Interaction of adsorbates with clean and metal-covered oxide surfaces: Vibrational spectroscopic studies

Dissertation

by

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Preface:

When I was a child I had a dream—to be a scientist like Albert Einstein and Niels Bohr, although it seems naive and impossible in today's research framework. Time elapses unconsciously, however I go far away from my dream more and more. But I don't want to give up although I have become old.

During the last three and half years I encountered many difficulties in my work. Especially, when I reached the end of my PhD study, I found it's very difficult to make clear even a very tiny problem. I can even imagine I was driving a small boat in the boundless sea of knowledge.

Yes, I have finished my PhD work and got many results. But I don't want to write this thesis like a result show, although, perhaps, no one would care about it except for publications. After finishing this thesis, I just hope it is worth of reading and can help its readers, if possible, to some extent, at least help them to think about the underlying problems in this thesis.

Thanks to my forthcoming daughter, she drove me to improve myself and write this thesis as soon as possible.

25.05.2009, Bochum
This thesis is partially based on following publications:

Chapter 3. Adsorption and Reactions on ZnO(10\overline{1}0)


Chapter 4. Adsorption on TiO$_2$(110) surface


Chapter 5. Adsorption on ZnO(000\overline{1}) surface


Other publications:


1. Introduction .................................................................................................................. 3
   1.1 General remarks ........................................................................................................... 3
   1.2 What can we do in surface science studies? ................................................................. 4
   1.3 From metals to metal oxides ........................................................................................ 6
   1.4 This thesis .................................................................................................................... 9

2. Experiment .................................................................................................................. 11
   2.1 Experimental setup ..................................................................................................... 11
   2.2 High resolution electron energy loss spectroscopy (HREELS) .................................... 13
   2.3 Thermal desorption spectroscopy (TDS) .................................................................... 16
       Shape analysis ............................................................................................................. 17
       Quantitative analysis .................................................................................................. 18
   2.4 Low energy electron diffraction (LEED) .................................................................. 21

3. Small molecular adsorbates on ZnO(10\text{10}) .................................................... 23
   3.1 CO$_2$ adsorption on the ZnO(10\text{10}) surface ....................................................... 23
   3.2 Co-adsorption of CO and CO$_2$ on ZnO(10\text{10}) surface ..................................... 33
   3.3 H$_2$O adsorption on the ZnO(10\text{10}) surface ......................................................... 37

4. Small molecular adsorbates on TiO$_2$(110) ........................................................... 44
   4.1 CH$_3$O adsorption on the TiO$_2$(110) surface ......................................................... 45
       CH$_3$O Adsorption on the Perfect TiO$_2$(110) Surface .............................................. 47
       CH$_3$O Aadsorption on Defective TiO$_2$(110) Surfaces ............................................. 52
   4.2 H adsorption on the TiO$_2$(110) surface ................................................................ 60

5. Small molecular adsorbates on ZnO(000\text{1}) .................................................... 69
5.1 The structure of the ZnO(000\text{\bar{1}}) surface .................................................................69

5.2 Hydrogen adsorption on the ZnO(000\text{\bar{1}}) surface .......................................................75

5.3 HCOOH adsorption on the ZnO(000\text{\bar{1}}) surface ............................................................83

5.4 CO\textsubscript{2} adsorption on the ZnO(000\text{\bar{1}}) surface ....................................................93

6. Cu deposition on ZnO(000\text{\bar{1}}) ......................................................................................100

   6.1 Structure of Cu clusters on the ZnO(000\text{\bar{1}}) surface ......................................................100

   6.2 The chemical state of Cu on ZnO(000\text{\bar{1}}) surface .......................................................103

   6.3 Diffusion of Cu into ZnO(000\text{\bar{1}}) bulk .........................................................................105

7. Summary and outlook ........................................................................................................110

    7.1 Summary ............................................................................................................................110

    7.2 Outlook ............................................................................................................................113

Appendix 1: Discussion on the effect of Titanium sublimation pump (TSP) on CO\textsubscript{2} adsorption experiments .........................................................................................................................114

Appendix 2 Illustrations and symbols of different vibrational modes ........................................118

Appendix 3: Fourier deconvolution process of HREEL spectra .............................................119

Appendix 4: Shape analysis of TD spectra—some examples ..................................................124

Appendix 5: Discussion on the expression of density of electrons in conduction band for doped semiconductor ..........................................................................................................................127

Bibliography ..........................................................................................................................129

Acknowledgements ..............................................................................................................143

Curriculum Vitae ..................................................................................................................144
1. Introduction

1.1 General remarks

The term catalyst was first introduced by Berzelius in 1835 referring to certain substances that accelerate a chemical reaction without being consumed during the reaction [1, 2]. Since then, catalysts have dramatically changed our daily life. However, until the 1960s, most work on finding catalyst was more empirical, i.e. experience-based [2]. A more straightforward or more scientific way was developed by surface science studies after the emergence of high-vacuum and electronic spectroscopic techniques. Understanding of catalytic processes on elemental level has become the heartland for exploring a new catalyst in the last several decades [1-7].

Along with the development of more complex catalytic processes, the presence of unexpected but inevitable side-products causes more and more problems. As a result, besides the original “catalytic” performance, the selectivity has become the other criterion for evaluating new catalysts [4, 8].

Although a certain reaction can be thermodynamically favorable from an energy point of view (ΔG < 0), the reaction rate is still a key point for a real industrial reaction. For instance, the reaction:

\[ CO (g) + 3H_2 (g) \rightarrow CH_3OH (l) \quad \Delta H = -128.5 \text{ kJ/mol and } \Delta G = -29.5 \text{ kJ/mol at } T = 298 \text{ K} \]

is thermodynamically favorable close to room temperature [9], but high reaction temperature and high pressure were still adopted in real processes to achieve relatively high reaction rates and reaction yields. Given enough time, any reaction (along with side reactions) will finally reach equilibrium with the distribution of all products depending on the change of ΔG in possible reaction pathways by an exponential relationship [10-12]. The largest fraction consequently comes from the lowest energy-containing product.

The reaction rate, based on the transition state theory (TST) [11, 12], is essentially related with kinetic barriers (or reaction barriers) and reaction temperature. To
increase reaction rate, one needs to increase the reaction temperature or decrease reaction barriers [5]. From an economical point of view, to decrease the reaction barrier would be a more feasible way since the increasing of temperature is a much energy-costly approach. The reaction barrier varies according to reaction pathways in which different intermediates could be presented. This fact provides chemists the possibility to find a catalyst that would guide the reaction along a different pathway with a smaller reaction barrier. From this aspect, the study of selectivity, in nature, is also a case of changing reaction barriers, but increasing the barrier for side reactions compared to the desired reactions [4]. In other words, catalyst changes the product distribution in addition to accelerating reaction rate. Additionally, the study of elevating reaction rates is often accompanied by the aim to avoid extreme reaction conditions (high temperature, high pressure etc.), which would be the same concept from an energy point of view.

Nowadays, most industrial catalytic processes are based on heterogeneous catalysis typically involving solid catalysts and gaseous or liquid reactants [2]. Heterogeneous catalytic processes may include four elementary steps [1]: (a) adsorption, (b) diffusion, (c) molecular rearrangement at active sites, (d) desorption. Herein, a good catalyst is considered to form intermediates with reactants not too strongly but also not too weakly bound. Too strong bonding leads to either a long residence time of the intermediate resulting in the decrease of reaction rate, or the blockage of the active sites resulting in the deactivation of the catalyst. Too weak bonding tends to cause desorption prior to the desired molecular rearrangement.

1.2 What can we do in surface science studies?
“Surface science” has been one of the most active research fields in the past years. This is partially due to the unique structural and electronic properties of surfaces after breaking the periodicity of bulk materials, and partially due to the development of vacuum techniques and surface analytic methods. One should also recall the fact that the most relevant existing catalytic processes, i.e. those heterogeneous ones with solid catalysts, take place at surfaces. In addition, besides the traditional “surface study”,
brand new electronic, catalytic and optical properties of electrons behaving in a confined dimension extend the surface study to a new perspective, including the study of thin films, nano-particles dispersed on surfaces.

King gave a summary of the methodological questions in the surface science approach to catalysis [13]:

(i) Where are the atoms comprising the surface? Why are they there? What structural changes accompany the surface processes?
(ii) What are the bond energies involved? What is the nature of the surface chemical bonds?
(iii) What factors control the bond making the breaking processes at surfaces?
(iv) How can these bond making and breaking processes be controlled?

In these questions, all the “what” and “where” questions can be answered by experimentalists individually, and even solely by theorists to a certain extent. But the “why” and “how” questions can only be answered through the combined efforts by experimentalists, theorists and engineers.

To my understanding, the role of experimental surface science studies is two-fold: interplay with the theory to understand the microscopic mechanisms of specific catalytic processes and interplay with the real catalysis to improve the catalytic efficiency. The theoretical and computational scientists build new theoretical models or calculation methods to explain the existing catalytic phenomena and even to predict the new catalysts with new properties. But, the fact that even the only-theory-based calculation, namely, the ab intio calculation, still treats theory with approximations to make the calculation feasible [14, 15], means that experimental results, especially on well-defined surface, are potentially needed to get a reasonable theoretical model.

From this aspect, the experimental surface science is not the end of studying catalysis, but the beginning. Generally, useful information derived from experimental surface science study can be on the adsorption geometry, adsorption site, adsorbate species, reaction barriers, reaction intermediates, binding energy, and surface structural and electronic properties. On the other hand, surface science studies should help engineers to understand reaction mechanisms and find the best way to improve catalytic
efficiency, including reaction yields, selectivity, depollution and avoiding of existing extreme reaction conditions, etc. However, one should be aware that most of surface studies are performed in ultra-high vacuum (UHV) conditions on well-defined single crystal surface, which inevitably causes the so-called “pressure gap” and “material gap” problematic between study conditions and catalytic application conditions [2, 16]. For the material gap, one must consider the existence of abundance of defects and grain bundaries on powder in contrast to the well-defined structure on single crystal. New model with extracting the structure-sensitive reaction could help to understand the inconsistency obtained on powder and on single crystal samples. For the pressure gap, the extrapolation from UHV to real catalytic condition is not always an effective way to bridge the gap since some new phases could arise when the pressure is increased by more than ten orders of magnitude [17]. This is because in UHV condition the reaction pathway with high barrier is not preferred although the product might contain relatively low free energy. Indeed, much effort has been spent to bridge these two gaps in the recent three decades, including the inherently efficient methods operating at more realistic conditions [18-20], sum frequency generation (SFG) and polarization-modulation infrared absorption spectroscopy (PM-IRAS), and the specially designed UHV apparatus [20-23].

Two kinds of study viewpoints about surface bonding mechanism provide the principal possibility to study adsorption on surfaces: (a) localized characters of the chemical bond between surface and adsorbates. This provides experimentalists the possibility to recognize adsorbed species using fingerprint techniques such as vibrational spectroscopy and photoelectron spectroscopy etc. (b) de-localized electron redistribution between surface and adsorbates. As a result, the study of surface electronic structure (valence and core level) plays an important role to investigate surface reactions. In fact, a comprehensive understanding would include both, just as the real system behaves.

1.3 From metals to metal oxides
Since the emergence of the techniques of high vacuum apparatus and electronic
spectroscopy the surface science approach to catalysis has been extensively developed. But most of the studies were carried out on metal substrates [1], whereas the information on oxide surfaces is still scarce due to experimental difficulties. In general, the difficulties include: (a) poor conductivity of oxides, which may lead to charge accumulation on the surface and cause the measurement to become invalid or deviate from the intrinsic value. (b) space charge regions. This is the consequence of poor conductivity and surface states (including intrinsic due to the breaking of periodicity and local molecular orbital and extrinsic due to the adsorbates or defects). The existence of space charge regions in oxide can affect on the surface chemical properties and makes the analysis more complicated. (c) poor quality of the surface structure. The partial segregation and desorption of oxygen atoms during the preparation process causes an imperfect stoichiometry of surface and near surface atoms, and in turn an uncertainty in the surface structure. This is more severe for a polar oxide surface in which the electrostatic instability can further result in a surface reconstruction, vacancies or steps on the surface. (d) intense surface phonons are a particular issue for vibrational spectroscopy as very strong surface phonons exhibit overwhelming domination of measured spectra and in some cases convolute with the vibrations of adsorbates to “create” new peaks in measured spectra.

Recently, studying oxides has become more active stimulated either by research interest for the metal/support interactions or by their catalytic activities themselves. At the same time, on the experimental side, researchers have adopted thin oxide films on metal substrate to avoid charge effect [24-26]. And some other analytical methods, such as molecular beam scattering (MB) [27, 28] and atomic force microscope (AFM) [29, 30] studies, become active due to the inherent insensitivity to charge effect.

Oxygen vacancies on oxide surfaces have been proposed to be important in dominating surface chemical properties. Studies of adsorption and reaction on intrinsic or artificially created oxygen vacancies on oxide surfaces has become blooming [31-33]. Even the self-organization of oxygen vacancies by electron induction has been reported [34], which has significance for fundamental and technical research. Besides, the presence of bulk interstitial defects can potentially
affect on the surface electronic and chemical properties [35, 36].
The study of metal nano-particles on oxide surfaces or metal diffusion into oxide bulk with forming doping effect has also attracted many research interests. On one hand metal nano-particles exhibit themselves excellent catalytic properties. Perhaps, this is owing to the good balance of less-coordination and band (orbital) dispersion of metal particles in the nanometer dimension. Too small metal particles have more un-coordinated orbitals in per unit volume but more strict requirement for the reactant orbitals due to the relatively monochromatic orbital energy level (horizontal line in energy diagram). Too large metal particles have higher orbital energy dispersion [37], but lower electron energy (lower position in energy diagram) and less uncoordinated orbitals. On the other hand the interaction between metal particles and the oxide support leads to a further change of electronic properties especially at the interface – although in some cases the mechanism is not well understood yet.
The diffusion of metal into oxide bulk leads to the change of electronic and photocatalytic properties, which has been one of the major focuses in semiconductor industry and photocatalysis in recent years. But the doping effect on “traditional” catalytic properties was rarely studied. This is understandable because the chemical bond between adsorbates and solid surface was considered quite localized while the ionized “donor” electrons are more delocalized. Indeed the delocalized electrons have less influence on the bonding upon gas adsorption to a lesser extent since the electron affinity of semiconductor (or insulator) is thought nearly independent of the position of Fermi level. This means the incoming adsorbate needs to align its orbital energy in a same value with respect to the oxide surface independent of the bulk doping [38, 39]. However, the doping can essentially change the electron distribution and consequently charge transfer between the solid surface and adsorbates if the adsorbate orbital is considered as a part of the solid. Although, in many cases, the Fermi level is pinned by a surface state, one should still be aware that the pinning of the Fermi level is always accompanied by the filling (or unfilling) of electrons in surface states including those created by adsorbates. In principle, the charge redistribution (or charge transfer) between solid surface and adsorbates can lead to certain effects on the
chemical bonds formed between them. Anyway, studying doping effect on the chemical properties of solid surface is a very interesting topic and worth of research attentions.

1.4 This thesis

All of this work is performed in the context of the collaborative research center SFB 558 “Metal-substrate interactions in heterogeneous catalysis” of the German research foundation (DFG). The case study is to understand microscopic reaction mechanism of the methanol synthesis process. Methanol is synthesized from syn-gas (CO, CO$_2$ and H$_2$) on Cu/ZnO/Al$_2$O$_3$ catalyst [40]. Several possible intermediates were observed or predicted in this reaction, such as formyl, formate, formaldehyde, formic acid and methoxy etc. [41-44]. The influence of H$_2$O on this reaction should also be taken into account since the real reaction is carried out under high-pressure conditions and the presence of H$_2$O is inevitable. In this thesis, the adsorption of syn-gas (CO, CO$_2$ and H$_2$), possible intermediates (HCOOH, CH$_2$O) as well as H$_2$O was studied on ZnO surface, including the non-polar ZnO(1010) and the polar O-ZnO(0001) surface. Gas adsorption on TiO$_2$(110) and on Cu deposited O-ZnO(0001) were also carried out and thus also presented in this thesis.

This thesis is organized as follows:

In chapter 2, the experimental setup (HREELS system) and methods (HREELS, TDS and LEED) are briefly reviewed.

In chapter 3, adsorption of CO$_2$, coadsorption of CO$_2$ and CO, and the H$_2$O adsorption on ZnO(1010) are investigated.

In chapter 4, the behavior of CH$_2$O and hydrogen adsorbed on TiO$_2$(110) is presented.

In chapter 5, the stability of ZnO(0001) is discussed and the adsorption of hydrogen, HCOOH and CO$_2$ on the surface are investigated.
In chapter 6, the structure, chemical state and diffusion to ZnO bulk of Cu clusters deposited on ZnO(000\textbar{}1) are presented.

In chapter 7, a summary of each previous chapter and outlook for future work are provided.
2. Experiment

In this chapter I present a brief introduction to the experimental setup and analytic methods used in this work. For the detailed operation of the setup one would fall back on the operation manual. In the analytic methods section, I will also discard a detailed discussion on principle, but focus more on some tips in terms of utility. The principal details can be found in the mentioned references.

2.1 Experimental setup

![Fig. 2.1 HREELS system used in this work. "PS" denotes "power supply".]

The work in this thesis was carried out in an ultra-high vacuum (UHV) system that contains two chambers, as shown in Fig. 2.1. The upper chamber (also called preparation chamber) is equipped with low energy electron diffraction (LEED) optics, Argon ion sputter gun for cleaning sample surface, mass spectrometer (Pfeiffer, Prisma) for thermal desorption spectroscopy (TDS) experiment, and metal evaporator for deposition of metal films. The base vacuum in upper chamber is $5 \times 10^{-11}$ mbar. The mass spectrometer is placed in the preparation chamber and differentially pumped with an ion getter pump. When carrying out TDS experiments, the sample surface is moved to approach the orifice of a shroud of the mass spectrometer with a distance of about 1 mm. The lower chamber (also called HREELS chamber) holds...
high-resolution electron energy loss spectroscopy (HREELS) (Delta 0.5, SPECS, Germany) with a straight-through resolution close to 1 meV. The incident angle of electron beam is fixed at 55° with respect to the sample surface normal. The rotatable analyzer can be positioned in either specular (reflective angle of 55°) or off-specular geometry. The base vacuum in the lower chamber is $2 \times 10^{-11}$ mbar. To maintain the very good vacuum, a gate valve is installed between the two chambers and kept closed during the preparation of samples.

The UHV chamber is pumped by a turbomolecular pump with large pumping speed (300 l/s) and an oil-free forevavuum system consisting of a small turbomolecular pump combined with a membrane pump. In the HREELS chamber, only an ion getter pump is running routinely. In both chambers there is a titanium sublimation pump (TSP) respectively. The TSP in preparation chamber runs more frequently depending on the vacuum condition. But for some refined experiments by using CO$_2$, the running of TSP should be very careful (see the Appendix 1).

The single crystal sample (usually 2 mm × 5 mm × 7 mm) was mounted on a Ta plate (thickness, 0.5 mm) by specifically designed thin Ta foils, with the thermocouple contacting the sample on the lateral side. Note that mounting sample is a very skill-based operation and special consideration should be paid on the contact between thermocouple (K-type) and sample. A calibration process by a known TDS peak is necessary for a new-mounted sample. The sample temperature can be changed from 90 K (cooled by liquid nitrogen) to 900 K (heated by resistance filament from the backside of the Ta plate).

Dosing of gas is realized by backfilling the chamber through different leak valves that connect the preparation chamber with gas bottles. For liquid sources like H$_2$O, HCOOH and CH$_3$OH, a glass tube with a metal flange to connect with vacuum system is used as container. Before dosing process, the liquid was cleaned by several freezing-melting cycles. For a solid source like N-(hydroxymethyl)-benzamide (decomposition temperature is 95 °C) to produce CH$_2$O, before dosing a degassing process is performed by overnight evacuation at an intermediate temperature (50-60 °C).
2.2 High resolution electron energy loss spectroscopy (HREELS)

As an electronic spectroscopy, HREELS has been proven to be one of the most powerful techniques for studying adsorption and reactions on single crystalline metal surfaces [45-48], electronic structures on semiconductor surfaces [49-51] and Fuchs-Kliewer phonons on oxide surfaces [52-54]. Compared with another wide-used vibrational spectroscopy, infrared (IR) spectroscopy, HREELS has a relative poor energy resolution, but high detection sensitivity. Indeed, the energy resolution of 1 to 5 meV of common-used HREELS, although insufficient for the analysis of the intrinsic vibrational line width [55], is good enough to identify adsorbed species and chemical shifts in most cases.

For the analysis of both IR and HREELS spectra, two selection rules must be considered [56, 57]: (a) Only the vibration with dynamic transition dipole moment is IR-active. (b) On metal surfaces, the vibration with dynamic transition dipole moment parallel to surface is IR-inactive. In fact, this is not the whole story, because HREELS can avoid these two selection rules by the impact interaction mechanism, and in some cases by employing negative ion resonances [58].

Several relevant interaction mechanisms are involved in the energy loss process:

(a) Dipole interaction

This is a long-range interaction between adsorbate dipole moment and electric field of the electron, which results in a very sharp peak close to specular direction in the angle distribution curve of electrons reflected from a surface (see Fig. 2.2). Dipole interaction is the most commonly used mechanism in HREELS to get the vibrational frequency of

![Fig. 2.2 Schematic angle distributions of dipole and impact interactions in HREELS.](image-url)
adsorbed species due to the high intensity and high signal to noise ratio. In this case, the analyzer is positioned in specular geometry and both selection rules take effect.

(b) Impact interaction

This is a short-range interaction between adsorbate and incident electrons. The comprehensive theoretical description is difficult, but we can understand it in a simple way: imagine that electrons transfer energy to adsorbates during the impact process just like the collision between two rigid balls, but in this case the transferred energy is limited to excite the vibration of chemical bonds. As a result, both selection rules don't work for the impact interaction mechanism. But the intensity from impact interaction is very low (two to three orders of amplitude lower than that of dipole interaction) and has a very broad angle distribution (see Fig. 2.2). The study in off-specular geometry provides a feasible way to separate impact interaction from the dipole interaction.

(c) Negative ion resonance

Although the dipole-inactive modes could be detected by off-specular measurements, their extremely weak signals still bring out much experimental difficulty. Another possible way to study the IR-inactive vibrations is negative ion resonance. For example, in a HREELS measurement of an IR-inactive adsorbate, it's possible that electrons are trapped by adsorbates for a short duration to form polar compounds in which vibrations are temporarily IR-active. However, unfortunately, negative ion resonance is rarely observed and unpredictable. The most use is to observe the physisorbed IR-inactive species.

(d) Plasmon excitation

This is a typical case especially for HREELS measurements on doped semiconductor and metal surfaces where the surface plasmons can be detected. It has been reported that the growth of metal particles deposited on oxide surfaces can be monitored by plasmon excitations. For doped semiconductors, if the doping concentration is not so high, a multi-scattering process can be remarkable. As a result, a broadening of the elastic peak can be observed. A quantitative analysis of the peak broadening can further enrich the study of doping process. In addition, the growth of thin films could
also be monitored by plasmon excitations [59, 60].

(e) Inter-band transition

In this case, HREELS is more addressed by the name of “EELS”. In the energy loss processes, besides the just mentioned interaction mechanisms, another contribution comes from the excitation of inter-band transitions. This allows us to study the electronic structures of substrates or even surface states. The scanning range of the energy loss is normally needed to extend to several electron volts (eV) and in this case a high resolution is not so necessary. At the same time, a relative high primary energy (several tens eV) should be adopted in order to compress the angle distribution of the reflected electrons to specular direction. Note also that EELS in this case is slightly different from that in transmission electron microscopy (TEM). In TEM, very high incident electron energy is adopted and the core level excitation is inclined to be concerned due to the relatively poor energy resolution.

![Fig. 2.3 (a) Raw HREEL spectra of 0.5 L CO\textsubscript{2} adsorbed on ZnO(10\overline{1}0) at 95 K. (b) the corresponding deconvoluted results.](image)

Although HREELS has been successfully used to metal surfaces, it encountered several problems when applied to oxide surfaces. In addition to the well-known problems of charge effect and poor surface quality which exist in nearly all electronic spectroscopy, a prominent problem in HREELS is the appearance of the intensive surface phonons on oxide surfaces [52, 53], although the surface phonons are of scientific interest in solid state physics studies [53]. Surface phonons of oxides
(including the multiple scattered phonons) dominate almost all interesting regions for the vibrations of chemical bonds from several tens to several hundreds meV. Fig. 2.3 (a) shows the HREEL spectra recorded on 0.5 L C\textsuperscript{18}O\textsubscript{2} adsorbed on ZnO(10\text{̄}10) at 100 K. No any adsorbate-related loss feature can be observed except for the strong surface phonons.

Most successful attempts to eliminate the effect of surface phonons include the experimental method by growing oxide thin film on metal supports [25, 26], and the numerical method by Fourier deconvolution process [61]. In this work, the latter one was adopted.

Fourier deconvolution process is based on the fact that the multiple scattered phonons can be expressed by a series of self-convolutions of the primary phonon. A numerical method to remove the multiple scattered phonons is possible. As is shown in Fig. 2.3 (b), after the Fourier deconvolution process of the raw spectrum, the HREEL spectrum clearly shows three loss peaks from the adsorbate. Detailed discussions about Fourier deconvolution process can be found in references and Appendix 2. An example for illustration and symbols of different vibrational modes can be found in Appendix 3.

In practical HREELS studies, an isotope substitution experiment is usually helpful to assign loss peaks, and the combination with TDS can provide more detailed information of the surface adsorption process.

### 2.3 Thermal desorption spectroscopy (TDS)

TDS (usually be addressed on single crystals in vacuum condition) or temperature programmed desorption (TPD, usually be addressed on powder samples in ordinary pressure ambient) is one of the most important surface techniques for studying adsorbed species [62-68].

