt–related IR bands with varying Pt content indicates a much smaller modification of the electronic properties under these conditions, in agreement with expectations. This argument is supported by the trend already observed in the TPD spectra, where the desorption peaks of CO on Pt sites, once fully formed, do not show any significant shifts in temperature, and the desorption peaks of CO\textsubscript{ad} on Ru show only a slight shift to lower temperatures with increasing Pt coverage. This leads to the conclusion that an increase in Pt coverage mainly results in an increase of the relative amount of Pt adsorption sites, while their chemical properties remain largely unchanged.

**4.2.4.3 Interaction of deuterium with Pt/Ru(0001)**

We now turn to the results of the D\textsubscript{2} TPD measurements, employing Pt/Ru(0001) surfaces with varying Pt coverage (up to \(\theta_{\text{Pt}} = 1.15 \text{ ML}\)) and, for comparison, the unmodified Ru(0001) surface. The respective sets of TPD spectra, with increasing D\textsubscript{2} exposures (at 90 K) for each surface, are shown in Figure 4.14. Furthermore, the TPD spectra obtained after the maximum D\textsubscript{2} dose of \(100 \times 10^{-6} \text{ mbar} \cdot \text{s}\) (\(60 \times 10^{-6} \text{ mbar} \cdot \text{s}\) for 0.75 ML Pt/Ru(0001)) from these surfaces are collected in Figure 4.15 to illustrate the changes in the desorption behaviour with increasing Pt coverage. Analogous to the CO TPD experiments, we will first discuss the
results of D\textsubscript{2} desorption from the unmodified Ru(0001) surface (Figure 4.14a) and a surface covered by a Pt monolayer film (Figure 4.14i).

**Figure 4.14:** \(\text{D}_2\) TPD spectra recorded on (a) unmodified Ru(0001), (b) – (h) different Pt\textsubscript{x}/Ru(0001) surfaces covered partly by Pt monolayer islands (Pt coverage given in each panel), and (i) Pt monolayer film (1.15 ML Pt on Ru(0001)) after \(\text{D}_2\) exposure at 90 K (heating rate: \(\beta = 5\text{ K s}^{-1}\)). \(\text{D}_2\) exposures \(\times 10^{-6}\text{ mbar s}: 0.2, 0.6, 1.0, 1.4, 2, 4, 10, 20, 40, 100\); for (g): 0.2, 0.6, 1.0, 1.4, 2, 4, 10, 20, 40, 60.

As in the case of CO adsorption, the deuterium coverage was determined by integration of the desorption spectra and normalization to the \(D\text{ad}\) saturation coverage of 1 ML on Ru(0001) [113]. For the Pt–free Ru(0001) surface, the spectra show a single peak, which is called the \(\beta_2\) state, for exposures up to \(4 \times 10^{-6}\text{ mbar s} (\theta_{\text{D}} = 0.59 \text{ ML}) [114]. As expected for recombative desorption, the \(\beta_2\) peak maximum shifts to lower temperatures with increasing \(D\text{ad}\) coverage. After higher exposures, an additional state (\(\beta_1\)) emerges at slightly lower temperature. This state is poorly resolved from the initial \(\beta_2\) state, indicating a relatively small difference in the activation energy for desorption between these two states [25,115]. At \(D\text{ad}\) saturation coverage, which is reached after a dose of \(100 \times 10^{-6}\text{ mbar s}, the onset for desorption is located
at ~275 K, the desorption maximum is centred at 320 K, and deuterium desorption stops at ~450 K. Peak temperature and the shape of the spectra displayed in Figure 4.14a are in complete agreement with data from the literature [114–118].

The D₂ TPD spectra recorded on a surface covered by a platinum monolayer (θ_{Pt} = 1.15 ML, Figure 4.14i) differ considerably from those obtained on pure Ru(0001) [115,117,118] or Pt(111) surfaces [119]. After the smallest D₂ exposure (E_{D₂} = 0.2×10⁻⁶ mbar·s), the spectra show desorption over a wide temperature region, with a first peak maximum at 300 K. Desorption ends at ~450 K. This first peak grows with increasing D₂ exposure and is centred at 260 K after 10×10⁻⁶ mbar·s D₂. Additionally, a new feature forms at lower temperature (~210 K) after this D₂ exposure. With further increasing D₂ exposures, the onset of deuterium desorption continues to shift to lower temperature, until it starts right at the beginning of the temperature ramp. In the high exposure range, a peak with a maximum at ~145 K develops, which dominates the spectrum after the maximum D₂ exposure of 100×10⁻⁶ mbar·s. This γ peak is attributed to desorption from the pseudomorphic Pt monolayer on the Ru(0001) substrate. Similar to the CO TPD results, the features at higher temperature (> 200 K) are assigned to D₂ desorption from defect sites of the monolayer film, including second layer Pt islands and still existing Pt–free Ru(0001) surface areas.

The D_{ad} coverage after the maximum exposure amounts to only 0.31 ML (see also below). The decrease of the apparent D_{ad} saturation coverage compared to unmodified Ru(0001) or Pt(111) can most simply explained by two effects: i) the significantly lower sticking probability on the Pt monolayer covered surface, and ii) the decrease of the adsorption energy, which leads to an onset of desorption essentially shortly after starting the heating ramp. This indicates that for high(er) coverages deuterium adsorption on the Pt monolayer approaches an adsorption – desorption equilibrium at 90 K, which limits stable adsorption (in the absence of a D₂ pressure) to coverages well below 1 ML D_{ad}. While the first contribution is assumed to be dominant, desorption after finishing the D₂ exposure cannot be ruled out. Test measurements, in which the maximum exposure was increased from 100×10⁻⁶ mbar·s to higher exposures, showed still a further growth in the γ peak and a measurable increase of the D_{ad} coverage. These very large exposures, however, have the disadvantage of slow accumulation of coadsorbed CO from the residual gas during adsorption. Therefore, they were not used routinely. Nevertheless, these data indicate that the maximum D_{ad} coverage accessible at 90 K on the Pt monolayer (in the γ peak, see below) is higher than reached here, presumably around 0.45 – 0.5 ML or more.
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Figure 4.15: $D_2$ TPD spectra recorded on the unmodified Ru(0001) surface, various Pt$_x$/Ru(0001) surfaces, and 1.15 ML Pt on Ru(0001) after a $D_2$ exposure of $100 \times 10^{-6}$ mbar·s ($60 \times 10^{-6}$ mbar·s for 0.75 ML Pt/Ru(0001)) at 90 K.

Next, we will discuss the $D_2$ TPD spectra obtained from bimetallic Pt/Ru(0001) surfaces with submonolayer Pt coverages (Figure 4.14(b–h)). After the lowest exposure ($\epsilon_{D_2} = 0.2 \times 10^{-6}$ mbar·s), the TPD spectra show $D_2$ desorption in a similar temperature range as observed for the unmodified Ru(0001) surface. Therefore, this feature is attributed to desorption from the Pt–free areas of the Ru(0001) surface ($\beta_2$ peak).

The $D_{ad}$ coverage obtained after this exposure is almost constant at $0.10 \pm 0.01$ ML for Pt–free Ru(0001) and Pt covered surfaces up to 0.6 ML Pt and decreases thereafter to $0.07 \pm 0.01$ ML.
on the 0.75 ML Pt covered surface. Finally, it drops to $0.02 \pm 0.01$ ML on the fully Pt monolayer covered surface (1.15 ML Pt). Similar to desorption from Ru(0001), the $\beta_2$ peak shifts with increasing $D_2$ exposure to lower temperature for all bimetallic surfaces. The temperature difference between the $\beta_1$ and $\beta_2$ peaks decreases with increasing Pt content so that these peaks merge for surfaces with higher Pt content ($\geq 0.5$ ML).

Similar to CO adsorption, the peak maximum and the position of the leading and trailing edges shift to successively lower temperatures with increasing Pt surface content. This is illustrated in Figure 4.16a for surfaces with up to 0.75 ML Pt. For the trailing edge, these shifts are less pronounced compared to CO adsorption (~50 K for deuterium desorption vs. ~60 K for CO adsorption). For the peak maximum and the leading edge, the shifts are comparable in size to CO adsorption, which results in a pronounced broadening of the desorption peak. While the peak spans over ~100 K (leading edge to trailing edge) for the unmodified Ru(0001) surface, its range increases to ~150 K for the surface with $\theta_{Pt} = 0.75$ ML. For the $D_{ad}$ saturated surfaces, the maximum of the $\beta_1$ peak also shifts to lower temperature with increasing Pt content. This is obvious from comparison of the $D_2$ TPD spectra after the maximum $D_2$ exposure of $100 \times 10^{-6}$ mbar-s in Figure 4.15. The temperatures of the peak maxima after $D_{ad}$ saturation are also plotted in Figure 4.16a. While it appears at 320 K for Pt–free Ru(0001), it has shifted to 283 K for the surface with 0.75 ML Pt. The physical reasons responsible for the observed peak shift and the simultaneous peak broadening are expected to be identical to those causing the peak shifts in CO desorption with increasing Pt surface content. This will be discussed in detail in the following section.

In addition to the $\beta$ peaks, which are assigned to desorption from the Pt–free Ru areas, we find increasing desorption also at lower temperature. In fact, for all bimetallic surfaces, $D_2$ desorption starts shortly after starting the heating ramp. For the surface with $\theta_{Pt} = 0.2$ ML Pt (Figure 4.14c), deuterium desorption below 210 K contributes 7% to the total desorption intensity after $D_{ad}$ saturation, while this number was only 2% for pure Ru(0001). (For unmodified Ru(0001), desorption in this temperature range can most probably be attributed to desorption from the periphery of the Ru(0001) surface, like the sample holder.) For surfaces with higher Pt contents, a new feature develops after higher deuterium exposures, with a peak at 147 K after $D_{ad}$ saturation ($\gamma$ peak). Following the assignment for the Pt monolayer covered surface (Figure 4.14i), this peak is due to desorption from the Pt monolayer islands. For surfaces with higher Pt content, up to $\theta_{Pt} = 0.75$ ML, the $\gamma$ peak gains successively in intensity.
In addition to the well separated \( \gamma \) and \( \beta \) peaks, there is also desorption in the temperature range between these peaks. Quantitative analysis of the TPD spectra reveals that this must be due to desorption from more stable Pt sites at the perimeter of the Pt islands. This will be discussed in more detail in the next section.

**Figure 4.16:** Temperature shifts of the prominent D\(_2\) TPD features from (a) the Ru part and (b) the Pt monolayer islands/Ru(0001). (a) Ru part: leading edge (▲), peak maximum (●) and trailing edge (▼) after the smallest D\(_2\) exposure (\( \epsilon_{D_2} = 0.2 \times 10^{-6} \) mbar·s); and \( \beta_1 \) peak maximum after D\(_{ad}\) saturation (○). (b) Pt monolayer islands/Ru(0001): \( \gamma \) peak maximum (●), and trailing edge (▼) after the largest D\(_2\) exposure.

Comparison of the integrated D\(_2\) TPD peak signal intensities from bimetallic surfaces with pure Ru(0001) shows a steady decrease of the D\(_{ad}\) saturation coverage (after an exposure of \( \epsilon_{D_2} = 100 \times 10^{-6} \) mbar·s) from 1 ML (Ru(0001) [113] or Pt(111) [120]) to 0.31 ML obtained on
the Pt monolayer covered surface (Figure 4.17a). The ‘maximum’ D_{ad} coverage of the bimetallic surfaces decreases almost linearly with increasing Pt content. In the next step, we evaluated the partial coverages in the high temperature (β peaks, between ~210 and 450 K) and low temperature (γ peak, between 90 and ~190 K) features of the D_{2} TPD spectra (Pt monolayer vs. Ru substrate). To reach acceptable agreement between the coverage fractions of the two surface components (Pt vs. Ru) and the partial D_{ad} coverages of these two parts, it was necessary to include the D_{2} desorption in the intermediate temperature range, between 190 and 210 K, into the desorption from the Pt covered areas (see above). As an example, for a surface with 0.35 ML Pt, the first two desorption regions up to 210 K contribute 17% (0.13 ML), whereas the part above 210 K includes 83% (0.63 ML) of the total D_{ad} coverage (0.76 ML). Comparison to the nominal surface contents of the two fractions (0.35 ML Pt vs. 0.65 ML Ru) indicates that a complete (1 × 1) D_{ad} layer with 1 ML D_{ad} is present on the Ru part after D_{ad} saturation, while the total maximum D_{ad} coverage, after exposure at 90 K, is well below the saturation coverage on pure Pt(111) [120] or Ru(0001) [113].

The local maximum D_{ad} coverage, determined separately for the Pt monolayer islands and the uncovered Ru areas (for cases where the two contributions could be reliably separated), are also plotted in Figure 4.17a. The local D_{ad} saturation coverage on the two surface regions is almost independent from the surface composition (Pt content). After D_{ad} saturation, the Ru areas always reach the maximum possible D_{ad} coverage of ~1 ML, while the D_{ad} coverage on the Pt islands is ~0.3 ML. The same value is obtained also for the closed Pt monolayer (1.15 ML Pt). For low Pt coverages (< 0.2 ML), the Pt-related D_{2} desorption signal cannot be discriminated unequivocally from the background signal, making a quantitative determination of the D_{ad} coverage on the Pt islands difficult. The finding of a constant maximum D_{ad} coverage of ~0.3 ML (after 100×10^{-6} mbar·s exposure), at least for Pt coverages above 0.2 ML, indicates that once a certain Pt island size is reached, any further increase in Pt coverage mainly serves to increase the amount of Pt adsorption sites without changing their chemical nature.
Figure 4.17: (a) $D_{\text{ad}}$ maximal coverage on Pt$_x$/Ru(0001) surfaces with varying Pt coverage (■), local maximal coverage on uncovered Ru areas (●) and Pt islands (▲); (b) Initial sticking coefficient $s_0$ for deuterium adsorption on Pt$_x$/Ru(0001) surfaces with varying Pt coverage.

The initial sticking coefficient $s_0$ is also affected by the presence of the Pt monolayer islands / cover layer (Figure 4.17b). For submonolayer Pt coverages, $s_0$ increases initially from 0.16 for the pure Ru(0001) to 0.2 for a Pt coverage of 0.1 ML, for higher Pt coverage $s_0$ decreases again to 0.09 for the 0.9 ML Pt covered surface. For Pt coverages beyond 1 ML (fully Pt covered surface), $s_0$ is further reduced, reaching, e.g., values of 0.04 and 0.055 for surfaces covered by 1.15 ML and 1.4 ML Pt (data not shown), respectively.

In a simple picture one would expect that the initial sticking coefficient $s_0$ decreases linearly with increasing Pt coverage to the value of the fully Pt monolayer covered surface ($s_0 = 0.04$).
Such kind of behaviour, which would be expected for D$_2$ adsorption on a surface consisting of two parts with constant intrinsic adsorption kinetics, is indicated by the dashed line in Figure 4.17b. Obviously, the experimental results differ significantly from that trend, and higher values are obtained for all submonolayer Pt coverages (e.g., 0.09 for $\theta_{Pt} = 0.9$ ML). Especially the increased sticking probability (compared to Ru(0001)) on surfaces with Pt coverages up to 0.35 ML Pt may seem surprising, considering the concomitant decrease in saturation coverage. These findings can most easily be explained by an increased number of defect sites at the edges of the Pt islands, which are well known to enhance the sticking probability for adsorption. In contrast to CO adsorption, surface diffusion of adsorbed deuterium (D$_{ad}$) is sufficiently fast on both parts of the bimetallic surfaces at 90 K to equilibrate the adlayer during adsorption. Therefore, spill-over effects during the TPD measurements, as observed for CO, do not exist for deuterium adsorption.

The low values of the initial sticking coefficient for D$_2$ adsorption on Pt monolayer covered surfaces point to the presence of an (increased) activation barrier. This can be understood from the Brønsted–Evans–Polanyi relation [121–123], which correlates the (de–)stabilization of the final (adsorption) state with a concomitant (de–)stabilization of the transition state. Therefore, the considerable destabilization of D$_{ad}$ on the Pt monolayer covered surface can be expected to raise the activation barrier for dissociative adsorption of D$_2$.

Overall, we arrive at similar findings as for CO adsorption. Neglecting smaller deviations in the adsorption kinetics, an increase in Pt coverage mainly results in an increase of the relative amount of Pt adsorption sites, while their chemical properties remain largely unchanged. Adsorption sites at the perimeter of the island edges, however, contribute significantly to the desorption intensity. Among others, this will be discussed in detail in the next section.

4.2.5 Discussion

In this section, a number of points will be addressed which have not been discussed in detail in the preceding sections and which are of general relevance for adsorption on bimetallic surfaces. These include i) the physical origin of the observed modification of the adsorption properties of the Pt/Ru(0001) systems, ii) characteristic differences in the adsorption properties of PtRu/Ru(0001) monolayer surface alloys and the Pt monolayer island covered Ru(0001) surface and iii) the deviations from a purely additive desorption behaviour, where
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desorption is additively composed of non–modified desorption from Pt monolayer islands and from Pt–free Ru(0001) areas. Effects related to the spill–over of CO$_{ad}$ from Pt monolayer islands to Pt–free Ru(0001) areas even on CO$_{ad}$ saturated surfaces will be discussed in Section 4.3.

i) The TPD spectra reveal for both adsorbate species a significant destabilization on the Pt monolayer islands compared to adsorption on the Ru(0001) substrate or to pure Pt(111). Compared to CO desorption from pure Pt(111) [85,98,111], the trailing edge of the first Pt related desorption peak ($\beta_1$ state) is shifted by ~150 K to lower temperature on Pt/Ru(0001) surfaces with intermediate to high Pt coverage (> 0.5 ML). Also the onset of CO desorption after CO saturation is shifted by ~150 K to 180 K. Based on the TPD results, the initial CO desorption energy decreases from ~140 kJ mol$^{-1}$ for pure Pt(111) [98,124] to only ~90 kJ mol$^{-1}$ for adsorption on the Pt islands of the bimetallic surface. Similarly, D$_2$ desorption from the Pt monolayer is shifted to significantly lower temperature. Considering the temperature shifts of the trailing edge of the Pt related feature in the TPD spectra from the Pt/Ru(0001) surfaces compared to pure Pt(111) [119], the activation energy for desorption can be estimated to be ~40 kJ mol$^{-1}$, compared to ~70 kJ mol$^{-1}$ for Pt(111) [125].

The modification of the adsorption properties (of both CO and D) on the Pt monolayer islands can be explained by a combination of geometric strain and electronic ligand effects [14,15,17,23,29,30,108,126]. Both, the compressive strain induced in the pseudomorphic Pt layer on the Ru substrate by the lattice mismatch of the two components (Pt: 2.77 Å, Ru: 2.70 Å) and the electronic interaction of the Pt atoms in the monolayer with the underlying Ru substrate (vertical ligand effects) tend to weaken the bonding of adsorbates to the surface. Strain and ligand effects have been explained in terms of the d–band model [14,15], the electronic ligand effects can also be rationalized by the stronger Pt – Ru bond as compared to a Pt – Pt bond, which weakens the adsorption strength of a Pt – adsorbate bond [17]. Using CO as probe molecule, Schlapka et al. [23] could demonstrate in a combined experimental and theoretical study that for the present system, CO adsorption on a Pt monolayer covered Ru(0001) substrate, the contribution from vertical electronic ligand effects is dominant with 60% of the observed decrease in adsorption energy, while compressive strain effects contribute the remaining 40%. Accordingly, the higher adsorption energy for adsorption on second layer islands as compared to adsorption on a Pt monolayer was explained by weaker electronic interactions between Pt surface layer and Ru(0001) substrate, leading to a backshift of the d–band centre closer to the Fermi level [23].
ii) Comparing adsorption on the present Pt_{0.0.0.2 ML}/Ru(0001) surfaces with PtRu/Ru(0001) monolayer surface alloys, there are significant differences. For Pt_{0.0.0.2 ML}/Ru(0001) surfaces with a Pt coverage beyond ~0.2 ML, the position of the Pt related CO (\( \beta_1 \)) and D₂ (\( \gamma \)) desorption features remains almost unchanged at the same position (cf. Figure 4.9 and Figure 4.16). This implies an almost unchanged chemical nature of the Pt adsorption sites for increasing Pt coverage up to 1 ML, with the exception of the island edge sites. This behaviour contrasts the development for CO and deuterium desorption from PtRu/Ru(0001) surface alloys [29,30]. In the latter case, a constant shift of the TPD features related to desorption from Pt sites was observed with increasing Pt concentration. For CO desorption, this shift was attributed to a combination of decreasing electronic interaction within the layer (lateral ligand effects), due to the decreasing number of Ru neighbours around a Pt atom, and an increasing overall compressive strain with increasing Pt concentration [29]. While the first effect should bring about a stabilization of CO adsorption, the second one should be destabilizing. From the shift of CO desorption to lower temperatures in the TPD spectra, it was concluded that the strain effects outbalance the intra–layer ligand effects in the case of this mixed alloy layer with increasing Pt concentration [29]. For deuterium adsorption/desorption, ensemble effects, i.e., the varying composition of the adsorption ensemble, have to be considered as well [30,127]. For recombinative desorption of Dₐd, a pentamer of surface atoms had been proposed as critical ensemble, where the adsorption energy decreases with increasing Pt content [91]. For Pt monolayer films and monolayer islands on Ru(0001) surfaces, the absence of significant shifts with increasing Pt content indicates that an increase in the Pt island size above a certain value does not influence the lateral strain or electronic interaction with the Ru substrate experienced by Pt atoms in the inner parts of the island any more. Thus, regarding their adsorption properties towards CO and D₂, the Pt submonolayer islands can be considered as locally closed monolayers. Therefore, lateral ligand and ensemble effects should be of minor importance for this bimetallic system.

iii) In order to test the idea of additive desorption, where the TPD spectra can be described as a sum of unmodified contributions from the Pt–free Ru(0001) areas and the Pt monolayer islands, we modelled the experimental TPD results of surfaces with intermediate Pt contents by computer simulations. While for CO adsorption, a straightforward and simple comparison of the simulated and experimental data is complicated because of the overlap between the desorption features arising from desorption from Ru(0001) and from Pt monolayer covered areas, this is much simpler and more unique for deuterium adsorption. Here the separation
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between these features is sufficient that one can clearly identify and distinguish between desorption from the two different areas.

The simulations are based on a numerical solution of the rate equations (Polanyi–Wigner equations) for second order recombinative deuterium desorption.

\( R_{Des} = -\frac{dN_D}{dt} = \sum_{i=1}^{j} \lambda_i \cdot \nu_i \cdot N_{D,i}^{m_i} \cdot e^{-E_{Des,i}(N_{D,i})/RT} \)  \hspace{1cm} (4.3)

In a simple approach, neglecting contributions from Pt island edge sites as well as adsorbate interdiffusion between different parts of the surface, the total desorption rate \( R_{Des} \) equals the sum of desorption from the different parts of the surface, which is described for each part by a Polanyi–Wigner equation. Here, \( \lambda_i \) is the fraction of the surface represented by the respective parts, \( \nu_i \) is the pre–exponential factor, \( N_{D,i} \) the number of occupied sites, \( m_i \) the desorption order (2 for recombinative deuterium desorption) and \( E_{Des} \) the coverage dependent activation energy for desorption from each component.

For our simulations of the surfaces covered by Pt islands with intermediate Pt content (0.35 and 0.5 ML Pt), we restricted ourselves to the two main parts contributing to deuterium desorption: (i) the unmodified Ru(0001) substrate (β peaks) and (ii) the perfect part of the Pt islands (γ peaks). Due to the lack of detailed information about the adsorption properties of other sites, in particular of sites at the perimeter between Pt islands and Ru substrate, we did not consider these sites in the present simulations. Furthermore, also interdiffusion between the different parts of the surface was not taken into account. The latter simplification was justified by test simulations where we allowed for instantaneous equilibration of the adlayer at each point of the desorption process, hence assuming infinitely fast –. These simulations revealed negligible changes in the resulting spectra. Obviously, the differences in deuterium binding energies, which determine the distribution of D\(_{ad}\) species under equilibrium conditions, are too large to induce sizeable transfer from one part of the surface to the other in the course of the desorption experiment. This situation would change, however, when considering systems with smaller differences in the adsorption properties. Accordingly, contributions from adsorbate interdiffusion may play a role when also sites with intermediate binding strength at the Pt island edges are taken into account, i.e., in a more realistic picture of the Pt/Ru(0001) surfaces (see below).
The desorption traces simulated for $D_{\text{ad}}$ saturated Pt/Ru(0001) surfaces with 0.35 and 0.5 ML Pt are shown in Figure 4.18a and b, respectively, together with the corresponding experimental $D_2$ TPD spectra from Figure 4.14 after an exposure of $100 \times 10^{-6}$ mbar·s. For these simulations, the relative intensities of the simulated peaks were adjusted to the experimental results by varying the contribution factors $\lambda_i$.

