Experimental investigations of model catalytic surface reactions on metal and metal oxide surfaces

Kess Marks
Experimental investigations of model catalytic surface reactions on metal and metal oxide surfaces

Kess Marks

Abstract

In the development of renewable energies catalysis plays an important role, for example in the production of H₂ gas that drives fuel cells, or in the decomposition of annoying by-products of renewable energy production. Most catalysts and catalytic processes currently used in the industry have their roots in macroscopic empirical investigations and trial and error-based optimization. In order to be able to design novel catalytic processes more efficiently, detailed understanding of the catalyst-reactant interaction and the dynamics of the microscopic reaction steps is needed. The present thesis aims to contribute to the fundamental understanding of catalyst reactant systems by means of experiments using model systems in Ultra High Vacuum. For this purpose, several surface science techniques were employed such as vibrational sum-frequency generation (SFG), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and femtochemistry.

In the present thesis the results of three different projects are presented. The first concerns the adsorption and decomposition of naphthalene on Ni(111). Using scanning tunnelling microscopy (STM) and density functional theory (DFT) we identify the adsorption energy and geometry of the naphthalene molecule. Using SFG and TPD we investigate the temperature dependent breakdown of the naphthalene molecule and identify geometrical changes of the adsorbate as an intermediate step in the decomposition reaction. Additionally, we observe poisoning of the surface due to graphene growth using both STM and XPS and explore the possible effect of co-adsorption with oxygen on the reaction pathway and the poisoning of the catalyst.

The second section concerns the adsorption and decomposition of ethanol and methanol on cuprous oxide (Cu₂O). Using mainly XPS and SFG we show that ethanol adsorbs dissociatively on Cu₂O(100) and (111) and that methanol adsorbs dissociatively on the (100) but molecularly on the (111) surface. Furthermore, we identify intermediate surface species and products of the temperature dependent dehydrogenation of both alcohols and show that the (111) surface is the more effective catalyst for decomposition.

The third section explores the physics of non-thermal excitation methods and discusses CO oxidation on ruthenium (0001) induced by an optical laser and by X-rays from a free electron laser. Based on these femtochemistry experiments we discuss in particular the energy transfer both for direct excitation and for substrate mediated excitations. We show that we were able to control the branching ratios of competing mechanisms and understand the role of non-thermal electrons in the mechanisms of optical laser excitation. Furthermore, we show that it is possible to induce CO oxidation by direct X-ray core hole excitation and can rationalize the relaxation process that leads to CO oxidation.

Stockholm 2019
http://urn.kb.se/resolve?urn=urn:nbn:se:su:diva-171385

ISBN 978-91-7797-707-0

Department of Physics

Stockholm University, 106 91 Stockholm
EXPERIMENTAL INVESTIGATIONS OF MODEL CATALYTIC SURFACE REACTIONS ON METAL AND METAL OXIDE SURFACES

Kess Marks
Experimental investigations of model catalytic surface reactions on metal and metal oxide surfaces

Kess Marks
Populärvetenskaplig sammanfattning

Vid utveckling av förnybara energikällor spelar katalys en viktig roll. Till exempel i produktionen av vätsgas som driver bränsleceller, eller i nedbrytningen av besvärliga biprodukter från förnybar energiproduktion som naftalen. För att kunna utforma effektivare katalytiska processer krävs detaljerad förståelse av interaktionen mellan katalysator och reaktant, och om dynamiken i de mikroskopiska reaktionsstegen. Denna avhandling syftar till att bidra med grundläggande förståelse av katalysator-reaktantsystem genom experiment med modellsystem i ultrahögvakuum. För detta ändamål användes flera tekniker inom ytfysik såsom vibrationssumfrekvensspektroskopi, röntgenfotoollektronspektroskopi, och femtosek. I den här avhandlingen presenteras resultat från tre olika projekt som alla handlar om ytreaktioner.

Det första projektet handlar om nedbrytning av naftalen på en katalysatoryta av nickel. Vi identifierar adsorptionsenergin och geometrin för naftalenmolekylen på nickel. Vi observerar också geometriska förändringar av naftalenadsorbatet som ett mellansteg i reaktionen.

Det andra projektet avser adsorption och nedbrytning av etanol och metanol på kopparoxid (Cu₂O). Vi visar att etanol och metanol absorberar dissociativt på kopparoxid, och att olika ytsnitt föredrar brytning av olika bindningar i molekylen.