In TDS experiment, sample is heated linearly (in some cases hyperbolic heating is also adopted) to high temperature with the adsorbate molecules desorbing from the sample surface. The desorbing molecules are then collected by a mass spectrometer.
Finally, a curve of desorbing rate with respect to the sample temperature is obtained. The analysis of TDS results is based on the well-known Wigner-Polanyi equation:

\[
R_{des}(\theta) = -\frac{d\theta}{dt} = n \cdot \theta^\nu \cdot \exp\left(-\frac{\Delta E}{RT}\right)
\]

\(R_{des}\)… desorption rate

\(\theta\)… surface coverage

\(n\)… pre-exponential factor

\(\nu\)… reaction order

\(\Delta E\)… activation energy for desorption

When the sample is heated to high temperatures, the exponential term will increase and will make \(R_{des}\) larger, and at the same time adsorbates desorb from sample surface and make \(R_{des}\) smaller (\(\theta\) becomes smaller). As a result, a TD spectrum always shows mountain-like shape. In general, the analysis of TD spectra includes two branches: quantitative analysis and shape analysis. In both cases, a series of TD spectra with different initial coverages are necessary.

Note that the re-adsorption of the desorbing molecules is unlikely on single crystal surfaces in UHV conditions and so is not considered in this work.

**Shape analysis**

Shape analysis can help us to get an overall impression on the adsorption process, such as the number of stable adsorbed phases, reaction order and the presence of lateral interaction. Generally, in TD spectra, the different desorption peaks come from different adsorbed phases each of which has a different binding energy. Further analysis with different initial coverages would bring us a rough impression of the reaction order. For example, with increasing coverages the zero-order desorption (normally desorption of physisorbed species) shows a blue shift of desorption rate maximum \(T_{max}\), whereas the first order desorption shows a constant \(T_{max}\) and an asymmetric shape of the desorption spectra. The second order desorption exhibits a red shift of \(T_{max}\) and symmetric shape of the desorption spectra with increasing coverages.
It is difficult to precisely determine the reaction orders just from the shape analysis, because lateral interactions between adsorbates are mostly present and lead to a coverage-dependent activation energy, $\Delta E$. The increased activation energy with coverage results in a blue shift of the temperature for desorption rate maximum ($T_{\text{max}}$), and vice versa. In some cases (normally for the 2nd order reaction), the coverage-dependent $\nu_n$ should also be considered. Some simulated examples for shape analysis can be found in Appendix 4.

To identify reaction order from TDS results, in many cases, makes sense since reactions don't always take place in the straightforward way as simple as we imagine, i.e., directly from reactant to final product. The possible reaction pathway and intermediates can change the reaction order and control the overall reaction. In other words, the rate-limiting process dominates the overall reaction order and later the observed TDS features. The analysis of reaction order can help us to understand the desorption process. For example, a reaction order of 2 means that the rate-limiting step during desorption is recombination, while a reaction order of 1/2 possibly indicates diffusion and desorption process at step edges.

**Quantitative analysis**

For the precise determination of reaction orders, further confirmation from quantitative analysis is needed. In addition, quantitative analysis of TD spectra can provide the information of one of the most important parameters, activation energy for desorption, $\Delta E$. This value is frequently used as the binding energy since in most cases the adsorption process is non-active or the activation energy of adsorption is so small compared with the binding energy that the former can be reasonably neglected. The quantitative analysis is essentially based on the Wigner-Polanyi equation. In fact, the methods for quantitative analysis are various since it is more like a data fitting process. One can use linear heating or hyperbolic heating for TDS experiments and pick up the $T_{\text{max}}$ or full width at half maximum (FWHM), or even full width at 3/4 maximum as the experimental data to fit the desired parameters [63, 64]. The most simple and widely used method is to use linear heating and fit the parameters by using
\(T_{\text{max}}\) and corresponding initial coverages. In this work, linear heating is adopted, 
\[ T = T_0 + \beta \cdot t, \]
where \(\beta\) denotes heating rate.

First let us assume that the differential pumping rate is constant and high enough, and that the ion current in the mass spectrometer is proportional to the desorption rate for each specific desorbed species. Thus, the temperature for desorption rate maximum, \(T_{\text{max}}\), can be deduced by letting the deviation of desorption rate equal zero (note that in TDS experiment we plot the desorption rate with respect to temperature):

\[
\frac{dR_{\text{des}}(\theta)}{dT} = -\beta \cdot \frac{dR_{\text{des}}(\theta)}{dt} = -\beta \cdot \frac{d^2\theta}{dt^2} = 0 \tag{2.2}
\]

one can get the expression:

\[
\frac{\Delta E}{RT_{\text{max}}^2} = \frac{1}{\beta} \cdot \nu_n \cdot n \cdot \theta^{n-1} \cdot \exp\left(-\frac{\Delta E}{RT_{\text{max}}}\right) \tag{2.3}
\]

For \(n=1\), expression (2.3) yields:

\[
\frac{\Delta E}{RT_{\text{max}}^2} = \frac{1}{\beta} \cdot \nu_1 \cdot \exp\left(-\frac{\Delta E}{RT_{\text{max}}}\right) \tag{2.4}
\]

an analytic solution for \(\Delta E\) is difficult, but a numerical solution, e.g. by Newton's iteration, is available. Furthermore, a simple approximate solution can be obtained by reasonably assuming the value of \(\nu_1/\beta\) located in the range of \(10^8 \text{ K}^{-1}\) to \(10^{13} \text{ K}^{-1}\) range, where relationship between \(\Delta E\) and \(T_{\text{max}}\) shows a good linearity. The expression (2.4) becomes:

\[
\Delta E = RT_{\text{max}} \cdot \ln\left(\frac{\nu_1}{\beta}\right) - 3.64
\]

this is the famous Redhead-formula [62], and the approximation would essentially bring out around 1.5% relative deviation.

For detailed analysis, let's change the form of expression (2.4)

\[
\ln\left(\frac{T_{\text{max}}}{\beta}\right) = \frac{\Delta E}{RT_{\text{max}}} + \ln\left(\frac{\Delta E}{\nu_1 R}\right) \tag{2.5}
\]

For a specific initial coverage, by varying heating rate, a series of different \(T_{\text{max}}\)
values will be observed in TD spectra. When plotting \( \ln \left( \frac{T_{\text{max}}^2}{\beta} \right) \) with respect to \( \frac{1}{T_{\text{max}}} \), one would get a straight line. From the slope of straight line, \( \Delta E \) can be obtained, and from the intercept on y-axis one can get the information of \( \nu_1 \). If a totally different shape of curve is obtained, one should consider the possibility of other order desorption process.

For \( n=2 \), expression (2.3) yields:

\[
\frac{\Delta E}{R T_{\text{max}}^2} = \frac{2}{\beta} \cdot \nu_2 \cdot \theta \cdot \exp \left( -\frac{\Delta E}{R T_{\text{max}}} \right) \quad (2.6)
\]

Again, numerical methods can be applied to get \( \Delta E \) from \( T_{\text{max}} \) if we know the initial coverage \( \theta_{\text{ini}} \), \( \nu_2 \) and \( \beta \). For detailed information of \( \nu_2 \), one can also use the analysis method used in expression (2.5) by varying heating rate.

\[
\ln \left( \frac{T_{\text{max}}^2}{\beta} \right) = \frac{\Delta E}{R T_{\text{max}}} + \ln \left( \frac{\Delta E}{2 R \nu_2} \right) \quad (2.7)
\]

When plotting \( \ln \left( \frac{T_{\text{max}}^2}{\beta} \right) \) with respect to \( \frac{1}{T_{\text{max}}} \), \( \Delta E \) can be obtained from the slope of the straight line, while from the intercept on y-axis one can get the information of \( \nu_2 \).

Here, one potential problem is that for a reasonable accuracy the heating rate should be varied by at least two orders in magnitude. This is difficult, especially for oxide samples. For second order desorption, one can also use the similar method, but vary the initial coverage with keeping a constant heating rate. But determining the initial coverage is usually difficult since the maximum coverage of chemisorption is not always one monolayer.

For \( n=0 \), from expression (2.3) we will see that the right side becomes zero. As a result, the \( \Delta E \) should be zero to keep the equation valid. This is of course not right since the activation of zero would mean that desorption process can occur at any temperatures and consequently no adsorption can be formed. This inconsistency results from the fact that the desorption rate of zero order desorption is
coverage-independent as implied in expression (2.1), and it will increase continuously until the completion of desorption process. After reaching the maximum of desorption rate, there will be a sharp drop in the desorption rate (a discontinuity in mathematics). The deduction of \( T_{\text{max}} \) by expression (2.2) would be invalid. Other analysis method should be introduced for zero order desorption.

Let's come back to the Wigner-Polanyi equation again, for zero order desorption, the Wigner-Polanyi equation becomes:

\[
\frac{-d\theta}{dt} = v_0 \cdot \exp \left( -\frac{\Delta E}{RT} \right) \tag{2.8}
\]

Recall that the ion current \( I_{\text{ion}} \) recorded by mass spectrometer is proportional to the desorption rate, then we can change the form of expression (2.8) to:

\[
I_{\text{ion}} = k \cdot v_0 \cdot \exp \left( -\frac{\Delta E}{RT} \right) \tag{2.9}
\]

where \( k \) is a constant.

An analytically straightforward form of expression (2.9) is:

\[
\ln(I_{\text{ion}}) = -\frac{\Delta E}{RT} + \ln(k \cdot v_0) \tag{2.10}
\]

When plotting \( \ln(I_{\text{ion}}) \) with respect to \( \frac{1}{T} \) one can get the information about \( \Delta E \) from the slope of the straight line.

### 2.4 Low energy electron diffraction (LEED)

LEED is one of the most widely used and powerful surface analytic techniques in early surface science studies [69, 70]. The electron energies used in LEED are generally located at 30–300 eV. This is due to the following two reasons. First, the mean free path of electron in solid shows very small value in this energy region, which makes LEED very surface sensitive. Second, in this energy region the wavelength of electron is comparable to lattice constant of solid, which makes LEED suitable for studying solid surface.

In LEED experiment, an energy-tunable electron beam bombards on sample surface (in most cases perpendicular to the surface) and is reflected by the sample surface.
After filtering inelastically scattered electrons by applying a retarding potential, only elastically scattered electrons are recorded by a fluorescent screen. The elastically scattered electrons form diffraction pattern on the fluorescent screen, which is considered as the reciprocal structure and reflects the periodicity of the sample surface.

LEED is usually used in two ways to study surface structure: LEED pattern and LEED IV-curves analysis. From LEED pattern one can check the surface quality and periodicity. Surface reconstruction or superstructure formed by adsorbates can also be well studied by LEED patterns. Note that from LEED pattern we can only get the information about surface periodicity, and no any local structure including position and orientation can be deduced from this method. The local structure information of surface can be obtained from LEED IV-curves in which the multi-scattering process of electrons is considered. However, the explanation of LEED IV-curves is a complicated process since prediction and test processes are involved. In this work, the structures of different oxide surfaces are checked only by recording LEED patterns.
3. Small molecular adsorbates on ZnO(10\textbar 1\bar 0)

As one of non-polar ZnO surfaces, the ZnO(10\textbar 1\bar 0) was found to be the dominant exposed face in ZnO powders, as demonstrated by x-ray diffraction (XRD) and transmission electron microscopy (TEM) studies [71]. Its well-defined and stable surface structure brings various advantages for experimental procedures including preparation, characterization and analysis [72]. Furthermore, it also provides an ideal structure model for theoretical works to explore the mechanisms of adsorption and reactions on this surface. In this chapter, I present the HREELS, TDS and LEED results of CO\textsubscript{2} adsorption, co-adsorption of CO and CO\textsubscript{2}, as well as H\textsubscript{2}O adsorption on the ZnO(10\textbar 1\bar 0) surface.

![Fig. 3.1 Stick-and-ball model of the non-polar ZnO(10\textbar 1\bar 0) surface.](image)

Fig. 3.1 shows the stick-and-ball model of non-polar ZnO(10\textbar 1\bar 0) surface. It consists of rows of slightly tilted Zn-O dimers that are formed by threefold coordinated Zn and O atoms. The Zn-O distance along [0001] direction is 5.21 Å and the O-O or Zn-Zn distance along [11\textbar 2\bar 0] direction is 3.25 Å [73]. It was claimed that, on this surface, the Zn-O dimer vacancies are more favorable compared to single vacancies [74].

3.1 CO\textsubscript{2} adsorption on the ZnO(10\textbar 1\bar 0) surface

The interaction of CO\textsubscript{2} with the non-polar ZnO(10\textbar 1\bar 0) surface at 95 K was studied by HREELS, TDS and LEED. It was found that an unusual tridentate carbonate species is formed via the strong interaction of CO\textsubscript{2} with Zn-O dimers on the stoichiometric
surface. Several ordered adsorption phases were identified. These stable phases with different binding energies were attributed to the consequence of charge transfer between substrate and adsorbates.

In previous work, the study of activation of CO$_2$ was limited to just few special topics due to the low energy content and high kinetic barrier in many CO$_2$-containing reaction pathways [9, 75]. In heterogeneous catalysis, the interaction of CO$_2$ with ZnO or Cu/ZnO has attracted much research interest in the recent two decades stimulated by the synthesis of methanol from syngas (CO/CO$_2$/H$_2$), where CO$_2$ was considered as one of the carbon sources [44, 76]. The study of CO$_2$ activation was mainly carried out on metal surfaces, especially on some alkali modified metal surfaces [77-79]. On oxide surfaces, however, the study was scarcely performed [80-82]. This deficit is due to the well-known electric conductivity problem on single crystalline oxide surfaces and partially due to the complexity of oxide surface structures compared to metal. Additionally, HREELS study on oxide crystalline surfaces encounters one more difficulty resulting from the very strong surface phonons (Fuchs-Kliewer phonons) [53, 83]. Growing oxide thin films on bulk metal supports has been applied by some groups to avoid the surface phonons and charge effect [25, 26]. However, the potential deviation in chemical properties of metal supported oxide film is still under debates [25].

![Structure model of (2×1) tridentate carbonate species on ZnO(1010) surface.](image)

In one previous work, the adsorption of CO$_2$ on ZnO(1010) surface was investigated to lead to a strong interaction with the substrate forming (1×1) and (2×1) stable
tridentate carbonate species [84]. In both phases, CO$_2$ bonds to the surface through C to surface oxygen and two up bended oxygen atoms bond to the surface Zn along [0001] direction. The (2×1) superstructure is formed along [11\_2\_0] direction with every two Zn-O pairs covered by one carbonate species, as shown in Fig. 3.2. In a further combined helium atom scattering (HAS) and theoretical study [85], a 2.3-fold periodicity of carbonate along [11\_2\_0] direction was observed and assigned to the coexistence of (2×1) and (3×1) periodic phases.

![Fig. 3.3 TD spectra of various exposures of CO$_2$ adsorbed on the ZnO(10\_1\_0) surface at 95 K. The heating rate was 1.5 K/s.](image)

Fig. 3.3 presents the TDS results of various amount of CO$_2$ adsorbed on ZnO(10\_1\_0) at 95 K. For a low CO$_2$ exposure (0.2 L and 0.5 L), only one desorption peak is found at 325 K. With increasing the CO$_2$ exposure to higher amounts, the peak at 325 K reaches saturation and four new peaks arise subsequently in the low temperature region at 297, 240, 200 and 125 K. The 125 K peak has been assigned to the physisorbed CO$_2$ by HREELS study and DFT calculation [84, 85]. For each other desorption peaks at 200 K, 240 K, 297 K and 325 K, the peak position has no shift corresponding to different initial coverage, indicating a negligible lateral interaction, although CO$_2$ in gas phase always show strong intermolecular interaction due to the relative large quadrupole moment of CO$_2$ molecule [9]. Assuming a pre-exponential factor of $10^{13}$ s$^{-1}$ for first order desorption of CO$_2$ adsorbed on ZnO(10\_1\_0), the
binding energies of the four adsorption states at 200, 240, 297 and 325 K correspond to binding energy of 51.8, 62.6, 77.9 and 85.5 kJ/mol, respectively. The peaks at 200 K and 325 K are attributed to (1×1) and (2×1) chemisorbed tridentate phases and the two weak peaks at 240 K and 297 K were tentatively explained as the adsorption of CO$_2$ at the defective sites in the previous work [84].

To identify the origin of 240 K and 297 K desorption peaks, CO$_2$ adsorption was performed on the defective ZnO(10$\bar{1}$0) surface, which is created artificially by Ar$^+$ ion sputtering. Fig. 3.4 shows the TDS data obtained by exposing differently Ar-ion-sputtered ZnO(10$\bar{1}$0) surfaces to 5 L CO$_2$ at 95 K. A slight sputtering can reduce the peak intensity to a large extent of the chemisorbed CO$_2$ (the topmost curve in Fig. 3.4). Note that, this information can be easily obtained by taking the amount of physisorbed CO$_2$ peak as reference. With increasing the sputtering intensity, the desorption peak at around 200 K decreases its intensity to near zero, whereas the desorption peak at around 325 K decreases its intensity very slowly and, at the same time, becomes broad. The TDS results reveals that the peaks at 240 K and 297 K are not attributed to the adsorption of CO$_2$ at defective sites on ZnO(10$\bar{1}$0), since after Ar ion sputtering the defective sites become abundant and the related desorption peaks would increase their intensities. Therefore, these two desorption peaks should be assigned to new stable phases of carbonate on the perfect part of ZnO(10$\bar{1}$0). The
Fig. 3.5 (a) HREEL spectra of 5 L CO\textsubscript{2} dosed ZnO(10\bar{1}0) at 95 K and further annealing the sample to the indicated temperatures. The bottom curve shows the HREEL spectrum of the clean ZnO(10\bar{1}0) surface. (b) HREEL spectrum of 5 L C\textsuperscript{18}O\textsubscript{2} adsorbed ZnO(10\bar{1}0) surface at 95 K.

The long tail at high temperature side can be explained by adsorption on defect sites such as the (000\bar{1}) step on which CO\textsubscript{2} adsorption shows a very broad desorption peak up to 600 K [86]. The origin of these two peaks will be discussed in more detail in the following subsection.

Fig. 3.5(a) shows a series of HREEL spectra obtained by adsorption of 5 L CO\textsubscript{2} on ZnO(10\bar{1}0) at 95 K and further annealing to various indicated temperatures. All the spectra are given after Fourier deconvolution to remove the multiple Fuchs-Kliewer phonons. The bottom curve in Fig. 3.5a shows the HREEL spectrum of clean surface.

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Summary of the HREELS results and assignments of tridentate carbonate on ZnO(10\bar{1}0).</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 K</td>
<td>104</td>
</tr>
<tr>
<td>300 K</td>
<td>104</td>
</tr>
<tr>
<td>Assignments</td>
<td>(\pi(\text{CO}_3))</td>
</tr>
</tbody>
</table>

* no loss peak available
and no adsorbate-related losses are detected. Note that the loss feature at around 136 meV results from the residual overtone of the primary surface phonon due to the imperfection of the deconvolution process [61]. All the loss energies and the corresponding mode assignments were summarized in Table 3.1 [84]. Upon heating to higher temperatures, no new peaks appear in the HREELS data (see Fig 3.5a), indicating that the molecular species constituting the different phases must be identical or at least very similar. Refined analysis of the HREEL spectra shows a small red shift of the ν_s(OCO) and ν_as(OCO) modes at temperatures higher than 200 K, which is consistent with the calculated vibrational frequencies of low-coverage tridentate carbonate on ZnO(10\overline{1}0) [84, 85]. The assignment of carbonate related modes is further confirmed by isotope substitution experiments using C\textsuperscript{18}O\textsubscript{2}. As shown in Fig. 3.5(b), taken after exposing ZnO(10\overline{1}0) to 5 L C\textsuperscript{18}O\textsubscript{2} at 95 K, all the O-related vibrations shift to lower frequency with a same isotope shift (due to the isotope effect) ratio of 1.02 [58].

Fig. 3.6 exhibits the LEED patterns recorded after 5 L CO\textsubscript{2} adsorption on ZnO(10\overline{1}0)
surface at 95 K and after annealing to the indicated temperatures. All the LEED patterns were recorded at 95 K and the electron energy was fixed at 72 eV. At 95 K, the LEED pattern shows a sharp (1×1) structure, which is similar to the clean surface. Annealing to 130 K to remove the physisorbed CO$_2$ just slightly reduces the sharpness of the diffraction spots, and no resolvable structure change is observed. After annealing to 170 K, besides further reduction of the sharpness of the diffraction spots, some blur spots arise between each row of the diffraction spots. After annealing to 220 K, a very clear (2×1) superstructure is observed along [11\bar{2}0] direction. This superstructure has been observed and attributed to the (2×1) tridentate carbonate species in the previous work [84, 85]. Annealing to 270 K makes the (2×1) structure obscure and a different superstructure seems to appear. Indeed, a similar complex superstructure was also observed by HAS [85]. A 2.3-fold periodicity, caused by combination of (2×1) and (3×1) superstructure, was obtained after dosing 0.7 L CO$_2$ to ZnO(10\bar{1}0) surface above 270 K. After annealing to 300 K and 330 K, the LEED patterns exhibit features like that on clean ZnO(10\bar{1}0) surface.

Overall, several stable superstructures of tridentate carbonate are formed (as confirmed by LEED and TDS), whereas the geometry of adsorbates undergoes nearly no change (as judged from HREEL S) and no apparent lateral interaction is present.

![Figure 3.7](image_url)

**Fig. 3.7** TD spectra of 5 L C\textsuperscript{18}O\textsubscript{2} adsorbed on the ZnO(10\bar{1}0) surface at 95 K. The heating rate was 1.5 K/s.
from TDS). The existence of different stable phases of carbonate species can be attributed to different amount of charge transfer between substrate and adsorbates. In order to get more detailed information about the localized chemical bond between carbonates and substrate, TDS experiments with isotope $^{18}$O$_2$ were further carried out. In Fig. 3.7, 5 L $^{18}$O$_2$ was dosed to ZnO(10$ar{1}$0) surface at 95 K and in the subsequent TDS experiment mass 44, 48 and 48 were monitored. Mass 48 corresponds to $^{18}$O$_2$ and means no exchange of oxygen between $^{18}$O$_2$ and surface; mass 46 is attributed to $^{16}$O$^{18}$O, indicating an oxygen exchange process during TDS experiment. The desorption of $^{16}$O$_2$ (mass 44) is in principle impossible, since one CO$_2$ molecule bonds to only one surface-oxygen through the C atom. For mass 44 and 46, the contribution from the cracking pattern of $^{18}$O$_2$ has been subtracted. The main desorption species in Fig. 3.7 is mass 48 ($^{18}$O$_2$), while mass 46 ($^{18}$O$^{16}$O) is mainly located between 270 and 370 K. Just a small amount of $^{18}$O$^{16}$O is observed between 200 and 270 K. No mass 44 ($^{16}$O$_2$) is detected throughout the TDS temperature range, which is consistent with the above argument. The exchange of oxygen can be achieved only through breaking one of the two oxygen-Zn bonds and taking the surface oxygen during desorption (see Fig. 3.2). The extent of oxygen exchange depends on the relative probabilities to break C-O$_{\text{suf}}$ and C-O$_{\text{ad}}$ bonds, and thus implying the relative bond strength of C-O$_{\text{suf}}$ compared to the two oxygen-Zn bonds (see Fig. 3.2). The present TDS data reveal that CO$_2$ at low coverages is more strongly bound to the ZnO(10$ar{1}$0) surface yielding desorption peak of $^{18}$O$^{16}$O at higher temperatures due to the exchange with surface $^{16}$O atoms.

From the electronic structure of CO$_2$ in gas and activated state [9], it is known that the filling of both two degenerated $2\pi_u$ molecular orbital is favored when the CO$_2$ activation reaction occurs. This is characterized by bending of the linear OCO geometry of the free CO$_2$ molecule. A larger amount filling of $2\pi_u$ orbital leads to stronger bond strength between C and surface oxygen on one hand, and smaller bond angle of OCO on the other hand. The smaller bond angle would further increase the bond length of two O-Zn bonds and consequently weaken them. For the large
carbonate coverage, the average charge transfer from surface to each carbonate species becomes smaller. As a result, the binding energy of carbonate decreases and the oxygen exchange becomes indistinctive due to the weakening of C-O_{surf} bond, and vice versa for the low coverage.

This speculation was further confirmed by the following co-adsorption experiment with CO and H$_2$O. Fig. 3.8(a) presents the TD spectrum of 2 L H$_2$O adsorption followed by 5 L CO$_2$ adsorption on ZnO(1010) surface at 95 K. The desorption peak of CO$_2$ at around 300 K disappears and only the desorption peaks at lower temperatures are observed. In contrast to coadsorption with H$_2$O, exposing the clean ZnO(1010) surface to 2 L CO followed by 5 L CO$_2$ at 95 K results in the desorption of CO$_2$ at high temperature region (see Fig. 3.8b).

H$_2$O adsorption on ZnO(1010) leads to partial dissociation forming a (2\times1) superstructure [87, 88]. The oxygen row along [11\overline{2}0] direction is half covered by
OH species. In the case of CO adsorption on ZnO(1010), however, the CO molecule is bound only to Zn sites and the bond is strengthened by the pre-adsorbed CO₂ [89]. Besides the site-blocking effect by H₂O or CO molecules, it is relevant to consider the electronic state of H₂O and CO. For H₂O adsorbed on ZnO(1010), H₂O mainly acts as a proton donor to the surface; for the CO adsorption on ZnO(1010), CO is more like an electron donor. By this means, the pre-adsorbed H₂O and CO affect the charge transfer between substrate and the following adsorbed CO₂. Pre-adsorbed H₂O would decrease and pre-adsorbed CO would increase the charge transfer between ZnO substrate and carbonate specie to some extent, respectively.

As shown in Fig. 3.4, CO₂ adsorption on the sputtered ZnO(1010) surface just gives rise to the new broad desorption feature at high temperature range, while the desorption peak at 325 K referring to CO₂ adsorbed on perfect ZnO(1010) surface is not disappeared. Here, one should note that besides creating defective sites, the Ar ion sputtering process also leads to destruction of surface periodicity, which potentially benefits the charge transfer between CO₂ and substrate.

For the charge transfer from substrate to CO₂, the maximum extent of filling of electrons in the two degenerated 2πₜ₀ orbital is four from energy point of view. No fractional electron is allowed to transfer and fill in the molecular orbital. The integer charge transfer of 1, 2, 3 and 4 is possibly corresponding to the different stable superstructures, although no any experimental indication of (4×1) has been reported. The speculation is consistent with the theoretical prediction that (4×1), (3×1) and (2×1) phases have higher binding energy than other investigated superstructures [85]. The thermal desorption peaks at 240 K and 297 K in Fig. 3.3 are likely attributed to the desorption from (2×1) and (3×1) carbonate superstructure, respectively, which is consistent with the LEED patterns obtained after annealing the carbonate-saturated ZnO(1010) surface to 220 K and 270 K.