For both parts of the surface, the pre-exponential factor was kept constant at $10^{-2}$ cm$^2$ s$^{-1}$. Applying transition state theory, this value corresponds to desorption from a mobile adsorbate phase on the surface [128] and similar values were also derived for hydrogen desorption from unmodified Ru(0001) [115,117]. The activation energy for desorption was described for both surfaces by the same coverage-dependent development, decreasing almost linearly from 102 to 76 kJ mol$^{-1}$ (at saturation) for the Ru part and from 41 to 35 kJ mol$^{-1}$ (at saturation) for the Pt part. The barrier for desorption from the Ru(0001) part closely resembles that used in earlier simulations of hydrogen desorption from Pt–free Ru(0001) at low $D_{\text{ad}}$ coverage [25], but decreases faster with (local) $D_{\text{ad}}$ coverage, to 76 kJ mol$^{-1}$ instead of 85 kJ mol$^{-1}$ at $D_{\text{ad}}$ saturation. This accounts formally for the observed peak broadening in the presence of Pt monolayer islands, although a microscopic explanation is still missing. Finally, the $D_{\text{ad}}$ saturation coverage on the Pt–covered part of the surface was set to 0.30 ML.

Comparison of computer simulations and experimental results shows for both surfaces for the $\beta$ peak range (desorption from Ru sites) reasonably good agreement in the trailing edge, while the shoulder extending from the peak maximum to lower temperature and the desorption intensity in the intermediate range (190 – 210 K) are completely missing in the simulations of both examples. For the $\gamma$ peaks, on the other hand, there is rather good agreement again between experimental and simulated spectra. The discrepancy between measured and simulated TPD spectra in the intermediate temperature range between the $\gamma$ and $\beta$ features (190 – 210 K) and in the low temperature shoulder below the $\beta_1$ peak, can be explained by the presence of additional adsorption sites on the Pt monolayer island modified Ru(0001) surfaces with a binding strength between that of the unmodified Ru(0001) surface and that on the Pt monolayer covered surface. These desorption features are tentatively related to desorption from the edge sites of the Pt monolayer islands (190 – 210 K) and to desorption from the Ru sites at the step edges (low temperature shoulder in the $\beta$ peak).
4 Results and discussion

Figure 4.18: Simulated (full line) and experimental (dashed line, see Figure 4.14) TPD spectra after D$_2$ exposures of 100×10$^{-6}$ mbar·s from bimetallic Pt/Ru(0001) surfaces with (a) 0.35 and (b) 0.5 ML Pt.

In the first case, the adsorption bond should be stronger than in the central part of the Pt islands, in the second case, electronic modifications of the Ru surface atoms at the step by the adjacent Pt atoms should result in a weaker adsorbate bond as compared to adsorption on the ideal Ru(0001) surface.

The contribution factors $\lambda_i$ are listed in Table 1. For a consistent picture, the desorption intensity missing in the simulated spectra is summarized in $\lambda_2$, which includes desorption from both Pt and Ru perimeter sites.
4 Results and discussion

<table>
<thead>
<tr>
<th>Pt coverage / ML</th>
<th>$\lambda_1$</th>
<th>$\lambda_2$</th>
<th>$\lambda_3$</th>
</tr>
</thead>
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<tr>
<td>0.35</td>
<td>0.56</td>
<td>0.10</td>
<td>0.34</td>
</tr>
<tr>
<td>0.50</td>
<td>0.44</td>
<td>0.08</td>
<td>0.48</td>
</tr>
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</table>

Table 1: Surface contribution factors for the simulation of D$_2$ TPD spectra. $\lambda_1$: Ru part (210 – 450 K), $\lambda_2$: intermediate range (190 – 210 K, not covered by simulation), $\lambda_3$: Pt islands/Ru (110 – 190 K).

Assuming that these sites are fully occupied at saturation ($\theta_D = 1.0$), these sites contribute with 0.10 (0.35 ML Pt) and 0.08 (0.5 ML Pt) to the adsorption sites on the surface, respectively. Since a quantitative separation between the two types of sites is hardly possible, they are combined in a single $\lambda$ value. Most simply, each type of sites contributes about half to the desorption intensity in this part. In that case, the fractions of the surface covered by Pt monolayer islands and the Pt–free Ru(0001) surface area should be given by $\lambda_1 + \lambda_2/2$ and by $\lambda_3 + \lambda_2/2$, respectively. The resulting values of 0.39 and 0.52 ML Pt agree reasonably well with the values determined by XPS of 0.35 and 0.50 ML Pt, respectively, supporting the validity of this approach.

Considering the morphology of the partly Pt covered Ru(0001) surfaces, which is characterized by almost hexagonally shaped, monolayer islands at lower Pt coverages (diameter ~10 nm at < 0.2 ML, ~20 nm at 0.3 – 0.4 ML), via partly merged, larger Pt islands for intermediate Pt coverages to an almost closed Pt overlayer with some remaining holes in the layer and the formation of second layer Pt islands on top of the monolayer for high Pt coverage approaching 1 ML [49,50], the fraction of edge atoms, however, is very small. For instance, a number of ~0.028 ML was derived from an analysis of STM measurements for a surface with 0.3 ML Pt [48]. Agreement between this value and the fraction of the surface with intermediate binding energies derived from the TPD spectra, as evidenced by the $\lambda_2$ values, is only possible if these steps affect the measured activation energies for desorption in a stripe with a width of approximately two adsorption sites, both on the Ru side and at the Pt side. Though this might sound surprising on a first view, since electronic effects of the Pt islands on the neighbouring Ru substrate are intuitively assumed to level off quickly, it should be noted that the lateral range of step effects had not been explored so far in detail. Density functional theory based calculations have been initiated to learn more on this surprising effect.

As a further characteristic feature of the TPD spectra for both CO and deuterium desorption, we observed a significant down–shift of the Ru–related high temperature peak over the whole
range of surface compositions compared to the unmodified Ru(0001) surface (cf. Figure 4.9 and Figure 4.16). This affects both the trailing edge and the peak temperature. Such kind of shifts appeared in a number of bimetallic adsorption systems, and therefore may represent a more general phenomenon [25,54,65,129–131]. Also this cannot be rationalized in the framework of the desorption models described above. According to a transition state theory (TST) description of desorption, this would imply either a reduction of the activation energy for desorption, in the present case by ~3 to 5 kJ mol\(^{-1}\), or a comparable increase of the pre–exponential factor. Contributions from configurational entropy, which were shown to affect the pre–exponential factor in the case of desorption from surface alloys [132], should be very small for the present bimetallic surfaces considering the size of the Pt islands and the remaining Pt–free Ru(0001) patches. Hence, the origin for the systematic down–shift of the Ru–related high temperature desorption peak, which we consider to be a general phenomenon for desorption from bimetallic surfaces, is not clear at the moment. Further work to explore this phenomenon has been started, but is outside the scope of the present paper.

iv) Finally, we want to discuss the spill–over effects observed for CO\(_{\text{ad}}\) on partly Pt covered surfaces even upon CO\(_{\text{ad}}\) saturation. Since these were described in more detail in a recent publication [109], we will only summarize the main aspects. After adsorption at low temperature (90 K), where surface diffusion is largely hindered, CO\(_{\text{ad}}\) was found to diffuse from the Pt monolayer covered areas to Pt–free Ru(0001) areas as soon as surface diffusion was thermally activated during the TPD run. While this is well known and obvious for lower CO\(_{\text{ad}}\) coverages, where the additional CO\(_{\text{ad}}\) can be easily accommodated on the Pt–free Ru(0001) areas, we found that this happens also on CO\(_{\text{ad}}\) saturated Pt\(_{0.4}\) ML/Ru(0001) surfaces, where further adsorption from the gas phase is not possible. We interpreted this in terms of a model, where additional uptake of CO\(_{\text{ad}}\) into the saturated CO adlayer on the Pt–free Ru(0001) areas is possible by spill–over of CO\(_{\text{ad}}\), but not by adsorption from the gas phase.

This was verified both by TPD and IR measurements. In TPD measurements (see Figure 4.10), it showed up in the continuous down–shift of the onset for desorption from the CO\(_{\text{ad}}\) saturated surface with increasing Pt coverage in the intermediate Pt coverage range (0.1 – 0.5 ML). In a simple model, with desorption from the two parts of the surface being independent, one would expect increasing desorption from Pt monolayer covered areas with a constant onset temperature over the entire submonolayer Pt range up to completion of a Pt monolayer film for desorption from CO\(_{\text{ad}}\) saturated surfaces. If we assume that CO adsorption at 90 K results in immobile CO\(_{\text{ad}}\) species and hence in a homogeneous CO adlayer on the
(inhomogeneous) bimetallic PtXML/Ru(0001) surface, spill–over of CO_{ad} during the desorption run, before the onset of desorption, leads to a loss of CO_{ad} coverage on the Pt monolayer islands and a corresponding CO_{ad} coverage increase on the Pt–free Ru(0001) areas. Obviously, such kind of spill–over is possible even on an apparently CO_{ad} saturated surface. Due to the limited uptake capacity of the CO_{ad} ‘saturated’ Ru(0001) areas, however, the amount of CO_{ad} able to transfer from Pt–covered to Pt–free areas decreases with increasing Pt coverage. Correspondingly, the remaining CO_{ad} coverage on the Pt–covered areas, at the onset of desorption, increases with increasing Pt coverage, which results in the continuous down–shift of the onset temperature observed for CO_{ad} saturated surfaces (Figure 4.8 and Figure 4.9).

Upon adsorption at 150 K and above, where CO_{ad} surface diffusion is activated, spill–over of CO_{ad} can occur during adsorption, and the Pt–covered areas are fully saturated by adsorbed CO. This results in an onset temperature which is identical to that on a monolayer Pt film already at low Pt coverages (Figure 4.10). In IR measurements, the additional uptake of CO_{ad} on the Pt–free Ru(0001) areas results in an up–shift of the CO_{ad} vibrational frequency, e.g., for a CO_{ad} saturated surface with 0.2 ML Pt from 2058 to 2068 cm\(^{-1}\) after CO adsorption at 90 K or 150 K, respectively [109].

These findings have important consequences. They indicate that CO adsorption on Ru(0001) is kinetically limited at high coverages. Inclusion of CO from the gas phase into a ‘saturated’ CO adlayer is kinetically inhibited, although energetically higher CO_{ad} densities are possible. Additional uptake is facilitated, however, by spill–over from areas where CO_{ad} is less strongly adsorbed, with the difference in adsorption energies providing the driving force. We propose that such kind of kinetic limitations in the adsorption of CO or other molecules into high coverage adlayers represent a general phenomenon, and that thermally activated spill–over on bimetallic surfaces may assist to reach the thermodynamically determined maximum coverage. This is possible for bimetallic surfaces with separated A– and B–type areas with pronounced differences in adsorption energy for the respective adsorbate, where the difference in adsorption energy provides the necessary driving force for the spill–over process [109].
4 Results and discussion

4.2.6 Conclusions

This chapter combined the results of investigation on the adsorption and desorption properties of CO and D$_2$ on series of structurally well-defined, bimetallic Pt/Ru(0001) surfaces, where an increasing part of the Ru(0001) substrate is covered by large, pseudomorphic Pt monolayer islands (small and medium Pt coverages) or by a contiguous Pt monolayer film at high submonolayer Pt coverages. Focus of this work was on the question whether adsorption on these surfaces can be described as purely additive, by simple superposition of adsorption on the Pt and Ru surface areas, or whether additional effects have to be considered as well, affecting the adsorption on / desorption from the two surface types. Detailed TPD and IR measurements lead to the following conclusions:

1. In agreement with earlier work, we find CO adsorption on the Pt monolayer covered areas to be substantially weaker than on Pt(111) or on Ru(0001), which was explained by a combination of electronic strain and vertical ligand effects. Both effects lead to a destabilization of adsorbates for adsorption on pseudomorphic Pt monolayer islands on Ru(0001) by lowering the d-band centre of Pt. CO adsorption on Pt–free Ru(0001) areas largely resembles that on a Pt–free Ru(0001) surface, except for a down–shift of the CO$_{ad}$(Ru) related TPD peaks (β peaks) (shift of the trailing edge by 60 K). The physical origin of this down–shift, which appears to be characteristic for desorption from bimetallic surfaces with coexisting large areas of two surface types with very different adsorption energies, is not yet clear. Entropy effects (configurational entropy), however, can be excluded.

2. Spill–over of CO$_{ad}$ from the Pt–covered to the Pt–free Ru(0001) areas, which is driven by the very different CO adsorption energies on those areas, can increase the local CO$_{ad}$ coverage on the Pt–free Ru(0001) areas to values well above the CO$_{ad}$ saturation coverage on Ru(0001). This indicates that the CO$_{ad}$ saturation coverage obtained upon direct CO adsorption on Ru(0001) is kinetically limited rather than by thermodynamics. Kinetically limited saturation coverages are proposed to be a general phenomenon in adsorption, spill–over processes on bimetallic surfaces offer the possibility to reach the thermodynamically limited saturation coverage, by opening an additional adsorption channel.

For adsorption at 90 K, where CO$_{ad}$ surface diffusion is inhibited, spill–over becomes possible only during the TPD experiment, leading to deviations in the TPD spectra in the high CO$_{ad}$ coverage regime. The CO$_{ad}$(Pt) related features are fully populated only at
higher Pt coverages, where the extent of CO$_{\text{ad}}$–spill–over is increasingly limited. For adsorption at 150 K, CO$_{\text{ad}}$–surface diffusion and spill–over are possible during adsorption, and these states are populated also at low and medium submonolayer Pt coverages.

3. For CO adsorption, where the desorption peaks related to the Pt covered parts of the surfaces (200 – 350 K) are well above the adsorption temperature (90 K), the saturation coverage is only slightly changed, although the CO adsorption energy is considerably weakened (from 140 kJ mol$^{-1}$ for Pt(111) to 90 kJ mol$^{-1}$ for monolayer Pt islands). Due to an overlap of the Pt– and Ru–related features in the TPD spectra, a quantitative analysis of the CO$_{\text{ad}}$ coverage on the Pt and Ru areas is not possible.

4. The absence of significant changes in the initial sticking coefficient for CO adsorption with increasing Pt coverage indicates that the Pt monolayer has little effect on the CO adsorption dynamics. For all Pt coverages, the variation of the sticking coefficient with CO$_{\text{ad}}$ coverage points to adsorption via a (extrinsic) precursor state, as described by the Kisliuk model, in agreement with findings for CO adsorption on Pt(111) and Ru(0001).

5. Adsorption of deuterium on the Pt/Ru(0001) surfaces reveals a similar weakening of the adsorption bond on the Pt monolayer covered areas as observed for CO$_{\text{ad}}$, which is attributed to a similar combination of electronic strain and vertical ligand effects (lowering of the d–band centre). The adsorption energy on the Pt monolayer covered areas is $\sim$40 kJ mol$^{-1}$, compared to $\sim$70 kJ mol$^{-1}$ on Pt(111) (both in the low D$_{\text{ad}}$ coverage limit).

6. Different from CO desorption, deuterium desorption from the Pt–covered and the Pt–free parts of the surface can be evaluated separately, since the respective desorption peaks do not overlap. The spectra reveal a similar kind of down–shift of the peak related to deuterium desorption from the Pt–free Ru(0001) surface areas with increasing Pt coverage as observed for CO desorption (see point 1). Simulations of the deuterium desorption clearly indicate that these shifts cannot be explained by surface diffusion, i.e., by interdiffusion between the Pt–free and Pt–covered surface areas, at least as long as no other sites with intermediate binding energies are included. Hence, the physical origin of this shift is equally open as for CO desorption.

Furthermore, the spectra also exhibit substantial intensity in the range between the two peaks, at $\sim$190 – 210 K, which is tentatively attributed to desorption from sites along the perimeter of the Pt islands, both at the Pt side (strongly binding Pt sites, desorption in the intermediate range) and at the Ru side (weakly binding Ru sites, desorption at the
low temperature side of the $\beta$ peak). From the intensity in these areas it is concluded, that adsorption sites in a stripe of approximately two sites width on each side of the step are affected by the step and the presence of the respective other metal.

7. Surface diffusion of $D_{\text{ad}}$ is activated at 90 K, therefore spill–over effects as observed for $CO_{\text{ad}}$ are absent. There is no indication of a measurably higher $D_{\text{ad}}$ saturation coverage on the Pt–free Ru(0001) surface areas ($\theta_{\text{Sat}}(D) = 1.0 \text{ ML}$) compared to a Pt–free Ru(0001) surface, which could be reached via spill–over of adsorbates.

8. The apparent $D_{\text{ad}}$ saturation coverage reached after $100 \times 10^{-6}$ mbar$\cdot$s $D_2$ decreases steadily with increasing Pt coverage. This is mainly due to the steady increase of the Pt covered areas, on which the adlayer coverage is rather low, while the local $D_{\text{ad}}$ coverages on the Pt–free and Pt–covered areas are approximately independent of the Pt coverage (1.0 and $\sim 0.3$ ML $D_{\text{ad}}$, respectively). The low apparent saturation coverage on the Pt–covered areas is mainly attributed to the very low sticking coefficient on these areas, which would allow for a further increase in $D_{\text{ad}}$ coverage for (much) higher exposures, contributions due to the onset of desorption at higher coverages during adsorption (adsorption – desorption equilibrium), cannot be ruled out.

9. After an initial increase from 0.16 for a Pt–free Ru(0001) substrate to 0.2 for a surface with 0.1 ML Pt, the initial sticking coefficient for $D_2$ adsorption decreases slowly and in a non–linear way with increasing Pt coverage to $\sim 0.04$ for a surface covered by a Pt monolayer film. The much lower sticking coefficient on the latter surface is tentatively explained by an increasing activation barrier for $D_2$ adsorption, as expected from the much weaker adsorption energy on that surface via the Brønsted–Evans–Polanyi effect, the non–linear decay with increasing Pt coverage is attributed to enhanced sticking at Pt island edges in the range of small and medium Pt coverages.

In total, the interaction of the probe molecules CO and $D_2$ with bimetallic Pt/Ru(0001) surfaces revealed a number of distinct effects, which are considered to be characteristic for adsorption on bimetallic surfaces consisting of large areas with distinctly different adsorption properties, such as spill–over effects, pronounced edge effects, and a general down–shift of the desorption peak related to the strongly adsorbing surface part (here Ru(0001)), as compared to adsorption on a pure surface of the latter type.
4 Results and discussion

4.3 CO spill–over effects on Pt/Ru(0001) film surfaces

The results presented in this section served as basis for two publications, [109a] and [109b].

4.3.1 Abstract

CO spill–over on Ru(0001) surfaces partly covered by Pt monolayer islands (Pt/Ru(0001)) has been studied by TPD and IRAS. CO molecules adsorbed at 90 K display only a very limited mobility on the Pt islands. The increases in mobility caused by annealing the adlayer to 150 K leads to a diffusion of CO$_{\text{ad}}$ molecules to the Pt free Ru areas, even at CO$_{\text{ad}}$ coverages which preclude further adsorption from the gas phase on the Ru parts of the surface. The same effect is observed for direct CO adsorption at 150 K, leading to CO$_{\text{ad}}$ saturation coverages on these areas which are considerably higher than after adsorption at 90 K. IRAS spectra indicate that partial CO$_{\text{ad}}$ coverages on the Pt free Ru(0001) areas are considerably higher than the CO saturation coverage on Ru(0001). This indicates that the CO$_{\text{ad}}$ saturation coverage of 0.68 ML resulting from direct adsorption on Ru(0001) is limited kinetically rather than thermodynamically. Literature data indicate that this effect is not limited to the Pt/Ru(0001) surface, but may be found on a wide range of bimetallic systems.

4.3.2 Introduction

Several previous studies addressed the mobility of CO adsorbed on bimetallic surfaces, in particular the diffusion of CO$_{\text{ad}}$ from the weaker binding surface component to the stronger binding one [84,108,133–137]. For example, the Cu/Ru(0001) system showed that the CO$_{\text{ad}}$ mobility increases at 120 – 175 K, leading to a migration of CO$_{\text{ad}}$ molecules adsorbed at 85 K from the Cu islands to the Ru(0001) substrate, the driving force for the diffusion process being the difference in the adsorption energies between the Cu and Ru components of the surface[133,134]. For Cu/Rh(100), He et al. [135,136] found that CO adsorbed on the surface at 90 – 100 K diffuses from Cu to Rh after annealing to 150 – 270 K. Similar observations were reported for the Pd/W(110) system [137]. For the Pt/Ru(0001) system, Jakob et al. found that the CO$_{\text{ad}}$ mobility is low at 90 K and migration from Pt to Ru is suppressed at this temperature [84,108]. For low CO coverages ($\theta_{\text{CO}} = 0.01$ ML) on a 0.4 ML Pt surface,
annealing to 104 K resulted in the migration of all CO\textsubscript{ad} molecules adsorbed on Pt islands to the Pt–Ru steps at the island edges. Annealing to higher temperatures resulted in the diffusion of all CO\textsubscript{ad} from Pt sites to the Ru(0001) substrate [108].

Studies on Cu/Rh(100) [135,136] and Pd/W(110) [137] observed CO diffusion upon annealing to higher temperatures not only for low CO coverages but also for surfaces nominally saturated with CO (at the respective adsorption temperatures of 85 – 100 K). While not explicitly mentioned by the authors, figures in [133,134] show some evidence that this also occurs on Cu/Ru(0001) after annealing a CO\textsubscript{ad} layer adsorbed at 85 K to 150 K. One aspect of these observations, which has not been addressed in these studies, is the change in CO\textsubscript{ad} coverage on both parts of the surface caused by the CO\textsubscript{ad} diffusion process. Obviously, the partial CO\textsubscript{ad} coverage will increase on the stronger binding part of the surface and it was assumed that this can only occur if the CO\textsubscript{ad} coverage on the stronger binding part is below saturation before the diffusion process starts [135,136]. An alternative explanation is that the higher mobility of CO at higher temperatures leads to a more ordered adlayer, which in turn facilitates the uptake of additional CO [80]. In the following section I will show that on the Pt/Ru(0001) surface CO\textsubscript{ad} is transferred from the Pt islands to the Ru areas via neither of these mechanisms. Instead, if the partial CO\textsubscript{ad} coverage after adsorption at low temperature is similar to the saturation coverage on the pure surface, CO\textsubscript{ad} diffusion between the surface components at higher temperatures leads to a partial CO coverage on the stronger binding component (Ru(0001)) which exceeds the CO saturation coverage on the pure Ru(0001) surface.

The increase of the partial CO coverage on one part of the bimetallic surface after annealing to higher temperatures indicates that CO adsorption at this temperature should allow higher total CO\textsubscript{ad} coverages, since the adsorption sites which are vacated on the weaker binding part of the surface can be filled up by adsorption from the gas phase. The results of TPD experiments on CO adsorption on submonolayer Pt films on Ru(0001) [104] indicate that this is in fact the case. On these surfaces, CO\textsubscript{ad} coverages after adsorption at 150 K were found to be significantly higher than after adsorption at 90 K. On surfaces with Pt coverages up to 0.3 ML the total CO\textsubscript{ad} coverage after adsorption at 150 K even exceeds the saturation coverage on pure Ru(0001). At the same time, the TPD spectra show additional desorption states in the temperature range associated with desorption from Pt islands [104]. At a first glance this might indicate that additional CO is adsorbed on the Pt islands, however, it appears more likely that these TPD features are absent in TPD spectra of CO adsorbed at 90 K
due to the inevitable diffusion of CO$_{\text{ad}}$ from Pt to Ru sites in the course of the TPD experiment.

In this section I present results of additional TPD and IRAS experiments conducted on submonolayer Pt films on Ru(0001) in order to further investigate the effects of annealing of CO$_{\text{ad}}$ layers and CO adsorption at 150 K on the partial CO$_{\text{ad}}$ coverage on different parts of the bimetallic surface. The combination of both methods is important, since TPD allows the determination of total CO$_{\text{ad}}$ coverages via integration of the TPD spectra, while IRAS is employed to provide information about the occupation of Pt and Ru sites at the respective temperatures.

4.3.3 Experimental

The TPD and IRAS experiments presented in this section were carried out with the same experimental setup and applying the procedures described in Section 3.