Slutligen visar vi att det finns många användbara verktyg tillgängliga för att studera ytreaktioner och att en kombination av tekniker, både experimentella och teoretiska, kan skapa bättre förståelse för katalytiska ytreaktioner. I alla projekt som presenteras här kunde vi kasta nytt ljus över reaktionsmekanismerna som är involverade i katalytiska ytreaktioner och vi undersökte metoder att förändra eller påverka reaktionsresultatet. Varje studie som presenteras här är en byggsten i en större bild av förståelse för katalys och katalytisk design, som vi kan fortsätta bygga på.
List of papers

The following papers, referred to by their roman numerals, are included in the present thesis, the status of unpublished papers is indicated in parentheses ():

PAPER I. **Naphthalene on Ni(111): Experimental and Theoretical Insights into Adsorption, Dehydrogenation, and Carbon Passivation.**
DOI: 10.1021/acs.jpcc.7b07757

PAPER II. **Investigation of the surface species during temperature dependent dehydrogenation of naphthalene on Ni(111).**
DOI: 10.1063/1.5098533

PAPER III. **Adsorption and decomposition of naphthalene on oxygen pre-covered Ni(111).**
K. Marks, M. G. Yazdi, T. Hansson, K. Engvall, D. J. Harding, M. Göthelid, and H. Öström. *(Manuscript)*

PAPER IV. **Adsorption and Decomposition of Ethanol on Cu₂O(111) and (100).**
DOI: 10.1021/acs.jpcc.9b05394

PAPER V. **Dehydrogenation of methanol on Cu₂O(100) and (111).**
DOI: 10.1063/1.4989472
PAPER VI. Indication of non-thermal contribution to visible femtosecond laser-induced CO oxidation on Ru(0001)  
DOI: 10.1063/1.4928646

PAPER VII. Atom-specific activation in CO oxidation.  
DOI: 10.1063/1.5044579

Reprints were made with permission from the publishers.
Author’s contribution

Paper I: I was involved in the TPD and STM measurements and responsible for the analysis of the TPD measurements. I was actively involved in the proofreading and editing of the paper.

Paper II: I wrote the paper. I was responsible for the SFG measurements including both experiment and analysis. I took part in the XPS measurements and was responsible for the interpretation of XPS and DFT results.

Paper III: I wrote the manuscript. I was responsible for the execution and analysis of the SFG and TPD experiments.

Paper IV: I wrote the paper. I was responsible for the SFG and TPD experiments and I worked on the analysis and interpretation of the fitted XPS data.

Paper V: I was responsible for the SFG measurements, including experiment, analysis and writing of the SFG related part of the paper. Additionally, I took part in the proofreading and editing of the paper.

Paper VI: I did part of the experimental work and I took part in the proofreading and editing of the paper.

Paper VII: I took responsibility for the sample preparation during the beamtime, did part of the experimental work and I took part in the proofreading and editing of the paper and support material.

Note on content of the present thesis
The present thesis is largely based on my licentiate thesis “Experimental femtosecond-laser based investigations of model catalytic surface reactions.” The sections 2.3, 3.3.1-3, 3.4.3, 3.7 and 3.81 are practically identical to sections in my licentiate thesis. For the sections 1.1, 2.2, 3.2, 3.4.1–2, 3.5, 3.6, 4.2.3 and 4.3.2 the text of my licentiate has been adapted and rewritten to better fit the present thesis, but the sections still contain phrasing similar to the licentiate thesis.
Table of contents:

Populärvetenskaplig sammanfattning iii
List of papers v
Author’s contribution vii
Table of contents: ix
List of abbreviations xi

1. Introduction
   1.1 Motivation 1
   1.2 Some historical perspective 2
   1.3 Scope of the present thesis 5

2. Chemical reactions on surfaces 7
   2.1 Surface-adsorbate interactions 7
   2.2 Surface catalysis 10
   2.3 Activating and controlling surface reactions 14

3. Experimental equipment and methods 21
   3.1 Some general remarks 21
   3.2 Ultra-High Vacuum (UHV) equipment 22
   3.3 Photon generation 24
   3.4 Sum Frequency Generation (SFG) Spectroscopy 29
   3.5 X-ray Photoelectron Spectroscopy (XPS) 36
   3.6 Temperature Programmed Desorption (TPD) 39
   3.7 Femtochemistry 42
   3.8 Spatially resolved techniques 47
   3.9 Theoretic calculations of surface adsorbate systems 51