In conclusion, we have studied the interaction CO₂ with ZnO(1010) at 95 K using...
HREELS, TDS and LEED. CO$_2$ adsorption on ZnO(10\{1\}0) at 95 K leads to the formation of an unusual tridentate carbonate species with different ordered phases. Several ordered structures are observed and attributed to the consequence of different amount of charge transfer between CO$_2$ and surface oxygen.

3.2 Co-adsorption of CO and CO$_2$ on ZnO(10\{1\}0) surface

In this work, a significant increase of CO binding energy on CO$_2$ modified ZnO(10\{1\}0) was observed. This effect is attributed to the increase of Lewis acidity of the surface Zn$^{2+}$ cations after CO$_2$ adsorption, which results from the charge transfer between CO$_2$ and ZnO(10\{1\}0) surface.

Fig. 3.9 presents TD spectra after exposing the ZnO(10\{1\}0) surface to various amount of CO at 95 K. The inset shows the integrated CO desorption peak area as a function of the exposure. With increasing CO exposure, the CO desorption peak exhibits lower desorption temperature, indicating a relatively strong lateral repulsion between adsorbed CO species on ZnO(10\{1\}0) surface. The TD spectrum of 45 L CO exposure shows no increase in peak area compared with that of 2 L CO exposure, which means that the CO coverage on ZnO(10 \{1\} 0) reaches maximum. By assuming a

![Fig. 3.9 TD spectra of various CO exposures on the ZnO(10\{1\}0) surface at 95 K. The inset indicates the integration of CO desorption peaks with respect to the exposure. The heating rate is 1.5 K/s.]

33
pre-exponential factor of $10^{13}$ s$^{-1}$ for first order desorption, we can get the binding energy for CO desorption of 29.8 to 32.7 kJ/mol for the presented CO exposure in Fig. 3.9. In fact a similar weak binding energy of CO was also reported on ZnO powder samples [90, 91]. The binding energy of the low-coverage limit of CO can be roughly estimated by extrapolation by the existing data points and amounts to 33.2 kJ/mol.

Fig. 3.10 shows the TD spectra of CO adsorbed on different CO$_2$ modified ZnO(10$ar{1}$0) surfaces at 95 K. In each experiment, ZnO(10$ar{1}$0) was first exposed to 2 L CO$_2$ and then annealed to indicated temperatures. The modified sample was exposed to 2 L CO.

Fig. 3.10 TD spectra of co-adsorbed CO and CO$_2$ on ZnO(10$ar{1}$0) surfaces at 95 K. In each experiment, ZnO(10$ar{1}$0) was first exposed to 2 L CO$_2$ and then annealed to indicated temperatures. The modified sample was exposed to 2 L CO.

surfaces at 95 K. ZnO(10$ar{1}$0) was first exposed to 2 L CO$_2$, and then annealed to different temperatures to remove part of adsorbed CO$_2$. CO adsorption was then performed on these modified surfaces. With increasing annealing temperatures, the desorption peak of CO$_2$ decreases gradually in intensity, while the peak area of CO increases first and then decreases again. The increase of CO adsorption amount is partially attributed to the weakening of site blocking effect by CO$_2$ since the desorption of CO$_2$ releases surface sites for further CO adsorption. More importantly, the desorption temperature of CO is also found to increase with elevating the CO$_2$ coverage, which indicates an increase of binding energy of CO to surface. Note that
the increase is significant even taking the binding energy of low-coverage limit of CO as reference. The binding energy of CO with respect to the relative coverage of CO$_2$ is summarized in Fig. 3.11. The binding energy of CO increases from 29.8 kJ/mol on the clean ZnO(10\(\overline{1}0\)) surface to 54.4 kJ/mol on the monolayer CO$_2$ modified ZnO(10\(\overline{1}0\)) surface.

Indeed, as we discussed in the above subsection, CO$_2$ adsorbed on ZnO(10\(\overline{1}0\)) takes electron from surface and the amount depends on the carbonate coverage. Since CO acts as an electron donor [92], the increase of Lewis acidity of the surface Zn$^{2+}$ cations can potentially promote the charge transfer between CO and surface.

Fig. 3.12 presents the HREEL spectra of CO adsorbed on CO$_2$ modified ZnO(10\(\overline{1}0\)) surfaces at 95 K. Curve A shows the HREEL spectrum on the clean ZnO(10\(\overline{1}0\)) surface. No adsorbate-related losses can be detected. CO adsorption on clean ZnO(10\(\overline{1}0\)) (curve B) results in the appearance of a small loss at 272 meV that is assigned to the stretching vibration of CO, \(\nu\)(CO) [93, 94]. The HREEL spectrum recorded after exposure of 2 L CO$_2$ followed by 2 L CO on ZnO(10\(\overline{1}0\)) at 95 K (curve C) shows tridentate carbonate-related losses at 123, 165 and 201 meV as well as the band at 292 meV assigned to the physisorbed CO$_2$, whereas no CO-related band is detected. This is due to the adsorption site blocking by monolayer carbonate as further demonstrated by the corresponding TDS results (see Fig. 3.10f). If half monolayer of
carbonate is removed from surface, the CO adsorption can reach a maximum coverage, and the HREEL spectrum (Fig. 3.12D) shows the presence of both tridentate carbonate and CO-related losses. The ν(CO) of CO reveals a slight blue shift to 273 meV while the carbonate-related losses are slightly red-shifted. Actually, this red shift of νₚ(OCO) and νₚₛ(OCO) was also found for CO₂ adsorbed on ZnO(1010) at low coverages where carbonate shows higher binding energy. The red shift induced by the coadsorption of carbonate and CO could be related to the charge transfer between CO molecule and pre-covered carbonate species. The blue shift of ν(CO) is not well understood. However, the present results reveal that the increasing of CO binding energy is not associated with electron back donation from surface to CO molecule 2π* orbital that will result in a significant red-shift of ν(CO), as observed on metal surfaces. We would attribute the increasing of CO binding energy to the electron donation from CO 5σ orbital to the modified ZnO surface, as supported by the DFT calculations [89]. The ν(CO) is not sensitive to this charge transfer since the 5s electrons mainly locate at C side.

In the co-adsorption experiment shown in Fig. 3.10, the CO coverage in Fig. 3.10(d) shows peak area three times larger than that in Fig. 3.10(a). This increase in CO
coverage implies a reduction of lateral repulsion between adsorbed CO species by the pre-adsorbed CO$_2$. This effect together with the site blocking effect on CO coverage reaches a good balance on the half monolayer CO$_2$ modified ZnO(10$ar{1}$0) surface.

### 3.3 H$_2$O adsorption on the ZnO(10$ar{1}$0) surface

![Ball and stick model of half dissociated H$_2$O on non-polar ZnO(10$ar{1}$0) surface from perspective view.](image)

H$_2$O, acting as an important and inevitable participant or even impurity in most of industrial chemical reactions, has attracted a lot of scientific attentions [87, 95-101]. The water-solid interactions can be dominant in many surface reactions, such as water-gas shift, methanol synthesis and stream reforming reaction [102, 103]. However, in some special cases, the unexpected H$_2$O ad-layer on substrate can lead to a change of the original physical and chemical properties [104]. Especially, H$_2$O usually shows high reactivity towards the active sites and block other reactions in many surface catalytic reactions [105-108]. In a more common way, surfaces are wetted by H$_2$O adlayers in which the hydrogen bond between H$_2$O molecules or between H$_2$O and substrate dominates the chemical and physical properties [100]. The existence of these hydrogen bonds gives rise to energy shift of OH stretching vibrations, which depend on the strength of the bonds [23, 88, 109]. This provides a possibility to identify the hydrogen bond in different coverage of H$_2$O layers.

H$_2$O adsorption on this surface has been studied theoretically [87, 101] and experimentally [88, 99] It was found that at room temperature monolayer water is partially dissociated forming a (2×1) superstructure (as shown in Fig. 3.13). The
driving force of the partial dissociation was proposed to be the unusually strong hydrogen bonding interactions of water to both neighboring adsorbate molecules and the surface O atoms [88]. The dissociation barrier was calculated to be smaller than 0.05 eV per molecule [99], which hints that the dissociation of H$_2$O on ZnO(1010) can be activated even at very low temperatures. However, an experimental observation by LEED (in macroscopic region) and vibrational spectroscopy (to determine the dissociated species) at low temperature is still scarce. Furthermore, the recognition of the hydrogen bonds in multi-, double and monolayer H$_2$O could provide a more straightforward understanding for the H$_2$O partial dissociation in monolayer [88, 109].

Fig. 3.14 shows the TDS results of various H$_2$O exposures to ZnO(1010) surface at 90 K. For H$_2$O exposure of 0.05 L, the desorption spectrum is dominated by the peak at 370 K. With increasing the H$_2$O exposure to 0.2 L, besides the increase of peak intensity at 370 K, a resolvable small shoulder at around 430 K shows up. These two peaks have been assigned to the chemisorbed H$_2$O molecule and hydroxyl group on ZnO(1010) surface [88], respectively. Further increasing the H$_2$O exposure to 0.5 L leads to an intensity increase of the molecular H$_2$O desorption peak to saturation. After the H$_2$O exposure exceeds 0.5 L (see Fig. 3.14, 2L and 4 L exposures), two new
peaks at 141 K and 160 K arise at lower temperatures. The inset in Fig. 3.14 shows the TD spectra of 4 L and 10 L H$_2$O exposures. The peak located at 141 K is obviously assigned to multilayer H$_2$O due to the unsaturated feature and the blue shift of the peak position for higher H$_2$O coverage, which is the typical character of the zero-order desorption. The peak at 160 K, therefore, is attributed to double layer H$_2$O adsorbed on ZnO(10\overline{1}0) surface. Actually, similar TDS results of H$_2$O were reported on TiO$_2$(110), where the multi-, double and mono-layer water desorptions were observed at 155, 174 and 270 K, respectively [110].

Fig. 3.15 exhibits the LEED patterns recorded on clean and H$_2$O covered ZnO(10\overline{1}0) surfaces, respectively. The experiments were carried out at 90 K and the electron energy was fixed at 72 eV for both cases. A perfect (1×1) surface is obtained on the clean ZnO(10\overline{1}0) surface (Fig. 3.15a), indicating a good preparing procedure for the sample. As shown in Fig. 3.15b, the LEED pattern of 1 L H$_2$O covered surface shows a clear (2×1) superstructure along [11\overline{2}0] direction. This phenomenon is consistent with the previous theoretical prediction [87, 101] and experimental results [88, 99] that H$_2$O adsorption on ZnO(10\overline{1}0) at RT leads to a self-dissociation forming a (2×1) superstructure. The possibility that every two Zn sites along [11\overline{2}0] are occupied by one H$_2$O molecule with the rest of Zn sites unoccupied, which could also give rise to a (2×1) superstructure in LEED, is clearly ruled out by our coadsorption experiments of H$_2$O and CO. When the H$_2$O-modified (2×1) ZnO(10\overline{1}0) surface was further exposed
to 10 L CO at 90 K, no CO desorption was detected in the corresponding TD spectra (data not shown). This means that on H₂O covered (2×1) ZnO(10̅10) surface all Zn sites are occupied by H₂O molecules. The present low temperature LEED experiment, in addition, indicates a very low energy barrier for H₂O dissociation as suggested by DFT calculations [99]. The desorption peak at 370 K and the shoulder at high temperature side are reasonably assigned to the molecular H₂O desorption and the recombinative desorption of OH species, respectively, because the recombination desorption barrier of OH groups is expected to be higher than that of H₂O molecule. Since half of the H₂O molecules are dissociated, for the monolayer H₂O adsorbed on ZnO(10̅10), one would expect same peak area from molecularly adsorbed H₂O and OH species in TDS. The obvious smaller peak area of 450 K compared with the 370 K peak can be explained by the balance between molecular H₂O and the dissociative state, which was reported by Dulub on the same surface [99].

In Fig. 3.16 the HREEL spectra obtained after different H₂O exposures on ZnO(10̅10) at 90 K are presented. The spectra were given in deconvoluted results. Fig. 3.16a was recorded on the clean ZnO(10̅10) surface at 90 K and no adsorbate-related losses are

![Fig. 3.16 HREEL spectra recorded for (a) the clean ZnO(10̅10) surface and after exposure to various amounts of water at 90 K: (b) 0.5 L, (c) 2 L, (d) 4 L, (e) 10 L. The spectra were recorded at 90 K.](image-url)
observed. For the small amount of H\textsubscript{2}O exposure (as shown in Fig. 3.16b, which corresponds to monolayer H\textsubscript{2}O adsorption), the dominant peaks are located at 122, 206 (poorly resolved), 389 and 456 meV. With increasing the H\textsubscript{2}O exposure to 2 L (Fig. 3.16c), which corresponds to double layer H\textsubscript{2}O adsorbed on the surface, a new loss at 441 meV arises, while the 206 meV and 389 meV peaks increase in intensity.

Further increasing the H\textsubscript{2}O exposure to 4 L (Fig. 3.16d), which corresponds to the multiplayer H\textsubscript{2}O adsorbed on the surface, leads to several new changes of the spectra: (a) A new broad peak at 430 meV shows up and the peaks at 389 and 441 meV are not resolvable anymore. (b) The 456 meV peak shifts to 460 meV. (c) The 122 meV peak disappears and the 206 meV peak increases its intensity. Fig. 3.16e shows the EEL spectrum obtained after 10 L H\textsubscript{2}O exposure at 90 K. All the peaks increase in intensity, whereas no peak shift compared to Fig. 3.16d is observed.

Fig. 3.17 presents the TD spectra of 1 L H\textsubscript{2}O adsorbed on ZnO(10\bar{1}0) at 90 K (curve a) and subsequently annealing to 370 K (curve b). The inset of Fig. 3.17 shows the corresponding HREEL spectra. After annealing to 370 K the loss peak at 389 meV disappears. From the TDS data it is known that at 370 K the molecularly adsorbed H\textsubscript{2}O is largely desorbed. We therefore attribute the loss peak at 389 meV to the vibration mode existing in the molecularly chemisorbed H\textsubscript{2}O layer. The only possibility of so high vibrational energy is the stretching mode of...
OH in H\textsubscript{2}O. Therefore, we can further attribute the loss peak at 389 meV to the stretching vibrational mode of OH with hydrogen bond, which can significantly cause red shift of the vibrational energy.

The loss feature at 122 meV can be assigned to the bending mode, ρ(OH), of OH species created by H\textsubscript{2}O partial dissociation. The decrease and even disappearance of ρ(OH) for thicker layer H\textsubscript{2}O adsorption, as shown from Fig. 3.16b to Fig. 3.16e, can be explained as the screening effect by double and multilayer H\textsubscript{2}O. The scissor mode, δ(γOH), of H\textsubscript{2}O, which is located at 206 meV, just exists in molecular H\textsubscript{2}O and increases its intensity with increasing the H\textsubscript{2}O exposure (from Fig. 3.16b to Fig. 3.16e). The losses higher than 380 meV result from the OH stretching mode, ν(OH). It exhibits energy shift according to different chemical surroundings. For instance, the energy of ν(OH) from isolated hydroxyl is different from that of H\textsubscript{2}O although they have overlapping in many cases [95]. According to our previous work on ZnO(10\textsubscript{1}0) surface [88], the loss at 460 meV is attributed to the ν(OH) of isolated H\textsubscript{2}O and the loss at 456 meV results from the ν(OH) of isolated hydroxyl group. On the other hand, the ν(OH) mode of H\textsubscript{2}O with H-bond should shift to lower energy region depending on the strength of the H-bond. The peaks at 389 meV, 430 meV and 441 meV are assigned to the ν(OH) mode of H\textsubscript{2}O with H-bond. The very broad peak at 430 meV is due to the random orientation of H-bond in multi-layer H\textsubscript{2}O. It increases in intensity with increasing the thickness of H\textsubscript{2}O adlayer. The shifts of ν(OH) in mono-, double

<table>
<thead>
<tr>
<th>Exposure (L)</th>
<th>H\textsubscript{2}O species</th>
<th>Energy loss (meV)</th>
<th>Shift of ν(OH) with H-bonding (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>Mono-layer</td>
<td>389, 460</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>Bi-layer</td>
<td>(389*), 441, 460</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>Multi-layer</td>
<td>(389*), 430, 460</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>Multi-layer</td>
<td>430, 460</td>
<td>30</td>
</tr>
</tbody>
</table>

* From the co-existence of mono-layer OH
and multi-layer H$_2$O amount to 71 meV, 19 meV and 30 meV, respectively. A collation of the strength of H-bond in different H$_2$O layers adsorbed on ZnO(10$ar{1}$0) can be achieved: H-bond$_{(\text{mono})}$ > H-bond$_{(\text{multi})}$ > H-bond$_{(\text{double})}$. Surprisingly, the energy of the v(OH) mode in monolayer H$_2$O is much lower than those in double and multilayer H$_2$O, indicating unusually strong H-bond interactions in monolayer H$_2$O. This is likely the origin of the low barrier of H$_2$O self-dissociation upon adsorbing on the ZnO(10$ar{1}$0). The HREELS data are summarized in Table 3.2.

In conclusion, the interaction of H$_2$O with ZnO(10$ar{1}$0) surface at 90 K was studied by HREELS, TDS and LEED. The partial self-dissociation of H$_2$O on ZnO(10$ar{1}$0) with a very low dissociation barrier was observed forming a stable (2×1) superstructure. The growth of H$_2$O was clearly monitored by HREELS and TDS. The energy shift of the v(OH) mode depends on the strength of H-bonds of H$_2$O and was used to distinguish between different H$_2$O adsorption layers on ZnO(10$ar{1}$0). The unusually strong H-bond interactions in monolayer H$_2$O is likely responsible to the low barrier self-dissociation of H$_2$O on this surface.
4. Small molecular adsorbates on TiO$_2$(110)

TiO$_2$ is one of the most studied oxides in surface science due to its particular properties [111], including photo-catalytic properties as catalyst for electron-hole generation [112, 113] or water dissociation [114], bio-compatibility, heterogeneous catalytic properties as the support for CO oxidation [115], electronic properties as varistor, and even the chemical stability as a corrosion-protective material and white pigment. As the most thermodynamically stable surface of TiO$_2$, rutile TiO$_2$(110) has attracted much more research attentions than other faces and been considered as a prototype system in surface science studies of metal oxides.

![Stick-and-ball model of TiO$_2$(110)](image)

**Fig. 4.1** Stick-and-ball model of TiO$_2$(110) in perspective view together with surface oxygen vacancies and reaction intermediate, diolate species formed after formaldehyde activation on two adjacent bridge O-vacancies. (Ti: bright gray ball, O: red ball)

Fig. 4.1 shows a stick-and-ball model of rutile TiO$_2$(110) surface. A stochiometric surface exposes 2-fold coordinated oxygen (bridge oxygen, O$_{2C}$), 3-fold coordinated oxygen (lattice oxygen, O$_{3C}$) and 5-fold coordinated Ti (T$_{5C}$). The lattice oxygen is coordinatively saturated and shows less chemical reactivity. The T$_{5C}$ and O$_{3C}$ atoms are 1-fold coordinatively unsaturated and usually show chemical reactivity toward gas adsorption and reactions. Furthermore, like for many other oxide surfaces, the oxygen vacancies on the surface also exhibit high activity. Two methods are normally applied to create oxygen vacancies on this surface: annealing at high temperature and sputtering with Ar$^+$ ion. In general, annealing method can only create the bridge...
oxygen vacancies and the amount depends on the annealing temperature [116, 117]. Alternatively, Ar$^+$ ion sputtering method can create the more chemical reactive oxygen vacancies, namely, lattice oxygen vacancies.

In this chapter, the work of CH$_2$O and H adsorption on TiO$_2$(110) surface is presented.

4.1 CH$_2$O adsorption on the TiO$_2$(110) surface

In this work, CH$_2$O adsorption on perfect and defective surface (either by high temperature annealing or by Ar$^+$ ion sputtering) was studied. Polymerization production was found to form on the perfect TiO$_2$(110) surface along Ti$_5$C rows. The binding energy of paraformaldehyde polymers depend on the chain length. On the defective TiO$_2$(110) surface, the adsorbed CH$_2$O is reduced to ethylene at oxygen vacancies. The formation of ethylene reflects the diffusion and recombination process of the adsorbate species, dioxy-methylene. The sputtered surface can contain as much as 40% of oxygen vacancies. The more reactive site was found to be the lattice oxygen vacancies created only by Ar$^+$ ion sputtering, on which CH$_2$O is reduced to ethylene even at temperature as low as 150 K.

Many catalytic reactions rely on the dynamic equilibrium between the addition and removal of oxygen atoms from the surface. For example, CO oxidation in a Mars van Krevelen type on RuO$_2$(110) surfaces [118-120] as well as oxidative de-hydrogenation of alcohols [121] and hydrocarbons [122] all rely on the dynamics between surface oxygen vacancies and gas phase oxygen pressure. In surface science for most of these oxidation/reduction processes the decomposition (dissociation) pathways are studied where the number of moles consumed is equal or less to the number of moles produced. This preference is in part due to what it generally referred to as the pressure gap; simply stated as high vacuum favouring dissociation and high pressure favouring association. However, some counter examples are persistent in surface reactions where surface-adsorbate interactions lead to building up of large molecules via carbon-carbon, carbon-oxygen and carbon-nitrogen bond formation.
These coupling reactions are among the most essential chemical reactions in nature. In UHV carbon-carbon bond formation was reported on O-defected TiO$_2$ [123-127] and UO$_2$ single crystals [128-130]. Oxidative coupling of acetylene to furan was also detected on Pd(111) single crystal surfaces [131].

Organometallic and organic chemists have early on recognised that Ti compounds are active for coupling reactions of carbonyl compounds via carbon-carbon bond formation. During this catalytic process Ti atoms are oxidized, ultimately to Ti$^{4+}$, a reaction termed McMurry reaction [132, 133]. Orbital symmetry is given as the reason for the high activity of the surface Ti-species, although detailed studies are not reported. It is also worth mentioning that this reaction is not observed on many other transition metals and of all the transition metals investigated Ti is the most active. The reductive coupling of carbonyls on reduced TiO$_2$(001) single crystals was studied by TPD and XPS [123-128] The results indicated that a diolate type species (-OCH$_2$CH$_2$O-) is most likely formed as an intermediate between the carbonyl (R(R’)C=O) and the symmetric hydrocarbon (R(R’)=C(C(R’))R). This conclusion was based on the appearance of an XPS C1s signal at about 286.5 eV, a value which is found between the C1s of hydrocarbons (ca. 285 eV) and that of carbonyls (ca. 288 eV). However, photoelectron spectroscopy provides indirect evidence of the surface species formed during the reaction. No unambiguous evidence for the formation of a diolate species on TiO$_2$ single crystal surfaces has been reported.

High resolution electron energy loss spectroscopy (HREELS) has been used extensively to characterize adsorbed species on metal single crystal surfaces (see e.g. Ref. [134-139]). In contrast to metals, the application of this technique to oxide surfaces is rather scarce. This lack of information is to a large extent due to the intense Fuchs-Kliewer phonon losses [140] which make the adsorbate-related losses very difficult to detect. Two methods to overcome this problem have been proposed in the literature: Fourier deconvolution of combination losses [141, 142] and collection of spectra under conditions where impact scattering is enhanced [143]. More recently, using a combination of both methods, high-quality HREELS data have been reported for different adsorbates on ZnO and TiO$_2$ surfaces [72, 84, 88, 93, 144, 145].
The successful application of HREELS to oxides and the advanced understanding of the surface structure of TiO$_2$ (110) rutile single crystal allow for a detailed investigation of one of the most fundamental and essential reaction in chemistry: the carbon-carbon bond formation reaction. Association of molecules to higher ones is not only central to industrial catalysis and chemical manufacture in general but is at the origin of any process in nature where complex compounds are made from simpler monomer or precursors. In this work we focus on the reaction of formaldehyde, the simplest of the carbonyls, on the surfaces of stoichiometric and reduced rutile TiO$_2$(110) using HREELS and thermal desorption spectroscopy (TDS). It is shown that formaldehyde can form ethylene by reductive coupling (2 CH$_2$O + 2Vo $\rightarrow$ CH$_2$=CH$_2$ + 2 Os), where V$_O$ denotes an O vacancy and s for surface. This reaction, although the simplest of all reductive carbonyl coupling reactions, is complex, and not understood on an elementary level. A key intermediate between the adsorbed formaldehyde and the desorbing ethylene is a diolate species (-OCH$_2$CH$_2$O-) bonded to Ti atoms. This stable intermediate species has not been unambiguously identified on any metal oxide single crystal surface prior to this work.

**CH$_2$O Adsorption on the Perfect TiO$_2$(110) Surface.**

Fig. 4.2 presents TD spectra recorded after exposing the defect-free TiO$_2$(110) surface to various amounts of CH$_2$O at 100 K. With increasing exposure to CH$_2$O three peaks located at 290, 268 and 128 K are observed for m/e 29 (the parent ion of CH$_2$O). The relative coverage of CH$_2$O was determined from the ratio of the integrated peak areas (see inset of Fig. 4.2). The following masses were also investigated but no signals were detected: m/e 2, 18, 26, 27, 44. A small amount of m/e 31 (CH$_3$OH) was observed but its intensity was less than 0.6 % of that of m/e 29 and as a result, was not further considered. At low coverage only one formaldehyde desorption peak at 290 K is seen; increasing surface exposure results in an increase of the total desorption at the same temperature. At higher exposures (2 L and above) a peak at 268 K develops and becomes dominant at 5 L. The peak at 128 K observed at high coverage is assigned to physisorbed CH$_2$O. It is also worth noting that for the 5 L exposure the main
The desorption peak becomes very broad between 150 K and 350 K. This hints to a non-uniform distribution of \( \text{CH}_2\text{O} \) species on the \( \text{TiO}_2(110) \) surface, which will be discussed later.

**Fig. 4.2** TD spectra of \( \text{CH}_2\text{O} \) adsorbed on the perfect \( \text{TiO}_2(110) \) surface at 100 K with various exposures. The heating rate was 1.5 K/s. 1 L = \( 1.33 \times 10^{-6} \) mbar s. The inset shows the relative coverage of \( \text{CH}_2\text{O} \) as function of exposure.