4.3.4 Results

In this section, the CO$_{\text{ad}}$ spill–over from Pt to Ru and CO adsorption at 150 K, which was touched on in Section 4.2.4.1, will be discussed in more detail. As has been mentioned in the above sections, the Pt/Ru(0001) surface consists of large, compact Pt monolayer islands. For a Pt coverage of 0.2 ML, the islands reach a diameter of 10 – 20 nm. Considering this, the adsorption of CO and D$_2$ on Pt/Ru(0001) surfaces with submonolayer coverages of Pt can be expected to be a superposition of adsorption on the Pt monolayer islands (similar to adsorption on a Pt monolayer) and on the uncovered parts of the Ru(0001) surface (similar to the pure Ru(0001) surface). While for adsorption of D$_2$, this expectation is confirmed to a large degree, TPD spectra of saturated CO$_{\text{ad}}$ layers recorded after adsorption at 90 K on surfaces with Pt coverages below 0.5 ML do not display all of the features that are eventually found on the Pt monolayer (Figure 4.8). Additionally, in the same Pt coverage range, the low–temperature edge of the CO TPD spectra at CO$_{\text{ad}}$ saturation displays a continuous shift to lower temperatures with increasing Pt coverage (Figure 4.9b), indicating that CO adsorption on the Pt monolayer islands differs from CO adsorption on a closed Pt monolayer. As shown in Figure 4.10 and Figure 4.19, adsorption of CO at 150 K on 0.3 ML Pt leads to increased
CO uptake (compared to adsorption at 90 K), shifting the onset of desorption from \(\sim 230 \text{ K}\) to \(\sim 200 \text{ K}\) and populating the \(\beta_3\) state, which is populated on surfaces with Pt coverages \(\geq 0.5 \text{ ML}\), but missing for lower Pt coverages after saturation at 90 K.

Figure 4.19 shows results of similar CO TPD experiments for surfaces with 0.15 – 1.0 ML Pt. In order to guarantee CO\(_{\text{ad}}\) saturation at 150 K, exposures of \(120 \times 10^{-6} \text{ mbar}\cdot\text{s}\) were used at this temperature. At 90 K exposures of \(30 \times 10^{-6} \text{ mbar}\cdot\text{s}\) CO were sufficient to saturate the surface with CO\(_{\text{ad}}\), increased exposures did not result in a measurable increase of the CO\(_{\text{ad}}\) coverage, for comparison a CO TPD spectrum recorded after \(120 \times 10^{-6} \text{ mbar}\cdot\text{s}\) at 90 K is included in Figure 4.19b.

**Figure 4.19:** CO TPD spectra (at CO saturation) on surfaces with increasing Pt coverages. CO exposures \(\times 10^{-6} \text{ mbar}\cdot\text{s}: (\cdots) 30 \text{ at } 90 \text{ K}, (\cdot\cdot\cdot) 120 \text{ at } 150 \text{ K}, (\cdots\cdots) 120 \text{ at } 90 \text{ K}.\)
The observations for the 0.15 ML Pt surface (Figure 4.19a) are similar to those made for 0.3 ML Pt (Figure 4.10 and Figure 4.19b), after CO\textsubscript{ad} saturation the onset of desorption shifts from 245 K for CO adsorbed at 90 K to 205 K for adsorption at 150 K. At the same time, the CO\textsubscript{ad} saturation coverage increases from 0.71 ML to 0.81 ML CO\textsubscript{ad}. Unlike in the case of 0.3 ML Pt, the $\beta_3$ state is not populated upon increasing the adsorption temperature to 150 K. It is difficult to speculate on the origins of the $\beta_3$ state, however, it appears that more or less extended Pt islands which are formed at Pt coverages $\geq$ 0.3 ML Pt are necessary to form the corresponding CO adsorbate structure. The picture for the surfaces with 0.5 and 1.0 ML Pt (Figure 4.19c and d) is rather different. In these cases, the onset of desorption is located at $\sim$200 K for both adsorption temperatures, the $\beta_3$ state is already populated at 90 K and shows a only slight increase in intensity for adsorption at 150 K, leading to a relatively small increase of the CO\textsubscript{ad} saturation coverage from 0.59 and 0.57 ML at 90 K to 0.63 and 0.61 ML at 150 K. The effect of varying Pt coverage on the CO\textsubscript{ad} saturation coverage after CO adsorption at 150 K will be discussed in more detail in the following sections.

The saturation coverage of 0.81 ML CO\textsubscript{ad} for adsorption at 150 K on the 0.15 ML Pt surface is considerably higher than the saturation coverage on pure Ru(0001) ($\theta_{\text{sat}(\text{CO})} = 0.68$ ML) or a closed Pt monolayer ($\theta_{\text{sat}(\text{CO})} = 0.57$ ML). If the parts of the Ru(0001) surface not covered by Pt are fully saturated with CO\textsubscript{ad} with a partial saturation coverage of 0.68 ML CO\textsubscript{ad}, 0.23 ML CO have to be adsorbed on the Pt islands, resulting in a partial CO\textsubscript{ad} coverage of 1.55 ML, which is essentially impossible. Therefore it follows that a large part of the CO which desorbs in the low–temperature feature of the TPD spectra, must originate from Pt–free Ru areas, already for CO adsorption at 90 K. The onset of desorption from Ru at lower temperature (compared to pure Ru(0001)) indicates a considerable decrease of the CO adsorption energy at saturation on the Ru parts of the bimetallic surface compared to pure Ru(0001). This decrease of adsorption energy is most likely explained by a higher CO\textsubscript{ad} saturation coverage which can be reached on Pt free Ru areas compared to pure Ru(0001).

Conversely, in IR spectra recorded after CO adsorption on Pt/Ru(0001) surfaces at 90 K (Figure 4.13 and black spectrum in Figure 4.20), the IR band related to CO adsorbed on Ru is located at 2060 cm\textsuperscript{-1} for the CO saturation coverage, while the band of CO adsorbed on Pt islands is located at $\sim$2090 cm\textsuperscript{-1}, which are the same wavenumbers as on pure Ru(0001) and on a closed Pt monolayer, respectively. It bears repeating that the position of the CO–Ru band is strongly dependent on the CO\textsubscript{ad} coverage, both on pure Ru(0001) [78] and on the bimetallic surfaces investigated in this work. In contrast the CO–Pt band is only weakly dependent on
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The CO\textsubscript{ad} coverage, especially close to CO\textsubscript{ad} saturation (see Section 4.2.4.2). This indicates that after adsorption at 90 K, the partial CO\textsubscript{ad} coverages on the Pt islands and Ru parts of the surface are more in line with a model that features separate adsorption of CO on the Pt and Ru parts of the surface without any interchange phenomena, and the increase in partial CO\textsubscript{ad} coverage on the Ru parts of the surface occurs only after the start of the heating ramp during the TPD experiment.

In order to further investigate this phenomenon, a series of IR experiments were carried out to compare the adsorption of CO at 90 and 150 K. Figure 4.20 shows spectra recorded on Pt film surfaces with varying Pt coverages. In each case, the first spectrum (from bottom to top) was recorded after a CO exposure of $30\times10^{-6}$ mbar·s at 90 K, the second spectrum was recorded from the same adsorbate layer after annealing to 150 K, finally a third spectrum was recorded after a CO exposure of $120\times10^{-6}$ mbar·s at 150 K. The spectra recorded after adsorption at 90 K are in agreement with the IR spectra already presented in Section 4.2.4.2, the CO–Ru band is observed at roughly the same wavenumber as on pure Ru(0001).

![Figure 4.20: IR spectra of different Pt/Ru(0001) surfaces (Pt coverage given in each panel). (---) CO saturation coverage at 90 K, (—) after annealing to 150 K, (——) CO saturation coverage at 150 K.](image-url)
After annealing to 150 K, the spectra from all three surfaces show a shift of the CO–Ru band to higher wavenumbers, indicating an increase of the CO$_{\text{ad}}$ coverage on the Ru areas of the surface caused by diffusion of CO$_{\text{ad}}$ molecules from the Pt islands to the Ru areas. The shift of the CO–Ru band increases with increasing Pt coverage; this can be explained by the increasing ratio of Pt to Ru adsorption sites. With increasing Pt coverage, the amount of CO$_{\text{ad}}$ molecules that can potentially diffuse from the Pt islands increases, while the amount of Ru adsorption sites, which can adsorb these molecules decreases. This leads to a higher increase of the partial CO$_{\text{ad}}$ coverage on the Ru areas with increasing Pt coverage. For the same reason, the highest total CO coverages are found on bimetallic surfaces with small Pt coverages (Figure 4.10). IR spectra recorded after CO adsorption at 150 K show that the CO–Ru band appears at even higher wavenumbers compared to spectra recorded after annealing to 150 K. Unlike in the former case though, the band is observed at the same wavenumber (2068 cm$^{-1}$) for all three Pt coverages. This indicates that adsorption of CO at 150 K leads to considerably higher CO$_{\text{ad}}$ coverages on the Ru areas of the bimetallic surfaces compared to Ru(0001) and that the maximal local CO$_{\text{ad}}$ coverages which can be achieved in this way are independent of the Pt coverage, at least up to 0.3 ML Pt. It is interesting to note that, while annealing a CO$_{\text{ad}}$ layer adsorbed at 90 K to 150 K leads to the diffusion of considerable amounts of CO molecules from Pt to Ru, the resulting CO$_{\text{ad}}$ coverage on the Ru areas is noticeably smaller than after CO adsorption at 150 K. Additionally, the CO–Pt band on all three surfaces is still clearly observable after the annealing step, with no noticeable decrease in intensity. This leads to the conclusion that the annealing step causes the diffusion of only a limited amount of CO from the Pt islands, even when more CO could be adsorbed on the Ru areas. A possible explanation for this observation is the formation of an equilibrium between the CO adsorbed on Pt islands and Ru areas at 150 K. As can be seen in the TPD spectra, there is a considerable overlap between the CO desorption features from Pt islands and Ru areas, indicating similar adsorption energies for the most favorable adsorption sites on Pt islands and the least favorable sites on Ru. The difference in adsorption energies on Pt and Ru is expected to decrease during the diffusion process, as the CO$_{\text{ad}}$ coverage on Pt islands decreases with a corresponding increase in CO coverage on the Ru areas, reducing the driving force for the diffusion. During CO adsorption at 150 K, the perturbation of this equilibrium by replacement of the diffused CO$_{\text{ad}}$ molecules on Pt islands via adsorption from the gas phase leads to the diffusion of additional CO$_{\text{ad}}$ to the Ru areas until local saturation coverage is reached.

The overlap of the CO adsorption energies on the two parts of the surface is further demonstrated in Figure 4.21. In this experiment, a surface with 0.3 ML Pt was exposed to
120×10⁻⁶ mbar·s CO at 150 K and stepwise annealed to higher temperatures, with an IR spectrum recorded after each annealing step.

**Figure 4.21:** IR spectra recorded on 0.3 ML Pt after an exposure of 120×10⁻⁶ mbar·s CO at 150 K. Subsequently the surface was annealed in steps with an IR spectrum recorded after each step (annealing temperature given at each spectrum).

Already at 190 K, the Ru band displays a slight shift to smaller wavenumbers, followed by a continuous downshift with increasing temperature. 190 K corresponds to the earliest onset of desorption observed in the TPD spectrum on this surface after adsorption at 150 K. This indicates that the desorption range of CO on Pt is completely overlapped by a part of the CO desorption range from Ru, which means that the differential CO adsorption energy at the high partial coverages, which can be achieved on Ru parts of the surface at 150 K, is in the same
range as the adsorption energy of the most weakly bound CO$_{\text{ad}}$ on Pt sites. This reinforces the assumption that the diffusion of CO from Pt to Ru at 150 K after adsorption at 90 K is limited by the formation of an equilibrium between the CO$_{\text{ad}}$ layers on both parts of the surface.

Interestingly, the same CO$_{\text{ad}}$ coverage that can be achieved with a CO exposure of $120 \times 10^{-6}$ mbar·s (red dotted spectrum in Figure 4.22, overlapped by black spectrum for the highest CO$_{\text{ad}}$ coverage) at 150 K can also be achieved by four steps of $30 \times 10^{-6}$ mbar·s exposures at 90 K with an annealing step to 150 K between exposures (black spectra in Figure 4.22). Conversely, a CO exposure of $30 \times 10^{-6}$ mbar·s followed by annealing to 150 K and a subsequent exposure to $90 \times 10^{-6}$ mbar·s at 90 K (blue dashed spectrum in Figure 4.22) results only in a slightly higher CO uptake than a $(30 + 30) \times 10^{-6}$ mbar·s exposure sequence with an annealing step between exposures.

![Figure 4.22: TPD spectra recorded on 0.3 ML Pt after: (—) 1,2,3 and 4 exposures to $30 \times 10^{-6}$ mbar·s CO at 90 K with an annealing step to 150 K between exposures. (---) Exposure to $30 \times 10^{-6}$ mbar·s CO at 90 K, annealing to 150 K and a second exposure to $90 \times 10^{-6}$ mbar·s CO at 90 K. (∙∙∙) Exposure to $120 \times 10^{-6}$ mbar·s CO at 150 K.](image)

These results again show that the CO$_{\text{ad}}$ diffusion from Pt islands to the Ru substrate is not limited only by temperature. While increasing the temperature to 150 K is necessary to achieve a high enough CO$_{\text{ad}}$ mobility to initiate the diffusion process, a comparatively high CO$_{\text{ad}}$ coverage on the Pt islands is also necessary to achieve a sufficiently high disparity.
between the adsorption energies of CO on Pt and Ru for the process to continue until the Ru areas are saturated with CO$_{ad}$.

The results so far indicate that CO$_{ad}$ coverages above 0.68 ML should be possible on a Ru(0001) surface. A way to achieve this on the pure Ru(0001) surface is CO adsorption at high pressure. Figure 4.23 show the IR spectrum of CO$_{ad}$ at equilibrium with the gas phase at 100 mbar on pure Ru(0001) at 300 K (dashed red line), compared to a spectrum of a saturated CO$_{ad}$ layer under UHV at 315 K (black line). The band of the UHV spectrum is found at 2044 cm$^{-1}$ which corresponds to a CO coverage of ~0.57 ML. The band of the high pressure spectrum is located at 2072 cm$^{-1}$, the blue–shift of 28 cm$^{-1}$ indicates that a considerably higher CO coverage can be achieved with higher CO pressures at a comparable temperature. The shift is still 10 cm$^{-1}$ compared to the saturation spectrum of CO$_{ad}$ at 90 K under UHV conditions (Figure 4.5), which shows that CO adsorption under high pressure results in a coverage well above the UHV saturation coverage of 0.68 ML, even without facilitation by a second metal.

**Figure 4.23:** IR spectra of CO adsorbed on Ru(0001). (—) after $30\times10^{-6}$ mbar s CO at 315 K, (---) in 100 mbar CO at 300 K.
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4.3.5 Discussion

An interesting aspect of the CO spill–over process at 150 K is that the CO$_{\text{ad}}$ coverage, which can be achieved on the Ru parts of the bimetallic surface, exceeds the CO$_{\text{ad}}$ saturation coverage on pure Ru(0001) (saturation coverage is defined here as the maximal coverage which can be achieved at a given temperature). Technically, the lower CO$_{\text{ad}}$ saturation coverages at 90 K on Ru(0001) and Ru parts of the Pt/Ru(0001) surfaces could be explained by a “frozen” non–compact structure of the CO adlayer caused by the low mobility of CO$_{\text{ad}}$ at this temperature, the formation of a more ordered compact structure would allow the adsorption of additional CO$_{\text{ad}}$ at higher temperatures. However, this possibility can be excluded due to the fact that an increase in CO coverage for adsorption temperatures higher than 90 K is not observed for pure Ru(0001) [78] or a closed Pt film (inset in Figure 4.10).

The adsorption of CO on Ru(0001) has been investigated by several experimental methods and is well characterized. The preferred adsorption site is the on–top site, at a coverage of $\theta$(CO) = 0.33 ML, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorbate structure is formed which is stabilized by repulsion between CO$_{\text{ad}}$ molecules on nearest neighbor sites and attractive interactions between molecules adsorbed at next nearest neighbor sites [47,138]. At $\theta$(CO) = 0.5 ML, CO adsorbs in a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure. Due to the considerable repulsive interactions between the adsorbed CO molecules in this coverage range, a shift away from the most favorable on–top position is necessary in order to maximize the CO$_{\text{ad}}$–CO$_{\text{ad}}$ distance. Adsorption beyond this coverage proceeds via insertion of CO between the molecules forming the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure and concomitant rearrangement and compression of the adsorbate structure in order to minimize CO$_{\text{ad}}$–CO$_{\text{ad}}$ repulsion [47,138]. Alternatively, Jakob et al. [139] proposed that due to a strong preference for on–top adsorption, CO molecules adsorbed in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure remain at their original on–top sites throughout the entire CO$_{\text{ad}}$ coverage range. In this picture additional CO$_{\text{ad}}$ molecules have to occupy nearest neighbor sites to the molecules originally adsorbed in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Since this results in considerable CO$_{\text{ad}}$–CO$_{\text{ad}}$ repulsion, the CO$_{\text{ad}}$ molecules have to adopt a tilted configuration in order to reduce the repulsive interactions [139].

Assuming that at the saturation coverage of $\theta$(CO) = 0.68 ML [47], the CO$_{\text{ad}}$ layer forms a compressed hexagonal structure, the lateral CO$_{\text{ad}}$–CO$_{\text{ad}}$ distance is calculated to be 3.44 Å. With a CO diameter of 3 Å (as derived from XRD experiments on Ru$_3$(CO)$_{12}$ [138,140]) a hexagonally close–packed layer should contain $1.41\times10^{15}$ molecules cm$^{-2}$, resulting in a CO
4 Results and discussion

coverage of 0.89 ML. This indicates that CO adsorption stops well before a truly close-packed CO adlayer is formed. One explanation for this is that at coverages ≥ 0.68 ML CO\textsubscript{ad} the system energy increase due to increasing CO\textsubscript{ad}–CO\textsubscript{ad} repulsion is not compensated anymore by the decrease in system energy due to the formation of new Ru–CO bonds.

An alternative explanation is that the CO\textsubscript{ad} saturation coverage on Ru(0001) is kinetically limited. At low coverages (≤ 0.2 ML), CO adsorption is non-activated [47]. However, once the \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure is formed, the CO layer has to be compressed in order to allow the adsorption of additional CO molecules – a process which is likely to be activated. For CO adsorption on a saturated CO\textsubscript{ad} layer on Ru(0001), literature data indicates that the activation barrier is at least 1.2 eV [141].

In view of the results of spill-over experiments presented above, a thermodynamic limit for the CO\textsubscript{ad} saturation coverage of 0.68 ML on Ru(0001) appears unlikely. The increase in energy due to compression of the CO\textsubscript{ad} layer and a shift of adsorbed molecules to less favorable sites is expected to be equal for adsorption of additional CO molecules from the gas phase and diffusion from Pt islands to the Ru substrate. At the same time, the energy decrease resulting from the change of a Pt–CO bond to a Ru–CO bond (when CO\textsubscript{ad} diffuses from Pt to Ru) would be considerably smaller than for the formation of a Ru–CO bond with a molecule from the gas phase. Therefore, it is likely that the activation barrier for CO\textsubscript{ad} diffusion from Pt islands to the Ru substrate is considerably smaller than the barrier for adsorption from the gas phase. The experiments presented in Figure 4.22 show that the CO\textsubscript{ad} layer on the Pt/Ru(0001) surface reaches equilibrium upon annealing to 150 K, indicating that the activation barrier for diffusion from Pt to Ru is easily overcome at this temperature. This results in the adsorption of additional CO on the Ru areas.

Although it is clear that the partial CO\textsubscript{ad} coverages on the Ru part of the bimetallic surface after adsorption at 150 K are higher than 0.68 ML, the actual coverage is difficult to determine. Assuming a partial coverage of 0.57 ML CO\textsubscript{ad} on Pt islands (i.e., the same coverage as on 1 ML Pt), the partial CO\textsubscript{ad} coverage on the Ru parts is calculated to linearly decrease from 0.85 ML CO\textsubscript{ad} on a surface with 0.15 ML Pt to 0.7 ML CO\textsubscript{ad} for the 0.55 ML Pt surface. This is contradicted by IR experiments, where the Ru–CO band is observed at 2068 cm\(^{-1}\) for all Pt coverages up to 0.6 ML Pt, indicating similar CO\textsubscript{ad} coverages which are independent of the Pt coverage. The likely explanation for this discrepancy, is that the partial CO\textsubscript{ad} coverage on the Pt islands does not necessarily correspond to the CO\textsubscript{ad} saturation
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Coverage on a Pt monolayer. Indeed the plot of \( \theta_{\text{sat}}(\text{CO}) \) vs. \( \theta(\text{Pt}) \) in Figure 4.8 shows a non-linear trend, indicating that the partial CO\(_{\text{ad}}\) coverages on Pt film surfaces are not identical to the CO\(_{\text{ad}}\) coverages on the pure constituents of these surfaces (i.e., Ru(0001) and a Pt monolayer). In any case, even the highest calculated partial coverage of 0.85 ML CO\(_{\text{ad}}\) on the Ru parts of the surface is still ~5% lower than would be expected for a close-packed CO adlayer. It is therefore not immediately clear whether the partial CO\(_{\text{ad}}\) coverage on Ru parts of the bimetallic surfaces, which results from CO\(_{\text{ad}}\) diffusion from Pt islands at 150 K, is still kinetically limited, or constitutes a thermodynamic limit.

CO\(_{\text{ad}}\) diffusion at temperatures around 150 K has been observed for many bimetallic systems where a metal substrate is covered by submonolayer films of a different metal. No systematic studies have been reported which explicitly aimed at the investigation of the CO\(_{\text{ad}}\) spill–over effect and its influence on the partial CO\(_{\text{ad}}\) coverage on parts of a bimetallic surface via CO\(_{\text{ad}}\) diffusion at higher temperatures, compared to CO adsorption from the gas phase. However, a number of conclusions can be derived from data reported in literature for various bimetallic systems.

In the case of the Cu/Ru(0001) system, with two–dimensional Cu submonolayer films deposited on Ru(0001), Vickerman et al. [142] reported CO\(_{\text{ad}}\) saturation coverages for CO adsorption at 150 K. For small Cu coverages (0.05 – 0.15 ML Cu), they reported CO\(_{\text{ad}}\) saturation coverages noticeably higher (~10%) than for Ru(0001). These authors did not perform measurements at lower temperatures, which makes a direct comparison impossible. However, the CO\(_{\text{ad}}\) saturation coverage on Ru(0001) is known to be independent from temperature (see above), at the same time an increase of the partial CO\(_{\text{ad}}\) coverage on the Cu part of the surface as the reason for the increase in total CO\(_{\text{ad}}\) coverage is rather unlikely, considering the high amounts of additionally adsorbed CO and the small amounts of Cu adsorption sites involved. For these reasons it appears reasonable to conclude that the CO uptake on the Ru part of Cu/Ru(0001) surfaces at 150 K is higher than on Ru(0001).

Hoffmann et al. investigated the adsorption of CO on Cu/Ru(0001) films by IRAS [133]. Annealing a saturated CO\(_{\text{ad}}\) layer adsorbed at 85 K on 0.53 ML Cu they observed a slight blue–shift of the Ru–CO band from 2057 to 2060 cm\(^{-1}\). For a surface with 0.6 ML Cu, annealing of an identically prepared CO adlayer to 200 K resulted in a blue–shift of the Ru–CO band from 2055 to 2066 cm\(^{-1}\). Considering that the authors found the CO band on pure Ru(0001) at 2056 cm\(^{-1}\) at CO\(_{\text{ad}}\) saturation (at 80 K), these results seem to indicate that, similar to our findings for Pt/Ru(0001), partial CO\(_{\text{ad}}\) coverages can be reached on the Ru areas via the
spill–over process which exceed those found on pure Ru(0001). However, unlike in the case of the Pt/Ru(0001) system, annealing of Cu/Ru(0001) surfaces to 150 – 200 K results in partial desorption of the CO adsorbed on the Cu islands, since CO desorption on these surfaces begins already at ~120 K [32,129,142]. The reduction in CO coverage on the Cu islands is expected to lead to a decreased driving force for the spill–over process at high CO\textsubscript{ad} coverages, additionally it also leads to a red–shift of the Cu–CO band. The authors therefore concluded that the blue–shift observed for the Ru–CO band upon annealing to 150 – 200 K is caused by increased dipole coupling due to a smaller frequency mismatch between CO molecules adsorbed on Cu and Ru, rather than by an increase of the partial CO coverage on the Ru part of the surface. An additional explanation is that the desorption and diffusion processes occur simultaneously, leading to a partial diffusion of CO\textsubscript{ad} from Cu to Ru. In this case the blue–shift of the Ru–CO band would at least partially be caused by an increase of the local CO\textsubscript{ad} coverage on Ru.