4. Results and discussion summary 53
   4.1 Studies of naphthalene on Ni(111) 53
   4.2 Studies of alcohols on Cu2O 62
   4.3 Studies of CO oxidation on Ru(0001) 69

5. Conclusions & Outlook 75

6. Acknowledgements 79

7. References 81
List of abbreviations

2PC Two Pulse Correlation
2TM Two Temperature Model
AES Auger Electron Spectroscopy
AFM Atomic Force Microscope
BBO Barium Borate
BESSY II Berlin Electron Storage Ring Society for Synchrotron Radiation
CCD Charged Coupled Device
DAFC Direct Alcohol Fuel Cell
DC Direct Current
DFT Density Functional Theory
DI(M)ET Desorption Induced by (Multiple) Electronic Transitions
FEL Free Electron Laser
FWHM Full Width at Half Maximum
GGA Generalized Gradient Approximation
HF Hartree-Fock
IR Infrared
LCLS Linear Coherent Light Source
LDA Local Density Approximation
LEED Low Energy Electron Diffraction
LH Langmuir-Hinshelwood
MAX IV Swedish National Laboratory for Accelerator Physics
ML Monolayer
nDFG non-collinear Difference Frequency Generation
NEB Nudged Elastic Band
PAH Polyaromatic Hydrocarbon
PBE Perdew-Burke-Ernzerhof
PES Potential Energy Surface
QMS Quadrupole Mass Spectrometer
RF Radio Frequency
SFG Sum Frequency Generation
STM Scanning Tunnelling Microscopy
TOF Time-Of-Flight
TOPAS Optical Parametric Amplifier
TPD Temperature Programmed Desorption
TSP Titanium Sublimation Pump
UHV Ultra-High Vacuum
X-FEL X-ray Free Electron Laser
XPS X-ray Photoelectron Spectroscopy

xi
1. Introduction

1.1 Motivation
Both in nature and in industry catalytic reactions ensure the efficient production of almost everything we need, from the processing of food into glucose by enzymes in our body to the production of fertilizer that helps grow the food we eat, to the generation of renewable energy that powers the laptop we use to write our dissertations, catalysis is all around.

A catalytic reaction is a chemical reaction made more efficient by the presence of a substance that we call a catalyst [1, 2]. Catalysts take part, but are not consumed in chemical reactions and their role is to increase reaction rates, lower the energy required to drive a reaction or to maximize a specific product output. We can differentiate between homogeneous and heterogeneous catalytic reactions, where the former refers to reactions in which the reactants and the catalyst are in the same chemical phase (gas, solid, liquid), and the latter refers to reactions in which the catalyst and reactants are in different chemical phases [1]. Homogeneous catalysis is usual in nature where many reactions take place inside cells where both reactants and catalysts are in a dissolved state. Heterogeneous catalysis is commonly preferred in industry since it allows for easy separation of solid catalysts and gaseous or liquid reaction products.

It comes as no surprise that increasing the efficiency of reactions is important to industry since it decreases the costs of production. However, besides the financial benefit, catalysts have a clear environmental impact that is significant to all of us. Catalytic reactions require less energy, consume resources more efficiently and have less unwanted side products (waste).
through increased selectivity [3]. Thus (heterogenous) catalysis can help us shape a greener, more sustainable society.

An example of an everyday catalyst is the three-way catalytic converter that is incorporated in modern cars to decrease the toxicity of the car exhaust [2, 4]. A precious metal catalyst (platinum, palladium or rhodium) facilitates the reaction of toxic carbon monoxide (CO) and nitrous oxides (NO\textsubscript{x}) to less dangerous carbon dioxide (CO\textsubscript{2}) and nitrogen and oxygen gas. Thus, CO, a gas toxic to humans [5], is replaced by the less harmful CO\textsubscript{2}. However, the contribution of CO\textsubscript{2} to climate change, as demonstrated by the IPCC [6], renders this solution imperfect. Another important catalytic example is the Fischer-Tropsch process, which is the conversion of CO\textsubscript{2} and hydrogen gas (H\textsubscript{2}) to hydrocarbons that can be used as synthetic fuel. This reaction takes place in the presence of metal catalysts such as cobalt, iron, ruthenium and nickel [7]. Similar to the catalytic converter, Fisher-Tropsch catalysts consist of precious metals, which are not only expensive, but also rare. Therefore, there is a need for the development of more effective and affordable catalysts to drive a more efficient chemistry in general.