**Fig. 4.3** HREEL spectra of (a), (b) clean \( \text{TiO}_2(110) \) surface, (c) 5 L \( \text{CH}_2\text{O} \) adsorbed on the perfect \( \text{TiO}_2(110) \) surface at 100 K. After c the sample was subsequently annealed to (d) 200 K, (e) 260 K, (f) 400 K. Curve (a) is the raw spectrum, and the Fourier deconvoluted spectra are shown in curves b-f. In curves c and d the surface phonon at 189 meV is not completely removed. All the spectra were taken at 100 K.
In Fig. 4.3, HREEL spectra are presented which were recorded for the stoichiometric TiO$_2$(110) surface before and after adsorption of formaldehyde at 100 K. The raw spectrum of the clean TiO$_2$(110) surface (curve a) shows intense primary surface phonon bands at 45, 54 and 94 meV as well as their combination and multiple excitations. The latter could be completely removed by Fourier deconvolution (curve b), and the corresponding spectrum demonstrates the presence of a clean, contamination-free TiO$_2$(110) surface (Note that in curves c, d, and f the surface phonon at 189 meV is still detected as a weak feature). After exposure of 5 L CH$_2$O at 100 K, new loss peaks are detected at 137, 143 (shoulder), 156, 174, 185, 210 and 363 meV (Fig. 4.3c). By comparison with IR results of free CH$_2$O molecules [146], the loss features at 143, 156, 210 and 363 meV are assigned to wagging $\omega$(CH$_2$), rocking $\rho$(CH$_2$), stretching $\nu$(C=O), and asymmetric stretching $\nu_a$(CH$_2$) modes of physisorbed CH$_2$O, respectively. This assignment is confirmed by the sequential annealing experiment shown in Fig. 4.3d, where all the physisorbed CH$_2$O-related bands are found to disappear upon heating the sample to 200 K. This observation is consistent with the assignment of the low temperature TDS peak at 128 K to physisorbed species (Fig. 4.2). Accordingly, the remaining loss features at 137, 174 and 363 meV in Fig. 4.3d must be related to chemisorbed CH$_2$O.

As was shown previously by many groups [147, 148], CH$_2$O adsorbed on metal or metal oxide surfaces at low temperature often polymerizes to yield paraformaldehyde. In our HREELS data, the loss peak at 137 meV is a typical feature of the O-C-O units in paraformaldehyde and corresponds to the C-O stretching vibration. A chemisorbed CH$_2$O monomer is generally bonded to the oxide surface in an oxygen end-on $\eta^1$(O) configuration [148, 149] giving a typical $\nu$(C=O) mode at around 205 meV due to the slightly reduced C=O bond. Based on our vibrational data, the presence of isolated chemisorbed CH$_2$O molecules on TiO$_2$(110) can be excluded. After further annealing to 260 K (Fig. 4.3e) no new peaks show up, while the losses at 137, 174 and 363 meV decrease in intensity. The two desorption states at 268 K and 290 K in TDS are therefore assigned to the decomposition of the same surface species,
Table 4.1 Vibrational energies (meV) and mode assignments of CH$_2$O adsorbed on fully oxidized TiO$_2$(110) surfaces at 100 K.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Modes</th>
<th>T = 100 K</th>
<th>T = 200 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraformaldehyde</td>
<td>$\nu$(C-O)</td>
<td>137</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>$\delta$(CH$_2$)</td>
<td>177</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>$\nu$(CH$_2$)</td>
<td>363</td>
<td>363</td>
</tr>
<tr>
<td>Physisorbed formaldehyde</td>
<td>$\omega$(CH$_2$)</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho$(CH$_2$)</td>
<td>156</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta$(CH$_2$)</td>
<td>185$^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu$(C=O)</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu$(CH$_2$)</td>
<td>363</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ not resolved from the surface phonon.

paraformaldehyde. All HREELS data and the corresponding assignments are summarized in Table 4.1.

In order to further assert about the adsorption site of paraformaldehyde, co-adsorption experiments of CH$_2$O and CO were conducted (Fig. 4.4). It is known that CO is adsorbed on five-fold coordinated Ti$_{5c}$ cations [145, 150]. Thus, if CH$_2$O also adsorbs on the metal ions competitive adsorption will take place which is expected to follow thermodynamic laws: the species with the stronger adsorption energy will prevail.

Fig. 4.4 presents the TDS data obtained after exposing the TiO$_2$(110) surface first to 2

![TDS spectrum](image.png)

**Fig. 4.4** TD spectra recorded after coadsorption of CO and CH$_2$O on the perfect TiO$_2$(110) surface: 3 L CH$_2$O on TiO$_2$(110) at 100 K followed by 2 L CO at 100 K. The insert shows TD spectrum of 2 L CO on defect-free TiO$_2$(110) at 100 K.
L of CH$_2$O and then to 2 L CO at 100 K. No CO desorption is found in the TD spectrum, confirming that the Ti$_{5c}$ sites are occupied by CH$_2$O molecules, thus preventing the adsorption of CO. The insert of Fig. 4.4 shows a TD spectrum of 2 L CO adsorbed on the clean TiO$_2$(110) surface at 100 K. A desorption peak at 130 K is detected and corresponds to a CO binding energy of $\sim 33$ kJ/mol (obtained by applying a standard Redhead-analysis with a frequency factor of $1 \cdot 10^{13}$ s$^{-1}$), in good agreement with previous results on fully oxidized TiO$_2$(110) [145, 151]. As expected, similar results are observed if the order of adsorption is reversed, indicating that all O atoms in the paraformaldehyde oligomer chain bind to Ti$_{5c}$ sites. It should be noted that there is a mismatch between the large Ti-Ti separation in TiO$_2$ (2.96 Å along the [001] direction) and the CH$_2$O unit length in (CH$_2$O)$_n$ of 2.35 Å [152]. As a result, many of the interior oxygen atoms in the polymer chain must be bound to the surface via electrostatic interactions. The appearance of two desorption phases (268 and 290 K) and the broadening of the TDS peak are likely to originate from the paraformaldehyde oligomer chains with different lengths and/or different modes of interaction.

A coadsorption of CH$_2$O and atomic hydrogen was also carried out on the perfect TiO$_2$(110) surface at 100 K. After 2 L CH$_2$O adsorption on TiO$_2$(110) surface at 100

![Fig. 4.5 TD spectra of CH$_3$OH on perfect TiO$_2$(110) surface after (a) only CH$_2$O adsorption, (b) coadsorption of CH$_2$O and 1000 L atomic hydrogen at 120 K. The solid line shows the guide for eyes.](image-url)
K, the modified surface was further exposed to 1000 L atomic hydrogen at 100 K, performed by dissociating H\(_2\) on a hot tungsten filament in line-of-sight from the substrate as described in previous works [145, 153]. The resulting TDS data (desorbed species, peak shapes and desorption temperatures) were found to be similar to those recorded after exposure to 2 L CH\(_2\)O at 100 K. The only significant difference is the observation of a small amount of CH\(_3\)OH (see Fig. 4.5), revealing the formation of methanol through the hydrogenation of formaldehyde.

**CH\(_2\)O Adsorption on Defective TiO\(_2\)(110) Surfaces.**

As was mentioned above, bridge O vacancies can be created by heating the sample to high temperatures [154-156]. The increase in vacancy density is not associated with a considerable rearrangement of the surface, as indicated by results from both STM and LEED [111]. Dosing of 5 L CH\(_2\)O to a TiO\(_2\)(110) surface that has been annealed at 900 K for 5 minutes yields significantly different TDS data. The results presented in Fig. 4.6b show a new feature in the high temperature region. A peak of mass 26 is observed at 620 K and corresponds to the desorption of C\(_2\)H\(_4\). TDS results recorded after longer annealing times (900 K, 10 min) only reveal a small increase in the intensity of this peak, accompanied by a slight temperature shift (see Fig. 4.6c). The

![TDS data of 5 L CH\(_2\)O adsorbed on over-annealed TiO\(_2\)(110) surfaces at 100 K.](image)

(a) CH\(_2\)O; (b), (c) C\(_2\)H\(_4\). The sample was over-annealed (a), (b) at 900 K for 5 min; (c) at 900 K for 10 min.
same desorption species, C$_2$H$_4$, was also observed in previous work [157] and the yield of C$_2$H$_4$ as reduction product was found to be proportional to the concentration of surface O vacancies. In Fig. 4.6c, the ratio of ethylene to formaldehyde is found to be equal to 3.7%. Correction factors for mass spectrometer sensitivity have been considered. Assuming full saturation of all Ti$_{5c}$ sites with formaldehyde and that the formation of one ethylene molecule leads to two oxygen atoms filling O vacancies, we calculated an initial O-defect concentration of 7.4 % (or $\approx 3.9 \times 10^{13}$ O vacancy/cm$^2$).

Fig. 4.7 displays TD spectra recorded after exposing a series of Ar ions sputtered TiO$_2$(110) surfaces to CH$_2$O at room temperature. Besides a very small amount of molecular desorption of CH$_2$O (curve A), desorption of ethylene at about 550 K is clearly observed (curve B), even at the weakest sputtering conditions used (4.0 $\mu$A·min). As shown in the inset of Fig. 4.7B, increasing the sputtering intensity results

![Fig. 4.7](image-url)

**Fig. 4.7** TDS data recorded after exposing sputtered TiO$_2$(110) surface to 5 L CH$_2$O at 300 K with various sputtering parameters (indicated in the lower part): (A) CH$_2$O; (B) C$_2$H$_4$. The energy of Argon ion was fixed at 600 eV and the sputtering parameters were given in the product between sputtering ion current and sputtering time ($\mu$A·min). The inset shows the integrated areas of CH$_2$O and C$_2$H$_4$ as function of sputtering intensity.
in considerable increase of the ethylene desorption (formation), reaching a maximum value of 19% at about 40 μA·min. Molecular desorption of CH₂O from the same surface, in contrast, is found to clearly decrease with increasing the sputtering intensity. The corresponding maximum concentration of oxygen vacancies created by Ar⁺ sputtering is computed equal to 38%.

Compared with the results on the fully oxidized (perfect) and over-annealed TiO₂(110) surfaces (Fig. 4.8), the yield of ethylene increases dramatically for the sputtered surface (note that for the perfect TiO₂(110) surface no ethylene desorption is detected), whereas the molecular desorption of CH₂O is largely reduced. These observations strongly indicate that the deoxygenation reaction of CH₂O occurs on surface oxygen vacancies. This finding is further supported by the co-adsorption experiments with
H$_2$O. Water adsorption on TiO$_2$(110) surface has been intensively studied and it was shown that the adsorption on O vacancy sites at room temperature causes a dissociation of H$_2$O molecules forming two OH species (and the filling of the O vacancies) [158, 159]. We have conducted TDS experiments of formaldehyde (2 L) on an Ar-ion sputtered TiO$_2$(110) surface that has been pre-exposed to 2 L of water at room temperature. No desorption of ethylene was observed (see Fig. 4.8d), as expected from the above reaction mechanism requiring the presence of O vacancies.

In order to elucidate the mechanism of formaldehyde activation at O vacancies, we have carried out HREELS experiments. Fig. 4.9 presents a comparison of vibrational data recorded after CH$_2$O adsorption on perfect and defective surfaces. After exposing the perfect TiO$_2$(110) surface to 5 L CH$_2$O at 300 K followed by annealing to 400 K, the corresponding HREEL spectrum only shows the features of a clean surface, clearly CH$_2$O has completely desorbed at this temperature, in good agreement with the TDS results. However, the HREEL spectrum (Fig. 4.9b) obtained on the defective TiO$_2$(110) surface prepared by Ar$^+$ sputtering, exhibits a number of distinct loss features, revealing the presence of chemisorbed species formed via CH$_2$O adsorption on O vacancy sites. The fact that no $\nu$(C=O) mode (at around 210 meV) was observed

![Fig. 4.9 HREELS data recorded after exposing differently modified TiO$_2$(110) surfaces to 5 L CH$_2$O at 300 K followed by annealing to 400 K. (a) The fully oxidized (perfect) surface; (b) Ar-ions sputtered TiO$_2$(110) surface. Both HREELS experiments were recorded at room temperature. Curve (b) was given as a raw spectrum. All the spectra were taken at 300 K in specular direction with an incidence angle of 55° and with a primary energy of 10 eV.](image)
Table 4.2 Assignments of HREELS data for the diolate molecule formed on defective TiO$_2$(110) surfaces and comparison with other works from ethylene glycol and the computed (at the DFT/B3LYP-6-31G**) frequencies from a Ti$_2$Cl$_2$C$_2$H$_3$O$_2$ cluster. All numbers are given in meV.

<table>
<thead>
<tr>
<th>Modes</th>
<th>Ethylene Glycol</th>
<th>O-CH$_2$-CH$_2$-O on Mo(110)</th>
<th>HREELS data</th>
<th>Computed results</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{as}$(C-O)</td>
<td>129</td>
<td>-</td>
<td>138</td>
<td>137</td>
</tr>
<tr>
<td>$\nu_s$(C-O)</td>
<td>135</td>
<td>128</td>
<td>143</td>
<td>145</td>
</tr>
<tr>
<td>$\nu$(C-C)</td>
<td>107</td>
<td>111</td>
<td>a</td>
<td>114</td>
</tr>
<tr>
<td>$\nu$(C-C)$+\omega$(CH$_2$)</td>
<td>-</td>
<td>-</td>
<td>174</td>
<td>174</td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>181</td>
<td>179</td>
<td>180</td>
<td>180-186</td>
</tr>
<tr>
<td>$\nu$(CH$_2$)</td>
<td>356</td>
<td>352</td>
<td>353</td>
<td>378</td>
</tr>
<tr>
<td>$\nu_{as}$(CH$_2$)</td>
<td>364</td>
<td>361</td>
<td>363</td>
<td>385</td>
</tr>
</tbody>
</table>

*a not resolved

hints a dissociative adsorption of CH$_2$O on O vacancies.

On the basis of the similarity of the frequencies in the HREELS data with those of ethylene glycol, both in liquid [160] and adsorbed on Mo(110) [161] (see Table 4.2), we propose the presence of a diolate species (-OCH$_2$CH$_2$O-). This assignment is clearly supported by DFT calculations. As shown in Table 4.2, the computed frequencies of diolate in a TiCl$_2$-OCH$_2$CH$_2$O-TiCl$_2$ cluster are in good agreement with the experimental results. The losses observed at 138, 143, 180, 353 and 363 meV are assigned to $\nu_{as}$(O-OCH$_2$CH$_2$O-), $\nu_s$(-O-CH$_2$-H$_2$C-O-), $\delta$(CH$_2$), $\nu_s$(CH$_2$) and $\nu_{as}$(CH$_2$) modes, respectively. The peak at 174 meV is attributed to a vibration of mixed character involving C-C stretching and CH$_2$ wagging.

The diolate species can be formed through activation of two formaldehyde molecules adsorbed at adjacent O vacancy sites (see Fig. 4.1). Actually, this type of double O vacancies has been observed on TiO$_2$(011)-2×1 surface prepared by electron irradiation in a recent STM study [162]. In our work, the oxygen vacancies on TiO$_2$(110) are created mainly by Ar$^+$ sputtering, and a large vacancy concentration of about 38 % of a monolayer is achieved. More recently, the diffusion barrier $E_b$ of bridge O vacancies on TiO$_2$(110) was determined by both STM and DFT calculations [163] to be equal to 1.15 eV, revealing that oxygen vacancies exhibit rather limited mobility at room temperature. The corresponding hopping rate $h$ can be calculated
according to $h = v \exp(-E_b/k_bT)$, where $v$ is the preexponential factor ($1.58 \times 10^{12} \text{ s}^{-1}$) and $k_b$ is the Boltzmann constant. Based on the given data a hopping rate of bridge oxygen vacancies is estimated to be as low as $\sim 7 \times 10^{-8} \text{ s}^{-1}$ at 300 K. This leads to a nonuniform distribution of O vacancies created by Ar$^+$ sputtering at 300 K, revealing the presence of double or multiple O vacancies on the sputtered TiO$_2$(110) surface. We propose that upon annealing the diolate species undergoes deoxygenation leading to the formation of C$_2$H$_4$ as the final product. Two oxygen atoms of the diolate species are left on the surface to fill up two O vacancies.

In addition, it should be noted that the reductive reaction of CH$_2$O to C$_2$H$_4$ on the defective TiO$_2$(110) surface could be complicated and other reaction mechanisms can also be involved. In particular, the TiO$_2$(110) surface prepared by over-annealing should be dominated by the single O vacancies due to the repulsive interaction between vacancies [163]. In that regard it is worth discussing the mechanism invoked for the reductive coupling of carbonyl reactions in general. Organometallic chemists have studied this reaction in details. This reaction is also known as McMurry reaction [132] although several variants of it have also been reported in particular by Lippard group [164]. Based on crystal structure and spectroscopic and kinetic methods two following mechanisms have been identified:

where [M] is a zero-valent metal. The net reaction involves the loss of four electrons from the surface (or the compound) reducing the carbonyl compound to the symmetric olefin. The radical species has been observed in numerous works [132, 165]. It has to be stressed that these two mechanisms exist depending on the nature of the metal and the reaction conditions. In the case of M = Ti mechanism 1 predominates, while when M = W or U mechanism 2 is observed. It is clear that both mechanisms require heavily reduced metals and strong $\pi$ - $d$ orbital interactions. Our
present work indicates that the reductive coupling on the heavily reduced TiO$_2$(110) surface is efficient. Based on our spectroscopic results this reaction most likely involves diolate type species as the intermediate (mechanism 1). This species can be formed not only via adsorption of two CH$_2$O molecules on adjacent O vacancies as described above, but also probably via activation of formaldehyde on single O vacancy sites. A schematic representation of the latter process is shown in Scheme 4.1,

**SCHEME 4.1**

![Scheme 4.1 Diagram]

with details as follows:

A. Oxygen point defects (represented by an open square) have been reported to involve two Ti atoms each with a +3 oxidation state. These two Ti atoms are however not equivalent: one is along the [001] direction (formerly
six-fold coordinated to oxygen atoms) and the other is a Ti five-fold coordinated along the [110] direction [166].

Formaldehyde preferentially adsorbs on these oxygen defects along the [001] direction. The adsorption of formaldehyde leads to the possible formation of a radical species as previously identified by EPR over Ti complexes for the same reaction [165].

B. The reaction of the initially adsorbed formaldehyde with an adjacent bridging oxygen atoms leads to the formation of a dioxy-methylene species (-OCH\(_2\)O-). These species has been observed from formaldehyde over several metal oxides by FTIR [167] and are postulated as reaction intermediate for the coupling of formaldehyde to ethylene over reduced TiO\(_2\) (110) surface [151].

C. The diffusion of these species is facilitated at higher temperatures and would involve the breaking and making of one carbon-oxygen bond.

D. The reaction of two adjacent species would result in the formation of a diolate species.

E. Upon further heating, breaking of two carbon-oxygen bonds, facilitated by the energy gained to oxidize the surface, would lead to the formation of ethylene that desorbs from the surface instantaneously.

Finally, an additional weak desorption peak of ethylene is observed in the TDS data at around 160 K (see Fig. 4.8), indicating that the reductive reaction of CH\(_2\)O to C\(_2\)H\(_4\) occurs also in the low temperature region. This finding may indicate the existence of more active defect sites on TiO\(_2\)(110) such as lattice O vacancies created by Ar\(^+\) sputtering.

In summary, formaldehyde adsorption on perfect and defective TiO\(_2\)(110) surfaces has been studied by TDS and HREELS. On the perfect TiO\(_2\)(110) surface, it was found that adsorption of CH\(_2\)O at 100 K leads to physisorbed CH\(_2\)O and polymerization of CH\(_2\)O yielding paraformaldehyde. The latter is bound to the surface via O-Ti bonds at the five-fold coordinated surface Ti\(_{5c}\) ions. Upon heating the paraformaldehyde oligomer chain decomposes and releases CH\(_2\)O. On defective surfaces, created by both over-annealing or Ar\(^+\) sputtering, formaldehyde is more
strongly adsorbed at O vacancy sites. For the sputtered surface a reaction intermediate species, diolate (-OCH₂CH₂O-), is clearly identified by HREELS. The observed vibrational frequencies are in good agreement with those obtained by DFT calculations. Upon heating a reductive reaction takes place to form ethylene which desorbs from the surface. Further studies for other organic molecules on TiO₂(110) are needed in order to elucidate whether similar carbon-carbon coupling reactions forming olefins take place at the reduced sites, surface oxide vacancies. In addition, our results demonstrated that HREELS is not only a powerful method to study adsorption and reaction of molecules at perfect oxide surfaces, but also can be used to characterize the interaction of adsorbates with defect sites.

4.2 H adsorption on the TiO₂(110) surface

In this work, we devoted much effort to the explanation of the experimental observation by both STM and HREELS that H adsorbed on TiO₂(110) surface prefers to diffuse into the bulk. Atomic hydrogen was used during exposure on account of the extremely small sticking coefficient of molecular hydrogen. After exposing 2000 L atomic hydrogen to TiO₂(110) surface, the STM images showed that the surface was covered by 66% OH on bridge oxygen rows. At the same time, the stretching vibrational mode of the OH species, ν(OH), was observed in HREEL spectra. But in the sequent TDS experiments, nearly no H₂ (or H₂O) could be detected, and after that no ν(OH) could be observed in HREELS. A conclusion was drawn that the hydrogen atoms of surface hydroxyl groups diffuse into the bulk during heating process. The theoretical works by DFT calculations further supported this conclusion and claimed that the reason is attributed to the smaller activation barrier for H diffusion into TiO₂ bulk than that for desorption as H₂. In addition, the existence of subsurface H was also observed by theoretical [168] and STM works [169].

Hydroxyl groups formed on TiO₂(110) surface was thought to be important for a number of applications, including the photo-catalysis where the light is converted to
chemical energy by photo-induced cleavage of water to O₂ and H₂ [112]. Unfortunately, the structure and properties of hydroxylated TiO₂(110) are still not well understood. Experimentally, hydroxyl groups can be formed by exposing TiO₂(110) surface to either water or atomic hydrogen. For the water adsorption, the hydroxyl groups are created through water dissociation at bridge oxygen vacancies [95, 110, 156]. A large amount of hydroxyl groups seems unlikely since the oxygen vacancies on the TiO₂(110) surface are not abundant due to the nice electrostatic stability of this surface. A previous STM study reported a disordered hydroxyl coverage of 0.25 ML on the TiO₂(110) surface by exposing the surface to atomic hydrogen [170]. However, a recent helium atom scattering (HAS) study revealed an ordered (1×1) hydroxyl adlayer [153]. This inconsistency is surprising since the TiO₂ has been received much experimental and theoretical studies in recent years.

In order to get a deeper understanding on the structure and properties of hydroxylated TiO₂(110) surface, several experimental methods including TDS, HREELS and STM were carried out on atomic hydrogen exposed TiO₂(110) surface. Additionally, a detailed theoretical study was also performed on this system.

The STM experiments were conducted in a two-chamber SEM/STM system (JEOL, JSPM-4500S) [73]. The HREELS (Delta 0.5, SPECS, Germany, nominal resolution 1 meV) and TDS experiments were performed in a separate UHV system. The TiO₂(110) samples used in this study were cleaned using cycles consisting of 20 min Ar⁺ sputtering (800-1000 eV) at room temperature (RT) and 30 min annealing (850-900 K). The samples had a dark blue color, indicating a slight O-deficiency. The details on H exposure can be found in Ref. [171]. Relative H atom exposures are given in L (1

**Fig. 4.10** Stick-and-ball model of the bulk-truncated TiO₂(110) surface.
Langmuir = $1.33 \times 10^{-6}$ mbar·s) assuming that the H atom flux is proportional to the H$_2$ total pressure ($1 \times 10^{-7}$ - $4 \times 10^{-6}$ mbar).

Periodic DFT slab calculations have been carried out using the VASP program [172-174]. The core electrons are described by pseudopotentials whereas a plane-wave basis set (cutoff 400 eV) represents valence electrons. The PW91 functional is used. A four TiO$_2$-layer thick slab is used to model the surface (see Fig. 4.10); the two uppermost layers are allowed to relax. The optimized bulk values are used as slab cell parameters ($a_{\text{slab}} = c_{\text{bulk}} = 2.964$ Å, $b_{\text{slab}} = \sqrt{2}a_{\text{bulk}} = 6.507$ Å). Hydrogen adsorption is modeled by adding neutral H atoms to one side of the slab. A thicker slab fully optimized has been utilized for modeling diffusion processes (see below).

![Fig. 4.11](image)

**Fig. 4.11** (a, b) STM images of the TiO$_2$(110)-(1×1) surface determined with sample bias voltages of (a) 2.0 V, (b) 1.3 V. Tunneling current was set at 0.05 nA. Inset in (b): a high resolution image, tunneling conditions: 1.5 V and 0.35 nA; (c, d) STM images of the TiO$_2$(110)-(1×1) surface after exposure to atomic hydrogen with different H$_2$ dosing amounts: (c) ~ 150 L H$_2$ and (d) ~1200 L H$_2$. Tunneling conditions: 2.0 V, 0.05 nA in (c) and 2.0 V, 0.02 nA in (d). Adapted from reference [175].

Fig. 4.11 shows a series of typical STM images of a clean TiO$_2$(110)-(1×1) substrate. Bright lines along the [001] direction correspond to the rows of 5-fold coordinated Ti atoms [176, 177]. The inset in Fig. 4.11(b) demonstrates atomic resolution also along the [001] direction. There are three kinds of atomic scale features in Fig. 4.11a, denoted by ‘A’, ‘B’ and ‘C’. Type A features are of uniform size and are invisible at low bias voltages [170] (see Fig. 4.11b) and are, in accordance with previous work, assigned to hydroxyls formed by the dissociation of water molecules from the residual gas [170, 178]. Type B features are located on Ti rows and are assigned to subsurface defects [177]. Type C features bridge two neighboring Ti rows and are attributed to oxygen vacancies.
Fig. 4.11c shows an STM image of the TiO$_2$(110)-(1×1) surface recorded after exposure to atomic hydrogen (150 L H$_2$). The Ti rows (solid white lines) are still visible. The short rows of protrusions on the dashed black lines are assigned to OH species; the corresponding coverage amounts to 0.4 ML. When increasing the H-exposure to 1200 L, the STM image (see Fig. 4.11d) reveals an increased density of OH species with coverage of about 0.7 ML. Although there are still a number of H atom vacancies with respect to a perfect (1×1)-structure, the images shown in Fig. 4.11d would be consistent with the (1×1) diffraction pattern seen in the HAS data [153]. A disordered OH adlayer with a coverage of 0.25 ML as reported previously [170], could not be observed in our experiments. We speculate that at least some of the OH visible in the previously published STM data result from H$_2$O dissociation at defects [179]. We observed OH-rows resulting from H atom adsorption only for exposures of about two orders of magnitude higher than those reported in the previous works [170].