In IRAS experiments conducted on Pd films on W(110) by Kuhn et al. [137], two IR bands were observed for the CO\textsubscript{ad} saturation coverage after adsorption at 90 K, on a 0.14 ML Pd surface the CO–Pd band is found at 2126 cm\textsuperscript{−1} and the W–CO band at 2033 cm\textsuperscript{−1}. After annealing the sample to 190 K, the Pd–CO band was red–shifted to 2108 cm\textsuperscript{−1} while the W–CO band displayed a blue–shift to 2045 cm\textsuperscript{−1}. Since at 190 K no desorption of CO\textsubscript{ad} takes place on this system, the shifts can be only attributed to a diffusion of CO\textsubscript{ad} from the Pd film to the W substrate. The lack of IR data for the adsorption of CO on pure W(110) precludes a direct comparison between the CO\textsubscript{ad} coverage on W(110) after adsorption at 90 K and on the W part of the bimetallic surface after annealing to 190 K. However, the observed blue–shift of 12 cm\textsuperscript{−1} for the W–CO band following the annealing step indicates that the CO\textsubscript{ad} coverage on the W part of the surface increases considerably, compared to the CO\textsubscript{ad} coverage after adsorption at 90 K.

TPD spectra recorded at CO saturation on Cu/Rh(100) surfaces with varying Cu coverages [135,143] show a behavior similar to the TPD spectra recorded on Pt/Ru(0001) films (Figure 4.8). The implications of this behavior are described at the beginning of Section 4.3.4. In short it appears possible that CO\textsubscript{ad} molecules originally adsorbed on the Cu islands migrate to the Cu–free parts of the Rh substrate when the sample temperature increases during the TPD experiment. IRAS experiments conducted by He et al. [135,136] conclusively showed that CO adsorbed on the Cu islands at 90 K diffuses to the Rh substrate when the sample is annealed to 140 – 210 K. While this process obviously leads to an increase of the partial CO\textsubscript{ad} coverage
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on the Cu–free Rh areas, the authors assumed that this is possible because the Rh adsorption sites are underoccupied after adsorption at 90 K on these surfaces (compared to pure Rh(100)). The situation is further complicated by the fact that the Rh–CO band shows a slight red–shift after the annealing step. The authors proposed that this might be caused by a rearrangement of the CO layer from a compressed structure to a more relaxed one, though it is difficult to see how this can be concomitant to an increase in CO coverage.

Unfortunately, no experiments can be found in literature where TPD experiments were carried out at different adsorption temperatures on bimetallic surfaces, which would allow a direct comparison of CO$_{\text{ad}}$ coverages with and without a possible enhancement of CO uptake due to surface diffusion of CO at higher temperatures.

Similarly high CO$_{\text{ad}}$ coverages as on the Ru parts of the Pt/Ru(0001) surface can also be achieved on pure Ru(0001) in a high pressure atmosphere (100 mbar). While my experiments do not allow to determine the exact CO coverage in this case, a recent XPS study of CO adsorption on Ru(0001) in high pressure CO atmosphere [144] determined a CO$_{\text{ad}}$ coverage of 0.88 ML at pressures of $1.3 \times 10^{-2} - 1.3$ mbar at 300 K, only slightly smaller than the coverage calculated for a close–packed hexagonal layer (0.89 ML). In fact, already pressures above $1.3 \times 10^{-6}$ mbar resulted in coverages above the UHV coverage of 0.68 ML CO$_{\text{ad}}$. From their XPS results, the authors concluded that the additional CO (above 0.68 ML) is adsorbed in a bridge site, in contrast to the results of my IR experiment in a high pressure CO atmosphere which show only a single band in the range associated with on top adsorption which is simply blue–shifted compared to IR spectra recorded in UHV, similar to the IR spectra recorded on the bimetallic Pt/Ru(0001) surface after CO$_{\text{ad}}$ diffusion/adsorption at 150 K. It is difficult to speculate on the reasons for this difference; a possible explanation might be that the pressure in my experiments was two orders of magnitude higher, however, it is not immediately clear why the CO adlayer should go from an exclusive on–top configuration under UHV conditions to a mix of on–top and bridge bound CO$_{\text{ad}}$ at pressures slightly above UHV and revert back to a layer exclusively composed of on–top CO$_{\text{ad}}$ at higher pressures. Additional investigations would be necessary in order to elucidate the exact structure of the CO adlayer in this coverage range.

Finally it should be noted that the resulting CO$_{\text{ad}}$ saturation coverage is much higher than obtained on other close packed platinum metal surfaces, even under high pressure conditions. Due to the larger lattice constant in, e.g., Pd(111) or Pt(111), this effect is even more pronounced when considering the absolute density of the CO adlayer rather than the CO$_{\text{ad}}$
coverage. This is certainly related to the strong metal – CO interaction, further work, however is required for a more detailed insight in the physical origin for this phenomenon.

4.3.6 Conclusions

The combined results of the experiments presented above lead to the following conclusions:

1. The shift of the onset of desorption to higher temperatures and absence of the $\beta_2$ and $\beta_3$ desorption features in CO TPD spectra of Pt film surfaces with low Pt coverages after adsorption at 90 K, compared to spectra of surfaces with higher Pt coverage, is caused by the diffusion of CO$_{ad}$ from Pt islands to the free Ru areas when the sample temperature increases to 150 K during the TPD experiment.

2. For CO adsorption at 150 K, the spill-over is activated during adsorption, resulting in higher total CO$_{ad}$ coverages as the CO$_{ad}$ lost from the Pt islands is replaced by CO adsorbing from the gas phase.

3. The increase in total CO$_{ad}$ coverage for adsorption at 150 K compared to adsorption at 90 K is caused by an increase in the partial CO$_{ad}$ coverage on Pt free Ru areas, while the CO$_{ad}$ saturation coverage on Pt islands appears to be independent of the adsorption temperature for $T \leq 200$ K (i.e., the onset temperature for CO desorption from Pt islands). For this reason the highest total CO$_{ad}$ coverages at 150 K are found for bimetallic surfaces with small Pt coverages and accordingly high ratios of Ru/Pt adsorption sites.

4. The CO$_{ad}$ saturation coverage of 0.68 ML on Ru(0001) under UHV conditions appears to be the result of an activation barrier which cannot be overcome via adsorption from the gas phase. On Pt/Ru(0001) film surfaces with submonolayer Pt coverages, an additional adsorption pathway via CO$_{ad}$ diffusion from Pt islands exists. Due to a lower activation barrier, this allows the adsorption of considerably higher amounts of CO$_{ad}$ on the Ru parts of the bimetallic surface compared to pure Ru(0001) substrate.

5. Literature data indicate that the effect described above may not be limited to the Pt/Ru(0001) system, but instead represent a general feature of bimetallic systems where CO$_{ad}$ diffusion between the two parts of the surface is inhibited at low temperatures. However, systematic and focused experiments are required in order to derive fully conclusive results.
4.4 Coadsorption of CO and deuterium on bimetallic, monolayer Pt–island/film covered Ru(0001) surfaces

The following section is the draft of a paper intended for submission at a later time.

4.4.1 Abstract

As part of a systematic study on the influence of Pt on the coadsorption of CO and deuterium on Pt modified Ru(0001) surfaces, we systematically investigated the (co-)adsorption and desorption behaviour of these gases on a sequence of structurally well–defined Ru(0001) surfaces, which were covered to an increasing extent by Pt monolayer islands, up to a closed Pt monolayer (Pt_{ML}/Ru(0001)). This follows earlier reports on the coadsorption of these gases on monolayer PtRu surface alloys on Ru(0001) and on the adsorption of CO and D₂, respectively on Pt/Ru(0001) surfaces. The (co–)adsorption and desorption behaviour was characterized by temperature programmed desorption and IR spectroscopy. The results show distinct modifications in the adsorption behaviour of both species, compared to the separate adsorption of the respective molecules. The adsorption energy and coverage of D₂ were found to decrease with increasing amounts of coadsorbed CO. A similar effect is imposed by an increasing Pt coverage. These modifications, resulting from interactions between the adsorbed species within the coadsorbate layer, are discussed with regard to the morphology of the bimetallic surface in an attempt to understand the influence of the surface structure on the coadsorption process.

4.4.2 Introduction

The interaction of hydrogen and CO with bimetallic PtRu surfaces has attracted great interest due to the suitability of these systems as electrocatalysts and anode material in advanced low temperature Polymer Electrolyte Membrane Fuel Cells (PEMFC). Their advantage over pure platinum anode catalysts is mainly their superior CO tolerance [145]. This makes them useful as catalysts for the catalytic conversion of CO contaminated H₂–rich fuel gas, which is generated in the reformate–process of hydrocarbons, as well as for the direct conversion of methanol on Direct Methanol Fuel Cells (DMFC) [105,106]. A bifunctional mechanism has
been proposed as explanation for the enhanced CO tolerance in the past [146,147]. Using pure platinum as anode material in the fuel cell, the electrolyte activity is reduced by the presence of CO\textsubscript{ad} which blocks the surface. The Ru part of the surface was supposed to more easily dissociate H\textsubscript{2}O and generate adsorbed oxygen species such as OH\textsubscript{ad}, facilitating the oxidation of adsorbed CO to CO\textsubscript{2} which is then easily removed from the surface. More recently, temperature programmed desorption (TPD) [23,26,29,104,108] and DFT [61] studies on the interaction of CO with bimetallic PtRu surface introduced an additional possible explanation for the improved CO tolerance. According to these works, electronic and strain effects which cause a significant reduction of the binding strength of CO on Pt monolayer islands on Ru(0001) and on PtRu surface alloys may also contribute to the improved CO tolerance by facilitating the removal of CO under steady state conditions. At the same time, studies on the adsorption of D\textsubscript{2} conducted on these surfaces [30,104] showed a similar decrease of adsorption energy for D\textsubscript{2}, which leads to the question whether the displacement of CO by hydrogen is possible on bimetallic PtRu surfaces.

The coadsorption of CO and hydrogen (deuterium) on Ru(0001) has been the subject of several studies. TPD experiments by Peebles et al. [148] demonstrated that neither of the pre–adsorbed species is displaced by exposure to the respective other species at 100 K, shifts of the thermal desorption states of D\textsubscript{2} in TPD spectra indicated a repulsive interaction between the coadsorbed species. This observation was supported by Mak et al., who explained a decrease of the H\textsubscript{ad} diffusion coefficient, with increasing CO coverage in coadsorbate layers, by adsorbate – adsorbate repulsion and formation of segregated islands of the coadsorbed species [149]. While no adsorption of deuterium on a saturated CO\textsubscript{ad} layer was observed, appreciable quantities of CO could be adsorbed in the reverse case at 100 K [107,110,148]. Additionally CO was found to completely displace pre–adsorbed hydrogen from the surface at 250 K [150]. Riedmüller et al. found that adsorption of CO on a perfect hydrogen layer with a coverage of 1 ML was an activated process with an activation barrier of $\geq 25$ kJ mol$^{-1}$ [141,151]. It was also demonstrated that imperfections in the H\textsubscript{ad} layer open an alternative non–activated adsorption pathway which results in the formation of small isolated CO islands in the H\textsubscript{ad} layer [150]. For the reverse case of adsorption of hydrogen on a closed CO adlayer, Ueta et al. calculated an activation barrier of ca. 40 kJ mol$^{-1}$ [152]. IR experiments show that the band of CO coadsorbed with hydrogen experiences a general shift to higher wavenumbers [107,153] irrespective of dosing sequence and the ratio of D\textsubscript{ad}/CO\textsubscript{ad}. DFT calculations show that in the case of small amounts of adsorbed CO molecules embedded in a hydrogen layer, this shift can be attributed to electrostatic interactions within the coadsorbate layer [153]. No
studies observed the formation of reaction products during coadsorption of CO and molecular hydrogen under UHV conditions. In contrast, Mitchell et al. reported the formation of formyl and formaldehyde species upon exposure of a CO saturated Ru(0001) surface to atomic hydrogen at sample temperatures below 130 K. These products decomposed upon annealing, leading to the desorption of molecular CO and hydrogen [154]. Recent molecular beam experiments by Ueta et al. found evidence for the formation of stabilized Dₓ–COᵧ species on the surface for medium CO pre–coverages and higher D₂ beam energies [155].

An early study by Baldwin et al. on the coadsorption of CO and H₂ on Pt(111) indicated the possibility of the formation of a CO–H adsorption complex on the surface [156]. More recent studies, however, concluded that the two adsorbate species form segregated islands on Pt(111) as a consequence of repulsive adsorbate – adsorbate interactions [157–159]. Similar to Ru(0001), coadsorption of H₂ and CO caused a temperature shift of the H₂ desorption peak in TPD spectra, while no displacement of hydrogen by post–exposure of a Hₐd layer to CO was observed. Furthermore adsorption of considerable amounts of CO was possible on a Hₐd saturated Pt(111) surface at 100 K [160].

Extensive studies have been conducted to investigate many aspects of the coadsorption of CO and D₂ on PtRu/Ru(0001) surface alloys [28,107,110]. The surface of this model system consists of Pt and Ru atoms which are randomly intermixed in the top layer. The presence of coadsorbed CO leads to a significant destabilization of Dₐd. Likewise increasing the fraction of Pt atoms in the surface alloy leads to additional destabilization. The destabilization is sufficient that displacement of Dₐd from the surface is activated already at 100 K. An alternative model system with a different surface morphology, consisting of submonolayer Pt films on Ru(0001) can provide additional insight into the interactions of coadsorbed CO and hydrogen species on bimetallic PtRu surfaces. The results of a study on the separate adsorption of CO and D₂ on Pt submonolayer films on Ru(0001) have been published previously [84,104,108]. The results of TPD and IR experiments showed that adsorption energies of both molecules were considerably weaker on the Pt islands, compared to Ru(0001) or Pt(111). Increasing Pt coverages were found to have a strongly negative effect on the D₂ sticking probability and saturation coverage. Conversely, for CO adsorption sticking probability and saturation coverage were mostly unaffected by increasing Pt coverage, while the adsorption energy of CO was significantly weaker on the Pt parts of the surface.
4 Results and discussion

In this chapter, I present results of TPD and IRAS experiments of coadsorption of D\textsubscript{2} and CO on submonolayer Pt films on Ru (0001) with varying Pt coverages (up to a closed Pt layer). The first part deals with influence of the coadsorbate species on each other, as well as their distribution on the surface following different exposure sequences at 90 K under UHV conditions. A second part elucidates the effect of increasing temperature on the coadsorbate layer and the displacement of pre–adsorbed CO and D\textsubscript{2} by the respective other species at different temperatures and pressures. Finally, the results are compared to the results of similar coadsorption experiments on PtRu/Ru(0001) surface alloys [28,107,110].

4.4.3 Experimental

The experiments described in this section were carried out on the UHV system described in detail in Section 3.1. For sample preparation procedures and details on data acquisition, I refer to Sections 3.2 and 3.3, respectively.

4.4.4 Results and discussion

4.4.4.1 Coadsorption on Ru(0001)

In order to establish a base for elucidating the influence of Pt monolayer islands on the coadsorption of CO and D\textsubscript{2} on surfaces with varying Pt coverage, two series of coadsorption experiments were carried out on the Pt–free Ru(0001) surface. In these experiments, two different dosing sequences were used. In the first sequence, the sample was exposed to increasing amounts of CO at 90 K, followed by an exposure to 40×10\textsuperscript{-6} mbar·s D\textsubscript{2}, which according to tests is sufficient to saturate the pure CO\textsubscript{ad}–free Ru(0001) surface with D\textsubscript{ad}. The TPD spectra recorded after this dosing sequence are shown in Figure 4.24. For the CO TPD spectra, no changes in peak shape or temperature are observed compared to adsorption of CO without post–adsorption of D\textsubscript{2}. This can easily be explained by the stronger binding of CO\textsubscript{ad}, which allows CO\textsubscript{ad} desorption only after deuterium desorption is almost completed. Evaluation of the CO\textsubscript{ad} coverage with and without subsequent exposure to D\textsubscript{2} shows similar values, indicating that displacement of CO\textsubscript{ad} by deuterium is inhibited at 90 K. Background
adsorption of CO during exposure to D₂ is below 0.01 ML, as indicated by the CO desorption trace obtained upon exposures to pure D₂ (dashed line in Figure 4.24a).

**Figure 4.24:** TPD spectra recorded on Ru(0001) after pre-exposure to increasing amounts of CO, followed by exposure to 40×10⁻⁶ mbar·s D₂. (CO exposures ×10⁻⁶ mbar·s: 0.15, 1.05, 1.9, 3.0, 30) at 100 K. Colors denote CO and D₂ spectra recorded from the same TPD run. Dashed line: spectrum after saturation with pure D₂ (no coadsorption). (a) CO TPD spectra, (b) D₂ TPD spectra.

The D₂ TPD spectra (Figure 4.24b) show a pronounced decline in intensity with increasing COₐd coverage, indicating that the uptake of deuterium is strongly hindered by pre-adsorbed CO. A comparatively small CO pre-coverage of 0.05 ML leads to a decrease of the Dₐd saturation coverage by 20%, indicating that under these conditions a single CO molecule blocks on average 4 Dₐd sites. The amount of blocked Dₐd sites decreases to ~2 for
Results and discussion

intermediate CO$_{ad}$ pre–coverages (0.3 – 0.5 ML CO) and to below 2 when approaching CO saturation. This can be explained by the low mobility of CO$_{ad}$ on the surface at 90 K. For very low CO$_{ad}$ coverages this results in single CO$_{ad}$ species randomly distributed on the surface, at higher coverages CO$_{ad}$ tends to coalesce into islands, leading to a decrease of the average number of blocked sites per CO$_{ad}$ (since several CO$_{ad}$ now block the same sites). For a fully CO$_{ad}$ covered surface (0.68 ML CO), adsorption of D$_2$ is completely inhibited. In all cases the D$_2$ desorption features stay within the envelope of the spectrum recorded on the CO$_{ad}$–free, D$_{ad}$–saturated Ru(0001) (dashed line in Figure 4.24). At the second–highest CO$_{ad}$ pre–coverage (lowest observed D$_{ad}$ coverage), the peak maximum is at 280 K, for higher D$_{ad}$ coverages (lower CO pre–coverages) the maximum shifts successively back to the temperature found for desorption from a purely D$_{ad}$ saturated Ru(0001) surface (without coadsorbed CO). Overall, these results indicate that the repulsive interactions between CO$_{ad}$ and D$_{ad}$ in a saturated adlayer are of similar magnitude as those in a saturated pure D$_{ad}$ layer.

Further information on the coadsorption of CO and D$_2$ was obtained by IR spectroscopy (Figure 4.25). Unlike TPD, IRAS allows to probe the influence of coadsorbed D$_{ad}$ on the CO adsorption properties within the coadsorbate layer at a given temperature (e.g., at the adsorption temperature). The experiments were carried out by first exposing the sample to CO and recording an IR spectrum of the pure CO adlayer (dashed lines in Figure 4.25), followed by exposure to 40×10$^{-6}$ mbar∙s D$_2$, followed by recording first an IR spectrum of the coadsorbed layer and then the TPD spectrum. The D$_{ad}$ and CO$_{ad}$ coverages determined by the TPD spectra are given in Figure 4.25, for CO exposures see Figure 4.24. For all coadsorbed adlayers a blue–shift of the C–O stretch frequency of 2 – 7 cm$^{-1}$ is found (with the highest values at medium CO$_{ad}$ pre–coverages), compared to the pure CO adlayer of the same CO$_{ad}$ coverage, induced by the presence of coadsorbed deuterium. In addition, there is an inhomogeneous broadening of the band as well as a decrease in band intensity for intermediate CO$_{ad}$ coverages.

Overall, these findings agree well with those of previous studies of the same system [107]. A combined IR and DFT study on the coadsorption of a small amount of CO molecules (~0.02 ML) in a hydrogen adlayer on Ru(0001) [153] showed that the blue–shift of the CO band arises mainly from electrostatic interactions (Stark effect) between the CO molecules and the neighbouring D$_{ad}$ species, at the same time the chemical shift was found to be negligible.
Figure 4.25: IR spectra recorded on Ru(0001) after pre-exposure to increasing amounts of CO, followed by $40 \times 10^{-6}$ mbar-s D$_2$ at 100 K. Colors and exposures correspond to TPD spectra in Figure 4.24. IR spectra recorded before post-adsorption of D$_2$ are added for comparison (dashed lines).

A second set of experiments was conducted with the reverse exposure sequence. After adsorbing increasing amounts of deuterium, the sample was exposed to a CO dose sufficient to saturate the pure Ru(0001) surface $(30 \times 10^{-6}$ mbar-s). The TPD spectra resulting from this dosing sequence are displayed in Figure 4.26. As already observed for the previous dosing sequence, coadsorption with deuterium does not modify the CO TPD spectra compared to adsorption of the same amount of pure CO. Integration of the CO desorption spectra shows an essentially linear decrease of CO$_{ad}$ saturation coverage with increasing pre-coverage of deuterium (Figure 4.39). Unlike the reverse case, however, CO adsorption is still possible on a surface saturated with D$_{ad}$, with a CO uptake of 0.11 ML CO. The linear dependence of the CO$_{ad}$ coverage on the D$_{ad}$ pre-coverage agrees well with results of similar experiments.
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reported in the literature [107,148]. The simple linear dependence seems to indicate that the
decrease of the CO uptake with increasing D_{ad} pre–coverage is caused by a blocking of
adsorption sites by D_{ad}, while D–CO interactions do not play a significant role.

Figure 4.26: TPD spectra recorded on Ru(0001) after pre–exposure to increasing amounts of D₂, followed by
30×10^{-6} mbar-s CO. (D₂ exposures ×10^{-6} mbar-s: 0.24, 0.8, 4, 12, 24, 40). Colors denote CO and D₂ spectra
recorded from the same TPD run. Dashed lines: spectra after saturation with pure CO and D₂ respectively; (a)
CO TPD spectra, (b) D₂ TPD spectra.

The uptake of CO on a surface pre–saturated with deuterium agrees quantitatively with the
value reported by Peebles et al for coadsorption at 100 K [148], Diemant et al. found a higher
value of 0.19 ML CO (at 100 K) [107]. Riedmüller et al. did not report numeric values for the
CO_{ad} coverage in their experiments, the very low sticking probability (< 0.02 at 100 K) of CO
on a D\textsuperscript{ad} saturated surface found by them possibly indicates a much lower CO\textsubscript{ad} coverage in their experiments [151].

The D\textsubscript{2} desorption spectra (Figure 4.26b) are shifted to considerably lower temperatures compared to desorption of pure D\textsubscript{2}. Unlike the case of the reverse dosing sequence, a significant part of the pre–adsorbed deuterium desorbs outside the envelope of the saturation spectrum of pure D\textsubscript{2} (dashed line in Figure 4.26b), at lower temperatures. For the TPD spectrum of a surface saturated with 1 ML D\textsubscript{ad} the onset of desorption is shifted to lower temperatures by 35 K, upon the post–adsorption of 0.11 ML CO\textsubscript{ad}, indicating a significant decrease in the adsorption energy of D\textsubscript{ad}. This shows that deuterium adsorption is influenced much more strongly by CO post–adsorption than by pre–adsorbed CO. For the lowest dose of D\textsubscript{2} (0.24×10\textsuperscript{-6} mbar\cdot s) the maximum of the desorption peak is shifted to 245 K, around 160 K lower than at the same D\textsubscript{ad} coverage on a clean Ru(0001) surface (see Figure 4.14a). Higher D\textsubscript{2} pre–exposures cause a continuous shift back to higher temperatures. The back–shift is most pronounced for the trailing edge and the peak maximum, while the leading edge does not shift as much, leading to a peak broadening with increasing D\textsubscript{ad} pre–coverage. However, even on a surface pre–saturated with 40×10\textsuperscript{-6} mbar\cdot s D\textsubscript{2}, a considerable part of the adsorbed deuterium desorbs below 250 K (onset of desorption for a pure D\textsubscript{ad}layer). Integration of the D\textsubscript{2} TPD spectra after exposure to the maximal dose of 40×10\textsuperscript{-6} mbar\cdot s D\textsubscript{2} with and without subsequent CO adsorption shows no detectable displacement of D\textsubscript{2} by post–dosed CO at 90 K.