Most catalysts and catalytic processes currently used in the industry have their roots in macroscopic empirical investigations and trial and error based optimization. This method has proven effective, but time consuming. It would be desirable to be able to simply design and construct the optimal catalyst for a specific process, instead of testing hundreds of possible catalysts and finding which one works best. In order to design novel catalytic processes more efficiently, a detailed understanding of the catalyst-reactant interaction and the dynamics of the microscopic reaction steps is needed.

Catalytic reactions only take place on the surface of the catalyst where reactants can adsorb and interact, therefore surface science research is tightly connected to catalysis. Already in 1922 Langmuir recognized the complexity of reactions on surfaces and suggested that in order to comprehend surface reactions we should confine our efforts to simplified (model) systems such as single crystal surfaces [8]. The present thesis aims to do just that: to contribute to the fundamental understanding of catalyst-reactant systems by experimental investigations of reactions on single crystal surfaces.

1.2 Some historical perspective
Experiments on single crystals as suggested by Langmuir in the early 1900s were complicated at the time since it was impossible to maintain well-defined clean single crystal surfaces. This all changed with the development of Ultra-High Vacuum (UHV) technology in the 1940s and 50s. UHV made it possible to conduct experiments at pressures below 10\textsuperscript{-8} torr which is required to keep
a surface nominally clean for the typical duration of an experiment (hours) [9, 10]. Early surface science experiments involved mainly thermodynamic measurements of adsorption-desorption isotherms and the heat of adsorption. With the availability of clean samples thanks to UHV technology and the development of surface sensitive techniques, focus shifted to investigations of the structure and chemical bonding of adsorbate-surface systems. The sensitivity of an experimental method is pivotal for surface experiments partly because adsorbate-surface systems have fewer molecules and thus lower signal in general, and partly because the surface signal needs to be distinguishable from the bulk signal of the crystal.

The commercial availability of UHV systems, in combination with the development of surface sensitive techniques such as low-energy electron diffraction (LEED) and electron spectroscopies such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), is generally considered the birth of modern surface science [9]. In LEED experiments the surface is bombarded with low-energy electrons to obtain information on the ordering of surface and adsorbate layers. This macroscopic technique allowed for a better understanding of adsorbate layer structure and additionally gave surface scientists a means to monitor the cleanliness of the surface. Electron spectroscopies use the principle that electrons or photons of high enough energy can eject electrons from the atom’s core levels to the vacuum, carrying information on the chemical composition and environment of the atom it was ejected from. Although initially not developed as surface techniques, XPS and AES have a high surface specificity, probing only the first few surface layers, and once this was realised in the late 1960s surface scientists embraced these methods and made them their own.

The advancement and development of spectroscopic techniques is limited by the availability of light sources that produce photons of a certain character. It is thus no surprise that as X-ray absorption spectroscopies expanded and branched out X-ray sources such as synchrotrons were developed to produce X-rays with an increased brightness, coherence and monochromaticity[11]. Another light source that through its development has had a significant impact on the field of surface science (and far beyond) is the laser. Developed in the 1960s and producing photons in the ultraviolet (UV), visible and infrared (IR) range, the laser considerably increased the experimental possibilities of the already existing spectroscopic techniques. Not only did it allow for measurements with superior resolution, it also opened up the possibility of spectroscopy time-dependently (femtochemistry) and the field of nonlinear optics.
Pioneering work in femtochemistry was performed in the 70s and 80s by A.H. Zewail who used ultrafast laser pulses to observe transition states in real time during reactions in gas phase [12]. In order to follow a chemical reaction in real time one needs to have access to pulses shorter than the timeframe of the process you are studying as well as a well-defined time-zero, which is exactly what ultrafast lasers with pulses of either picosecond or femtosecond pulse length provide. In femtochemistry a laser pulse is used to activate a reaction (pumping) which then is probed spectroscopically at a well-defined time after the pumping of the reaction. The time delay between pump and probe can be varied which allows different stages of the reaction process to be investigated. Although the presence of a surface adds complexity to the dynamics of a reaction, Zewail’s approach can be applied to surface reactions as well.