Surprisingly, even larger exposures to H did not lead to the expected “filling-up” of the H vacancies visible in Fig. 4.11d. Even after much higher exposures to H atoms images similar to the one shown in Fig. 4.11c were obtained. We never observed H coverages exceeding 0.7 ML.

A possible explanation for the apparent absence of a perfect H(1×1) monolayer might be

### Table 4.3 Total energy and binding energy $E_b$ per H atom for the hydrogenated (1×1) slabs, calculated as the difference between the hydrogenated slab and the bare slab plus atomic hydrogen (in eV). First, one hydrogen is adsorbed, and for the fully covered O$_{2C}$-H slab a second hydrogen is considered.

<table>
<thead>
<tr>
<th>system</th>
<th>Total Energy</th>
<th>first H $E_b$</th>
<th>second H $E_b$</th>
<th>Average $E_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-1.118</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>-6.778</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bare surface</td>
<td>-210.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H on O$_{2C}$</td>
<td>-214.24</td>
<td>2.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H on O$_{3C}$</td>
<td>-213.49</td>
<td>1.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H on T$_{5C}$</td>
<td>-211.73</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H on O$_{sub}$</td>
<td>-214.07</td>
<td>2.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2H: O$<em>{2C}$ + O$</em>{sub}$</td>
<td>-217.24</td>
<td>2.52</td>
<td>1.88</td>
<td>2.20</td>
</tr>
<tr>
<td>2H: O$<em>{2C}$ + O$</em>{3C}$</td>
<td>-216.90</td>
<td>2.52</td>
<td>1.54</td>
<td>2.03</td>
</tr>
<tr>
<td>2H: O$<em>{2C}$ + T$</em>{3C}$</td>
<td>-216.45</td>
<td>2.52</td>
<td>1.08</td>
<td>1.80</td>
</tr>
</tbody>
</table>
be that the impinging H atoms also form Ti-H species, which then block adjacent O adsorption sites (and which may not be seen in the STM data). In order to test this hypothesis we have calculated the binding energy $E_b$ of one atomic hydrogen atom bonded to different surface sites in a $(1 \times 1)$ unit cell (Table 4.3). The surface sites considered are the bridging $O_{2C}$, 3-fold $O_{3C}$, under-coordinated titanium $Ti_{5C}$ and a subsurface $O_{sub}$. The calculations reveal that the $O_{2C}$-H, which is tilted in the $[1\bar{1}0]$ direction, is the most stable species ($E_b = 2.52$ eV), followed by $O_{sub}$-H (2.34 eV) $O_{3C}$-H (1.76 eV) and $Ti_{5C}$-H (0.01 eV). Next, we considered the presence of two H atoms in the unit cell, with one of them occupying a $O_{2C}$ site. Also in this case the Ti-H species is the least favorable H-containing surface species, the binding energy of

![Diagram](image)

**Fig. 4.12** (a) HREELS spectra recorded for the clean TiO$_2$(110) surface (curves A and B) and after exposure to 2000 L atomic hydrogen at room temperature and subsequent annealing to the indicated temperatures (curves C-F). Curve A displays the raw spectrum, and the Fourier-deconvoluted spectra are shown in curves B-F. (b) TDS data recorded after exposing the clean TiO$_2$(110) surface to 2000 L atomic hydrogen at 300 K (curve A: H$_2$, curve B: H$_2$O) and after exposing the room temperature hydrogenated surface to 50 L CO at 95 K (curve C: CO).

The absence of Ti-H species is confirmed by the results of vibrational spectroscopy. Fig. 4.12(a) shows the HREELS data for the clean TiO$_2$(110) surface recorded at room
temperature. Curve A presents the raw spectrum that is dominated by the intense primary phonon losses (45, 55 and 94 meV) as well as their combination and multiple excitations [110]. After exposing the TiO$_2$(110) surface to 2000 L atomic hydrogen at room temperature a new loss at 456 meV (curve C) is observed, which can be unambiguously assigned to the O-H stretching mode. The frequency is in fact rather similar to the corresponding species on a ZnO(10\bar{1}0) surface [93]. Despite significant effort no Ti-H stretching modes could be observed in the HREELS data, indicating that no surface Ti-H species are formed when exposing to H-atoms at room temperature. This conclusion is corroborated by the following coadsorption experiment: The TiO$_2$(110) surface was first saturated by atomic hydrogen at room temperature. When this surface was subsequently exposed to 50 L of CO at 95 K, the corresponding TD spectrum (curve C in Fig. 4.12(b)) exhibits a desorption peak at 129 K, revealing that CO is adsorbed on the hydroxylated TiO$_2$(110) surface at 95 K, thus confirming that the Ti sites are available for CO adsorption.

At this point we conclude that there is only one H containing species on the surface, the bridging O$_2$C-H hydroxyl group. There are no Ti-H species on the surface, which is consistent with expectations for this easily reducible oxide [180, 181]. Note that on more irreducible metal oxide surfaces like ZnO metal-H species have been observed [93]. The possibility that the presence of Ti-H species prohibits the completion of the OH(1 \times 1)-adlayer can thus be safely ruled out.

When trying to obtain independent information from thermal desorption spectroscopy, TDS, a second disturbing observation was made. TDS data recorded after exposing TiO$_2$(110) to 2000 L of atomic H at room temperature show no signs of H$_2$ or H$_2$O desorption (see curves A and B in Fig. 4.12(b)). This is in pronounced contrast to H adsorption on metals [182] and on other oxides, where corresponding H$_2$ or H$_2$O desorption maxima could be clearly observed in TDS [93, 183]. Upon heating the H atoms clearly leave the surface (as seen by HREELS and HAS). Since we can rule out desorption, the only way to rationalize our findings is to propose that the H atoms migrate into the bulk and thus “disappear” from the
detection zone of the surface sensitive techniques. This is a rather unexpected finding which, if true, would have important consequences for the technical applications of TiO$_2$.

![Fig. 4.13](image)

**Fig. 4.13** (a) Side view of the (1 × 1) unit cell used to calculate the insertion of H in rutile TiO$_2$, bridging hydroxyl O$_{2C}$-H group is always present; (b) Energy profile for H penetration from the surface O$_{3C}$ to internal cavities I to IV, in eV. Selected structures for minima (bottom) and transition structures (top) are shown. In parentheses the energy values relative to the starting point (bottom), in square brackets the barriers (top). The x axis shows the vertical z position relative to the initial O$_{3C}$-H position, in Å. The y axis shows energy relative to the starting point. Adapted from reference [175].

The DFT results for H binding energies listed in Table 4.3 clearly demonstrate that the subsurface O$_{sub}$-H is a rather stable species. In order to obtain estimates on the activation energy required for subsurface migration we carried out a detailed theoretical analysis using TiO$_2$ slabs with a considerable larger thickness (8 layers) with all surface O$_{2C}$ sites hydroxylated. When a second H atom was placed initially on the surface O$_{3C}$ site, and then moved towards the cavities I, II, III and IV (see Fig. 4.13) the potential energy diagrams depicted in Fig. 4.13 were obtained. Two observations are important: First, the total energies are all lower than those on the surface and second, the corresponding activation energy is 1.11 eV. The fairly large binding energy of H atoms in the bulk can be rationalized by considering the formation of hydrogen bonds with the other oxygens inside the cavity; such stabilizing interactions are, of course, absent at the undercoordinated surface sites. A more detailed account of these effects will be provided in a future publication.
Altogether these results confirm the stability of subsurface hydroxyls and the corresponding relatively low activation energies for migration of H into the bulk can explain the experimental TDS findings. Note, that there are a few accounts of hydrogen incorporation into a rutile TiO$_2$ lattice [184-186].

It remains to explain why the H atom coverage cannot exceed a critical value and form a perfect (1×1) adlayer as in the case of H on other oxide surfaces (e.g. ZnO(10̅10), [73]). Since site-blocking by the formation of other surface species can be ruled out (see above) another likely explanation could be that repulsive interactions between adjacent OH species limit the maximal coverage. Indeed, calculations for larger unit-cells simulating H coverages from 0.5 ML to 1.5 ML reveal a pronounced decrease of the H atom binding energy with coverage. When using the DFT calculations in the framework of a thermodynamic analysis [187], considering the equilibrium between adsorbed H-atoms and H$_2$ molecules in the gas phase, we find that for the experimental conditions (300 K and 10$^{-6}$ mbar of H$_2$ pressure) the coverage is predicted to be 0.66 ML, in good agreement with the experimental observations.

In conclusion, a combined experimental and theoretical approach has been used to gain insight into the behavior of hydrogen atoms on TiO$_2$(110) surface. Exposing TiO$_2$(110) to atomic H yields a quasi (1×1) adlayer consisting of 0.66 ML hydroxyl groups. Heating of the hydroxylated sample does not lead to recombinative desorption of H$_2$ (or H$_2$O) molecules, but to a migration of H atoms into the TiO$_2$ bulk, as demonstrated by TDS and HREELS results. This finding is supported by DFT-calculations, which reveals the presence of an activation barrier of 1.11 eV for migration into the bulk, in contrast to the recombinative desorption barrier as H$_2$ of 2.64 eV.

Still, there are some underlying problems in this system not well understood:

(a) No H$_2$ desorption was observed throughout the experiments even after the sample was heated to 900 K. This temperature is high enough to overcome the possible
desorption barrier of 2.26 eV/molecule. Moreover, the diffusion to TiO$_2$ bulk and desorption (let's say two sides of one reaction pathway) would be non-equilibrium since on the vacuum side the product can be removed quickly and can't re-adsorb on the surface.

(b) If the atomic hydrogen adsorbs on bridge oxygen sites to form hydroxyl species, where does the electron of atomic hydrogen go? It is known that the bridge oxygen on TiO$_2$(110) has no unfilled bonding orbitals to accept electron. If the electron goes to the 3d orbital of Ti$_{5C}$ or Ti$_{6C}$, an 2-D metallic character would be presented on the surface because the conduction band of TiO$_2$ is mainly contributed by Ti 3d orbitals [188, 189].

(c) Chemically, there should be no difference between hydroxyl group formed by atomic hydrogen adsorption on O$_{br}$ sites and by H$_2$O dissociation at bridge oxygen vacancies. Also, as described in paper, the less than monolayer (66%) coverage is due to the repulsion force between hydroxyl groups. This means the hydroxyl group formed by H$_2$O dissociation on 4% oxygen vacancies would have higher binding energy. Indeed, a small amount of H$_2$O desorption can be detected in the TDS experiments for H$_2$O adsorption on TiO$_2$(110). In principle the adsorbed species with lower binding energy would desorb first, which means the 66% hydroxyl groups would be more like to desorb as H$_2$O since we have observed the H$_2$O desorption from the small coverage of hydroxyl.

(d) It is more reasonable to compare the calculated diffusion barrier with the activation barrier for desorption as H$_2$O, but not as a H$_2$. 
5. Small molecular adsorbates on ZnO(000\(\bar{1}\))

As a polar surface, ZnO(000\(\bar{1}\)) exhibits much complexity in surface structure. Many structural models have been proposed to explain experimental observations (as will be discussed below). In addition, atomically resolved images of this surface are still rarely reported due to either the experimental difficulties or the complex structure of this surface [190-193]. But one consistency in experimental work is the existence of abundant of oxygen vacancies on this surface. In this chapter, I present the work on the structure of ZnO(000\(\bar{1}\)) surface, and \(\text{H}_2\), HCOOH and CO\(_2\) adsorption on the ZnO(000\(\bar{1}\)) surface.

![Stick-and-ball model of the wurtzite ZnO structure from a perspective view.](image)

Fig. 5.1 Stick-and-ball model of the wurtzite ZnO structure from a perspective view.

5.1 The structure of the ZnO(000\(\bar{1}\)) surface

Fig. 5.1 shows the perspective view of the wurtzite ZnO bulk structure. Along the [0001] direction, the structure can be characterized by the repeating-stack of Zn-O double layers. The difference of the charge between oxygen and Zn layers lead to a dipole moment in the Zn-O double layers. The in-plane dipole moment can be compensated by the neighbor double layers, while the out-of-plane dipole moment
will diverge with increasing layer number [194, 195]. As a result, a macroscopic dipole moment builds up along the [0001] direction cross the crystal. This macroscopic dipole moment can essentially elevate the Madelung potential of two surfaces termination, namely, the oxygen terminated surface O-ZnO(000\(\bar{1}\)) and the Zn terminated surface Zn-ZnO(0001). Energetically, this elevated Madelung potential possibly (not necessarily) causes the instability of the two polar surfaces. Several spontaneous reactions of the surface can occur to diminish the Madelung potential [194, 195]: (a) adsorption of charged ions. (b) charge transfer between two counterpart polar surfaces. (c) surface reconstructions (including the formation of disordered steps).

The research interest in the structure of these two polar ZnO surfaces perhaps comes from the existence of a non-negligible fraction of these two polar surfaces in ZnO powders, which means they are quite favorable in nature. The study of such polar surfaces is also an interesting fundamental problem. The O-ZnO surface was investigated by STM and found be unreconstructed with no significant defect concentration [192]. The further study by surface X-ray diffraction (SXRD) and ab initio calculation attributed the unreconstructed structure to the surface relaxation and charge transfer between the two polar surfaces. It was speculated that, as a result of the charge transfer, the two polar surfaces exhibit metallicity [196]. But, unfortunately, the surface metallic character was not approved by HREELS experiment under H free conditions, in which a significant broadening of the quasi-elastic peak due to the excitation of free charge carriers in subsurface region would be expected [105]. Furthermore, a photoluminescence (PL) combined with surface Kelvin probe (SKP) study observed a strong spontaneous polarization along [0001] direction and just a small difference of the band bending of the (0001) and (000\(\bar{1}\)) surfaces of ZnO [197]. The authors claimed that the charge transfer between two surfaces is not the dominant contribution to the stabilization of the two polar surfaces. Also, a DFT study showed a strong contraction of the topmost Zn-O double layers on both sides [198]. Although consistent with the result on the ZnO(000\(\bar{1}\)) surface, it deviated on ZnO(0001) surface
for which STM has shown a different stabilization mechanism by forming triangular islands and holes [199, 200], which means the charge transfer mechanism alone is not adequate to understand the stabilization mechanism of these two polar surfaces.

A very surface sensitive technique, helium atomic scattering (HAS), was also performed on ZnO(000\(\bar{1}\)) surface. Different from the preview work, it showed a (3×1) reconstruction on the clean surface [28, 106, 107]. Later, by using CO as a probe molecule, it was claimed that the ZnO(000\(\bar{1}\)) is either reconstructed or hydrogen covered [201]. In addition, the hydroxylated ZnO(000\(\bar{1}\)) surface shows high resistance to hydrogen etching that occurs on other ZnO surfaces [202], which might be due to the high stability of hydroxyl groups on this surface. Note also that a (1×1) OH covered surface is suggested to be thermodynamically unfavorable, and half monolayer of OH coverage with formation of (2×1) superstructure was calculated to be the most thermodynamically stable phase [203]. The experimental observation of a (1×1) OH covered surface could be explained by a kinetic stabilization mechanism [106, 107].

The experimental observation of (3×1) superstructure of clean ZnO(000\(\bar{1}\)) surface is difficult since such a surface is so reactive that H\(_2\)O in UHV can adsorb on the surface very fast to cure the reconstruction. This was confirmed by X-ray photoelectron (XPS) experiment that the O1s curve always shows signal from OH species under the common preparation condition [72, 204]. The observation of H-free O1s signal can only be achieved under very careful preparation condition [106]. In addition, a DFT calculation of the phase diagram of ZnO(000\(\bar{1}\)) with oxygen and hydrogen atmosphere also proposed that a defect free surface is only possible under the condition of high oxygen partial pressure with nearly no presence of hydrogen [203].

In this work, we provide additional evidence for the existence of a clean, H-free and (3×1) reconstructed ZnO(000\(\bar{1}\)) surface.

The first evidence is from the LEED results shown in Fig. 5.2. The clean ZnO(000\(\bar{1}\))
surface shows a hexagonal structure with (3×1) reconstruction (Fig. 5.2, left panel). The different symmetry of LEED pattern (6-fold) and ideal ZnO(000\bar{1}) surface (3-fold) was explained by presence of single height steps (double layer) [205]. This explanation is also consistent with the HAS result that abundant of steps are presented on the ZnO(000\bar{1}) surface [206]. By exposing the clean surface to H₂O or atomic H (Fig. 5.2, right panel), the (3×1) LEED pattern turns to (1×1). And if the clean surface is left under UHV condition for some time (e.g. 1×10⁻¹⁰ mbar for 1 h), the (3×1) pattern becomes undistinguishable and (1×1) is more likely formed. The (3×1) reconstruction could be achieved by removing of one row of oxygen in every three oxygen rows, although other mechanism such as presence of (3×1) step is also possible to result in the (3×1) LEED pattern.

HREELS experiments were also performed on clean and H₂O covered ZnO(000\bar{1}) surface. Fig. 5.3(a) shows the HREELS results on the clean, (3×1) reconstructed ZnO(000\bar{1}) at room temperature. No loss feature can be detected related OH species. In contrast, as shown in Fig. 5.3(b), very intense loss feature located at around 449 meV shows up after 2 L H₂O adsorption. The loss feature at 449 meV can be assigned to the stretching vibrational mode of OH, ν(OH). Since other H₂O related loss features are presented in the HREEL spectrum, we can assign the loss feature at 449 meV to ν(OH) of the isolated OH, which further indicates a dissociative adsorption of H₂O molecules at oxygen vacancies. In addition, on the clean surface a small loss feature at around 45 meV is observed which was assigned to the vibrations of defective sites [207]. After exposing to 2 L H₂O, the loss peak disappears, which
confirms deduction of dissociative adsorption of H₂O at defective sites. The HREEL spectra on the atomic hydrogen covered ZnO(000$\bar{1}$) is not shown here due to the relative poor spectrum quality caused by the metallization effect upon atomic hydrogen adsorption, the LEED pattern of which also exhibits the same (1×1) structure for the H₂O covered surface.

Fig. 5.4 presents the TDS results of H₂O adsorbed on the ZnO(000$\bar{1}$) surface. Three H₂O desorption peaks are observed at 418 K, 615 K and 710 K respectively. No H₂ desorption was detected in the measured temperature range from 300 K to 850 K. The three different H₂O adsorption peaks imply several different stable OH species formed on the surface. Since 1/3 ML of oxygen vacancies are thought to be existing on the
clean surface and each H$_2$O molecule gives two OH species upon adsorbing at an oxygen vacancies, we would expect that the (1×1) OH covered surface can not be fulfilled just by H$_2$O adsorption while 1/3 of surface oxygen are uncovered. Note also that the experiment was performed at RT and any physisorption of H$_2$O on this surface can be ruled out.

Further atomic hydrogen adsorption on H$_2$O covered surface confirmed this speculation. As is shown in Fig. 5.5, after 4 L H$_2$O adsorption on the ZnO(000\bar{1}) surface, the sample was further exposed to 500 L H/H$_2$ adsorption. The TD spectra show two desorption species, H$_2$O and H$_2$. The H$_2$ desorption comes from the H species in the bulk ZnO that are formed by the diffusion of hydrogen atoms into ZnO bulk during the adsorption process [105]. H$_2$O desorption peaks exhibit similar shape with that from the H$_2$O exposed surface, but the analysis of the peak area shows around 1.5 times more than that from H$_2$O exposed surface, $A_{H_2O+H} : A_{H_2O} = 3 : 2$. The increase of H$_2$O desorption can be attributed to the additional formation of OH species by atomic hydrogen adsorption on the 1/3 ML uncovered surface oxygen. Pure H$_2$O adsorption on ZnO(000\bar{1}) results in 2/3 ML of OH species on the surface and 1/3 ML of H$_2$O during the following TDS experiment. But after atomic hydrogen adsorption on the pure H$_2$O exposed surface, an (1×1) OH covered surface can be fulfilled and 1/2 ML of H$_2$O will be observed in the following thermal desorption process.

![Fig. 5.5 TD spectra of 4 L H$_2$O adsorption followed by 500 L H/H$_2$ adsorption on the ZnO(000\bar{1}) surface at RT. The heating rate is 1.5 K/s.](image)
Combining the results from LEED, HREELS and the ratio of $A_{H_2O+H} : A_{H_2O} = 3 : 2$ in TDS experiment, we conclude that the clean, H-free and (3×1) reconstructed ZnO(000\(\bar{1}\)) surface does exist.

Still, there are some points in this work not well understood:

(a) the explanation of (3×1) LEED pattern. From LEED pattern only the information of surface periodicity can be obtained. The missing of 1/3 of oxygen rows would be not the only possibility to yield (3×1) LEED pattern although a better understanding is still scarce. Indeed, one previous work observed streak structure in LEED on the same surface [208] and explained by the presence of two double Zn-O layers [205, 209]. Note also that this is different from the satellite diffraction spots observed in many film/substrate systems due to the mismatch of lattice constant and multi-scattering from large unit cell [210-212]. As a summary, although the streak structure in previous work is different from the observation in this work, such effect should still be considered when explaining superstructure in LEED on oxide surface.

(b) the transformation of LEED pattern from (3×1) to (1×1) is not exactly as described in above paragraphs by exposing the clean surface to enough amount of H$_2$O or atomic H, but more like a trigger effect that a very small amount of H$_2$O exposure (smaller than 0.1 L) can dispel the (3×1) and form a sharp (1×1) LEED pattern.

(c) the presence of three H$_2$O desorption peaks perhaps is the evidence of (1×1) and (2×1) stable phase of OH species although the (1×1) phase is thermodynamically unstable. The high temperature peak at around 700 K is more reasonably to be assigned to the OH species formed at step edges.

5.2 Hydrogen adsorption on the ZnO(000\(\bar{1}\)) surface

In this work, the electronic effects of H atoms at interstitial sites in ZnO have been investigated by high resolution electron energy loss spectroscopy (HREELS). A
reversible doping is achieved by exposing single crystalline (000\textbar{1})-oriented ZnO substrates to atomic hydrogen. At low temperatures, interstitial H atoms form shallow donor states. At sufficiently high temperatures, the electrons are excited into the conduction band. We use EELS to demonstrate the presence of plasmons resulting from this finite density of charge carriers in the conduction band. Above temperatures of 100 K, a strong, plasmon-induced broadening of the quasielastic peak in the HREELS data is observed. The analysis of the temperature dependence yields a donor level ionization energy of 25 ± 5 meV.

Undoped ZnO exhibits n-conduction properties, a fact that—despite numerous experimental and theoretical studies [213-217]—is still not thoroughly understood. It has long been known that the incorporation of H atoms in the bulk increases the electrical conductivity of ZnO. In fact, ZnO can be used as a detector for hydrogen atoms [218-221]. From the temperature dependence of the electrical conductivity, it is thought that the incorporation of H atoms at interstitial sites gives rise to shallow donor states with an ionization energy of 51 meV [222]. This value, however, is not consistent with donor activation energies of 35 ± 5 meV as obtained from electron paramagnetic resonance (EPR) spectroscopy [215]. It has been proposed that the electrical conductivity experiments are affected by other bulk defects such as oxygen vacancies, which can also interact with H atoms and may have different effects. The n-doping properties of H in ZnO have been corroborated by recent theoretical work [213], where it was proposed that interstitial H atoms always act as donors in ZnO. A reliable value for the ionization (or exciton binding) energy, however, could not be obtained from these calculations.

The experiments were carried out in an UHV apparatus with a base pressure better than 5×10^{-11} mbar, equipped with an HREEL spectrometer [190], LEED optics and a mass spectrometer [88, 223]. The O-terminated ZnO(000\textbar{1}) surface (O-ZnO) was prepared using sputtering and annealing cycles as described previously [106, 107]. The LEED pattern recorded for the clean O-ZnO surface exhibited (3×1)
superstructure spots, as reported previously [72]. This clean, reconstructed (3×1) O-ZnO surface is very reactive towards H$_2$O adsorption and quickly converts into a very stable, structurally well-defined, OH-terminated surface exhibiting a (1×1) LEED pattern termed HO-ZnO [72, 106, 107]. Exposure to atomic hydrogen was performed by dissociating H$_2$ on a hot tungsten filament situated in the line of sight from the substrate. H$_2$O was dosed on the ZnO surface by backfilling the UHV vessel with water vapor. In the following exposures will be given in units of Langmuir (L), with 1 L = 1.33×10$^{-6}$ mbar•s. The width of the quasielastic signal in the EELS data, $\Delta_{\text{app}}$, showed a small day-to-day variation. For the analysis of the data the most recent value of $\Delta_{\text{app}}$ was used.

The EELS data for the clean (1×3) O-ZnO surface shown in Fig. 5.6A are dominated by intense Fuchs-Kliewer phonon losses (fundamental and multiples) located at 68, 135, 203 and 269 meV [33, 53, 224]. For the HO-ZnO substrate, a new loss arising from the OH stretching vibration of the surface hydroxyl species is seen at 449 meV (3621 cm$^{-1}$), shown in Fig. 1B, a frequency which is close to the value of 3670 cm$^{-1}$ reported for OH species on the mixed-terminated ZnO(10oda) surface [88, 93]. The weak feature at 45 meV was also observed in previous works [225, 226] and was
attributed to a vibrational mode localized at defects.