After saturation of the Ru(0001) surface with D\textsubscript{ad} and subsequent exposure to 30×10\textsuperscript{-6} mbar\cdot s CO, the total adsorbate coverage (1 ML D\textsubscript{2} + 0.11 ML CO) exceeds 1 ML, and is well above the saturation coverage of the individual adsorbates. Obviously the weakening of the deuterium adsorption due to CO\textsubscript{ad} induced compression of the D\textsubscript{ad} layer, which is evidenced by the downshift of the desorption peaks in the D\textsubscript{2} TPD spectra, is overcompensated by the energy gained upon adsorption of additional CO molecules. Conversely for the separate adsorption of the respective adsorbates, adsorption above the respective saturation coverages is kinetically inhibited, while thermodynamically higher coverages are possible [118] (see also Section 4.3). The absence of a similar temperature downshift and the lower maximal coverage found for the reverse dosing sequence (pre–adsorption of CO, post–exposure to D\textsubscript{2}) points to a kinetically limited compression (similar to adsorption of pure D\textsubscript{2}) of the D\textsubscript{ad} layer in that case with much weaker repulsive interactions.
4 Results and discussion

Peebles et al. [148] found a similar development of the D$_2$ TPD spectra with increasing D$_{ad}$ pre–coverage and postulated a phase separation of the D$_{ad}$ and CO$_{ad}$ species in the coadsorbed layer. Molecular beam experiments and DFT calculations by Riedmüller et al. [151] showed the presence of an activation barrier of 25 kJ mol$^{-1}$ for CO adsorption on a Ru(0001) surface fully covered by deuterium. Adsorption via an additional, non–activated adsorption channel was attributed to CO adsorption at defects in the D adlayer, most likely CO molecules adsorbed from the residual gas before deliberate exposure. Based on the results of TPD and He–atom scattering experiments, Riedmüller et al. [150] concluded that CO adsorption on a H$_{ad}$ pre–saturated surface at 250 K proceeds via the formation of CO$_{ad}$ islands, which are imbedded in the H$_{ad}$ layer. The much lower temperature of 100 K in our experiments does not allow the formation of CO islands on the clean Ru(0001) surface, due to the low mobility of CO at this temperature. On the other hand, since the adsorption of CO into a saturated layer of D$_{ad}$ occurs in the vicinity of sites already occupied by CO molecules adsorbed from the background [151], it is reasonable to assume that even at 100 K the CO$_{ad}$ molecules in a coadsorbate layer are clustered in small islands and are not evenly distributed on the surface.

The non–activated adsorption mechanism may also provide an explanation for the different values for CO uptake reported in literature for the surface saturated with deuterium. Different experimental setups cannot be guaranteed to have the same CO partial pressure in the residual gas and even for the same setup this may vary depending on the experiments conducted previously; additionally the time necessary to cool down the sample for TPD experiments may vary considerably for different experimental setups leading to different exposures to the residual gas. Different CO partial pressures in the residual gas atmosphere can therefore lead to varying amounts of CO$_{ad}$ adsorbed from the background in the D$_{ad}$ layer, which in turn lead to variations in the CO uptake.

The influence of coadsorbed deuterium on the adsorption properties of CO in this dosing sequence was also investigated by IRAS. IR spectra recorded at 90 K from coadsorbate layers with different amounts of pre–adsorbed deuterium are compiled in Figure 4.27 (exposures and experimental procedures see Figure 4.26). Compared to pure CO adlayers with similar coverages (dashed lines in Figure 4.27), the IR bands are shifted to higher wavenumbers. The shift amounts to 4 cm$^{-1}$ after preadsorption of only 0.09 ML of deuterium (0.58 ML CO$_{ad}$ coadsorbed). For higher D$_{ad}$ pre–coverages the shift increases, e.g., to 18 cm$^{-1}$ for a coadsorbed layer with 0.87 ML D$_{ad}$ + 0.2 ML CO$_{ad}$. Analogous to the above discussion, this shift is largely attributed to electrostatic interactions (depolarization) and dynamic coupling.
between the adsorbed species. In addition, a contribution from a chemical shift seems likely considering the stronger repulsive interactions between the different adsorbate species evidenced by the TPD results.

Figure 4.27: IR spectra recorded on Ru(0001) after pre–exposure to increasing amounts of D\textsubscript{2}, followed by 30×10\textsuperscript{−6} mbar-s CO exposure. Colors and exposures correspond to those in the TPD spectra in Figure 4.26. IR spectra recorded on pure CO layers are added for comparison (dashed lines).

Comparing coadsorbate layers with different amounts of pre–adsorbed deuterium the CO\textsubscript{ad} related IR band shifts to lower wavenumbers with increasing D\textsubscript{ad} pre–coverage (and concomitant decreasing CO\textsubscript{ad} coverage). Analogous to adsorption of pure CO only, this shift can be mostly attributed to decreasing dipole – dipole coupling due to an overall decrease of the CO\textsubscript{ad} coverage. However, the shift between the lowest CO\textsubscript{ad} coverage (0.11 ML) and the highest (0.58 ML) amounts to 25 cm\textsuperscript{−1} in the case of coadsorption, while it is 36 cm\textsuperscript{−1} for the
adsorption of pure CO. This is likely the consequence of a clustering of CO$_{\text{ad}}$ within the coadsorbate layer, which leads to a slower attenuation of the dipole–dipole coupling with decreasing total CO$_{\text{ad}}$ coverage, caused by higher local coverage in the CO$_{\text{ad}}$ islands. The integrated intensity of the IR bands is lower for all coadsorbate layers compared to those of the pure CO adlayers with identical coverage. The difference is most pronounced for CO coverages around 0.3 ML and below. Most likely, this difference is due to depolarization and dynamic coupling effects arising in the densely packed CO$_{\text{ad}}$ islands embedded in the D$_{\text{ad}}$ layer. Additionally, a considerable increase in the band width is detected for the same CO$_{\text{ad}}$ coverage range. This is tentatively attributed to an inhomogeneous broadening caused by CO adsorption in varying environments (CO$_{\text{ad}}$ islands of different sizes within the D$_{\text{ad}}$ layer) [39]. Taken together, the IR results point to the formation of CO$_{\text{ad}}$ islands within the D$_{\text{ad}}$ layer, following the exposure of a D$_{\text{ad}}$ covered Ru(0001) surface to CO at 100 K.

4.4.4.2 Coadsorption on Pt/Ru(0001) (low Pt coverage)

In this section, results of experiments on the coadsorption of CO and D$_2$ obtained from Pt/Ru(0001) films with low Pt coverage (up to 0.3 ML Pt) will be presented. Figure 4.28 shows coadsorption D$_2$ TPD spectra recorded from film surfaces with 0.15 and 0.25 ML Pt, respectively. Analogous to the previous Ru(0001) measurements, the sample was exposed to different doses of CO first, followed by a dose of $40 \times 10^{-6}$ mbar·s of D$_2$. In the case of the CO TPD spectra again no difference is observed compared to results without coadsorption (see Figure 4.7), since D$_2$ desorption is completed before the onset of CO desorption. The effects of preadsorbed CO on the adsorption properties of D$_2$ in this Pt coverage range are rather similar to those observed for pure Ru(0001). For the lowest pre–coverage with D$_{\text{ad}}$ the D$_2$ TPD peaks are shifted by ~180 K to lower temperatures, compared to the same D$_{\text{ad}}$ coverage without coadsorbed CO (see Figure 4.14). With increasing D$_{\text{ad}}$ pre–coverage D$_2$ desorption shifts back to higher temperatures. For all coadsorption layers, the desorption of D$_2$ is observed to stay within the envelope given by the TPD spectrum recorded after exposure to $40 \times 10^{-6}$ mbar·s of pure D$_2$ (dashed lines) and no additional desorption states are present. Desorption in the low–temperature region (desorption from Pt islands) is considerably lower compared to the TPD spectra of pure D$_2$. 
Figure 4.28: TPD spectra recorded on (a) 0.15 and (b) 0.25 ML Pt after pre-exposure to increasing amounts of CO, followed by $40 \times 10^{-6}$ mbar s $D_2$. The upper panels show $D_2$ TPD results, the lower panels CO TPD results. (CO exposures $\times 10^{-6}$ mbar s: (a) 0.15, 0.75, 1.5, 2.25, 3.0, 30; (b) 0.15, 0.45, 1.05, 1.5, 2.25, 4.5, 30). Dashed lines: spectra recorded after an exposure of $40 \times 10^{-6}$ mbar s of pure $D_2$ (no coadsorption).

On the surface with 0.25 ML of Pt, a clear desorption peak is detectable only for $D_{\text{ad}}$ coverages above 0.45 ML, at this $D_{\text{ad}}$ coverage the peak is located at 135 K, for next lower CO pre-coverage resulting in $D_{\text{ad}}$ coverage of 0.6 ML the peak maximum shifts to 140 K. Separate integration of the low- and high-temperature $D_2$ desorption features on the surface with 0.25 ML of Pt shows that for the lowest CO pre-coverage (0.06 ML) 2.5% of the coadsorbed deuterium desorb in the low-temperature region, significantly less than in the case of adsorption of pure $D_2$ (5%). This indicates that the influence of pre-adsorbed CO is considerably higher on the Pt islands than on the uncovered Ru areas. In line with results obtained from Ru(0001), no CO displacement is observed, even though CO desorption on the Pt part of the surface takes place at much lower temperatures than on Ru(0001). However, the
onset of desorption is still ~100 K above the adsorption temperature (same as for the adsorption of pure CO). Consequently, no D₂ adsorption can be detected on a surface fully saturated with CO.

An anomalous structure of the D₂ TPD spectra is observed for both Pt coverages after a pre-exposure to 1.5×10⁻⁶ and 1.05×10⁻⁶ mbar⋅s CO, respectively. This desorption state deviates from the typical shape found for TPD spectra. Instead it shows a sharp maximum at the high-temperature end followed by a sharp drop-off of the trailing edge. The same structure was observed on the pure Ru(0001) for both dosing sequences after a pre-exposure to 1.9×10⁻⁶ mbar⋅s CO or 4×10⁻⁶ mbar⋅s D₂. In the case of Ru(0001), this kind of structure has already been reported in literature [107,161]. In all cases, the corresponding CO TPD spectrum shows a saturated high temperature peak attributed to the (\(\sqrt{3} \times \sqrt{3}\))R30° structure, which is formed for a local coverage of 0.33 ML CO on the Ru part of the surface. Due to attractive interactions between the adsorbed CO molecules this structure is particularly stable for CO adsorption [46,69]. In the case of a coadsorbed layer, this stabilization results in an additional driving force for the displacement of coadsorbed D_ad from the surface. It is notable, that this D₂ desorption feature has a similar shape as the low-temperature feature in the CO TPD spectrum on pure Ru(0001) or the Ru part of the bimetallic surface, which is formed following the sharp drop-off in the CO adsorption energy after the formation of the (\(\sqrt{3} \times \sqrt{3}\))R30° structure [46,69] (see also the blue spectra in Figure 4.26).

As in the case of Ru(0001), the same coadsorption sequence as used in the TPD experiments was investigated with IR spectroscopy on surfaces with 0.15 and 0.25 ML Pt. The results of these experiments are shown in Figure 4.29. Again the respective D_ad and CO_ad coverages are given in the figure. Spectra recorded from the pure CO layers before exposure to D₂ are included for comparison (dashed lines). Similar to the results on pure Ru(0001) (Figure 4.25), the coadsorption of D₂ with ~0.05 ML of pre-adsorbed CO causes a blue-shift of the IR band (13 and 17 cm⁻¹ for 0.15 and 0.25 ML Pt respectively). With increasing CO_ad pre-coverage, this blue-shift decreases continuously and disappears for high CO_ad coverages. In analogy to Ru(0001), this shift of the IR band is tentatively attributed to electrostatic interactions between the coadsorbed species. As in the case of adsorption of CO only, the Pt band is only detected at higher CO_ad coverages with intensities never above those found for CO only, demonstrating that no displacement of CO_ad from Ru to Pt sites takes place. This is expected, since \(\Delta E_{ad,CO} > \Delta E_{ad,D}\) (here \(\Delta E_{ad}\) is defined as difference in adsorption energy between the Ru
and Pt parts of the surface), in addition the mobility of CO\textsubscript{ad} on the surface at 90 K is not high enough for this kind of site exchange to take place (see Section 4.3).

Figure 4.29: IR spectra recorded on surfaces with 0.15 (a) and 0.25 (b) ML Pt after pre–exposure to increasing amounts of CO, followed by 40×10\textsuperscript{−6} mbar∙s D\textsubscript{2}. Colors and exposures correspond to TPD spectra in Figure 4.28. IR spectra recorded on pure CO layers before D\textsubscript{2} exposure are added for comparison (dashed lines).

Figure 4.30 shows D\textsubscript{2} TPD spectra of coadsorbed layers on surfaces with a Pt coverage of 0.11 and 0.3 ML, respectively. Here, the reversed dosing sequence was employed, with increasing D\textsubscript{2} exposures followed by 30×10\textsuperscript{−6} mbar∙s of CO. The CO exposure is high enough to saturate the surface with CO\textsubscript{ad} in the absence of pre–adsorbed D\textsubscript{2}. As with all previous coadsorption experiments, no modification of the CO TPD spectra is observed. In contrast, the modifications of D\textsubscript{2} spectra caused by CO post–adsorption are rather pronounced already for the minimal D\textsubscript{ad} coverage of 0.11 ML Pt. At the lowest D\textsubscript{ad} coverage (0.11 ML
D + 0.59 ML CO) there is only one desorption state with the maximum at 220 K (195 K for 0.3 ML Pt), which is still rather similar to the same D$_{ad}$ pre–coverage on Ru(0001).

![Figure 4.30: TPD spectra recorded on (a) 0.11 and (b) 0.3 ML Pt after pre–exposure to increasing amounts of D$_2$, followed by 30×10$^{-6}$ mbar s CO. The upper panels show D$_2$ TPD results, the lower panels CO TPD results. (D$_2$ exposures ×10$^{-6}$ mbar·s: (a) 0.25, 0.55, 1.2, 2.4, 4.0, 40; (b) 0.25, 0.55, 1.2, 4.0, 40). Spectra recorded after exposure to 40×10$^{-6}$ mbar·s D$_2$ (---) or 30×10$^{-6}$ mbar·s CO (···) are added for comparison.](image)

In contrast to adsorption on Ru(0001), however, where this state successively shifts to higher temperatures with increasing D$_{ad}$ pre–coverage, on the bimetallic surface this state shows only a slight shift to higher temperature, followed by a distinct shift to lower temperature by ~10 K after a D$_{ad}$ pre–coverage of ~0.57 ML is reached (olive spectrum in Figure 4.30a). On the surface with 0.3 ML of Pt the integrated intensity of this state is considerably higher than that of the high–temperature state leading to the conclusion that the D$_2$ desorption in this temperature range (150 – 250 K) originates from the bare Ru part of the bimetallic surface. At
the same time, two additional desorption states arise with increasing D₂ pre–exposures. The first is a high temperature state, which is located in the temperature range (250 – 450 K) of pure D₂ desorption from the Ru part of the surface. On the surface with 0.11 ML of Pt, for the maximum D₂ pre–exposure, this state has roughly the same shape as observed for desorption of pure D₂. On the surface with the higher Pt coverage of 0.3 ML, this state only reaches the peculiar shape which is associated with the fully saturated high temperature state in the CO TPD spectra (originating from the (√3 × √3)R30° structure of the CO adlayer, see above). A second low temperature state is located in the temperature range (100 – 190 K) which is attributed to desorption of pure D₂ from the Pt islands. On both surfaces, the integrated intensity in the low–temperature range is markedly higher than found in the case of desorption of pure D₂. For the surface with 0.11 ML Pt, without coadsorbed CO, only ~0.01 ML of D₂ desorb in the temperature range between 90 – 190 K, in the case of coadsorption, the D₂ desorption is several times higher (a full quantitative evaluation is impossible due to the overlap of this state with the one in the higher temperature range). Since this amount of D_ads cannot possibly be adsorbed on the Pt part of the surface (which makes up no more than 10% of adsorption sites on this surface), there are two possible explanations for the increased intensity in this temperature range: a) the deuterium belonging to this desorption feature is originally adsorbed on the Ru part of the surface at 90 K and is displaced from there to the Pt part by CO_ads molecules, either during the CO exposure or once the CO_ads mobility increases after the start of the heating ramp; b) the deuterium belonging to this desorption peak adsorbs on the Ru part at 90 K and is destabilized by the interactions with the coadsorbed CO_ads species sufficiently to shift the onset of desorption for D_ads on the Ru part of the surface close to the adsorption temperature. It is possible that this destabilization only occurs after the start of the heating ramp, when due to the spillover effect CO molecules diffuse from the Pt islands onto the Ru areas, leading to an increase of the local CO coverage on the Ru parts of the surface (see Section 4.3). This is discussed in more detail in a later section.

Even though the onset of desorption for pure D₂ is found close to the adsorption temperature of 90 K for all bimetallic surfaces, comparison of integrated intensities of the deuterium TPD spectra after an exposure to 40×10⁻⁶ mbar·s D₂ with and without coadsorbed CO shows no measurable displacement of D_ads by post–adsorbed CO in this Pt coverage range.

The results of IR measurement conducted with the same dosing sequence (first D₂, followed by CO) are shown in Figure 4.31. Again the CO_ads and D_ads coverages are given next to the IR
spectra and spectra of a pure CO adlayer with similar CO$_{ad}$ coverage are indicated by dashed lines.

Figure 4.31: IR spectra recorded on surfaces with (a) 0.11 and (b) 0.30 ML Pt after pre-exposure to increasing amounts of D$_2$, followed by 30×10$^{-6}$ mbar·s CO. Colors and exposures correspond to TPD spectra in Figure 4.30. IR spectra recorded on pure CO layers with similar CO coverage are added for comparison (dashed lines).

Starting with the 0.11 ML Pt surface, the overall development of the band of CO on the Ru part of the bimetallic surface with increasing D$_{ad}$ pre-coverage is rather similar to that observed on Pt-free Ru(0001). For the highest D$_{ad}$ pre-coverage (0.94 ML D$_{ad}$ + 0.15 ML CO$_{ad}$) the band is again shifted to higher wavenumbers by 14 cm$^{-1}$, this shift decreases to zero with decreasing D$_2$ pre-exposures (concomitant with increasing CO coverage). As in the case of Ru(0001), the Ru band also shows a decreased intensity and a broader shape compared to the adsorption of CO only. The modifications of the CO–Pt band caused by coadsorbed
deuterium are rather different in nature. For the pure CO$_{\text{ad}}$ layer, this band first appears at low CO$_{\text{ad}}$ coverages as a comparatively flat feature ~30 – 35 cm$^{-1}$ above the CO–Ru band, only at the highest CO coverage of 0.6 ML CO the band is clearly observed at 2088 cm$^{-1}$. For the coadsorbed layer on the other hand, the CO–Pt band is present throughout the whole CO coverage range, already for the lowest CO$_{\text{ad}}$ pre–coverage of 0.15 ML the band is observed at the same frequency and with the same intensity as at the highest CO$_{\text{ad}}$ coverage of 0.59 ML (with or without coadsorbed D$_{\text{ad}}$).

Observations for the CO–Pt band on the 0.3 ML Pt film surface are in line with those made for the lower Pt coverage of 0.11 ML. Unlike the case of adsorption of CO only (dashed lines in Figure 4.31), for coadsorbed adlayers the CO–Pt band is observed independent of the CO coverage in the same position and with almost the same intensity (95% for the lowest CO coverage) which are found for the highest CO$_{\text{ad}}$ coverage of 0.56 ML. Conversely, while the overall behaviour of the CO–Ru band of coadsorbed layers on the 0.11 ML Pt surface is very similar to that observed for Pt–free Ru(0001), increasing the Pt coverage to 0.3 ML has a pronounced effect on this band. Most important, the blue–shift of this feature upon coadsorption, which was observed for pure Ru(0001) and the surface with 0.11 ML Pt, disappears. A second effect caused by an increase of the Pt coverage concerns the intensity of the CO–Ru band. While a diminished intensity of this band has been already found for coadsorbed layers (compared to CO only) on the pure Ru(0001), the intensity decrease is considerably more pronounced on the bimetallic Pt/Ru surfaces. Taking a CO coverage of ~0.45 ML for comparison, pre–adsorbed D$_{\text{ad}}$ (~0.3 ML) causes a decrease of intensity of the CO–Ru band by 16% on Ru(0001) and 22% on the Pt film surfaces with 0.11 and 0.3 ML Pt.

Considering the high mobility of D$_{\text{ad}}$ on the surface and the difference in adsorption energies on the Pt islands and the uncovered Ru parts, it can be assumed that up to the local saturation coverage of 1 ML pre–adsorbed deuterium is localized mostly on the Ru parts of the bimetallic surface. Even for the maximum D$_2$ pre–exposure the Pt islands are still mostly free of D$_{\text{ad}}$ (see Section 4.2.4.3). At the same time, adsorption of CO on a pre–adsorbed D$_{\text{ad}}$ layer is found to be strongly hindered on Ru(0001) (see above). Considering that the CO–Pt band is at least 95% saturated for all (total) CO$_{\text{ad}}$ coverages in the coadsorbed layers, and taking into account the additional intensity decrease of the CO–Ru band, we can conclude that CO adsorption on a pre–adsorbed deuterium layer on the bimetallic surfaces takes place mostly on the Pt islands, while adsorption on the Ru parts of the surface is limited, analogous to D$_2$/CO coadsorption on Ru(0001).
4.4.4.3 Coadsorption on Pt/Ru(0001) (medium to high Pt coverage)

This section deals with coadsorption of D$_2$ and CO (using the same dosing sequences as in previous sections) on Pt films with coverages between 0.3 and ~1 ML of Pt. Figure 4.32 shows D$_2$ TPD spectra recorded from coadsorbed layers on Pt films with 0.5 and 0.95 ML, respectively, which were exposed to increasing doses of CO, followed by 40×10$^{-6}$ mbar∙s D$_2$. As in the case of the previous TPD experiments, the CO TPD spectra show no modifications due to coadsorbed D$_{ad}$, since the desorption temperature ranges of D$_2$ and CO do not overlap.

Starting with the 0.5 ML Pt surface, at the highest non–saturation CO pre–exposure (15×10$^{-6}$ mbar∙s CO, leading to 0.33 ML CO), the D$_2$ desorption maximum is at 208 K (red spectrum in Figure 4.32a), ~76 K lower than on the 0.25 ML Pt surface with a similar CO$_{ad}$ pre–coverage. At the same time, the D$_2$ uptake on a CO$_{ad}$ layer with this coverage is considerably lower (0.04 ML D$_{ad}$ vs 0.11 ML on the surface with 0.25 ML Pt). Compared to a TPD experiment with the same D$_{ad}$ coverage (and a higher CO$_{ad}$ pre–coverage) on the 0.25 ML Pt surface (green spectrum in Figure 4.28b), the desorption maximum is still 20 K lower. With decreasing CO pre–exposures, this desorption state grows in intensity and displays a moderate shift to higher temperatures (222 K for 0.17 ML CO + 0.13 ML D$_{ad}$, blue spectrum in Figure 4.32a). In contrast to the results observed for this dosing sequence on pure Ru(0001) and Pt films with lower Pt coverage, the intensity of this desorption state is clearly outside the envelope given by the TPD spectrum of pure D$_2$ (dashed line in Figure 4.32a). For even lower CO pre–exposures (< 0.75×10$^{-6}$ mbar∙s CO) this desorption state decreases in intensity, for the highest coadsorption D$_{ad}$ coverage of 0.43 ML (brown spectrum in Figure 4.32a) the D$_2$ desorption in this temperature range is only slightly above the desorption trace for desorption of pure D$_2$. Concomitant with the decrease in intensity of the first desorption peak, two additional states appear which are rather similar to those already observed on surfaces with lower Pt coverage (Figure 4.28). One is a high–temperature state in the temperature range usually associated with desorption from the uncovered Ru areas of the surface. The other one is found at temperatures around 150 K, i.e., the temperature range for desorption from the Pt film islands.

On the 0.95 ML Pt surface, the desorption maximum for the lowest D$_{ad}$ coadsorption coverage (0.28 ML CO + 0.04 ML D) is found at 187 K, again shifted to lower temperatures compared to surfaces with lower Pt coverage. With decreasing CO$_{ad}$ pre–exposures (down to 0.3×10$^{-6}$ mbar∙s CO), this desorption state grows in intensity and shows a moderate shift to
higher temperatures (199 K for 0.11 ML CO + 0.11 ML D₂) similar to the behavior on the 0.5 ML Pt surface. Unlike to the latter surface the desorption peak stays within the envelope of the TPD spectrum of pure D₂ at maximum coverage (dashed line in Figure 4.32b).

**Figure 4.32:** TPD spectra recorded on 0.5 and 0.95 ML of Pt after pre-exposure to increasing amounts of CO, followed by $40 \times 10^{-6}$ mbar·s D₂. The upper panels show D₂ TPD results, the lower panels CO TPD results. (CO exposures $\times 10^{-6}$ mbar·s: (a) 0.15, 0.45, 0.75, 1.05, 1.5, 30; (b) 0.075, 0.15, 0.3, 0.45, 0.75, 1.05, 30). Dashed lines: spectra recorded after an exposure of $40 \times 10^{-6}$ mbar·s of pure D₂ (no coadsorption).

For even lower CO pre-coverages, the D₂ TPD spectrum broadens as desorption of D₂ increases at both the lower and the higher temperature sides of the initial desorption peak, which for pure D₂ adsorption on this surface is associated with desorption from the Pt film and uncovered Ru areas/second Pt layer islands, respectively (see Section 4.2.4.3). As in the case of surfaces with lower Pt coverages, no significant adsorption of D₂ is detectable on a fully saturated CO layer for the surfaces with 0.5 and 0.95 ML of Pt.
IR spectra of coadsorbed layers on surfaces with 0.5 and 0.95 ML of Pt resulting from varying CO pre–exposures, followed by $40 \times 10^{-6}$ mbar·s of D$_2$, are compiled in Figure 4.33. Again, spectra recorded from the CO layer before post–dosing of D$_2$ are indicated by dashed lines. The behavior of the CO–Ru band on the 0.5 ML Pt surface (Figure 4.33a) is generally in line with the results observed on films with lower Pt coverages.

![Figure 4.33: IR spectra recorded on surfaces with (a) 0.5 and (b) 0.95 ML Pt after pre–exposure to increasing amounts of CO, followed by $40 \times 10^{-6}$ mbar·s D$_2$. Colors and exposures correspond to TPD spectra in Figure 4.32. IR spectra recorded on pure CO layers before D$_2$ exposure are added for comparison (dashed lines).](image)

At low CO pre–coverages, the band has a lower intensity and a broader shape compared to the CO only adlayer with the same coverage, additionally a blue–shift of $\sim 10 - 14$ cm$^{-1}$ is observed. The differences between the CO–Ru bands of pure and coadsorbed CO$_{ad}$ decrease progressively with increasing CO$_{ad}$ pre–coverage (decreasing coverage of post–adsorbed D$_{ad}$).
also in line with earlier results. The low coverage CO–Pt band of the CO only adlayer on 0.5 ML of Pt is rather broad with two maxima at 2085 and 2070 cm$^{-1}$. After post–exposure to 40×10$^{-6}$ mbar·s of D$_2$, the intensity of the band increases concomitant with an overall slight blue–shift of ~2 cm$^{-1}$. With increasing CO$_{ad}$ coverage the maximum at higher wavenumbers increases in intensity and progressively shifts to 2090 cm$^{-1}$ for a fully saturated CO$_{ad}$ layer. The maximum at lower wavenumbers also shows a slight blue–shift with increasing CO$_{ad}$ coverage but turns into a rather low intensity shoulder of the main CO–Pt band.

The increase in intensity of the CO–Pt band observed for lower CO coverages due to the post–exposure of a CO$_{ad}$ layer to 40×10$^{-6}$ mbar·s of D$_2$ is attenuated for higher CO$_{ad}$ coverages, but still observable up to at least 0.33 ML of CO$_{ad}$ (0.04 ML of D$_{ad}$ coadsorbed). While the CO–Ru band is not observed on the surface with 0.95 ML Pt, the CO–Pt band displays the same increase in intensity after D$_2$ post–exposure that was observed on the 0.5 ML Pt surface. A possible explanation for this increase in intensity would be an increased ordering of the CO$_{ad}$ layer on the Pt islands due to repulsive interactions with coadsorbed D$_{ad}$.

The next paragraphs will deal with results of coadsorption experiments on Pt film surfaces with Pt coverages of 0.41 – 1.15 ML, which were carried out with the reverse dosing sequence (pre–exposure to increasing doses of D$_2$ followed by a saturating dose of 30×10$^{-6}$ mbar·s of CO). Figure 4.34 shows D$_2$ TPD spectra recorded from coadsorbate layers on surfaces with Pt coverages of 0.41 and 0.65 ML, respectively. Again spectra resulting from the highest used exposure of 40×10$^{-6}$ mbar·s of pure D$_2$ (no coadsorption) are included for comparison (dashed lines).

The most significant difference observed in these spectra compared to the TPD spectra recorded from surfaces with lower Pt coverages is the lack of a distinct desorption state in the temperature range of desorption from uncovered Ru areas. At all D$_{ad}$ pre–coverages the largest fraction of D$_2$ desorbs in the temperature range between the two peaks associated with desorption of pure D$_2$ from Pt islands and Ru areas. Compared to surfaces with lower Pt coverages (Figure 4.30), desorption of coadsorbed D$_2$ at low D$_{ad}$ pre–coverages (~0.12 ML) is further shifted to lower temperatures (185 K for 0.41 ML Pt and 177 K for 0.65 ML). With increasing D$_2$ pre–exposures, the intensity of the initial desorption state increases until it reaches saturation. At the same time, a low–temperature desorption state appears and increases in intensity within the envelope of the low–temperature peak of pure D$_2$ (desorption from Pt islands). On the 0.41 ML Pt surface this feature is observed only in the spectra of the
two highest D$_{ad}$ coverages, while for 0.65 ML Pt it is present for all but the lowest D$_{ad}$ coverage.

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<tr>
<th>Temperature / K</th>
<th>CO desorption rate / ML s$^{-1}$</th>
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Figure 4.34: TPD spectra recorded on 0.41 and 0.65 ML Pt after pre–exposure to increasing amounts of D$_2$, followed by $30 \times 10^{-6}$ mbar·s CO. The upper panels show D$_2$ TPD results, the lower panels CO TPD results. (D$_2$ exposures $\times 10^{-6}$ mbar·s: 0.25, 0.55, 1.2, 2.4, 40). Spectra recorded after exposure to $40 \times 10^{-6}$ mbar·s D$_2$ (---) or $30 \times 10^{-6}$ mbar·s CO (···) a re added for comparison.

Comparison of integrated intensities of the TPD spectra after the maximum exposure of $40 \times 10^{-6}$ mbar·s of D$_2$ with and without subsequent exposure to CO shows considerable displacement (induced desorption) of deuterium by post–dosed CO. On both surfaces, the amount of displaced D$_2$ is found to be equivalent to the amount of pure D$_2$ adsorbed on Pt islands without coadsorbed CO. This might indicate that, the desorption of D$_2$ induced by CO post–adsorption takes place only on the Pt islands, while D$_{ad}$ adsorbed on the Ru areas remains on the surface.
Results of IR experiments employing the same dosing sequence (varying doses of D\textsubscript{2} followed by 30×10\textsuperscript{-6} mbar·s of CO) at 90 K are shown in Figure 4.35. The switch from blue–shift to red–shift for the coadsorption CO–Ru band compared to the band of pure CO\textsubscript{ad} observed on the 0.3 ML Pt surface continues on the bimetallic surface with 0.41 ML of Pt. Here, a red–shift of 15 cm\textsuperscript{-1} is observed for the CO–Ru band of coadsorbed CO already for the highest D\textsubscript{2} pre–exposure (0.54 ML D\textsubscript{ad} + 0.36 ML CO\textsubscript{ad}). For the lowest D\textsubscript{ad} pre–coverage (0.12 ML D\textsubscript{ad} + 0.54 ML CO\textsubscript{ad}) the red–shift still amounts to 5 cm\textsuperscript{-1}. At the same time, the CO–Ru band continues to display a broader shape and a lower intensity compared to adsorption of pure CO. Due to the very low intensity of the CO–Ru band for Pt coverages above 0.6 ML (see Section 4.2.4.2), no definite statements can be made about the IR

Figure 4.35: IR spectra recorded on surfaces with 0.41 (a) and 0.65 (b) ML Pt after pre–exposure to increasing amounts of D\textsubscript{2}, followed by 30×10\textsuperscript{-6} mbar·s CO. Colors and exposures correspond to TPD spectra in Figure 4.34. IR spectra recorded on pure CO layers with similar coverages are added for comparison (dashed lines).
Results and discussion

Absorption properties of coadsorbed CO on the Ru areas for higher Pt coverages. In line with observations already made for the 0.3 ML Pt surface, the CO–Pt band on 0.41 and 0.65 ML of Pt is almost fully saturated (~95% intensity) throughout the whole range of D$_2$ pre–exposures and does not display a frequency shift compared to the band of a pure CO adlayer.

![Graph showing TPD spectra](image)

**Figure 4.36**: TPD spectra recorded on 0.95 (a) and 1.15 (b) ML Pt after pre–exposure to increasing amounts of D$_2$, followed by 30×10$^{-6}$ mbar·s CO. The upper panels show D$_2$ TPD results, the lower panels CO TPD results. (D$_2$ exposures ×10$^{-6}$ mbar·s: 0.55, 2.5, 8, 16, 40). Spectra recorded after exposure to 40×10$^{-6}$ mbar·s D$_2$ (---) or 30×10$^{-6}$ mbar·s CO (···) are added for comparison.

A further increase of the Pt coverage up to the closed monolayer range leads to further considerable changes in the desorption behavior of deuterium coadsorbed with CO. D$_2$ TPD spectra of coadsorbed layers on surfaces with 0.95 and 1.15 ML of Pt are presented in Figure 4.36. In line with the general trend observed so far desorption of coadsorbed deuterium is again shifted to lower temperatures compared to surfaces with lower Pt coverages. For both
surfaces only one major desorption state at ~150 K appears – the temperature range for D₂ desorption from the first Pt layer.

On the 0.95 ML surface, for the maximum D₂ pre-exposure of 40×10⁻⁶ mbar·s, this peak is almost congruent with the corresponding low-temperature desorption peak found for desorption of pure D₂ after the same exposure. For the Pt coverage of 1.15 ML on the other hand, this state shows considerably higher intensity than the spectrum of pure D₂. Additionally a low temperature shift of 10 K is observed for the leading edge of the desorption spectrum for the coadsorption case. Integrating the spectra shows that after exposure to 40×10⁻⁶ mbar·s D₂ a considerable amount of D₂ (~50% for 0.95 ML of Pt and ~65% for 1.15 ML) desorbs in the temperature range of 190 – 350 K on both surfaces in case of pure D₂ adsorption. In the case of coadsorption desorption in this temperature range is considerably lower for both surfaces, however, for the 0.95 ML surface ~35% of desorbing D₂ is still detected in this range while it amounts to only ~15% for the surface covered with 1.15 ML of Pt.

Figure 4.37 shows IR spectra recorded on the 0.95 and 1.15 ML Pt surfaces following the same exposure sequence. Colors and coverages given next to the spectra correspond to the TPD spectra in Figure 4.36. On the 0.95 ML Pt surface, only the CO–Pt band is observed showing the same intensity and frequency (2090 cm⁻¹) for all spectra recorded. It must be noted that on this surface due to the relatively low D₂ uptake the difference in CO coverage between the lowest and highest D₂ pre-exposure is relatively small (0.56 vs. 0.51 ML of CO). At the same time, the CO–Pt band was found to be relatively insensitive to variations in CO_ads coverage in this coverage range (see Figure 4.13) for pure CO adsorption. The same observations are also true for the CO–Pt band recorded from the coadsorbate layer on the surface covered by 1.15 ML of Pt. Additionally, a shoulder is detected on the high frequency side of the main band, which for pure CO is attributed to CO adsorption on the second Pt layer (see Section 4.2.4.2). In the case of coadsorbate layers, the intensity of this shoulder increases with decreasing D_ads pre-exposures. This indicates that at 90 K post-adsorbed CO molecules populate only the first Pt layer while pre-adsorbed D_ads is concentrated on the second layer, a total pre-coverage of 0.17 ML D_ads (resulting in local saturation for the second Pt layer) is enough to prevent CO adsorption on the second Pt layer. In this regard the second Pt layer and the uncovered Ru areas on bimetallic surfaces with submonolayer Pt coverages show a similar behavior. This is attributed to the much higher D_ads adsorption energy on these
surfaces, compared to the first Pt layer, which prevents the displacement of pre-adsorbed D$_{ad}$ by post-exposure to CO.

**Figure 4.37:** IR spectra recorded on surfaces with (a) 0.95 and (b) 1.15 ML Pt after pre-exposure to increasing amounts of D$_2$, followed by 30×10$^{-6}$ mbar s CO. Colors and exposures correspond to TPD spectra in Figure 4.36. IR spectra recorded on pure CO layers with similar coverages are added for comparison (dashed lines).

This effect likely explains the much higher intensity of the D$_2$ desorption peak at ~150 K on the 1.15 ML surface, compared to the TPD peak of pure D$_2$. In the case of D$_2$ only adsorption, a large part of the adsorbed D$_{ad}$ is located on the second Pt layer, from where it desorbs in the 200 – 400 K temperature range. In the case of coadsorption, interactions with the coadsorbed CO$_{ad}$ cause an additional reduction of the D$_{ad}$ adsorption energy leading to D$_2$ desorption at a lower temperature. As in the case of the bare Ru areas discussed above (Section 4.4.4.2), it is not clear whether this destabilization occurs already during CO adsorption at 90 K or only
after the start of the TPD experiment when the adsorbed CO becomes mobile. Additionally it is impossible to tell whether the pre–adsorbed D\textsubscript{ad} is displaced from the second onto the first Pt layer (from where it desorbs at \(\sim 150\) K) or whether the destabilization by coadsorbed CO\textsubscript{ad} is sufficient to lead to desorption of D\textsubscript{ad} from the second Pt layer at a lower temperature, compared to desorption of pure D\textsubscript{2}.

4.4.4.4 Coadsorbate coverage

Figure 4.38 shows the deuterium coverage reached on bimetallic surfaces with different Pt coverages pre–covered by different amounts of CO as determined by integration of the TPD spectra. For a similar coadsorption experiment on Ru(0001), Peebles et al. [148] used the equation:

\[
\theta(D_2) = \theta(D_2)_{sat} \left[1 - \frac{\theta(CO)}{\theta(CO)_{sat}}\right]^n
\]  

(4.4)

to fit the experimental results. They found a value of \(n = 2\) to give the best fit, concluding that CO\textsubscript{ad} blocks deuterium adsorption as a function of CO\textsubscript{ad} covered adsorption sites. For the experiments presented here, the same result is found for the clean Ru(0001) surface. The same equation can be also used to fit the results for bimetallic surfaces. With increasing Pt coverage the value for \(n\) is found to increase. For surfaces with lower Pt coverages of 0.15 and 0.25 ML, it is still close (\(n = 2.3\) and 2.5 respectively) to the value of \(n = 2\) found for Ru(0001). For the medium coverages of 0.5 and 0.65 ML Pt it increases further to \(n = 4\). Finally a value of \(n = 5\) is found for the 0.95 ML Pt surface. Since CO and D\textsubscript{2} do not occupy the same adsorption sites either on pure Ru(0001) or on the bimetallic surfaces (on–top sites for CO and fcc sites for D\textsubscript{2}) the blocking of deuterium adsorption must be attributed to an exclusion of adjacent deuterium adsorption sites by adsorbed CO molecules. Technically, a value of \(n = 2\) indicates that one adsorbed CO molecule prevents the adsorption of two D\textsubscript{ad} species or one D\textsubscript{2} molecule. It must be noted, however, that equation (4.4) is strictly valid only for the case where pre–adsorbed CO molecules are randomly distributed on the surface. This may be assumed as valid for the Ru(0001) surface at 90 K, where formation of ordered CO adsorbate structures is largely inhibited by the low mobility of CO molecules on the surface at this temperature [39,78].
4 Results and discussion

Figure 4.38: D\textsubscript{ad} coverage after a dose of 40×10\textsuperscript{−6} mbar·s D\textsubscript{2} following varying CO pre–exposures: (■) Ru(0001), (▲) 0.15 ML Pt, (▼) 0.25 ML Pt, (●) 0.5 ML Pt, (◆) 0.65 ML Pt, (▲) 0.95 ML Pt; dashed lines: graphs of the equation (4.4).

Considering the results of CO TPD and IR experiments (see Section 4.2.4.1 and 4.2.4.2), this assumption can be extended to the uncovered Ru areas of Pt/Ru bimetallic surfaces. In the case of the Pt islands, however, the considerably lower adsorption energy of CO on the Pt islands leads to an enhance mobility on the surface already at 90 K [108], causing preferential occupation of the most stable adsorption sites on the Pt islands and possibly formation of stabilized ordered adsorbate structures (similar to Ru(0001) at higher temperatures). Considering this, the numerical value for \( n \) found on the bimetallic films, can at best be regarded as the average for the entire surface, preventing quantitative conclusions about the blocking of deuterium adsorption by CO on the Pt islands. Qualitatively the increasing value of \( n \) found for increasing Pt coverages indicates that pre–adsorbed CO on the Pt film has a much stronger effect on subsequent adsorption of D\textsubscript{2} compared to pure Ru(0001) and the free Ru areas of bimetallic surfaces. This may be explained by the fact that D\textsubscript{2} adsorption is considerably weakened already on the clean Pt film surface, an exposure to 80×10\textsuperscript{−6} mbar·s D\textsubscript{2} (double the amount used in the coadsorption experiments) results in a local coverage of only \(~0.3\) ML D\textsubscript{ad} on Pt islands (see Section 4.2.4.3). Additionally, considering that due to their higher mobility on Pt islands pre–adsorbed CO molecules most likely occupy the most stable adsorption sites, the blocking effect of CO\textsubscript{ad} on deuterium adsorption is expected to be
stronger on the Pt islands than on the bare Ru areas, were CO$_{\text{ad}}$ is distributed randomly at 90 K.

Figure 4.39 shows the development of the CO$_{\text{ad}}$ coverage with varying D$_{\text{ad}}$ coadsorption coverages on clean Ru(0001) and Pt films with 0.3 and 0.65 ML Pt. The CO$_{\text{ad}}$ coverage was normalized to the CO$_{\text{ad}}$ saturation coverage in order to separate the influence of D$_2$ coadsorption from the variations of CO$_{\text{ad}}$ coverage caused by different Pt coverages as seen in Figure 4.8. For the Pt film with 0.3 ML Pt the decrease of CO$_{\text{ad}}$ coverage with increasing D$_{\text{ad}}$ coverage is initially not as pronounced as for pure Ru(0001). For D$_{\text{ad}}$ coverages above ~0.2 ML the slopes of both lines are roughly parallel, however, the CO coverage values for the 0.3 ML Pt film are consistently higher by ~0.05 – 0.07 throughout the entire D$_{\text{ad}}$ coverage range, indicating a smaller influence of pre–adsorbed D$_{\text{ad}}$ on the CO uptake for the bimetallic surface.

**Figure 4.39:** CO$_{\text{ad}}$ coverages (normalized to the CO saturation coverage) after coadsorption on (■) Ru(0001), (▲) 0.3 ML Pt and (●) 0.65 ML Pt. with varying D$_{\text{ad}}$ pre–coverages.

It must be noted that on the clean Ru(0001) surface and on the 0.3 ML Pt surface the D$_{\text{ad}}$ pre–coverage is equal to the resulting coadsorption coverage, since no D$_{\text{ad}}$ is displaced by post–dosed CO. On the surface with 0.65 ML Pt, the decrease of CO$_{\text{ad}}$ coverage with increasing D$_{\text{ad}}$ coadsorption coverages is considerably less pronounced than for Ru(0001) or 0.3 ML Pt, leading to higher normalized CO coadsorption coverages on this surface. In addition the slope
of the plot for the surface with 0.65 ML Pt decreases with increasing D_{ad} pre–coverage. This decrease can most likely be explained by the displacement of considerable amounts of D_{ad} by CO post–exposure on this surface, which allows higher CO uptakes for equal D_{ad} pre–coverages.

Figure 4.40: Adsorbate coverages on Pt film surfaces on Ru(0001) with varying Pt coverages after exposure to 40×10^{-6} mbar·s D_{2} followed by 30×10^{-6} mbar·s CO (■). (a) CO_{ad} coverage, (b) D_{ad} coverage. The corresponding coverages without coadsorption are added for comparison (□). Inset: total coadsorbate coverage, relative to the saturation coverage of the individual adsorbates.

The D_{ad} and CO_{ad} coverages resulting from the same dosing sequence after the maximum D_{2} pre–exposure of 40×10^{-6} mbar·s D_{2}, followed by 30×10^{-6} mbar·s CO, are compiled in Figure 4.40, coverages of both coadsorbates resulting from the same respective exposures without
coadsorption are added for comparison (open black symbols). Up to a Pt coverage of 0.3 ML, displacement of D\textsubscript{ad} by post–exposure to CO is found to be negligible. At higher Pt coverages between 0.3 and 0.65 ML post–exposure to CO results in considerable displacement of pre–adsorbed D\textsubscript{ad}. The amount of D\textsubscript{ad} calculated to remain adsorbed on these surfaces is roughly equivalent to the amount necessary to achieve a local coverage of 1 ML on the Ru areas. Considering that displacement of D\textsubscript{ad} apparently does not take place on the uncovered Ru areas and that the CO–Pt IR band is found to be almost fully saturated in all cases, it can be concluded that the Pt islands are mostly free of adsorbed deuterium after post–exposure to CO (with the possible exclusion of the most stable sites along the island edges) and covered almost exclusively by CO. The considerable amount of D\textsubscript{2}, which is found desorbing in the low–temperature range (attributed to D\textsubscript{2} desorption from Pt sites) in the TPD spectra, is likely to result from a rearrangement of the coadsorbate layer with increasing temperatures during the TPD experiment. For higher Pt coverages, the difference between the coverages of pure D\textsubscript{ad} and D\textsubscript{ad} coadsorbed with CO decreases somewhat, indicating that less deuterium is displaced by post–dosed CO. This can be attributed to the fact that for Pt coverages above ~0.9 ML the formation of a stronger binding second Pt layer begins before the completion of the first layer (see Section 3.2), as shown by IR spectra (Figure 4.37b) no D\textsubscript{ad} is displaced by CO from the second Pt layer. Due to the fact that Pt coverages are given as monolayer equivalents, the Pt surfaces in this coverage range effectively have a higher percentage of stronger binding adsorption sites on uncovered Ru areas and on the second Pt layer than is suggested by the nominal Pt coverage value. This effect is especially clear on the 1.15 ML Pt surface, where, due to the high mobility of D\textsubscript{ad} on the surface, most of the originally adsorbed 0.21 ML D\textsubscript{ad} will be located on the second Pt layer, leading to the displacement of only 0.04 ML D\textsubscript{ad} by post–adsorbed CO.

The CO\textsubscript{ad} coverage resulting from the exposure of a pre–adsorbed D\textsubscript{ad} layer to $30 \times 10^{-6}$ mbar·s\textsuperscript{-1} CO initially increases markedly with increasing Pt coverage (Figure 4.40a). While on pure Ru(0001) this dosing sequence results in the adsorption of only 0.12 ML CO (compared to 0.68 ML for adsorption of pure CO), on the 0.65 ML Pt surface CO uptake increases to 0.48 ML (0.57 ML for pure CO). For even higher Pt coverages CO uptake remains approximately constant at ~0.5 ML of CO, i.e. ~0.08 ML less than in the case of pure CO adsorption. These results can be explained by the increasing displacement of pre–adsorbed D\textsubscript{ad} with increasing Pt coverage. In addition, the blocking of CO adsorption by pre–adsorbed deuterium decreases simply due to the fact that the number of D\textsubscript{ad}–free sites increases with increasing Pt coverage.
The insert in Figure 4.40b shows the total relative coverage of the coadsorbate layers on surfaces with varying Pt coverage. In the case of CO\textsubscript{ad} 100% corresponds to the saturation coverage at 90 K on the respective surface. For deuterium, 100% is assumed to be 1 ML, even though this coverage cannot be achieved on the bimetallic surfaces with the exposures employed in these experiments. For the Ru(0001) surface, the total coverage achieved by post-dosing CO on 1 ML of D\textsubscript{ad} is 18% higher than the values found for separate adsorption of CO and D\textsubscript{2}. As noted above, this results from the fact that on the one hand deuterium cannot be displaced from Ru(0001) at 90 K, on the other hand the Ru(0001) surface can accommodate a D\textsubscript{ad} coverage > 1 ML even though adsorption of D\textsubscript{2} from the gas phase is kinetically hindered above 1 ML [118]. Therefore, repulsive interactions between the coadsorbed species result in a compression of the D\textsubscript{ad} part of the coadsorbate layer allowing adsorption of 0.12 ML CO in addition to 1 ML D\textsubscript{ad}. In contrast, the surfaces with coverages of 0.95 and 1.15 ML of Pt do not show coadsorbate coverages significantly higher than 100%. This can be explained by the rather low adsorption energy of deuterium on the first Pt layer. Since D\textsubscript{2} desorption already starts at the adsorption temperature of 90 K, a further decrease in adsorption energy caused by repulsive interactions with coadsorbed CO\textsubscript{ad} will result in D\textsubscript{2} desorption (and replacement by CO) instead of a compression of the D\textsubscript{ad} layer.