For the spectrum shown in Fig. 5.6B recorded for the HO-ZnO surfaces, the full width at half maximum (FWHM, $\Delta_{\text{tot}}$) of the quasielastic peak is equal to 6 meV, slightly larger than the FWHM of the resolution of HREELS apparatus, 4 meV, as determined in experiments on a clean Pt(111) substrate. Similar broadenings of the quasielastic signal in EELS have been observed for other semiconductors, Si [51, 227], GaAs [50] and Ge [228]. In following these previous works we attribute the broadening of $\Delta_{\text{tot}}$ seen for ZnO substrates to an interaction of the incident electrons with plasmons in the semiconductor (SC) substrates. Compared to a metal the carrier density in a SC is quite low, leading to plasmon energies in the meV-regime. Persson has derived an elegant formula [51] relating the broadening $\Delta$ (given by $\Delta_{\text{tot}}^2 = \Delta_{\text{app}}^2 + \Delta^2$) to experimental parameters, the carrier density $n_c$ and the substrate temperature $T$:

$$\Delta^2 = \frac{C}{4} \pi^2 \omega_p^2 \left[ \frac{2}{e^{k_{b} n_c / k_b T} - 1} + 1 \right] \cos \alpha$$

(5.1)

with

$$C = \frac{4}{\pi} \frac{1}{\varepsilon + 1} \frac{1}{\cos^2 \alpha} \frac{1}{k a_0}$$

and

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \varepsilon}} \quad \text{and} \quad \omega_p = \sqrt{\frac{n_e e^2}{m \varepsilon_0}}$$

(5.2)

with $\varepsilon$ the relative dielectric constant (4.6 for ZnO [229]), $k$ the wave vector of the incident electron, $a_0$ the Bohr radius, $m^*$ the effective mass of electrons in ZnO (0.19 $m_e$ for ZnO [230]), $\varepsilon_0$ the vacuum dielectric constant, $k_b$ the Boltzmann constant, $\omega_{sp}$ and $\omega_p$ are the surface and bulk plasmon frequencies, respectively, and $\alpha$ the electron angle of incidence ($55^\circ$).

From (5.1) and our experimental parameters and the materials constants for ZnO we obtain a carrier density of $9 \times 10^{13}$ cm$^{-3}$, a reasonable low value for a clean ZnO substrate. Upon exposing the HO-ZnO surface to atomic hydrogen (see Fig. 1C), $\Delta_{\text{tot}}$ strongly increases. No indications of additional individual losses could be detected in
the EELS data. In particular, we were unable to detect Zn-H vibrations, which have been observed at around 200 meV (1613 cm$^{-1}$) on other ZnO surfaces [93]. This is expected, since according to the current structural models for this surface [72] the HO-ZnO surfaces does not expose Zn atom. The increase of $\Delta_{\text{tot}}$ was found to be completely reversible: Heating the ZnO specimen (and thus removing the H atoms) reduced $\Delta_{\text{tot}}$ to its original value. We did not observe any indication of a band arising from bulk OH stretching vibrations at about 3327 cm$^{-1}$, which has been detected in IR transmission experiments [231].

A similar broadening upon exposure to atomic H has been reported for the ZnO(10\bar{1}0) surface, where the broadening was linked to the formation of a partially filled, H-induced electronic surface state [93]. In the present case, however, the surface is already hydroxylated and fully oxidized prior to H atom exposure. DFT calculations have shown that the surface hydroxylation is the most efficient means to stabilize the

![Fig. 5.7](image)

**Fig. 5.7** (a) Thermal desorption spectra for m/e=2, representing H$_2$, of the HO-ZnO surface (prepared by exposure to H$_2$O) before (solid cycles) and after (hollow cycles) exposure to 1000 L atomic H. (b) same as (a) but for m/e=18, representing water. The heating rate was 1.5 K/s.
polar surface termination of O-ZnO [232]. The complete hydroxylation of the HO-ZnO surface has been demonstrated by a study of CO adsorption on this surface [233] and is further evidenced by the presence of the OH stretching mode and the absence of any other features in the EELS data after H exposure.

The only possibility to explain our experimental observation is that the H atoms impinging on the HO-ZnO substrate diffuse into the bulk, forming H interstitials in the subsurface region. Their presence is clearly revealed by thermal desorption spectroscopy (TDS). As shown in Fig. 5.7(a), after loading the hydroxylated substrate with atomic hydrogen at 300 K, the TDS data reveal an additional H$_2$ desorption peak (m/e=2) at ~ 500 K. The H$_2$ peak was not seen for the HO-ZnO surface that was not exposed to H atoms. The shape of H$_2$O desorption peaks from the HO-ZnO surface, however, is unaffected by the exposure to H atoms, as seen in Fig. 5.7(b).

Using (5.1) we can calculate the carrier density $n_c$ from the broadening $\Delta$ and yield a value of $1\times10^{17}$ cm$^{-3}$. When the HO-ZnO substrate is heated to higher temperatures,

![Fig. 5.8](image)

**Fig. 5.8** (a) FWHM of the quasi-elastic peak, $\Delta$, in the HREEL spectra (measured at RT) as a function of annealing temperature $T_a$ after exposing the HO-ZnO surface to 1000 L atomic hydrogen at 300 K. (b) $d(\Delta^2)/dT$ as a function of the annealing temperature. Annealing rate: 1.5 K/s, total annealing time: < 2 min.
the broadening decreases continuously as shown in Fig. 5.8(a). Fig. 5.8(b) shows 
\( \frac{d(\Delta^2)}{dT} \) as a function of annealing temperature. The curve reveals two peaks at 455 
K and 515 K. By comparison with the hydrogen TDS results (Fig. 5.8(a)) the peak at 
515 K can be attributed to \( \text{H}_2 \) desorption from the surface. The maximum observed at 
455 K, on the other hand, is not detected in TDS experiments and, accordingly, must 
be due to diffusion of H atoms into deeper bulk regions. The corresponding diffusion 
barrier \( E_{\text{diff}} \) can be estimated from this temperature (455 K) according to 

\[
\frac{E_{\text{diff}}}{k_b T_{\text{max}}} = \frac{\nu}{\beta} \exp\left(\frac{E_{\text{diff}}}{k_b T_{\text{max}}}\right)
\]  

(5.3)

where \( \nu \) is a preexponential factor, \( \beta \) is the linear heating rate, and \( T_{\text{max}} \) is the 
temperature corresponding to the maximum diffusion rate. This equation is derived 
from 

\[
\frac{dn}{dt} = \beta \frac{dn}{dT} = -\nu n \exp\left(-\frac{E_{\text{diff}}}{k_b T}\right) \quad \text{and} \quad \frac{d^2n}{dt^2} = 0 
\] 

for the maximum diffusion rate. 

For a heating rate of \( \beta=1.5 \text{ K s}^{-1} \) and a preexponential factor \( \nu \) of \( 10^{13} \text{ s}^{-1} \), an activation 
energy of 1.26 eV is obtained, in reasonable agreement with the experimental value 
(\( \sim 1.0 \) eV) reported for H atom diffusion in bulk ZnO [218, 219]. For the \( \text{H}_2 \) 
desorption peak at 515 K, an activation energy for desorption of 1.44 eV is deduced, 
which also agrees well with the results of recent DFT calculations [234].

![Graph](image)

**Fig. 5.9.** The value of \( \Delta^2 \) as a function of different measurement temperatures \( T_m \) for HO-ZnO 
surface exposed to 1000 L atomic hydrogen at 100 K. The dashed line has been obtained using 
Eq. (1) assuming a temperature independent density of carriers, \( n_c \). The solid line is the result 
of a nonlinear least square fit assuming an ionization energy of the H-induced shallow donor 
of \( \varepsilon_d=25 \text{ meV} \) (see text).
Having provided compelling evidence that the increase of $\Delta$ seen in our EELS data results from a finite density of electrons in the conduction band, we next investigate the temperature dependence of $\Delta$ below 300 K, where any diffusion of H atom can be safely ruled out.

As shown in Fig. 5.9, $\Delta^2$ (and $\Delta$) increases continuously with temperature in the regime between 100 K and 300 K. In principle, such a temperature dependence is expected, see expression (5.1). A comparison of the experimental data with the dashed line in Fig. 5.9, however, reveals that the temperature dependence predicted by expression (5.1) is much too small to reproduce the experimental behavior. The only possibility to explain this strong temperature variation is to assume that the carrier density itself, $n_c$, depends on temperature. This is in accord with previous suggestions, that H-interstitials act as shallow donors with fairly small ionization energies [213].

For an n-type semiconductor, the CB charge density $n_c$ can be calculated from [235, 236]:

$$n_c = \left( \frac{N_d N_c(T)}{2} \right)^{1/2} \exp \left( -\frac{e_d}{2k_b T} \right) \quad (5.4a)$$

or

$$\ln n_c = \frac{1}{2} \ln \left( \frac{N_d N_{c,0}}{2} \right) - \frac{e_d}{2k_b T} + \frac{3}{4} \ln T \quad (5.4b)$$

where $N_d$ is the density of donor atoms, $N_c(T)$ the conduction band density of states.

Fig. 5.10 Schematic model for the shallow donor states created by H atoms in ZnO.
and $N_e(T) = 2N_{e,0} T^{3/2}$ with $N_{e,0} = \left( \frac{m^* k_B}{2\pi \hbar^2} \right)^{3/2}$. $\varepsilon_d$ denotes the donor state ionization energy, as shown in Fig. 5. 10. A detailed discussion on the origin of expression (5.4a) is presented in Appendix 5. If we insert the expression for $n_c$ in (5.4a) into (5.1) we can perform a nonlinear least squares regression analysis, which yields $\varepsilon_d = 25 \pm 5$ meV. The latter value is in reasonable agreement with the ionization energy of $35 \pm 5$ meV as obtained from a completely different method, electron paramagnetic resonance (EPR) [215]. This value, however, is substantially smaller than the value deduced from electrical conductivity experiments, 51 meV [222]. The higher value might result from contributions from other types of defects, such as oxygen vacancies, which are included in conductivity measurements.

In summary, our HREELS and TDS data demonstrate that exposing a fully hydroxylated ZnO(0001) surface to atomic hydrogen leads to the incorporation of subsurface interstitial H atoms. The shallow donor states created by this doping process can be thermally dissociated, thus populating the conduction band and, as a result, giving rise to plasmon losses seen in EELS. From the observed temperature dependence, an ionization energy of $25 \pm 5$ meV is obtained. In the future we will use this method to study the doping of ZnO by other elements, in particular metals.

5.3 HCOOH adsorption on the ZnO(0001) surface

The adsorption and interaction of HCOOH on the ZnO(0001) surface has been studied by HREELS and TDS. Exposing the ZnO(0001) surface to HCOOH at 100 K leads to either multi- or double layer HCOOH and formate species. The formate species can only be formed at oxygen vacancies through a dissociative adsorption of HCOOH with the ionized H diffusing into ZnO bulk. Heating the sample to higher temperatures induces a geometry conversion from the bidentate to monodentate formate species. Further heating of the sample leads to a dehydration process of the

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1 The theoretical work was performed by Janos Kiss.
monodentate formate species to CO and H₂O at around 500 K and full decomposition process to CO, CO₂ and H₂ at 550 K. In addition, an adsorbate-induced Zn desorption was also observed along with the formate full decomposition.

Formate species was predicted by DFT calculations to be one of the intermediates in the methanol synthesis process [42, 43]. Experimentally, formate species were observed after dissociative chemisorption of CH₃OH on ZnO surfaces [237, 238]. It has been shown by many groups that the adsorption of HCOOH on metal or metal oxide tends to form formate on the surface [239-245]. Several different adsorption geometries were proposed depending on surfaces and adsorption sites, namely, mono-dentate, bi-dentate and bridge structures [242, 246]. Upon heating, the formate species undergoes a decomposition releasing CO or CO₂ depending on the acidity of the anion sites [239] and the structure of formate species [247]. With the decomposition of formate, an adsorbate-induced desorption of Zn was also observed. It was considered that the desorption of Zn is attributed to the reduction of the surface by the adsorbates [237, 248]. In this work, a more detailed view on the properties of HCOOH adsorbed on ZnO(000̅1) surface is provided using HREELS and TDS.

![Fig. 5.10 TD spectra of 10 L HCOOH adsorbed on ZnO(000̅1) surface at 120 K. The heating rate is 1.5 K/s.](image-url)
Fig. 5.10 shows the TD spectra of 10 L HCOOH adsorbed on ZnO(000\bar{1}) surface at 120 K. The main desorption products are: HCOOH (mass 46), H\textsubscript{2} (mass 2), H\textsubscript{2}O (mass 18), CO (mass 28), CO\textsubscript{2} (mass 44) and trace amount of CH\textsubscript{2}O (mass 29 and 30) and Zn (mass 64). For CO, the contribution from the fragment of CO\textsubscript{2} has been subtracted. At low temperature region, only the molecularly desorption of HCOOH are observed at 155 K and 173 K which can be assigned to physisorbed multi- and double layer HCOOH. Above 200 K, no molecular desorption of HCOOH is observed and only the decomposition products, CO, CO\textsubscript{2}, H\textsubscript{2}H\textsubscript{2}O, and a trace amount of CH\textsubscript{2}O and Zn, are detected. A dominant peak located at 554 K consists of CO, CO\textsubscript{2}, H\textsubscript{2} and a trace amount of CH\textsubscript{2}O and Zn. A shoulder at the low temperature side of the CO peak is also resolvable. The H\textsubscript{2}O desorption peak covers a very wide temperature range from 200 K to 800 K, but decreases sharply at around 550 K, which is exactly the decomposition temperature of the formate species (see Fig. 5.10).

In Fig. 5.11, HREEL spectra on the clean and with various amount of HCOOH covered ZnO(000\bar{1}) surface at 120 K are shown. No loss feature is observed on the clean surface, indicating a perfectly clean surface, as well as a Fourier deconvolution
without artifacts process. The spectrum of 10 L HCOOH covered surface (Fig. 5.11b) exhibits the loss features at 120, 154, 174, 212, 341 and 368 meV that can be assigned to physisorbed HCOOH [249]. On the other hand, HREEL spectrum of low coverage HCOOH adsorbed on ZnO(000\(\bar{1}\)) at 120 K (Fig. 5.11d) shows totally different loss features at 132, 170, 199, 341, 359 and 449 meV. Those loss features were suggested by our DFT calculation and previous work [244] coming from the formate species that are formed by dissociative adsorption of HCOOH through breaking OH bond and leaving the ionized H to the bulk of ZnO. But the loss peak at 449 meV that was attributed to the surface OH species [105] was still observed in Fig. 5.11d. This OH species is thought to stem from the co-adsorption of background H\(_2\)O at the unsaturated oxygen vacancies since only a small amount of HCOOH is used that can't saturate the oxygen vacancies (Fig. 5.11d). This suggestion is further confirmed by the intermediate coverage of HCOOH on ZnO(000\(\bar{1}\)) (Fig. 5.11c), where no surface OH-related loss feature is seen in Fig. 5.11c, although its spectrum shows a combinative features of physisorbed HCOOH and formate species.

Co-adsorption of HCOOH and D\(_2\)O was also performed in order to determine the adsorption site of the formate species. The TD spectra after HCOOH adsorption followed by D\(_2\)O adsorption shows the same desorption peaks as that of HCOOH adsorbed on clean the ZnO(000\(\bar{1}\)) surface, and no D\(_2\)O (mass 20) desorption was detected (data not shown here). Since D\(_2\)O can only chemisorb on the ZnO(000\(\bar{1}\)) surface at oxygen vacancy sites [106, 107], we propose that the formate species are formed at oxygen vacancies, which is consistent with the argument in previous work that the formation of formate always requires a cation on the surface [239, 240, 243-245].
The absence of a loss feature at 449 meV in the spectra of Fig. 5.11b and Fig. 5.11c provides a solid evidence for the dissociative adsorption and the diffusion of the ionized H into ZnO bulk upon HCOOH adsorption. The very broad H$_2$O desorption peak in Fig. 5.10 provides another evidence for this explanation because the out-diffusion of H from bulk, as shown in previous work [105], also occurs in a large temperature range from 270 K to 750 K. The adsorption of background H$_2$O forming multilayer water would give rise to the desorption peak lower than 270 K, because either the out-diffusion of bulk H or the decomposition of the formate species is unlikely in this temperature range.

Fig. 5.12 shows a series of HREEL spectra of various HCOOH coverages on the ZnO(000\(\overline{1}\)) surface at 120 K after annealing to various temperatures. Below 160 K (as shown in Fig. 5.12a and Fig. 5.12b), the spectra mainly show the features of

![HREEL spectra of 10 L HCOOH adsorbed on ZnO(000\(\overline{1}\)) at 120 K after annealing to various temperatures. All measurements were performed at 120 K.](image)

**Fig. 5.12** HREEL spectra of 10 L HCOOH adsorbed on ZnO(000\(\overline{1}\)) at 120 K after annealing to various temperatures. All measurements were performed at 120 K.
physisorbed HCOOH, which is consistent with the TDS data in Fig. 5.10. After the desorption of molecular HCOOH, the loss features of the formate species appear at 131, 170, 199 and 360 meV. Three possible adsorption geometries of formate have been reported on other oxide surfaces [239, 244, 245], namely, mono-dentate, bi-dentate and bridge structures. One rule to distinguish these three geometries in vibrational spectra comes from the splitting of the symmetric stretch vibrational mode of (OCO), $\nu_{s}(\text{OCO})$, and the asymmetric stretch vibrational mode of (OCO). The splitting of monodentate formate is generally larger than 41 meV and the bidentate (including bridge structure) formate smaller than 33 meV [245]. In the bridge structure, the two oxygen atoms of formate would be bound to two different Zn atoms. For the ZnO(000$\bar{1}$) surface, the minimum distance of two adjacent Zn atoms along the [1120] direction is 3.25 Å, but the distance of two oxygen atoms in the free formate ion is just 2.25 Å [243]. So, the bridge structure can be ruled out for HCOOH adsorbed on the ZnO(000$\bar{1}$) surface. Consequently, the loss feature shown in Fig. 5.12c can be assigned to bidentate formate due to its relative small splitting of $\nu_{s}(\text{OCO})$ and $\nu_{as}(\text{OCO})$, accounting to 28 meV.

Heating the sample to 500 K, as shown in Fig. 5.12d, the intensity of formate loss features decreases. In addition, three new loss features at 161, 204 and 449 meV show up, indicating that new formate and OH species are formed along with the partial decomposition of the bidentate formate to CO and H$_2$O occurring at around 500 K. The new formate species can be assigned to monodentate structure due to a relatively large splitting of their $\nu_{s}(\text{OCO})$ and $\nu_{as}(\text{OCO})$ which amounts to 43 meV, indicating a geometry conversion along with the first decomposition process. At the same time the loss feature at 449 meV reappears. Indeed, a similar geometry transformation was also observed for HCOOH adsorbed on NiO(111) surface studied by DFT calculation [250], but not reported on ZnO surfaces. Additionally, the desorption of CO at 500 K (shown in Fig. 5.10 as the shoulder at low temperature side of CO desorption peak located at 550 K) indicates that, beside the geometry conversion from bidentate formate to monodentate formate, also a decomposition of formate to CO and H$_2$O
**Table 5.1** assignments of experimental and calculated results for monodentate and bidentate formate species in units of meV.

<table>
<thead>
<tr>
<th>Assignments</th>
<th>$\nu$(OH)</th>
<th>$\nu$(CH)</th>
<th>$\pi$(CH)</th>
<th>$\nu_{as}$(OCO)</th>
<th>$\nu_{s}$(OCO)</th>
<th>$\Delta\nu$(OCO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-dentate (Exp.)</td>
<td>449</td>
<td>360</td>
<td>131</td>
<td>204</td>
<td>161</td>
<td>43</td>
</tr>
<tr>
<td>Mono-dentate (Cal.)</td>
<td>*</td>
<td>358.8</td>
<td>121.4</td>
<td>204.6</td>
<td>137.9</td>
<td>66.7</td>
</tr>
<tr>
<td>Bi-dentate (Exp.)</td>
<td>449</td>
<td>360</td>
<td>131</td>
<td>199</td>
<td>171</td>
<td>28</td>
</tr>
<tr>
<td>Bi-dentate (Cal.)</td>
<td>*</td>
<td>372</td>
<td>120.4</td>
<td>186.4</td>
<td>155.6</td>
<td>30.8</td>
</tr>
</tbody>
</table>

*: not calculated.

takes place at 500 K.

After heating the sample to 620 K (Fig. 5.12e), only the loss feature at 449 meV is observed, indicating the accomplishment of the decomposition process of the monodentate formate, which is also consistent with the TDS data of Fig. 5.10. Annealing at 750 K (Fig. 5.12f) results in a HREEL spectrum as for a clean surface. A summary of experimental and theoretical results is presented in Table 5.1.

Fig. 5.13 shows the TD spectra of H$_2$O of different amount of HCOOH on ZnO(000$\bar{1}$) starting from room temperature. With increasing exposure of HCOOH, the area of H$_2$O desorption peak increases as shown in the inset of Fig. 5.13. By comparing the H$_2$O desorption peak with the out-diffusion and desorption peak in Ref. [105], the peak at around 400 K can be attributed to the out-diffusion of bulk proton and further

![Fig. 5.13](image)

**Fig. 5.13** H$_2$O desorption peaks evolve as a function with the exposure of HCOOH on ZnO(000$\bar{1}$) surface at room temperature. The inset shows the peak area of H$_2$O as a function with exposure of HCOOH.
desorption as H$_2$O molecules. The H$_2$O peak at around 530 K appears following the CO desorption peak at 500 K. The only source of H$_2$O and CO is formate. Since the monodentate formate has already formed at 500 K and at the same temperature OH is observed in EEL spectrum (Fig. 5.12d), we would propose the reaction pathway as follows:

At 500 K, one of the Zn-O bond breaks and bidentate formate converts to monodentate formate. At the same temperature part of the H atoms of the monodentate formate diffuses to surface oxygen site to form surface hydroxyl with the remaining -CO group desorbing from surface as CO molecule. Indeed, H$_2$O desorption is not coincident with CO desorption, but later than it. This is due to the different stabilities of CO and OH species on ZnO(000$\bar{1}$) surface. Interestingly, after the decomposition of HCOOH at 550 K, still a H$_2$O desorption peak is the observed in TD spectrum, as well as in the HREEL spectrum (Fig. 5.12e). H$_2$O adsorption from the background can be ruled out since the TDS experiments were carried out at room temperature within a very short time. The only possibility of H$_2$O desorption peak above 600 K is as the consequence of formate decomposition. As shown in Fig. 5.10, the decomposition of formate gives H$_2$, CO and CO$_2$. Either the two H atoms get together and form a H$_2$ molecule, or they re-adsorb on a surface oxygen forming an OH species.

In Fig. 5.10, a trace amount of Zn is also observed at the same temperature of formate decomposition. A similar phenomenon has been reported in Ref. [248], where the desorption of Zn was explained by the reduction of Zn$^{2+}$ to 0 of valency by reductive adsorbates.
Due to the very small ionization probability, Zn atoms show a very small intensity (ion current) in the mass spectrometer. It is difficult to calibrate the absolute amount of Zn. In this work, since the desorption of Zn can only come from the oxygen vacancies which have been occupied by formate species, the relative amount of desorbed Zn can be estimated by the amount of adsorbed formate.

Fig. 5.14 presents the signals of mass 44 in three continuous exposure-TDS cycles. In each experimental cycle, 5 L HCOOH was dosed onto the ZnO(000\(\bar{1}\)) surface at room temperature, which is thought to be enough to saturate the oxygen vacancies by forming formate species. In the first cycle, the HCOOH exposure was performed on the freshly prepared clean ZnO(000\(\bar{1}\)) surface. The maximum temperature of each TDS experiment is 630 K, below which the decomposition of formate is completed and no diffusion of bulk Zn and bulk O is considered [251]. As a result, with the desorption of Zn, the amount of formate species formed on oxygen vacancies will decrease accordingly in the following exposure-TDS cycle. Note that we have assumed that the amount of formate species can be represented by the amount of desorbed CO\(_2\). The inset in Fig. 5.14 shows the peak area of desorbed CO\(_2\) with

![Fig. 5.14 CO\(_2\) desorption peaks evolve as a function with the cycle of exposing HCOOH at room temperature: (a) on clean surface (b) the second cycle (c) the third cycle. During TDS experiment maximum temperature was restricted to 675 K.](image-url)
respect the experiment cycles. It shows a linear relationship, indicating the ratio of desorbed Zn to active Zn-formate species sites is constant. We define a constant

\[ R = \frac{A_i - A_{i+1}}{A_i} \]

where the \( A_i \) represents the peak area of i-th cycle. R would reflect the decrease of the amount of formate species in percent in each exposure-TDS cycle. R is calculated to 0.13. Indeed the amount of formate species comes from two contributions: the desorption of Zn removing oxygen vacancies and the desorption of H\(_2\)O creating new oxygen vacancies. Every HCOOH molecule adsorbed at oxygen vacancies can donate one proton that diffuses to the ZnO bulk and later desorbs as 1/2 H\(_2\)O creating 1/2 oxygen vacancy. This means if all Zn atoms of Zn-formate species desorb in the decomposition process, R would be the value of 0.5. A smaller value of R would indicate a partial desorption of Zn and the ratio of desorbed Zn to Zn-formate can be calculated by 0.5-R=0.5-0.13=0.37, which means only 37% of the Zn desorbs along with the decomposition of Zn-formate species.

Since the desorption of Zn associates with the reduction of the Zn\(^*\), we attribute this partial desorption of Zn in Zn-formate species to the existence of different chemical states of Zn on the surface. Indeed, as a covalent compound, the molecular orbitals on ZnO surface are quite localized. At single oxygen vacancies, each Zn has one dangling bond (slightly reduced) while at double oxygen vacancies one of the Zn has two dangling bonds (heavily reduced). Zn atoms at single vacancies are more likely to stay at surface and Zn atoms at double vacancies desorb along with the decomposition of Zn-formate species. Our result illuminates that the proportion of double vacancies among all surface oxygen vacancies is 37%.

In conclusion, we have investigated the adsorption of HCOOH on ZnO(000\(\bar{1}\)) surface at 120 K. Multilayer, double layer and chemisorbed HCOOH were observed in our experiment. The chemisorbed HCOOH undergoes a dissociative adsorption forming bidentate formate at oxygen vacancies with the ionized H-atom diffusing into the ZnO bulk. Heating the sample to high temperature leads to a geometry conversion from bidentate formate to monodentate formate. The latter decomposes to CO and H\(_2\)O or
CO, CO$_2$ and H$_2$ at different temperature with different decomposition mechanism. At last, the partial desorption of Zn reflects the different chemical states of formate species on ZnO(000$\bar{1}$).

5.4 CO$_2$ adsorption on the ZnO(000$\bar{1}$) surface$^2$

In this work, CO$_2$ adsorbed on the clean and hydrogen-free ZnO(000$\bar{1}$) surface was studied by high resolution electron loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) at 100 K and DFT calculations. Three different adsorption geometries for chemisorbed CO$_2$ were proposed by combination of experimental and calculated results. CO$_2$ adsorption at the oxygen vacancies leads to bidentate at single oxygen vacancies while at double oxygen vacancies to a planar (tridentate) carbonate species. Furthermore, CO$_2$ adsorbed on surface oxygen can also form stable monodentate carbonate with the C atoms bound to surface oxygen. The experimental results of the binding energy and vibrational energy of different carbonate species are in very good agreement with theoretical calculations.