### 4.4.4.5 Influence of increasing temperature on IR spectra

In the next section, the effects of increasing sample temperature on the coadsorbate layers as investigated by IR measurements will be presented. In these experiments, the sample was first exposed to $40 \times 10^{-6}$ mbar·s of D\textsubscript{2} + $30 \times 10^{-6}$ mbar·s of CO at 90 K, then annealed in 10 K steps with an IR spectrum recorded after each annealing step (the first spectrum was recorded at the adsorption temperature of 90 K). In Figure 4.41, the results for the Ru(0001) surface are presented. At first, the broad and weak IR band with maximum at 2028 cm\textsuperscript{-1} shows a general shift of intensity to higher wavenumbers up to 200 K. At around 250 K, the band shifts to 2007 cm\textsuperscript{-1}, simultaneous with a considerable increase in intensity. At 410 K, the band begins to shift to lower wavenumbers and decrease in intensity, indicating the onset of CO desorption. Comparison to the D\textsubscript{2} TPD spectrum of a coadsorbate adlayer prepared in an identical way (Figure 4.41b) indicates that the shift to lower wavenumbers at 250 K is most likely caused by a rearrangement of the CO adlayer (dissolution of small compressed CO
islands into larger, more ordered structures) upon the onset of D₂ desorption at this temperature.

Figure 4.41: (a) IR spectra recorded after an exposure to $40 \times 10^{-6}$ mbar⋅s D₂ followed by $30 \times 10^{-6}$ mbar⋅s CO on Ru(0001) at 90 K (initial coverage: 1 ML D + 0.13 ML CO) and stepwise heating (10 K steps), (b) D₂ TPD spectrum recorded after the same exposure sequence.

The development of the IR spectra with increasing substrate temperature on a 0.25 ML Pt surface is shown in Figure 4.42. At 90 K, the CO–Ru band is located at 2033 cm⁻¹. In the temperature range between 100 and 150 K, the band shows a marked broadening and decreased intensity while no change is observed for the CO–Pt band at 2088 cm⁻¹. The corresponding D₂ TPD spectrum shows that ~0.05 ML of D₂ desorb in this temperature range. Considering that the behavior of the CO–Ru band is rather similar to that of the CO–Ru band on Ru(0001) (where no D₂ desorption takes place in this temperature range), the changes
observed for this band up to 150 K are most likely caused by the increasing temperature rather than D$_2$ desorption.

Figure 4.42: (a) IR spectra recorded after an exposure to 40×10$^{-6}$ mbar∙s D$_2$ followed by 30×10$^{-6}$ mbar∙s CO on a surface with 0.25 ML of Pt at 90 K (initial coverage: 0.76 ML D + 0.24 ML CO) and stepwise heating (10 K steps), (b) D$_2$ TPD spectrum recorded after the same exposure sequence.

Upon reaching 160 K, the CO–Pt band shows a sharp decrease in intensity, until it vanishes almost completely at 200 K. Concomitantly, the low and broad CO–Ru band grows into a sharp peak at 2038 cm$^{-1}$. The IR results indicate a diffusion of the majority of adsorbed CO molecules from Pt islands to the Ru areas, concomitant with the onset of D$_2$ desorption from the major desorption feature at 160 K (Figure 4.42b). A further increase in temperature above 200 K causes a continuous shift of the CO–Ru band to lower wavenumbers (2029 cm$^{-1}$ at 300 K). Since no CO desorption is observed in this temperature range, this red–shift of the IR
band cannot be explained by a decreasing CO\textsubscript{ad} coverage. The observed red–shift can be seen as a retrograde blue–shift caused by the continuously decreasing amount of coadsorbed D\textsubscript{ad} (see Figure 4.31 and respective discussion). Finally, above 350 K the IR band displays the behavior expected to result from a decreasing CO\textsubscript{ad} coverage due to CO desorption in this temperature range.

**Figure 4.43:** (a) IR spectra recorded after an exposure to 40×10\textsuperscript{−6} mbar s D\textsubscript{2} followed by 30×10\textsuperscript{−6} mbar s CO on a surface with 0.5 ML of Pt at 90 K (initial coverage: 0.47 ML D + 0.39 ML CO) and stepwise heating (10 K steps), (b) D\textsubscript{2} TPD spectrum recorded after the same exposure sequence.

Figure 4.43 shows the results of the identical experiment on a surface with a Pt coverage of 0.5 ML. Similar to the results observed on the 0.25 ML Pt surface (Figure 4.42), the CO–Ru band at 2033 cm\textsuperscript{−1} at 90 K begins to decrease in intensity already after the first annealing step to 100 K. At 130 K it cannot be distinguished from the background anymore. At 150 K the
CO–Ru band reappears again at 2052 cm\(^{-1}\), a further increase in temperature results in an increased intensity and slight blue–shift of 3 cm\(^{-1}\), concomitant with a decrease in intensity and red–shift (from 2089 cm\(^{-1}\) to 2086 cm\(^{-1}\)) of the CO–Pt band. Both processes occur in the temperature range of the major desorption feature in the D\(_2\) TPD spectrum (Figure 4.43b). Finally, at 240 K both IR bands start a trend of decreasing intensity and a shift to lower wavenumbers accompanying the onset of CO desorption.

The major D\(_2\) desorption feature at ~200 K, which is observed for all bimetallic surfaces, for the dosing sequence were a pre–adsorbed D\(_{ad}\) layer is exposed to CO, (except those with a Pt coverage close to 1 ML) is absent on Ru(0001). While the desorption of coadsorbed D\(_2\) is shifted to lower temperatures on Ru(0001) compared to pure D\(_2\) desorption (see Figure 4.26), the additional low–temperature shift, found for D\(_2\) desorbing from the Ru areas of submonolayer Pt film surfaces, indicates the presence of an additional destabilizing effect caused by CO post–adsorption on these surfaces. Considering the results of the IR experiments above, it can be assumed to originate from an additional destabilization of D\(_{ad}\) in the coadsorbate layer on the Ru parts of the surface, caused by an increase of CO coverage due to the CO spill–over from Pt islands to Ru areas at temperatures above ~110 K (see Section 4.3). Since this process requires the presence of both, Pt islands and bare Ru areas, it is not observed on pure Ru(0001) and on bimetallic surfaces with Pt coverages close to 1 ML.

The conclusion, that the additional destabilization of D\(_{ad}\) occurs only after the start of the heating ramp during the TPD experiment and not already during the CO post–exposure, is further supported by the fact that a desorption feature in the same temperature range is also observed for the reverse dosing sequence on the surface with 0.5 ML Pt (Figure 4.32a). Here, a destabilization by post–adsorbed CO\(_{ad}\) can be excluded, while the spill–over of CO\(_{ad}\) from Pt islands to the Ru areas will occur for both dosing sequences. On surfaces with lower Pt coverages the desorption feature at ~200 K is not observed for this dosing sequence (CO followed by D\(_2\)), this is likely due to a smaller CO\(_{ad}\) coverage on the Pt islands compared to the reverse sequence (D\(_2\) followed by CO), where Pt islands are always saturated with CO\(_{ad}\).

4.4.4.6 Coadsorbate displacement

In this section, experiments investigating the displacement of pre–adsorbed D\(_{ad}\) (or CO\(_{ad}\)) by post–dosing of the respective other species will be discussed. Earlier investigations of D\(_2\)/CO
coadsorption on Ru(0001) showed no detectable displacement of pre–adsorbed CO by a post–exposure to D₂ in the temperature range of 100 – 200 K [107,148,162]. For the reversed dosing sequence it has been shown that displacement of pre–adsorbed deuterium by exposure to CO does not take place at temperatures of 100 K [107,110,148]. Conversely, at the higher temperature of 250 K, Riedmüller et al. observed quantitative displacement of pre–adsorbed Dₐd by post–dosed CO [150].

For comparison with experiments on Pt film surfaces, the displacement of deuterium by CO at up to 250 K on Ru(0001) was investigated by exposing the sample to 40×10⁻⁶ mbar·s D₂, followed by increasing doses of CO. Experiments at 100 K (Section 4.4.4.1) and 200 K (not shown) did not result in a measurable displacement of pre–adsorbed Dₐd by post–exposure to CO.

The results of experiments carried out at 250 K are shown in Figure 4.44. A comparison of integrated intensities after an exposure to 40×10⁻⁶ mbar·s D₂ at 90 and 250 K shows a slightly lower Dₐd coverage of 0.94 ML for the higher temperature. Exposure of this Dₐd layer to 30×10⁻⁶ mbar·s CO results in the displacement of a considerable amount of pre–adsorbed deuterium (red spectra in Figure 4.44) and in a final coverage of 0.51 ML Dₐd + 0.28 ML COₐd. It is interesting to note that coadsorption at this temperature results in a total coverage of 97% compared to the maximal coverage for separate adsorption of each species. Conversely, the same experiment at 90 K resulted in a total coverage of 118% (see inset Figure 4.40). This indicates that similar to the situation on Pt islands (at 90 K), post–adsorption of CO on Ru(0001) at 250 K does not result in a compression of the Dₐd layer and instead leads to direct COₐd induced desorption of deuterium. Increasing the CO post–exposure to 75×10⁻⁶ mbar·s, results in a CO spectrum that is identical to the spectrum of a saturated CO layer at 90 K. The displacement of Dₐd after this CO post–exposure is almost complete, integration of the remaining D₂ desorption trace (green spectrum in Figure 4.44a) shows that only 0.04 ML Dₐd still remain on the surface. Interestingly, desorption of D₂ after the higher CO exposure is concentrated at the high–temperature end of the temperature range of D₂ desorption, whereas post–exposure to CO at 90 K (and the smaller CO post–exposure at 250 K) results in a shift of D₂ desorption to the low–temperature end (compare red and green spectra in Figure 4.44a and Figure 4.26b). A possible origin of this D₂ desorption can be small amounts of lone Dₐd species trapped within an ordered CO adlayer which can recombine with a second Dₐd and desorb only after desorption of a part of the COₐd layer. The fact that the temperatures of the maxima (393 K and 496 K) of the remaining D₂ desorption trace
correspond roughly to the temperatures of the two desorption peaks in the CO TPD spectrum seems to point in this direction.

![TPD spectra recorded on Ru(0001) after a dose of 40×10⁻⁶ mbar·s D₂ at 250 K followed by increasing doses of CO. (a) D₂ (b) CO. CO exposures ×10⁻⁶ mbar·s: 0 (black), 30 (red), 75 (green). Dashed lines indicate spectra of saturated adlayers at 90 K without coadsorption.](image)

**Figure 4.44:** TPD spectra recorded on Ru(0001) after a dose of 40×10⁻⁶ mbar·s D₂ at 250 K followed by increasing doses of CO. (a) D₂ (b) CO. CO exposures ×10⁻⁶ mbar·s: 0 (black), 30 (red), 75 (green). Dashed lines indicate spectra of saturated adlayers at 90 K without coadsorption.

As has already been shown above, exposure of a CO adlayer pre–adsorbed on bimetallic Pt/Ru(0001) surfaces to varying doses of D₂ at 90 K does not result in a measurable displacement of CO. Figure 4.45 shows the results of experiments where surfaces with Pt coverages of 0.25 – 0.35 ML were first exposed to 30×10⁻⁶ mbar·s CO at 250 – 300 K, followed by D₂ exposures of 10³×10⁻⁶ – 10⁴×10⁻⁶ mbar·s.
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**Figure 4.45**: CO TPD spectra of bimetallic surfaces with varying Pt coverages after a pre–exposure to $30 \times 10^{-6}$ mbar·s CO followed by a dose of D$_2$. D$_2$ exposures $\times 10^{-6}$ mbar·s: (a) $10^3$ (at $10^{-7}$ mbar) at 300 K, (b) $10^4$ (at $10^{-5}$ mbar) at 250 K, (c) sample held at 300 K for 170 min. Spectra resulting from a CO exposure of $30 \times 10^{-6}$ mbar·s at the same temperature, without coadsorption, are shown in black.

At a first glance Figure 4.45 (a) and (b) seem to show a small but noticeable reduction of CO$_{ad}$ coverage after the D$_2$ post–exposure. However, an experiment where the sample was held at 300 K for 170 min (corresponding to the D$_2$ exposure time) in UHV atmosphere (Figure 4.45c) shows the same reduction in coverage, indicating that the loss of CO coverage in these experiments is caused simply by thermal desorption during the D$_2$ exposure and is not a result of CO$_{ad}$ displacement by D$_2$. In conclusion it can be stated that D$_2$ is not capable of displacing pre–adsorbed CO from Pt films on Ru(0001) at D$_2$ pressures of up to $10^{-5}$ mbar at any temperature.

The question remains, under which conditions a complete displacement of D$_2$ by post–dosed CO can take place? As can be seen in the left panels of Figure 4.46, increasing the CO post–exposure from $30 \times 10^{-6}$ to $75 \times 10^{-6}$ mbar·s at 90 K results in a small reduction of D$_{ad}$ coverage (from 0.74 to 0.69 ML D$_{ad}$). The CO coverage increases from 0.22 to 0.27 ML CO. On the one hand, this indicates that higher CO post–exposures lead to D$_2$ displacement also on bimetallic surfaces with low Pt coverages, on the other hand increasing the CO post–exposure by more than 100% results in the displacement of only 7% of D$_{ad}$, indicating that complete displacement of pre–adsorbed deuterium at 90 K can be achieved only with extremely high CO post–exposures, if at all. The right panels of Figure 4.46 show the results of a similar experiment conducted at 150 K. Here the surface again was exposed to $40 \times 10^{-6}$ mbar·s D$_2$ followed by increasing exposures to CO. Already a relatively small CO exposure of $15 \times 10^{-6}$ mbar·s results in a reduction of D$_{ad}$ coverage from 0.69 to 0.47 ML. Increasing the
CO post-exposure leads to increasing displacement of pre-adsorbed deuterium. A CO post-exposure of $150 \times 10^{-6}$ mbar·s results in a coadsorbate layer with 0.07 ML $D_{ad}$ + 0.66 ML CO.

![TPD spectra](image)

**Figure 4.46:** TPD spectra recorded on a surface with 0.3 ML of Pt after an exposure to $40 \times 10^{-6}$ mbar·s $D_2$ followed by increasing CO exposures at temperatures of (a) 90 and (b) 150 K. The upper panels show $D_2$ TPD results, the lower panels CO TPD results. CO exposures $\times 10^{-6}$ mbar·s: (90 K) 30, 75; (150 K) 15, 30, 75, 150, 225. Saturation spectra of the respective adsorbates without coadsorption are given for comparison (dashed lines).

However, a further increase of the CO post-exposure to $225 \times 10^{-6}$ mbar·s does not lead to a further reduction of the $D_{ad}$ coverage. Similar to the case of pure Ru(0001), a small residual coverage of $D_{ad}$ remains on the surface which cannot be displaced even with higher doses of CO. In the case of this bimetallic surface the remaining deuterium desorbs over the entire temperature range of $D_2$ desorption with two distinct maxima at 200 and 268 K and a broad desorption feature with low intensity at 300 – 500 K. As in the case of Ru(0001) this can be
attributed to single D\textsubscript{ad} species trapped within the CO adlayer. Another possibility is that these D\textsubscript{ad} species are adsorbed on the most favorable adsorption sites (edges of Pt islands and step decorations), where the interaction with coadsorbed CO\textsubscript{ad} does not result in a decrease of adsorption energy sufficient to induce desorption of D\textsubscript{2}.

**4.4.4.7 CO adsorption kinetics on a pre–adsorbed D\textsubscript{ad} layer**

This section is focused on the adsorption kinetics of CO on Pt films with varying Pt coverage pre–covered with deuterium. In these experiments, the bimetallic surfaces were first exposed to \(80 \times 10^{-6} \text{ mbar} \cdot \text{s}\) of D\textsubscript{2} followed by a series of increasing exposures of CO (up to \(30 \times 10^{-6} \text{ mbar} \cdot \text{s}\)), the respective TPS spectra can be found in the appendix. Integral sticking coefficients on the pre–adsorbed D\textsubscript{ad} layers were calculated identically to those for pure CO adsorption in Section 4.2.4.1.

The development of the sticking coefficients as a function of CO coverage is shown in Figure 4.47, the sticking coefficients for adsorption of CO on the clean films surfaces (without pre–adsorbed D\textsubscript{ad}) are shown for comparison. The sticking behavior of CO on pure Pt film surfaces was discussed in Section 4.2.5 where CO adsorption was found to proceed via a precursor mechanism, and the initial sticking coefficient \(s_0\) remained roughly constant at \(~0.7\) throughout the whole Pt coverage range. On D\textsubscript{ad} saturated Ru(0001) \(s_0\) decreases to 0.26. Effectively this means that 26\% of the CO molecules that initially impinge on the surface are adsorbed. Even allowing for the fact that \(~0.005 – 0.01\) ML of CO are imbedded in the D\textsubscript{ad} layer (due to adsorption from the residual gas) the rather high value seems to indicate the presence of a precursor state for CO also on the adsorbed deuterium layer. A rather similar value of 0.28 for \(s_0\) was found by T. Diemant using the same experimental setup [110], Peebles et al. observed a linear decrease of the relative sticking coefficient with increasing D\textsubscript{ad} pre–coverage, with a value of 0.2 – 0.3 for a surface saturated with deuterium. In contrast, Riedmüller et al. found a considerably lower value of \(s_0 = 0.017\) for CO adsorption on H\textsubscript{ad} pre–saturated Ru(0001) surface. The differences in these results could be the result of different amounts of defects in the H\textsubscript{ad} layer which serve as the pathway for non–activated CO adsorption [151].
 Already on a Pt film with a relatively low Pt coverage of 0.2 ML the value for the initial sticking coefficient more than doubles to 0.55. After this initial steep increase, $s_0$ increases further with increasing Pt coverage, finally converging with the values obtained for pure CO adsorption on surfaces with Pt coverages close to 1 ML. This trend is further illustrated in Figure 4.48.
In addition to the increase of the initial sticking coefficient with Pt coverage a modification of the evolution of the sticking coefficient with CO\textsubscript{ad} coverage is observed. On Ru(0001) the sticking coefficient shows a rapid, almost linear decrease to zero with increasing CO\textsubscript{ad} coverage. On the surface with 0.2 ML of Pt, the decrease of the sticking coefficient with increasing CO coverage is already significantly slower resulting in a higher maximal CO uptake. A further increase of the Pt coverage to ≥ 0.55 ML results in a shape of the \( s(\theta_{\text{CO}}) \) graph which is rather similar to those observed for the precursor mediated absorption adsorption of pure CO\textsubscript{ad}, an initial slight decrease of the sticking coefficient for low CO uptake followed by a sharp decrease close to the maximum CO\textsubscript{ad} coverage. This indicates an increased presence of the “normal” CO adsorption mechanism on surfaces with higher Pt coverages. Similar to the behaviour observed for CO uptake on D\textsubscript{ad} pre–covered Pt film surfaces (see above), the development of the CO adsorption kinetics with increasing Pt coverage is a consequence of the decreasing maximum D\textsubscript{ad} coverage (as shown in Section 4.2.4.3) and the facilitated displacement of pre–adsorbed deuterium on film surfaces with increasing Pt coverage.
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4.4.5 Comparison to coadsorption results on PtRu/Ru(0001) surface alloys

The influence of the surface morphology (as opposed to the chemical composition) can be further elucidated by comparison of the above results to the results of similar coadsorption experiments on PtRu/Ru(0001) surface alloys with random distribution of the two metal components in the surface layer. In general, the differences observed in the coadsorption TPD spectra of Pt/Ru(0001) film surfaces and PtRu/Ru(0001) surface alloys follow the same trend which was already observed for the separate adsorption of CO and D\textsubscript{2} (see Section 4.2.5). TPD spectra recorded from Pt film surfaces consist of several well discernible states which can be associated with desorption from the Pt islands and the uncovered Ru areas and which show little variation in temperature with increasing Pt coverage. Conversely, TPD spectra recorded on PtRu/Ru(0001) surface alloys display a single broad feature which spans a wide temperature range, with the intensity continuously shifting to lower temperature with increasing Pt content [107,110]. These differences can be explained by the different morphologies of films and surface alloys. In contrast to submonolayer Pt films, which consist of compact Pt islands surrounded by contiguous areas of uncovered Ru, PtRu surface alloys consist of a surface where Pt and Ru atoms are randomly intermixed which leads to a wide range of possible compositions for adsorption ensembles, with different adsorption energies, on this surface. Whereas the shapes of the coadsorption TPD spectra of films and surface alloys are rather different, the general trends regarding coadsorbate coverages and adsorption kinetics are generally similar for both kinds of surfaces. A destabilization of D\textsubscript{ad} by coadsorbed CO is observed on both surfaces, with the destabilization seemingly stronger for pre–adsorption of D\textsubscript{2} and post–exposure to CO than for the reverse sequence. Analogous to film surfaces, adsorption of CO is partially blocked by pre–adsorbed deuterium; however, adsorption of CO remains possible even on D\textsubscript{ad} saturated surface alloys. For the coadsorption sequence where the sample surface is pre–dosed by 40×10\textsuperscript{-6} mbar\textcdot s D\textsubscript{ad} followed by a 30×10\textsuperscript{-6} mbar\textcdot s CO (45×10\textsuperscript{-6} mbar\textcdot s D\textsubscript{ad} and 37.5×10\textsuperscript{-6} mbar\textcdot s CO were used in the experiments on PtRu surface alloys [110]), the trends for coadsorbate coverages are generally similar for both kinds of surfaces (see Figure 4.40 for film surfaces and [110] for surface alloys). Overall, the displacement of pre–adsorbed D\textsubscript{ad} at 90 K seems to be easier on the PtRu surface alloys compared to Pt film surfaces. On surface alloys, displacement of D\textsubscript{ad} is observed for all Pt percentages > 0 [110], while on Pt films it occurs in detectable quantities only above 0.3 ML Pt. Additionally while D\textsubscript{ad} coverages with and without coadsorption are higher on surface alloys than on films, the percentage of D\textsubscript{ad} displaced from the surface by CO post–exposure is generally 10 – 20% higher for surface alloys. The higher susceptibility
of surface alloys for D$_{\text{ad}}$ displacement likely results from the intermixing of Pt and Ru atoms in the surface alloy, which leads to a lower percentage of pure Ru or Pt adsorption ensembles compared to film surfaces. On the one hand, the lower percentage of pure Pt ensembles (weakest binding ensembles) enhances adsorption of D$_2$, on the other hand, the lower percentage of pure Ru ensembles (strongest binding ensembles) leads to a smaller fraction of D$_{\text{ad}}$, which is adsorbed strongly enough to resist displacement by post–dosed CO. The adsorption kinetics of CO on a D$_{\text{ad}}$ pre–covered surface again follow a similar trend on both kinds on surfaces. On the surface alloys, however, while the initial sticking coefficient $s_0$ continuously increases with increasing Pt content, the increase is more gradual compared to Pt films (see Figure 4.48) and the value of $s_0$ for pure CO adsorption is not reached even for Pt contents approaching 100% [110]. A possible explanation lies in the higher D$_{\text{ad}}$ coverages which can be achieved on surface alloys compared to film surfaces. Although the development of the CO sticking coefficient with $\theta$(CO) on D$_{\text{ad}}$ pre–covered surface alloys indicates the existence of a precursor mechanism for CO adsorption [110], similar to the one found on Pt film surfaces (see Section 4.4.4.7), the higher amount of D$_{\text{ad}}$–free adsorption sites can be expected to facilitate CO uptake on Pt film surfaces.