Many studies using other methods have been carried out for CO$_2$ adsorbed on ZnO(000$\bar{1}$) surface. A photoelectron spectroscopy (XPS and UPS) study showed that CO$_2$ can only be chemisorbed as bidentate carbonate at oxygen vacancies [81]. In another study by NEXAFS and FT-RAIRS, carbonate species were considered bidentate carbonate formed at (10$\bar{1}$0) step sites [252]. On the non-polar ZnO(10$\bar{1}$0) surface, CO$_2$ adsorption has been found in form of the tridentate carbonate on Zn-O dimers [84]. The experimental inconsistency possibly results from the complexity of the surface structure due to the electro-instability of this polar surface and sequentially abundant of oxygen vacancies [180, 195, 253]. In fact, it was also shown that the surface chemistry is sensitive to the surface structure or co-adsorption [89, 240].

$^2$ The theoretical work was performed by Jörg Kossmann.
Fig. 5.15 shows TD spectra of various amount of CO$_2$ adsorbed on the ZnO(000$\bar{1}$) surface at 120 K. Only desorption of CO$_2$ was observed in TDS experiment. After adsorption of 0.1 L CO$_2$ adsorbed on the ZnO(000$\bar{1}$) surface at 120 K two broaden desorption peaks at 490 K and 350 K are observed. With increasing exposure to CO$_2$, the peak at higher temperature becomes broaden, until the appearance of a sharp peak at 150 K for high exposure. The main features of the TD spectrum for 0.8 L CO$_2$ adsorbed on ZnO(000$\bar{1}$) at 120 K are the sharp peak at 150 K and the long tail roughly from 200 K to 600 K. The peak area, as shown in the inset of Fig. 5.15, increases linearly and then reaches saturation for 0.8 L of CO$_2$. The saturation might result from the lower temperature limit, 120 K on this sample. The very broad feature at high temperature region could be attributed to several contributions: the re-adsorption process, lateral interaction between adsorbates, different adsorption configurations. The possibility of re-adsorption can be ruled out since all experiments
were carried out in UHV chamber and during the TDS experiment a differential pump was used to evacuate the gas desorbing from sample surface. Indeed, on the non-polar ZnO(10\(\bar{1}0\)), CO\(_2\) desorption also shows a broad feature from 100 K to 350 K due to the different stable phases of adsorbate on surface [84]. In addition, the complexity of this surface structure has been frequently reported [72, 253-256]. This broad peak of CO\(_2\) on ZnO(000\(\bar{1}\)), on the other hand, would also provide an evidence of the complexity of this polar surface. In addition, since 1/3 ML oxygen vacancies is predicted for the clean ZnO(000\(\bar{1}\)) surface, the TD spectra in Fig. 5.15 indicate a high sticking coefficient of CO\(_2\) or high reactivity of ZnO(000\(\bar{1}\)) to CO\(_2\) adsorption.

To explore the origin of broad feature of CO\(_2\) desorption at high temperature region, a co-adsorption experiment of 2 L H\(_2\)O followed by 2 L CO\(_2\) was performed, as shown in Fig. 5.16. H\(_2\)O chemisorption on ZnO(000\(\bar{1}\)) surface leads to a dissociative adsorption at oxygen vacancy sites with leaving two hydroxyl species by every H\(_2\)O molecule and thus blocks the oxygen vacancies [72, 253, 257]. In Fig. 5.16, it is shown that desorption of CO\(_2\) at tail region disappears for the hydroxylated surface. A
straightforward conclusion can be drawn here: the tail region of the TD spectra in Fig. 5.15 results from the CO$_2$ adsorption at vacancies sites. One should also note that the desorption peak of CO$_2$ on hydroxylated surface has slightly a red-shift, which corresponding a small increase in binding energy. This could be the consequence of different electronic properties of ZnO(000$\bar{1}$) surface after H$_2$O adsorption. Since the vacancies are always randomly distributed on the surface and the relative amount is still small, the occurrence of different stable configurations due to the lateral interaction is unlikely. The long tail character would originate from the different adsorption configurations although the desorption peaks convolute with each other.

Fig. 5.17 presents the TD spectra from the adsorption of the isotope C$^{18}$O$_2$ on ZnO(000$\bar{1}$) at 120 K. Mass 48 (C$^{18}$O$_2$), mass 46 (C$^{18}$O$^{16}$O) and mass 44 (C$^{16}$O$_2$) were monitored in the experiment. The desorption peak are dominated by mass 48 and mass 46. Just a trace amount of mass 44 was detected. Since the $^{16}$O can only originate from the substrate, the desorption spectrum of mass 46 indicates an exchange of surface oxygen and C$^{18}$O$_2$, indicating that carbon atom bonds to the surface oxygen upon adsorption. At the same time the $^{18}$O from adsorbate should bond to the surface Zn at vacancy sites since the adsorption at tail region occurs at oxygen vacancies. This indicates that the possible adsorption configuration of CO$_2$ adsorbed

![Fig. 5.17 TD spectra of isotope C$^{18}$O$_2$ adsorbed on ZnO(000$\bar{1}$) surface at 120 K.](image.png)
Fig. 5.18 Proposed models for carbonate species on ZnO(000\bar{1}) surface.

at the vacancy sites would be bidentate or tridentate carbonate species as shown in Fig. 5.18(b) and Fig. 5.18(c).

Fig. 5.19 presents HREEL spectra of CO\textsubscript{2} adsorbed on ZnO(000\bar{1}) surfaces of different states. Compared with Fig. 5.19A, which exhibits the clean surface, the spectrum of 2 L CO\textsubscript{2} adsorbed on ZnO(000\bar{1}) at 120 K (Fig. 5.19B) shows several additional loss features at 107, 161, 196 and 207 meV. These loss features are the characteristics of carbonate species. No loss feature of physisorbed CO\textsubscript{2}, which would be located at 291 meV, was observed. To distinguish different carbonate species, an HREELS experiment of CO\textsubscript{2} adsorbed on hydroxylated ZnO(000\bar{1}) at 120 K was performed, as shown in Fig. 5.19C. On the hydroxylated ZnO(000\bar{1}) surface, all oxygen vacancies are blocked by H\textsubscript{2}O through dissociative adsorption. The available adsorption site for CO\textsubscript{2} could be the surface oxygen or hydroxyl group. We rule out the possibility of CO\textsubscript{2} reacting with hydroxyl group since the TDS peak of CO\textsubscript{2} on the hydroxylated surface at 150 K in Fig. 5.16 decreases compared with the adsorption on clean surface. Fig. 5.19C shows loss features at 127, 180 and 203 meV, which are consistent with the possible adsorption as monodentate carbonate. Fig 5.19D shows the HREEL spectrum of 2 L CO\textsubscript{2} adsorbed on ZnO(000\bar{1}) at 400 K. Only two weak
loss features were observed at 150 and 193 meV. DFT calculations were also performed for CO$_2$ adsorbed on different oxygen vacancy sites. The corresponding binding energy and vibrational energy were also calculated for a comparison with the experimental results. The most stable configuration of CO$_2$ adsorbed on ZnO(000$\bar{1}$), as shown in Fig. 5.18(c), was found to be CO$_2$ adsorption at double oxygen vacancies with a geometry of planar tridentate carbonate and the binding energy of 134 kJ/mol. This would correspond to the TDS peak centered at 490 K. By assuming the preexponential factor for CO$_2$ desorption from ZnO (first order desorption) of $10^{-13}$ s$^{-1}$ it yields a binding energy of 131 kJ/mol, in perfect agreement with calculated results. Fig. 5.19D, for 2 L CO$_2$ adsorbed on ZnO(000$\bar{1}$) at 400 K, shows the EELS spectrum of this configuration. On the other hand (see Fig. 5.18(b)), the adsorption at single oxygen vacancies leads to bi-dentate carbonate with

![HREEL spectra](image)

**Fig. 5.19** HREEL spectra of (A) Clean surface (B) 2 L CO$_2$ adsorbed on ZnO(000$\bar{1}$) at 120 K. (C) 2 L CO$_2$ adsorbed on hydroxylated ZnO(000$\bar{1}$) at 120 K (D) 2 L CO$_2$ adsorbed on ZnO(000$\bar{1}$) at room temperature. All experiment were performed at exposure temperature. The spectra were shown as the deconvoluted results.
Table 5.2 Summary of experimental (HREELS) and theoretical results (DFT calculation) of different carbonate species in units of meV.

<table>
<thead>
<tr>
<th>Assignments</th>
<th>(\pi(\text{CO}_3))</th>
<th>(\nu_s(\text{CO}))</th>
<th>(\nu_{as}(\text{CO}))</th>
<th>(\nu(\text{C}=\text{O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monodentate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.</td>
<td>a</td>
<td>180</td>
<td>203</td>
<td>b</td>
</tr>
<tr>
<td>Cal.</td>
<td>100</td>
<td>153</td>
<td>218</td>
<td>b</td>
</tr>
<tr>
<td><strong>Bidentate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.</td>
<td>a</td>
<td>109</td>
<td>161</td>
<td>207</td>
</tr>
<tr>
<td>Cal.</td>
<td>99</td>
<td>101</td>
<td>126</td>
<td>221</td>
</tr>
<tr>
<td><strong>Tridentate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.</td>
<td>a</td>
<td>150</td>
<td>193</td>
<td>b</td>
</tr>
<tr>
<td>Cal.</td>
<td>100</td>
<td>164</td>
<td>190</td>
<td>b</td>
</tr>
</tbody>
</table>

a not resolved
b vibrational mode not existence

The binding energy of 115 kJ/mol. The TDS peak centered at 350 K in Fig. 5.15 yields a binding energy of 93.3 kJ/mol, in reasonable agreement with calculated results. These two calculated configurations of CO\(_2\) adsorbed at oxygen vacancies further confirm the conclusion deduced from the isotope substitution experiment. As shown in the experiment, no physisorbed CO\(_2\) was observed in HREELS experiment for the temperature higher than 120 K. DFT calculations also show an intermediate stable species formed by adsorbing CO\(_2\) on the surface oxygen sites with monodentate carbonate geometry with carbon bound to surface oxygen (see Fig. 5.18(a)). This configuration would be corresponding to CO\(_2\) adsorbing on the hydroxylated ZnO(000\(\bar{1}\)) surface, the HREEL spectrum of which is presented in Fig. 5.19C. All experimental and calculated results are summarized in Table 5.2.

In conclusion, we have studied the adsorption and reaction of CO\(_2\) with ZnO(000\(\bar{1}\)) surface. The extremely stable state of CO\(_2\) adsorbed on ZnO(000\(\bar{1}\)) surface was observed and assigned to the planar tridentate carbonate at double oxygen vacancy sites. On the single oxygen vacancy sites the preferable adsorption geometry is the bidentate carbonate. At last, a monodentate carbonate species, which is formed by CO\(_2\) adsorption on the surface oxygen, was observed by both experiments and DFT calculations.
6. Cu deposition on ZnO(000$\bar{1}$)

The interaction between metal and oxide is technically important in many fields, such as material science, microelectronics and heterogeneous catalysis [24, 38, 208, 258, 259]. In catalysis, the precious metal nanoparticles dispersed on oxide surfaces can substantially reduce the cost. Furthermore, metal/oxide systems exhibit usually more superior catalytic properties. Besides the original catalytic properties of the precious metal, the size-effect of metal particles and their interaction with oxide supports also remarkably affect on the catalytic properties and has attracted more and more research attentions. The Cu/ZnO catalyst used for methanol synthesis is a nice example for the study of the so-called strong metal-support interactions (SMSI).

Several decades ago, ZnO was used as catalyst for synthesizing methanol from syngas (CO/CO$_2$/H$_2$). However, high pressure and high temperature were required. Later, the introduction of Cu into ZnO apparently reduced the reaction temperature and pressure [208]. The role of Cu is still less understood although many studies on this system have been carried out. It has been proposed that metallic copper particles alone [40, 103, 260], partially oxidized Cu (Cu$^+$ [261, 262]), the size-effect [263], the metal-oxide junction effect [264], or even the lattice strain and defects in Cu [265] exhibit catalytic activity for methanol synthesis.

In this chapter, the structure, chemical state and diffusion of Cu into ZnO bulk of Cu clusters deposited on the ZnO(000$\bar{1}$) surface are studied by HREELS, TDS and LEED.

6.1 Structure of Cu clusters on the ZnO(000$\bar{1}$) surface

Fig. 6.1 presents the LEED pattern recorded on clean and Cu deposited ZnO(000$\bar{1}$) surfaces. The clean surface shows a (1×3) superstructure as discussed in previous section. After deposition of 10 ML Cu at RT, the LEED result shows a bright and sharp diffraction spots (note that after deposition of Cu, a clear diffraction pattern can
only be obtained by using a different electron energy), indicating a good film quality and a possible layer-by-layer growth mode for relatively large Cu coverages on ZnO(000\(\bar{1}\)) at RT. Furthermore, the hexagonal structure of Cu deposited on ZnO(000\(\bar{1}\)) reveals the formation of Cu thin-film with (111) facets since the bulk Cu shows face cubic centered (fcc) structure (Note that this hexagonal structure is not contributed by ZnO because the electrons can not penetrate as thick as 10 ML Cu layer). This conclusion is further confirmed by the different in-plane lattice constants (see Fig. 6.1) determined by considering the electron energy and pattern dimensions. Direct calculation of the in-plane lattice constant of the Cu film is difficult and arbitrary, however a rough estimation is achieved by comparing two LEED patterns and assuming that the in-plane lattice constant of ZnO(000\(\bar{1}\)) has negligible deviation from its bulk. Given that the in-plane lattice constant of ZnO(000\(\bar{1}\)) amounts to 3.26\(\AA\),
the in-plane constant of the Cu film is calculated to be 2.5 Å. By taking account of the fcc structure and lattice constant (3.61 Å) of Cu, the in-plane lattice constant of the (111) face is calculated to be 2.55 Å, which is in very good agreement with the value derived from the LEED results.

For 10 ML Cu film grown at 110 K, the LEED experiment was also performed. The corresponding data show a strongly blurred diffraction pattern, implying an island-like growth mode at low temperatures. Fig. 6.2 shows the intensity of the HREELS elastic peak and the FWHM value as a function of temperature. The HREEL spectra were taken after 10 ML Cu deposition on ZnO(000\bar{1}) at 100 K and during the following annealing process. First, the HREELS intensity is dramatically decreased compared to that recorded on the clean surface that amounts to around 20 kilo-counts per second (kcps). The FWHM value keeps nearly constant in the experimental temperature range, indicating that no diffusion process of Cu into bulk ZnO occurs (details will be discussed in subsection 6.3). The HREELS intensity increases gradually with increasing the temperature, implying that the Cu-covered surface becomes more flat and film-like. Given that the surface roughness can only be improved by the lateral diffusion of Cu atoms, our HREELS data further suggests a relative small diffusion barrier of Cu atoms.

Fig. 6.3 presents the TD spectra of CO adsorbed on different Cu deposited ZnO(000\bar{1}) surfaces. CO adsorption on thick Cu layers (curve A) gives a main desorption peak at

![Fig. 6.3 TD spectra of 10 L CO adsorption at 100 K on (A) 30 ML Cu/ZnO, (B) 5 ML Cu/ZnO, (C) after annealing 5 ML Cu-covered ZnO surface to 700 K.](image)
172 K, which is assigned to CO bound to the Cu(111) face. The small desorption peak at 200 K is not well understood and since it always exists in our experiments we temporarily attribute it to the systematic problem. Fig. 6.3B shows the TD spectrum of CO adsorbed on 3 ML Cu/ZnO(000\textbar1) surface. The relatively broad feature indicates the complexity of Cu thin layer on ZnO(000\textbar1). After annealing to 750 K for 3 minutes (Fig. 6.3C), four desorption peaks at 124, 144, 162 and 200 K are clearly resolved, which are attributed to CO adsorbed on different Cu surfaces as supported by the previous work [266]. This finding indicates the presence of new indexed faces or steps of Cu layer created after annealing to higher temperatures, which leads to the aggregation of Cu clusters forming islands due to high intermolecular interaction of Cu atoms [267-269].

6.2 The chemical state of Cu on ZnO(000\textbar1) surface

In general, the chemical state of surface cations (in particular for transition metal cations) can be explored by vibrational spectroscopy using CO as probe molecule. It has been shown that the stretching vibration of adsorbed CO, $\nu$(CO), is sensitive to the potential of surface anions [24, 208]. A large red shift of $\nu$(CO) relative to gas phase (266 meV) implies usually a lower oxidation state of surface anions. This is attributed to the electron back donation from 3d metal orbital to the anti-bonding $2\pi^*$ orbital of CO, the filling of which can essentially reduce the bond strength and bond order [37]. Compared to the gas phase value, CO adsorbed on fully reduced metal surfaces (as an extremity) will give a red shift as large as 20-30 meV. Moreover, the $\nu$(CO) frequency depends also on the CO coverage and adsorption sites (on-top, bridge, hollow and step edge). Because of the relatively poor energy resolution of HREELS, a fine analysis including adsorption site is difficult. For comparison we have performed the experiments under two extreme conditions: fully oxidized and fully reduced Cu states. The latter corresponds to the thick Cu layer (more than 20 ML), whereas the fully oxidized Cu state is prepared through an intended post oxidation process in oxygen ambient.
Fig. 6.4 shows the HREEL spectra of CO adsorbed on different Cu/ZnO surfaces. On the 5 ML Cu covered surface the $\nu$(CO) band amounts to 257 meV (Fig. 6.4(a)), which is consistent with that of CO adsorbed on the top site of Cu surface [270-272]. When the Cu layer is fully oxidized (Cu$^{2+}$), the $\nu$(CO) band shows a blue shift to 262 meV, while the peak intensity reduces largely, indicating a weak adsorption of CO on fully oxidized Cu/ZnO(000$\bar{1}$) surface. From this finding a safe conclusion can be drawn: the thin Cu layer is not in the fully oxidized Cu$^{2+}$ state.

In Fig. 6.5, the $\nu$(CO) bands of C$^{18}$O adsorbed on different Cu/ZnO surfaces are further compared. On the 30 ML Cu-covered ZnO(000$\bar{1}$) surface with fully reduced Cu$^0$ state (Fig. 6.5(a)), the C$^{18}$-O stretching mode is observed at 250.5 meV, whereas
on 2 ML Cu-covered ZnO the $\nu(C^{18}O)$ band amounts to 253.5 meV (Fig. 6.5(b)), indicating that the thin Cu layer is not in fully reduced, metallic Cu$^0$ state. Based on the above results we draw the conclusion that the chemical state of thin Cu layer on ZnO(000$\overline{1}$) is Cu$^+$. Although the coexistence of other chemical states of thin layer Cu on ZnO(000$\overline{1}$) can not be definitively ruled out, the majority of active sites (e.g. Cu-ZnO interface) for CO adsorption should be Cu species with the Cu$^+$ state.

6.3 Diffusion of Cu into ZnO(000$\overline{1}$) bulk

The diffusion of H into ZnO(000$\overline{1}$) bulk has been observed and characterized by the broadening of the HREELS quasi-elastic peak as discussed in section 5.2. The doping of ZnO(000$\overline{1}$) induced by the H diffusion into the bulk leads to the formation of donor levels in the band gap of ZnO which are close to the conduction band. The similar broadening of the quasi-elastic peak in HREELS was also observed after annealing the Cu-covered ZnO(000$\overline{1}$) surface to high temperatures. This finding reveals the diffusion of Cu atoms into ZnO bulk during annealing. Indeed, the diffusion of Cu into ZnO bulk was also found on the Zn terminated ZnO surface by STM [267].

![HREEL spectra of 20 ML Cu-covered ZnO surface at 300 K and with annealing to indicated temperatures.](image)

**Fig. 6.6** HREEL spectra of 20 ML Cu-covered ZnO surface at 300 K and with annealing to indicated temperatures.
Fig. 6.6 shows a series of HREEL spectra recorded after annealing the 20 ML Cu-covered ZnO(000\overline{1}) surface to the indicated temperatures. As a reference, the HREEL spectrum of the clean ZnO(000\overline{1}) surface is also displayed in Fig. 6.6E. For the as-grown 20 ML Cu covered ZnO(000\overline{1}) surface (Fig. 6.6A) the spectrum exhibits characters of metal surfaces. All surface phonons of ZnO(000\overline{1}) are absent, which originates from the screening effect by thick Cu layers. After annealing the sample to 520 K (Fig. 6.6B), the fundamental surface phonon mode at 69 meV starts to appear in the spectrum, which increases in intensity with further increasing the annealing temperatures. At temperatures higher than 750 K, the multiple phonons at 136, 202 meV are also observed (Fig. 6.6C and Fig. 6.6D). After annealing to 900 K, the surface phonons show comparable intensities with those for the clean ZnO(000\overline{1}) surface.

The reappearance of ZnO surface phonons could be due to the following reasons: (a) the desorption of Cu atoms upon annealing to high temperatures. (b) the aggregation of Cu film to large islands during annealing. (c) the diffusion of Cu atoms into ZnO bulk. Actually all of these three possibilities have been observed in previous works. The zero order desorption of Cu on Al$_2$O$_3$/Mo(110) was found to take place at around 900 K [273, 274]. This is obviously not the case occurring in this study since the

![Desorption of 5 ML Cu on ZnO(000-1)](image)

**Fig. 6.7** TD spectrum of Cu of the 5 ML Cu-covered ZnO surface. For comparison the desorption of H$_2$O adsorbed from the background is also shown.
surface phonons reappear at temperatures far below 900 K. Indeed, nearly no desorption of Cu was observed in the corresponding TDS experiments (see Fig. 6.7). The mass 64 signal has only an upward bending at around 800 K, which would correspond to the desorption of Cu. For comparison, the desorption peak from background H\textsubscript{2}O adsorption was also shown in Fig. 6.7. Compared to the H\textsubscript{2}O signals the desorption of Cu is negligible. Therefore, we can rule out the first possibility; the reappearance of ZnO surface phonons should be attributed to the aggregation of Cu layers and/or diffusion of Cu atoms into ZnO bulk. After the former process, part of the ZnO(000\,\overline{1}) surface is again exposed to vacuum and can be monitored by HREELS. The aggregation of Cu film was also observed by STM studies in the group of Köhler [267, 269]. Finally, the diffusion of Cu to ZnO bulk can also lead to elimination of the screening effect, thus resulting in the reappearance of ZnO surface phonons.

Fig. 6.8 shows a series of TD spectra of CO adsorbed on 5 ML Cu-covered ZnO surfaces that are pre-annealed to different temperatures. The desorption amount of CO decreases dramatically with elevating the annealing temperatures. Because the annealing process causes the aggregation of Cu layers forming Cu islands, more Cu atoms are exposed. Thus, the desorption intensity of CO is expected to increase to some extent. The fact that the CO desorption amount is largely decreased during

Fig. 6.8 TD spectra of 10 L CO adsorbed on 5 ML Cu-covered ZnO surfaces pre-annealed to different temperatures
Fig. 6.9 The FWHM value as a function of annealing temperatures. The samples were prepared as follows: 5 ML Cu was first deposited on ZnO\((000\bar{1})\) at RT and annealed to 800 K for 5 minutes, and then cooled down to 100 K.

The annealing process implies a decrease of exposed Cu atoms, which can only be explained by diffusion of Cu atoms into ZnO bulk.

A more solid evidence for Cu diffusion into ZnO bulk results from the HREELS experiments results (see Fig. 6.6). After annealing the Cu-covered ZnO surface to higher temperatures the quasi-elastic peak in HREELS becomes broader. The FWHM value as a function of annealing temperatures is plotted in Fig. 6.9. The FWHM increases with heating to higher temperatures, which indicates directly a diffusion of Cu atoms into ZnO bulk. The doping of ZnO\((000\bar{1})\) by Cu leads to the formation of shallow donor states in the band gap. As we have discussed in section 5.2, the excitation of electrons into the conduction band results in the low-energy plasmon vibrations. Thus, a plasmon-induced broadening of the quasi-elastic peaks in the HREELS data is observed in Fig. 6.9. To further identify this mechanism on doped semiconductor surfaces, it's necessary to observe a temperature-dependent broadening according to expressions (5.1), (5.2) and (5.4a).

As shown in Fig. 6.10, 5 ML Cu was first deposited on ZnO\((000\bar{1})\) at RT and annealed to 800 K for 3 min, then cooled down to 100 K. The FWHM of the HREELS quasi-elastic peak was then measured at different temperatures. For doped semiconductors, the density of free charge carriers in the conduction band can be calculated according to the expression (5.4a). By the same manner as used in section...
5.2, the ionization energy of the Cu donor level is estimated to be 20 meV. This rather small ionization energy can be considered as the kinetic barrier for Cu-ZnO redox reactions, which provides a further evidence for the existence of the Cu$^+$ state in the thin Cu layer on ZnO(000$\bar{1}$) surface.

In summary, Cu deposition on O-ZnO leads to the formation of ordered Cu layers with the Cu(111) facets. For the small clusters the partial oxidation of Cu$^0$ into Cu$^+$ was clearly identified by the characteristic C-O stretching frequencies. Upon heating the Cu atoms undergo, instead of desorption, diffusion into the bulk. This is confirmed by a significant broadening of the quasi-elastic peak in HREELS, which corresponds to the existence of free charge carriers at ZnO surface region. These free charge carriers result from the thermal excitation of electrons at the donor level into the conduction band. The shallow donor states are created via diffusion of Cu atoms into the bulk. The analysis of the temperature dependence yields a shallow donor ionization energy of 20 meV. This unexpected doping effect of ZnO by Cu could have important consequences for its chemical activity and needs to be investigated systematically in future research.
7. Summary and outlook

7.1 Summary
We have shown that the combination of vibrational spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and electron diffraction method (LEED) can provide a comprehensive investigation for the adsorption and reaction behaviors of gas molecules on oxide and metal deposited oxide surfaces. Furthermore, the theoretical work also plays an important role for getting the insight of the studied system.

Adsorption and reactions of a number of molecules (hydrogen, water, carbon monoxide, carbon dioxide, formaldehyde, formic acid and methanol) on clean and metal deposited oxide single crystal surfaces (ZnO and TiO$_2$) have been studied by high resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and low energy electron diffraction (LEED).

On the most stable surface of ZnO, ZnO(10$ar{1}$0), CO$_2$ adsorption is found to form an unusual tridentate carbonate species. Several ordered phases can be observed and are explained as the consequence of charge transfer between CO$_2$ and substrates. As the result of charge transfer, the Lewis acidity of surface Zn cations increases due to the formation of neighboring carbonate species after CO$_2$ adsorption, which essentially leads to an increase of adsorption ability of co-adsorbed CO molecules. With increasing the coverage of pre-covered CO$_2$ the binding energy of CO increases monotonically. However, the site-blocking effect also arises. A good balance of the binding energy and coverage of CO is achieved when the surface is pre-covered by half monolayer of CO$_2$, where the CO coverage reaches the maximum value of 0.5 ML.

H$_2$O adsorption on ZnO(10$ar{1}$0) at 100 K results in the formation of mono-, double- and multi- layer H$_2$O species, which are clearly identified by the different O-H stretching modes of H$_2$O with H-bonding. In the monolayer coverage regime it was further found that H$_2$O is partially dissociated forming a (2×1) superstructure along [11$ar{2}$0] direction. Surprisingly, the frequency of the ν(O-H) mode of H$_2$O monolayer
has a large red shift compared to the values in double- and multi-layer H$_2$O. This findings reveals unusually strong hydrogen bonding interactions in monolayer H$_2$O to both neighbouring absorbate molecules and the surface O atoms, which is responsible for the partial dissociation of H$_2$O molecules on the perfect ZnO(10$ar{1}$0) surface at temperature as low as 100 K.

The interaction of formaldehyde (CH$_2$O) with TiO$_2$(110) surfaces was also investigated. CH$_2$O adsorption on the perfect TiO$_2$(110) surface leads to the polymerization production, paraformaldehyde, along Ti$_5$C rows. The binding energy of the paraformaldehyde polymers to surface depends on the chain length. On defective TiO$_2$(110) surfaces created by high temperature annealing and Ar$^+$ ion sputtering methods, the adsorbed CH$_2$O is reduced to ethylene at oxygen vacancies. The formation of ethylene results from the diffusion and recombination processes of the adsorbate species, dioxy-methylene. The artificially sputtered surface can contain as much as 40% of oxygen vacancies. The more reactive sites were found to be the lattice oxygen vacancies created only by Ar$^+$ ion sputtering, where CH$_2$O is reduced to ethylene even at temperatures as low low as 150K.

For H adsorption on TiO$_2$(110) at room temperature, a maximum hydroxyl coverage of 0.66 monolayer is achieved by exposing the clean surface to a large amount of atomic hydrogen. Upon heating, the surface hydrogen species, instead of desorption, undergoes a diffusion process into the TiO$_2$ bulk. This unusual behavior originates from the lower activation barrier for diffusion of hydrogen into bulk compared to that of recombinative desorption.

The existence of a hydrogen-free and unreconstructed polar ZnO(000$ar{1}$) surface is still under debate. We provided the experimental evidence for the stable surface structure of ZnO(000$ar{1}$) being either (3×1) reconstructed or (1×1) hydroxylated. The oxygen vacancies on H-free ZnO(000$ar{1}$) exhibit high catalytic activities toward a number of chemical reactions. It was found that CO$_2$ is activated at surface oxygens on ZnO(000$ar{1}$) forming three different carbonate species: monodentate on surface oxygen,
bidentate carbonate species at single oxygen vacancies and tridentate carbonate at double oxygen vacancies.

The interaction of formic acid (HCOOH) with the clean, H-free ZnO(000̅1) surface leads to the formation of bidentate formate species at oxygen vacancies. The bidentate formate species undergo a geometry conversion to mono-dentate formate and further a dehydration process upon annealing to 500 K. Heating the sample to 550 K leads to a full decomposition of mono-dentate formate to H₂, CO and CO₂. The desorption of Zn atoms during the decomposition process is analyzed and proposed to reveal the presence of different oxygen vacancies.

Exposing the fully hydroxylated ZnO(000̅1) surface to atomic hydrogen leads to a significant broadening of the quasi-elastic peak in HREELS, which results from the existence of free charge carriers in the ZnO surface region. These free charge carriers are created by the thermal excitation of electrons from the donor level into the conduction band. The shallow donor states are created via diffusion of H atoms into the bulk. The analysis of the temperature dependence yields a shallow donor ionization energy of 25 ± 5 meV.

Cu deposition on ZnO(000̅1) surface leads to the formation of well-defined islands exposing Cu(111) facets. For the small clusters the partial oxidation of Cu⁰ to Cu⁺ was clearly identified by the characteristic C-O stretching frequencies. Upon heating the Cu atoms undergo, instead of desorption, diffusion into the ZnO bulk. The doping of ZnO by Cu leads also to the formation of shallow donor states, from which the electrons can be thermally excited into the conduction band and, as a result, give rise to a plasmon-induced broadening of the quasi-elastic peak in HREELS. From the observed temperature dependence, the donor level ionization energy amounts to 20 meV, which reveals the low reaction barrier for the Cu-ZnO redox reaction. This unexpected doping effect of ZnO by Cu could have important consequences for its surface chemical activity and needs to be investigated systematically in future research.
7.2 Outlook

In this work, although much effort has been carried out to study the adsorption and reaction of gases on metal oxide surfaces, a deep understanding of metal substrate interaction, especially its effect on catalytic properties, is still scarce. Further studies, including new study methods, would be relevant.

**Study contents:**

1. The study of adsorption on metal deposited substrate. This includes the growth mode, the chemical state of metal particles (films) and their effect on the catalytic properties. The presence of vacancies and pre-covered H₂O could also influence the mentioned properties.

2. The doping of metal particles in oxide bulk leads to a change on electronic properties of the substrate, which can essentially change the charge distribution between adsorbates and substrates. As a result, the binding energy between adsorbates and substrates would be expected to increase to certain extent. This could be more prominent on powder sample since the dimension becomes smaller. A case study is the Cu doping effect on CO₂ adsorption properties that after Cu doping in ZnO the binding energy of CO₂ to ZnO increases. Combined techniques including HREELS, TDS, HAS and theoretical calculations are needed to get deep insight for this system.

**Study methods:**

1. In this work, the analysis of TDS results seems too straightforward although more detailed information could be obtained from them. The combination of shape and quantitative analysis of TDS would make the study more comprehensive.

2. The study from electronic and orbital point of view, which in many cases provides the original understanding for the reaction mechanism, could benefit the current study.

3. The possible functional extending of HREEL spectrometer for study of electronic structure, which would enrich the current study contents.
Appendix 1: Discussion on the effect of Titanium sublimation pump (TSP) on CO$_2$ adsorption experiments

When the experiment of CO$_2$ adsorption is performed in UHV chamber, especially when CO$_2$ just weakly reacts with sample and at the same time its reduction product, CO, strongly reacts with sample, the effect of Titanium sublimation pump should be considered. One example is given here of CO$_2$ adsorption on Cu/ZnO(000$\bar{1}$) surface.

In the work of CO$_2$ adsorption on Cu/ZnO(000$\bar{1}$), one of the “remarkable” results is that CO$_2$ can be reduced to CO by Cu film. Isotope substitution experiment using C$^{18}$O$_2$ further confirmed this conclusion, as shown in Fig A1.1. But, unfortunately, this is wrong. The problem is attributed to the effect of TSP, that during exposure of CO$_2$, part of backfilling CO$_2$ is reduced to CO by Ti films produced during the running of TSP, and further dramatically affects on experiments. Evidences are shown here.

Fig. A1.1 TD and HREEL spectra of 10 L C$^{18}$O$_2$ adsorbed on 30 ML Cu deposited ZnO(000-1) at 100 K.
As shown in literature, CO$_2$ can only weakly adsorb on Cu(111) surface, but strongly adsorb on some high Miller indexed surfaces with dissociation [9]. In chapter 6, we have shown that the growth of Cu on ZnO(0001) surface is along (111) face at room temperature (RT). Other faces appear only when annealing the sample to high temperature.

Fig. A1.2 shows a series of HREEL spectra of 20 ML Cu deposited on ZnO(0001) surface with different treatment. Note that the curves from (a) to (f) were recorded in sequence during the experiments. (a) 20 ML Cu was deposited on ZnO(0001) at RT. (b) after exposing the Cu/ZnO surface to 20 L C$_{18}$O$_2$ at RT. (c) after exposing the Cu/ZnO surface to 1000 L C$_{18}$O$_2$ at RT. (d) cooling the sample down to 100 K and exposing it to 20 L C$_{18}$O$_2$. (e) the sample was exposed to 5 L CO at 100 K. (f) running TSP for twice (40 A, 40 sec for each time) and 20 minutes later exposing the sample to 20 L C$_{18}$O$_2$.

After 20 ML Cu deposition on ZnO(0001) surface at RT, there is nearly no phonon observed (curve a). If this Cu/ZnO surface can really reduce CO$_2$ to CO, one oxygen atom would be left on the surface and the stretching vibrational mode of $\nu$(Cu-O) would be observed in HREELS. Note that at room temperature CO$_2$ (or CO) is not
stable on Cu film surface. Indeed, in curve (b) no change of the spectrum was observed. Possible small sticking coefficient was also considered and 1000 L C\textsuperscript{18}O\textsubscript{2} adsorption was further performed (curve c). Again, no change was observed in HREEL spectrum. Possibly, the ν(Cu-O) shows too small intensity to be detected by HREELS. But, at least, if the Cu/ZnO is fully covered by oxygen due to the “reduction” of CO\textsubscript{2}, no further CO\textsubscript{2} adsorption would be observed at low temperature. In curve (d), no ν(C\textsuperscript{18}-O) band was observed. But, wait, we can’t reach the conclusion right now that Cu/ZnO is fully covered by oxygen after 1000 L CO\textsubscript{2} adsorption on Cu/ZnO at room temperature. The other possibility as we wanted to testify hasn’t been ruled out. If the surface is now fully covered by oxygen, then how is the further CO adsorption? Curve (e) brings us the answer. CO does adsorb on this surface and the ν(CO) is exactly the same with CO adsorbed on the untreated Cu/ZnO surface. We can not consider this ν(CO) coming from the CO adsorption on CuO or Cu\textsubscript{2}O since it is very sensitive to the chemical state of substrate. TSP pump was then switch on for twice. 20 minutes later, after the vacuum became better, 20 L C\textsuperscript{18}O\textsubscript{2} was again exposed just like step (d). Interestingly, different from curve (d), this time we found the ν(C\textsuperscript{18}-O).

Now we come back to the speculation at beginning: during exposure of CO\textsubscript{2}, part of CO\textsubscript{2} is reduced to CO by Ti film from TSP. If it were true, then the result of curve (e) would be reasonable. In addition, the exposure of 1000 L C\textsuperscript{18}O\textsubscript{2} in step (c) would have another effect, not to saturate the sample, but to saturate the Ti film by oxygen. As a
result, the CO$_2$ adsorption in step (d) could not provide the reduction production, CO in the background. Note also that CO$_2$ itself doesn’t adsorb on Cu films at 100 K in this work.

One more piece of evidence comes from the ratio of mass 30/48 recorded by mass spectrometer during backfilling the chamber with 5.0×10$^{-7}$ mbar of C$^{18}$O$_2$ (Fig. A1.3). Four separated regions in the figure denote different experimental condition: (a) normal condition (b) after exposing 1000 L C$^{18}$O$_2$. (3) after step (b) and switching on the TSP (40 A, 80 sec). (d) after step (c) and 50 L C$^{18}$O$_2$ exposure.

Note that the ratio of mass 30/48 is not the ratio of C$^{18}$O to C$^{18}$O$_2$ since C$^{18}$O$_2$ has fragment of C$^{18}$O in mass spectrometer. But the ratio of C$^{18}$O$_2$ to the C$^{18}$O fragment is a constant and increase of the ratio would indicate an increase of CO proportion in the backfilling ambient. During C$^{18}$O$_2$ backfilling, the ratio of mass 48/30 was decreasing slowly from 0.22 to 0.16. After additional 1000 L C$^{18}$O$_2$ backfilling, the ratio had a sharp drop. If we run the TSP again (region C) the ratio returns back to the normal value as in region A. Further decreasing during C$^{18}$O$_2$ backfilling in region D is similar with that in region A.

The change of ratio of mass 30/48 clearly exhibits the TSP effect on CO$_2$ adsorption.

Indeed, in the CO$_2$ on Zn(10$\bar{1}$0) work, we also found tiny amount of CO product in TDS. So strong effect on Cu/ZnO system comes from the fact CO$_2$ doesn’t adsorb on Cu(111) surface at 100 K but CO does, as a result, even 5% of CO in CO$_2$ ambient can essentially affect the experimental observation. But in CO$_2$ on ZnO(10$\bar{1}$0) work, CO$_2$ can really adsorb and compete with CO.

In conclusion, when the experiment of CO$_2$ adsorption is performed in UHV chamber, especially when CO$_2$ just weakly reacts with sample and at the same time its reduction product, CO, strongly reacts with sample, the effect of Titanium sublimation pump should be considered.
Appendix 2 Illustrations and symbols of different vibrational modes

A typical example of vibrational modes for three-atom molecule (e.g. H$_2$O) adsorbed on solid surface is presented here. As shown in figure, the nonlinear adsorbate has three atoms. As a result, it has three (3N-6) internal vibrations and six integral vibrations (three rotation and three translation). One should note that during a specific vibration some irrelative atoms could have a possible movement to keep the conservation of momentum, which is not specified in this figure.
Appendix 3: Fourier deconvolution process of HREEL spectra

HREEL spectra on metal oxide surfaces show extensive surface phonons (including primary and multiple scattered phonons). A powerful way is to use the numerical method to remove the effect of multiple scattered phonons. Refer to Cox’s work [61] for principle. Here, I present the realization of Fourier deconvolution process by Origin. The program is attached in the end.

The program is written by “labtalk” language in Origin and put in Origin as a plug-in button (see the “FFT” button in Fig. A3.1). Clicking the “FFT” button, a dialog window appears as shown in Fig. A3.1. Input the experimental parameters including scanning range and scanning step and click “OK”, and then one can get two worksheets. The worksheet with name “Axxx” is the raw data and the worksheet with name “Rxxx” corresponds to the deconvoluted result (xxx represents the original file name).

Fig. A3.1

Attached program:

adecimalprogram://Pretreatmentadecimalprogram
//this file should be put in the origin directory
[start]
Menu id=34006;
run.section(Standard,NewWks); //new worksheet
wks.import.minBlock=11;
getfile *.dbf;open -w %A;    //open dbf file
run.section(labtalk_eels, begin);
[begin]
for(;wks.col1.name$==Nr;)
{
    run.section(labtalk_eels,run);
}
[run]
%Z=%[A,8];
getnumber "From -" from "To" to "Step" Step "Scan range";
//From*=-1;
ScanRange=From+To;
ResponseRange=2*From;
Delete Col(Nr);
col(Scan)*=1000;
wks.col1.type=4; //set first column as x axis
sum(col(ch1));  //normalize process start
maxtemp=sum.max;
col(ch1)=maxtemp;  // normalize process end
worksheet -d ResultsTemp;
worksheet -d ToFindPhonon;
mark -d col(scan) -b 1 -e 60; // cut the elastic peak off
sum(col(ch1));
Phonon=sum.max;
window -cd ToFindPhonon; // to normalize the last result to the elastic peak
worksheet -a 2;  // add two new columns
for(i=1;i<=From+To+1;i++)
    col(A)[i]=i-From-1;
col(b)=ResultsTemp_CH1(ResultsTemp_A); //interpolate the dataset with interval 1
for(i=0,LastPoint=0;i<10;i++)
    {
        LastPoint+=col(b)[From+To+1-i];
    }
AverageLastPoint=LastPoint/10;   //make an average of last ten data
for(i=From+To+2;i<1025;i++)
    {
        col(a)[i]=i-From-1;
        col(b)[i]=AverageLastPoint*(1-(i-1025+ScanRange)/(1025-ScanRange));
    }
col(scan)=col(a);
col(ch1)=col(b);  //results after interpolation
Delete col(a);
Delete col(b);
worksheet -c response;  //add a new column
for(i=1;i<1025;i++)
{
    if(i<=ResponseRange+1)
        col(response)[i]=col(ch1)[i];
    else
        col(response)[i]=col(ch1)[ResponseRange+1]*exp(-0.0005*i*i)/exp(-0.0005*(ResponseRange+1)*(ResponseRange+1));
}

/////////////////////fft process of the signal/////////////////////////
fft.reset();
fft.forward = 1;
fft.forward.timeData$ = ResultsTemp_scan;
fft.forward.tdelta = ResultsTemp_scan[2] - ResultsTemp_scan[1];
fft.forward.realData$ = Resultstemp_ch1;
window -t W fft FFT1;
fft.output.samplingdata$ = FFT1_Freq;
fft.output.realdata$ = FFT1_Real;
fft.output.imagdata$ = FFT1_Imag;
fft.output.ampdata$ = FFT1_r;
fft.output.phasedata$ = FFT1_Phi;
fft.output.powerdata$ = FFT1_Power;
fft.real = 1;
fft.normalize = 1;
fft.shifted = 1;
fft.windowing = 1;
fft.spectrum = 1;
fft.unwrap = 1;
fft.forward();
fft.reset();
fft.forward = 1;
fft.forward.timeData$ = ResultsTemp_scan;
fft.forward.tdelta = ResultsTemp_scan[2] - ResultsTemp_scan[1];
fft.forward.realData$ = ResultsTemp_response;
window -t W fft FFT2;
fft.output.samplingdata$ = FFT2_Freq;
fft.output.realdata$ = FFT2_Real;
fft.output.imagdata$ = FFT2_Imag;
fft.output.ampdata$ = FFT2_r;
fft.output.phasedata$ = FFT2_Phi;
fft.output.powerdata$ = FFT2_Power;
fft.real = 1;
fft.normalize = 1;
fft.shifted = 1;
fft.windowing = 1;
fft.spectrum = 1;
fft.unwrap = 1;
fft.forward();
get col(freq) -e row_number;  //get the max row number
create fft_results -w 4 frequency fft_signal fft_response T;
wks.col1.type=4;
wks.col1.width=15;  //set the width of first column
wks.col2.width=15;
wks.col3.width=15;

for(i=1;i<row_number;i++)
{
    col(Frequency)[i]=FFT1_Freq[i];
    col(signal)[i]=FFT1_R[i];
    col(response)[i]=FFT2_R[i];
    col(T)[i]=ln(col(signal)[i]/col(response)[i])*col(response)[i];
}

fft.reset();
fft.forward = 1;
fft.forward.timeData$ = FFTRESULTS_Frequency;
fft.forward.tdelta = FFTRESULTS_Frequency[2] - FFTRESULTS_Frequency[1];
fft.forward.realData$ = FFTRESULTS_T;
window -t W fft FFT3;
fft.output.samplingdata$ = FFT3_Freq;
fft.output.realdata$ = FFT3_R;
fft.output.imagdata$ = FFT3_Imag;
fft.output.ampdata$ = FFT3_r;
fft.output.phasedata$ = FFT3_Phi;
fft.output.powerdata$ = FFT3_Power;
fft.real = 1;
fft.normalize = 1;
fft.shifted = 1;
fft.windowing = 1;
fft.spectrum = 1;
fft.unwrap = 1;
fft.forward();

///////////////////////////////////////////////////////////////////////////////////
%W=R%Z;
worksheet -d %W;  //duplicate the worksheet
Delete col(real); // delete useless columns
Delete col(imag);  
Delete col(Phi);  
Delete col(power);  
mark -d col(r) -b 1 -e 512; // delete useless rows
mark -d col(r) -b 501 -e 513;

sum(col(r));  // normalize process start
maxtemp=sum.max;
col(r)/=maxtemp; // normalize process end
col(r)*=Phonon;  // normalize to the elastic peak but not the first phonon peak
work -n $(1) Scan$();
work -n $(2) CH1$(); // rename
mark -d col(Scan) -b (To+1) -e 500; // suitable for different scan range (e.g. -30~340meV)

window -cd fft1;
window -cd fft2;
window -cd fft3;
window -cd fftresults;
window -cd ResultsTemp;
Appendix 4: Shape analysis of TD spectra—some examples

Shape analysis of TD spectra is important to determine the reaction order and possible lateral interaction between adsorbate. Some simulated examples are presented here to show the typical shape features of different order desorption. Mathcad was used to do the simulation. As an example, the program for first order desorption is attached in the end.

Based on Wigner-Polanyi equation, the simulation can be realized by the simple programming idea:

\[
\begin{align*}
[R_{\text{des}}(\theta)] & = v_n \cdot [\theta^n] \cdot \exp\left(\frac{-\Delta E}{RT}\right) \quad (A4.1)
\end{align*}
\]

and

\[
\theta_{i+1} = \theta_i - [R_{\text{des}}(\theta)] \cdot \Delta T \quad (A4.2)
\]

where the subscript i is an integer, \(\Delta T\) stands for the simulated heating step.

By naming the initial coverage \(\theta_0\), we calculate \([R_{\text{des}}(\theta)]\) and \(\theta_1\) can be obtained by expression (A4.2). Go back to expression (A4.1) to calculate the next \([R_{\text{des}}(\theta)]\) and the iteration process starts. Actually, approximation was assumed in expression (A4.1) that \([R_{\text{des}}(\theta)]\) is the average desorption rate between \(T_i\) and \(T_{i+1} = T_i + \Delta T\).

The deviation from this approximation can be diminished through using smaller heating step.

Parameters for each simulated results are shown in figures.

Parameters for each simulated results are shown in figures.
Attached program and explanations:

The evolution of desorption shape with different coverage for the first order desorption. The binding energy increase from $E_D$ to $1.1E_D$ from the monolayer to the near-zero coverage.

Parameters: $\nu=10^{13}$ s$^{-1}$, $E_D=300$ meV, $\beta=5$ K/s

Reason for if: Due to the use of different time step, it is possible that $R$ becomes negative after some cycles (of course after the useful region)

$k$, as a variable, is used to change the parameters, e.g., $\nu$ and $\phi_0$, etc.

AA is used to show the change of $E_D$ (in percent) during the desorption process which is possibly caused by lateral interaction.
\[ e := 1.6 \times 10^{-19} \text{ C} \quad eV := e \cdot V \quad \text{meV} := \frac{eV}{1000} \quad \text{NA} := 6.02 \times 10^{23} \quad \text{RR} := \frac{8.31}{\text{NA} \cdot \text{K}} \]

\[ \beta := \frac{5}{s} \quad T_0 := 90K \quad \Delta t := 0.02s \quad \text{cycle} := 500 \]

\[ E_{d00} := 330 \text{meV} \quad v_{00} := 10^{13} \text{s}^{-1} \quad v_{000} := 10^{15} \quad \AA := -0.1 \]

\[
R(E_d, v, 00) := \\
\text{for } k \in 0..9 \\
\theta_{0,k} \leftarrow 00 \left(1 - \frac{k}{10}\right) \\
T_{0,k} \leftarrow T_0 \\
R_{0,k} \leftarrow v \cdot \theta_{0,k} \cdot \exp\left[-\frac{E_{d} + AA \cdot E_{d} \left(1 - \frac{\theta_{0,k}}{000}\right)}{RR \cdot T_{0,k}}\right] \\
\text{for } i \in 1..\text{cycle} \\
T_{i,k} \leftarrow T_{0,k} + \beta \cdot \Delta t \cdot i \\
\theta_{i,k} \leftarrow \theta_{i-1,k} - R_{i-1,k} \cdot \Delta t \\
R_{i,k} \leftarrow v \cdot \theta_{i,k} \cdot \exp\left[-\frac{E_{d} + AA \cdot E_{d} \left(1 - \frac{\theta_{i,k}}{000}\right)}{RR \cdot T_{i,k}}\right] \\
\text{if } R_{i,k} < 0 \\
j \leftarrow i \\
\text{break} \\
\text{for } i \in j..\text{cycle} \\
R_{i,k} \leftarrow 0 \\
\]

\[
\frac{R(E_{d00}, v_{000}, 000)}{000} = 1 
\]
Appendix 5: Discussion on the expression of density of electrons in conduction band for doped semiconductor

The expression of density of electrons in conduction band for doped semiconductor is written in expression (A5.1) or (A5.2). Indeed, both expressions can be found in different textbooks. A discussion on the validity of both expressions is presented in this section.

First, the expression of \( N_c(T) = 2 \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} \) is a definition, which can be called effective density of state (DOS) in conduction band (CB) (or we can just treat it as a constant). This name comes from the expression of electron density of conduction band for the intrinsic semiconductors, \( n = 2 \left( \frac{m_kT}{2\pi\hbar^2} \right)^{3/2} e^{(E_c - E_f)/kT} \), where \( E_c \) denotes the bottom of conduction band. This expression is written like the product of DOS (but not the real DOS in CB) and probability [275-279].

In some books the expression of \( n_c(T) \) was written as [276, 277],

\[
\sqrt{N_d} N_c(T) \exp(-\varepsilon_d / 2kT) \tag{A5.1}
\]

where the coefficient of 2 disappears compared to the expression used other books [278, 279], including in this work [105],

\[
\sqrt{\frac{N_d N_c(T)}{2}} \exp(-\varepsilon_d / 2kT) \tag{A5.2}
\]

The deviation, I think, originates from a very fundamental problem, that what is the electron energy distribution function (probability) on donor level (electrons which are not ionized),

\[
f(E) = \frac{1}{1 + e^{(E-E_c)/kT}} \tag{A5.3}
\]

or
\[ f(E) = \frac{1}{1 + 2 e^{(E-E_f)/kT}} \]  \hfill (A5.4)

Here, the coefficient of 2 in the latter expression results from the fact that, at donor level two electrons with different spin are not allowed at the same time, which means only one of the two states (spin-up and spin-down) is allowed for electrons at donor level due to the potential localized interaction of two electrons [275].

To calculate the electron density in conduction band, \( n_c \), we can not use the expression:

\[ n_c = N_d \cdot \int_{E_c}^{\infty} \frac{1}{1 + e^{(E-E_d)/kT}} dE \]  \hfill (A5.5)

but we must use:

\[ n_c = N_d \cdot \left( 1 - \frac{1}{1 + 2 e^{(E-E_f)/kT}} \right) \]  \hfill (A5.6)

For weak ionization case \( kT < E_c - E_d \), Fermi level locates at middle between donor level and the bottom of conduction band. We can get the electron density in conduction band:

\[ n_c(T) = \sqrt{\frac{N_d N_c(T)}{2}} \exp(-\varepsilon_d / 2kT) \]  \hfill (A5.7)
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