4.4.6 Summary

The coadsorption of CO and D$_2$ was investigated on Ru(0001) and submonolayer Pt films on Ru(0001) with varying Pt coverages. The results show that a closed CO$_{\text{ad}}$ layer completely blocks the adsorption of D$_2$. While adsorption of D$_2$ is still possible on a surface partially covered by CO$_{\text{ad}}$, repulsive interactions between the adsorbed species lead to a considerable decrease of the D$_{\text{ad}}$ adsorption energy. In the case of the reverse adsorption sequence, pre–adsorbed D$_{\text{ad}}$ also inhibits the post–adsorption of CO, however, adsorption of limited amounts of CO is possible even on a closed D$_{\text{ad}}$ layer on Ru(0001) and on Pt free parts of the Ru surface. This leads to exceptionally high combined coverages and an additional destabilization of the coadsorbed species. Pre–adsorbed D$_{\text{ad}}$ has the strongest influence on CO adsorption on Ru(0001) and on Pt films with low Pt coverage (≤ 0.3 ML Pt), on Pt films saturated with D$_{\text{ad}}$, both the initial sticking coefficient $s_0$ and the maximal CO$_{\text{ad}}$ coverage increase with increasing Pt coverage. This is trend can be explained by the considerably weaker D$_{\text{ad}}$ binding energy on Pt islands (compared to the Pt free Ru surface) which leads to a decreasing initial D$_{\text{ad}}$ coverage and facilitates the displacement of D$_{\text{ad}}$ by post–adsorbed CO$_{\text{ad}}$. 


For the same reason, the influence of pre–adsorbed CO\textsubscript{ad} on D\textsubscript{2} adsorption increases considerably with increasing Pt coverage.

The CO\textsubscript{ad} spill–over from Pt islands to the Ru areas, which occurs during the temperature increase at the start of the TPD experiment, leads to an additional destabilization of the D\textsubscript{ad} adsorbed on the bare Ru areas. This in turn leads to the formation of a new D\textsubscript{2} desorption feature ~100 K lower than the D\textsubscript{2} desorption peak found for desorption of D\textsubscript{2} only.

Displacement experiments showed that limited displacement of D\textsubscript{ad} by post–exposure to CO is possible at 90 K for Pt coverages above 0.3 ML. The displacement of D\textsubscript{ad} on these surfaces is limited only to the first Pt layer and does not take place on the Ru areas or the second Pt layer. At 100 K, the Pt free parts of the Ru substrate in general display similar properties with regards to CO/D\textsubscript{2} coadsorption as the pure Ru(0001) surface. The presence of Pt islands on the surface, however, results in an effect which is absent on Ru(0001). At higher temperatures (~150 K) diffusion of CO\textsubscript{ad} from Pt islands to the Ru areas results in an additional destabilization of D\textsubscript{ad} on the Ru parts of the surface, leading to either direct desorption of D\textsubscript{ad} or (less likely) to a displacement of D\textsubscript{ad} on the Pt islands followed by desorption. At 150 K, this results in almost complete displacement of D\textsubscript{ad} by post–adsorbed CO, with 0.05 – 0.07 ML D\textsubscript{ad} remaining on the surface. On pure Ru(0001), where this mechanism is absent, complete displacement of D\textsubscript{ad} by CO is possible only at temperatures of ≥ 250 K. Experiments with the reverse dosing sequence showed that pre–adsorbed CO cannot be displaced by D\textsubscript{2} post–exposures up to 10\textsuperscript{5} mbar•s at pressures up to 10\textsuperscript{−5} mbar at any temperature.
5. Summary

In this thesis the interactions of PdRu/Ru(0001) surface alloys and of Pt/Ru(0001) thin films with deuterium and CO were investigated under UHV conditions. The PdRu surface alloy consists of clustered Pd atoms embedded in the topmost Ru layer, while the Pt film surfaces are composed of compact Pt monolayer islands and step decorations on the Ru(0001) substrate. It was demonstrated that for both investigated bimetallic surfaces the two components possess distinctly different properties regarding adsorption of deuterium and CO. The Pd and Pt parts of the surface displayed significantly lower adsorption energies for both probe molecules, compared to the Pd(111) and Pt(111) surfaces. This was explained by strain and electronic effects resulting from the formation of the bimetallic surfaces. Pd islands in the PdRu surface alloy as well as Pt film islands show a structure which is pseudomorphous with regards to the underlying Ru(0001) substrate. For both metals, this results in considerable compressive lattice strain, since the lattice distance of the Ru(0001) surface is smaller than that of the (111) surfaces of Pd and Pt. A second effect playing a role in the modification of adsorption properties of Pd and Pt as parts of a bimetallic surface is the electronic interaction with the atoms of the Ru(0001) substrate. Both effects result in a down–shift of the d–band centre of the Pd and Pt atoms, which in turn leads to weaker interaction with adsorbed CO and deuterium. Interestingly, while the lattice strain imposed by the Ru(0001) substrate is considerably stronger for Pt than Pd (2.8% vs. 1.8%), both metals show an approximately similar lowering of the adsorption energy for CO and deuterium (compared to the pure (111) surfaces). This has been tentatively attributed to a stronger electronic interaction between Pd and the Ru(0001) substrate.

For CO adsorption, mixed ensemble effects were found to be negligible for both bimetallic surfaces. For the PdRu surface alloy this is partially a result of the segregation observed for the metals which make up the surface alloy, resulting in a limited number of mixed ensembles. Additionally, CO displays a strong preference for adsorption in the on–top configuration on Ru, which prevents adsorption on mixed ensembles. On the Pt film surface which consists of Pt islands on the Ru(0001) substrate, practically no mixed ensembles are present.

While the differences in adsorption energies on the pure Pd(111) and Pt(111) surfaces and on the respective parts of bimetallic surfaces were similar for D₂ and CO, the overall effect on adsorption was considerably more pronounced for D₂. COₐd saturation coverages on
bimetallic surfaces were hardly influenced by increasing Pd fractions or Pt coverages. Additionally, the CO adsorption kinetics showed little difference between adsorption on pure monometallic surfaces and the bimetallic surfaces, CO was found to adsorb via a precursor mediated adsorption mechanism in every case. Conversely, the deuterium saturation coverages and sticking coefficients show a pronounced decrease upon the addition of Pd or Pt to the Ru(0001) surface. This has been attributed to an increase of the activation barrier for adsorption on the Pd and Pt parts of the surface, caused by the down–shift of the d–band centre.

An additional effect which was observed on both bimetallic surfaces for both probe molecules is a slight shift of the Ru–related desorption features to lower temperatures compared to Ru(0001). This shift increases with increasing Pd fraction and Pt coverage, indicating a continuous decrease of adsorption energy on the Ru part of the surface. While the origins of this effect are not clear at the moment, literature data indicates that this is a general effect which is found on many bimetallic surfaces.

Furthermore it was shown in Section 4.3 that CO adsorbed on Pt islands of the Pt/Ru(0001) surface at 90 K, migrates to the Pt free Ru areas upon annealing to 150 K, driven by the difference in adsorption energies on Pt and Ru. This effect was observed even for surfaces nominally saturated with CO\textsubscript{ad}, leading to CO\textsubscript{ad} coverages on the Ru areas that are higher than the CO\textsubscript{ad} saturation coverage on pure Ru(0001). From this, it has been concluded that the CO saturation coverage on Ru(0001), which can be reached via adsorption from the gas phase under UHV conditions, is limited kinetically rather than thermodynamically. On the Pt/Ru(0001) surface diffusion of CO\textsubscript{ad} at 150 K offers a second pathway, which, due to a lower activation barrier allows the adsorption of additional CO on the Pt free areas of the Ru(0001) substrate. Literature data suggests that this may be a general effect in place on various bimetallic surfaces. For D\textsubscript{2}, no corresponding effect was observed, since surface diffusion of D\textsubscript{ad} is activated already at 90 K on the Pt/Ru(0001) surfaces. This is an interesting property of bimetallic surfaces which allows the uptake of higher CO\textsubscript{ad} coverages even on surfaces where the adsorption energies of CO are lower on the bimetallic surface compared to the pure constituents. The higher CO\textsubscript{ad} coverage however, is limited to the stronger binding surface component.

In Section 4.4, effects of coadsorption of D\textsubscript{2} and CO on Pt/Ru(0001) surfaces were examined. The pre–exposure of the sample surface to one species was observed to block the subsequent
adsorption of the respective other species. However, while no D\textsubscript{2} adsorption was possible on surfaces saturated with CO\textsubscript{ad}, limited CO adsorption was still possible on surfaces saturated with D\textsubscript{ad}. This was found to lead to total combined coverages which considerably exceeded coverages resulting from separate adsorption of CO and D\textsubscript{2}. Repulsive interactions between D\textsubscript{ad} and CO\textsubscript{ad} within the coadsorbate layer lead to a significant decrease of the adsorption energy of coadsorbed D\textsubscript{ad}. For the exposure sequence where CO is dosed on a pre–adsorbed D\textsubscript{ad} layer this leads to the displacement of considerable amounts of D\textsubscript{ad} from bimetallic surfaces at 90 K. Because of this, increasing Pt coverages lead to an increase in CO\textsubscript{ad} coverages which can be achieved on bimetallic surfaces pre–covered with D\textsubscript{ad}. In general, the influence of D\textsubscript{ad} on coadsorbed CO\textsubscript{ad} was found to decrease with increasing Pt coverage, while the reverse is true for the influence of CO\textsubscript{ad} on coadsorbed D\textsubscript{ad}. This was explained by the progressively weakened adsorption of D\textsubscript{2} caused by increasing Pt coverage.

While CO post–exposure of pre–adsorbed D\textsubscript{ad} layers leads to the displacement of limited amounts of D\textsubscript{ad} at 90 K from the Pt islands, no evidence was found for D\textsubscript{ad} displacement from Ru areas. In coadsorption experiments conducted at 150 K, CO post–exposure leads to essentially complete displacement of pre–adsorbed D\textsubscript{ad} from both parts of the surface. Conversely, exposure of pre–adsorbed CO\textsubscript{ad} layers to D\textsubscript{2} showed no evidence of CO\textsubscript{ad} displacement up to exposures of 10\textsuperscript{5} mbar·s D\textsubscript{2} at pressures up to 10\textsuperscript{−5} mbar at any temperature.

The combined results of adsorption experiments on the PdRu/Ru(0001) and Pt/Ru(0001) surfaces show that while the adsorption of both D\textsubscript{2} and CO is weakened compared to the pure metallic surface components, the effect is in general considerably more pronounced for D\textsubscript{2} than for CO. Unlike in the case of CO, for D\textsubscript{2} the combination of two metals has a negative impact on the maximum coverage as well as on the adsorption kinetics. Most likely this is caused by an activation barrier for D\textsubscript{2} adsorption on the weaker binding part of the surface. In the case of CO and D\textsubscript{2} coadsorption on Pt/Ru(0001), the interactions between the two adsorbates lead to an additional destabilization of D\textsubscript{ad}, causing increasing displacement/blocking of D\textsubscript{ad} by CO with increasing Pt coverage.

In conclusion, this work is a significant contribution to the understanding of chemical properties of bimetallic surfaces, especially the adsorption behaviour towards CO and D\textsubscript{2}, including the interplay of the two surface components during adsorption/desorption processes. Combined with other studies, it elucidates the influence of different surface morphologies on
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the adsorption behaviour of these surfaces. Additionally, comparison of the results to literature data shows that several phenomena, which have previously been described separately for different bimetallic surfaces, are likely a common feature of many bimetallic systems. In view of the results of the D$_2$/CO coadsorption experiments, especially regarding the high CO tolerance of PtRu electrodes in PEMFC applications, further experiments should be carried out in order to investigate the coadsorption under realistic pressures and with realistic compositions of the gas phase.
6 Zusammenfassung


Für die Adsorption von CO erwiesen sich Ensemble-Effekte als vernachlässigbar. Im Fall der PdRu-Oberflächenlegierung ergibt sich dies zum Teil aus der teilweisen Segregation der Pd- und Ru-Atome in der Oberfläche, was nur zu einer begrenzten Menge an gemischten Ensembles führt. Zusätzlich adsorbiert CO auf Ru bevorzugt in der on-top Konfiguration, was Adsorption auf gemischten Ensembles verhindert. Auf den Pt-Film-Oberflächen, die aus Pt-Inseln auf Ru(0001) bestehen, gibt es praktisch keine gemischten Ensembles.
Zusammenfassung


Des Weiteren wurde in Abschnitt 4.3 gezeigt, dass auf den Pt-Inseln der Pt/Ru(0001)-Oberfläche bei 90 K adsorbiertes CO beim Heizen auf 150 K auf die Pt-freien Ru-Flächen diffundiert, angetrieben durch den Unterschied der Adsorptionsenergien auf Pt und Ru. Dieser Effekt wurde auch auf Oberflächen festgestellt, die nominell mit CO\textsubscript{ad} gesättigt waren. Auf den Ru-Flächen führt dies zu CO\textsubscript{ad} Bedeckungen die über der Sättigungsbedeckung auf reinem Ru(0001) liegen. Daraus wurde gefolgt, dass CO-Sättigungsbedeckung auf Ru(0001) unter UHV-Bedingungen nicht durch Thermodynamik, sondern durch Kinetik begrenzt ist. Auf der Pt/Ru(0001)-Oberfläche bittet die Diffusion von CO\textsubscript{ad} bei 150 K einen zusätzlichen Pfad, der auf Grund einer kleineren Aktivierungsbarriere die Adsorption von zusätzlichen CO auf den Pt-freien Teilen des Ru(0001) Substrats erlaubt. Ergebnisse aus der Literatur deuten darauf hin, dass dies ein allgemeiner Effekt ist, der auf mehreren bimetallischen Oberflächen zu finden ist. Für D\textsubscript{2} wurde kein entsprechender Effekt gefunden,
da die Oberflächendiffusion von $D_{ad}$ schon bei 90 K aktiviert ist. Diese interessante Eigenschaft einiger bimetallischer Oberflächen erlaubt die Adsorption von größeren Mengen CO selbst auf Oberflächen mit Adsorptionsenergien, die deutlich unter den Adsorptionsenergien der reinen Komponenten liegen. Diese höheren CO$_{ad}$ Bedeckungen beschränken sich allerdings auf die stärker bindende Oberflächenkomponente.

In Abschnitt 4.4 wurde die Koadsorption von $D_2$ und CO auf Pt/Ru(0001) untersucht. Das Vorbelegen der Probenoberfläche mit einer Spezies blockiert die Oberfläche für die Adsorption der jeweiligen anderen Spezies. Während Adsorption von $D_2$ auf einer mit CO$_{ad}$ gesättigten Oberfläche nicht möglich ist, findet auf mit $D_2$ gesättigten Oberflächen immer noch Adsorption von kleineren Mengen CO statt. Daraus resultieren Gesamtbedeckungen ($D_{ad} + CO_{ad}$), die deutlich über den Sättigungsbedeckungen liegen, die sich aus der separaten Adsorption von $D_2$ und CO ergeben. Repulsive Wechselwirkungen zwischen $D_{ad}$ und CO$_{ad}$ innerhalb der Koadsorbatschicht führen zu einer deutlichen Schwächung der Adsorptionsenergie von $D_{ad}$. Das Dosieren von CO auf eine mit $D_{ad}$ vorbelegte bimetallische Oberfläche führt deshalb zur teilweisen Verdrängung von $D_{ad}$ bei 90 K. Aus diesem Grund führt eine Erhöhung der Pt-Bedeckung dazu, dass größere Mengen an CO auf mit $D_{ad}$ vorbelegten bimetallischen Oberflächen adsorbieren. Im Allgemeinen reduziert sich der Einfluss von $D_{ad}$ auf koadsorbiertes CO$_{ad}$ mit steigender Pt Bedeckung, das Gegenteil trifft auf den Einfluss von CO$_{ad}$ auf koadsorbiertes $D_{ad}$ zu. Dies ist auf die zunehmende Schwächung der $D_2$-Adsorption mit steigender Pt-Bedeckung zurückzuführen.

Während das Dosieren von CO auf eine mit $D_{ad}$ vorbelegte Oberfläche zu einer teilweisen Verdrängung von $D_{ad}$ von den Pt-Inseln führt, wurden keine Hinweise darauf gefunden, dass $D_{ad}$ von Ru-Flächen verdrängt wird. Entsprechende Koadsorptionsexperimente, die bei 150 K durchgeführt wurden, führen zu einer vollständigen Verdrängung von vorbelegtem $D_{ad}$ von beiden Teilen der Oberfläche. Im umgekehrten Fall, wurde beim Dosieren von $D_2$ auf eine mit CO$_{ad}$ vorbelegte Oberfläche, bei Angeboten bis zu $10^2$ mbar·s und Drücken bis $10^{-5}$ mbar, bei keiner Temperatur eine Verdrängung von CO$_{ad}$ festgestellt.

Die kombinierten Ergebnisse der Adsorptionsperimente auf PdRu/Ru(0001) und Pt/Ru(0001) zeigen, dass während eine Schwächung der Adsorption sowohl für $D_2$ wie auch für CO auftritt (vergleichen mit den entsprechenden monometallischen Oberflächen), dieser Effekt im Fall von $D_2$ deutlich stärker ausgeprägt ist. Anders als beim CO, wird im Fall von $D_2$ eine deutliche Verringerung der $D_{ad}$ Maximalbedeckung, so wie auch des
Zusammenfassung

Haftkoeffizienten mit steigendem Pd- bzw. Pt-Anteil festgestellt. Die wahrscheinlichste Ursache hierfür ist die Ausbildung einer Aktivierungsbarriere für die D₂ Adsorption auf dem schwächer bindenden Teil der Oberfläche. Im Fall der Koadsorption von D₂ und CO auf Pt/Ru(0001), führen die Wechselwirkungen zwischen den beiden Adsorbspezies zu einer zusätzlichen Destabilisierung von D_ads, was mit zunehmender Pt Bedeckung zunehmend zu einer Blockierung/Verdrängung von Deuterium durch CO führt.

7. Appendix

7.1 Data validation for experiments on Pt/Ru(0001)

In view of the experimental problems described in Section 3.4 it appeared necessary to test the reproducibility of the experiments presented in Sections 4.2 and 4.4 (CO and D₂ adsorption and coadsorption on Pt/Ru(0001) submonolayer films). One way to do this is to compare the features of CO and D₂ TPD spectra recorded during the separate adsorption experiments (Section 4.2) with the features of the pure CO and D₂ spectra recorded in the coadsorption series of experiments (Section 4.4). Since the Pt coverages in both series mostly do not correspond, it is sensible to compare the trends for peak maxima, leading and trailing edges of both series of TPD spectra with varying Pt coverages. Figure 7.1 displays these features for the CO TPD spectra. It is a combination of Figure 4.9 which showed the features of the TPD spectra from the CO adsorption series (full symbols), complemented by features of CO spectra recorded during the coadsorption experiments (empty symbols). The temperatures of the main features of the various TPD spectra of both series of experiments follow the same trend. With increasing Pt coverage, the deviations between data points of the two series are not larger than between data points within each respective series. Unlike in the case of CO, D₂ TPD spectra are modified by coadsorbed CO, which makes it impossible to tabulate TPD features after small D₂ exposures for the coadsorption series. Figure 7.2 therefore displays trends for peak maxima, leading and trailing edges for D₂ adsorption on different parts of the bimetallic surfaces after the maximal D₂ exposure used in the coadsorption experiments (40×10⁻⁶ mbar·s). As in the case of CO the data points for D₂ adsorption from the two different series of experiments follow the same trend with increasing Pt coverage, indicating a sufficient degree of reproducibility for CO and D₂ adsorption on the investigated bimetallic surfaces. Another data point to compare between the two series of experiments is the saturation/maximal coverage of both adsorbates on surfaces with different Pt coverages. As shown in Figure 7., the coverage trends for D₂ match very well, for CO there are small deviations in the range of 0.2 – 0.5 ML Pt, these, however, are well within the error bars.
Figure 7.1: Temperature shifts of the prominent CO TPD features from (a) the Ru part and (b) the Pt monolayer islands/Ru(0001). (a) Ru part: leading edge (▼), peak maximum (●) and trailing edge (▲) after the smallest CO exposure ($e_{\text{CO}} = 0.15 \times 10^{-6}$ mbar·s); and $\alpha_1$ peak maximum after CO$_{ad}$ saturation (■). (b) Pt monolayer islands/Ru(0001): leading edge (▼), $\beta_1$ (♦) and $\beta_3$ (■) peak maximum after CO$_{ad}$ saturation. Full symbols: results from adsorption experiments (Section 4.2), empty symbols: results from coadsorption experiments (Section 4.4).
Figure 7.2: Temperature shifts of the prominent D₂ TPD features from (a) the Ru part and (b) the Pt monolayer islands/Ru(0001). (a) Ru part: leading edge (▼), peak maximum (■) and trailing edge (▲) after a D₂ exposure of $40 \times 10^{-6}$ mbar s; (b) Pt monolayer islands/Ru(0001): leading edge (▼), peak maximum (■) and trailing edge (▲) after a D₂ exposure of $40 \times 10^{-6}$ mbar s. Full symbols: results from adsorption experiments (Section 4.2), empty symbols: results from coadsorption experiments (Section 4.4).
Figure 7.3: (a) CO saturation coverages at 90 K, (■) CO adsorption experiments (Section 4.2), (□) coadsorption experiments (Section 4.4); (b) maximal D$_2$ coverages at 90 K ($\varepsilon_{D_2} = 40\times10^{-6}$ mbar·s), (■) D$_2$ adsorption experiments (Section 4.2), (□) coadsorption experiments (Section 4.4).
One important question is whether the sticking probability or the dependence of coverage on exposure matches between the two series. Figure 7.4 shows the trends of $D_{ad}$ coverage vs. $D_2$ exposure for Pt coverages of 0 – 0.35 ML. At higher Pt coverages post–exposure to CO leads to partial displacement of $D_{ad}$, which makes it impossible to compare data recorded on surfaces with higher Pt coverages. The trends in the investigated Pt coverage range, however, match very well. The fact that the $D_{ad}$ coverage on 0.35 ML Pt is slightly lower for the coadsorption experiment than the $D_{ad}$ coverage on 0.3 ML Pt recorded in the adsorption experiment, this can likely be attributed to the slightly higher Pt coverage.

Figure 7.4: $D_2$ coverage vs. $D_2$ exposure for different Pt coverages. (■) Ru(0001), (●) 0.1 ML Pt, (▲) 0.3 ML Pt (0.35 for coadsorption). Full symbols: adsorption experiments (Section 4.2), empty symbols: coadsorption experiments (Section 4.4). The error bars are left out in order to decluter the graphic.

Figure 7.5 shows the same data for CO adsorption, similar to the $D_2$ data the trend for the two series of measurements correspond very well. The most obvious deviation is observed for the Pt coverage of 0.2/0.25 ML for CO exposures above $\sim 4 \times 10^{-6}$ mbar·s. A similar deviation is observed in Figure 7. for CO saturation coverages in this Pt coverage range, both times, however, the data points are within the respective experimental error bars.
A final point to consider is the stability and possible contamination of the investigated surfaces during an experimental sequence. In order to test for these effects, a D$_2$ TPD spectrum was recorded at the beginning and end of each sequence with the maximum D$_2$ exposure of 40×10$^{-6}$ mbar·s. Selected results of the coadsorption experiments are presented in Figure 7.6. The changes in the spectra for the respective Pt coverages are rather small and do not seem to follow a clear trend. The greatest change is observed for the medium Pt coverage of 0.5 ML, this change consists of a slight decrease in intensity of the high temperature (Ru related) feature, concomitant with a slight shift of the high temperature edge. Conversely the low temperature (Pt related) feature shows a slight increase in intensity and no temperature shifts. The origin of these changes is difficult to determine, the loss of intensity in the Ru
related feature might be ascribed to a contamination of the surface, possibly with carbon from traces of decomposing CO. However, the fact that the Pt related feature shows a slight increase in intensity makes this unlikely. In any case, the changes between the initial and final spectrum within an experimental sequence seem to be negligible.

**Figure 7.6:** $^2$D$_2$ TPD spectra ($^2$D$_2 = 40 \times 10^{-6}$ mbar s) recorded before (—) and after (---) the coadsorption experiment series on surfaces with different Pt coverages (given in the panels).
7.2 TPD spectra recorded during CO sticking coefficient measurements

**Figure 7.7:** TPD Spectra recorded after a D\(_2\) pre-exposure of 80×10\(^{-6}\) mbar·s followed by varying CO exposures for the CO sticking coefficient measurements in Section 4.4.4.7. Left column: CO, right column: D\(_2\). CO exposures ×10\(^{-6}\) mbar·s: 0.15, 0.53, 1.05, 1.5, 3, 4.5, 30.
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