The emergence of laser technology also gave birth to the field of nonlinear optics, for which the high intensity electromagnetic fields that are inherent to laser light, are a requirement. Nonlinear optics is the study of the response of materials to an applied optical field, if that response depends nonlinearly on the strength of that optical field. Of particular relevance is vibrational sum-frequency generation (SFG) spectroscopy, developed by the group of Y.R. Shen [13-15]. SFG is a nonlinear surface sensitive probe which uses two incoming light beams of different frequencies to measure the vibrational frequencies of adsorbates. Although the first experiments on nonlinear optics were performed already one year after the development of the laser, vibrational sum-frequency generation spectroscopy was put to use only in the late 1980’s and came to a bloom in the following decade.

Parallel to the advancement of different spectroscopic techniques that allow for the probing of the adsorbate-surface system on a molecular level, new microscopic techniques were developed in the 1980s as well. Atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) employ intrinsically different methods than the original optical microscopies, which are limited by the diffraction limit and cannot image atomic scale objects. AFM and STM can achieve atomic resolution imaging of the topography of the macroscopic surface and surface-adsorbate layers. This allows for a detailed understanding of the surface structure of catalytic materials and the adsorbate ordering and geometry on the surface [16, 17].

As with every other scientific field, surface science has benefitted enormously from advances in microelectronics and the resulting increase of computational power that is still ongoing. It not only became possible to do more complex experiments and data analysis (SFG and STM experiments would be unthinkable without electronics and computers), but also allowed for the application of density functional theory (DFT) [18, 19] to the surface-
adsorbate system. This made it a realistic option to pair experimental results with quantum chemical predictions of surface-adsorbate interactions and reaction dynamics allowing for a deeper understanding and improved interpretation of experimental results.

Surface science is a field that developed not by sequential steps, but rather by parallel developments in various fields of science and technology where at some point in time it was realized it could be applied to surface-adsorbate systems as well. Thus, in the past 60 years surface science has grown to be a well-established research field with a wide range of available methods and technologies to probe the various properties of surface-adsorbate systems. The surface scientist has but to perform the experiments.

1.3 **Scope of the present thesis**

In the present thesis, results of several experimental investigations into catalysis related surface systems are presented in the form of summaries of the appended scientific publications and manuscripts. The presentation of the results is preceded by an introduction to surface adsorbate interactions and chemical reactions at surfaces and a description of the experimental methods used to produce the results. The thesis will be concluded by a discussion on the significance of the scientific work presented and the need for further investigations.

The first part of the results section describes the temperature dependent dehydrogenation of naphthalene on Ni(111), where we identify a change in the geometry of the molecule with respect to the surface as a central part of the reaction mechanism. Additionally, we address the resultant formation of graphitic and carbidic surface carbon on the nickel surface and its consequences for catalysis as well as the influence of pre-adsorbed surface oxygen on the naphthalene dissociation. (Paper I, II and III)

The next project concerns the decomposition of methanol and ethanol on Cu$_2$O(111) and (100). It is shown that both molecules adsorb dissociatively on the (100) facet and in a mixed layer on the (111) facet. With regard to the decomposition we identify the (111) facet as the more efficient catalyst since dehydrogenation occurs at lower temperatures and breakdown is more complete. We identify a difference in selectivity for C-C and C-O bond cleavage between both surfaces. (Paper IV & V)

In the last part of the results section we will move away from thermally induced reactions and discuss how the branching ratio of CO oxidation on Ru(0001) can be controlled when other methods of excitation are employed. (Paper VI & VII)
2. Chemical reactions on surfaces

2.1 Surface-adsorbate interactions
The first step in any catalysis reaction is the adsorption of the reactant(s) on the catalyst surface. The molecules can adsorb on the surface either through the formation of a chemical bond (chemisorption) or through a weaker interaction caused by van der Waals forces (physisorption). Chemisorption is characterized by an intermingling of surface and adsorbate electron densities that gives rise to a chemical bond. This interaction is strong and allows the adsorbate to approach the surface quite closely. Physisorption is marked by a significantly weaker interaction and longer distances between the surface and the adsorbate [20].

We can view the interaction of a gas-phase molecule and the surface from a simplified energetic perspective using a Lennard-Jones potential as drawn in Figure 1a [9, 10, 21]. The energy of the surface-and-molecule system is drawn as a function of the distance between the surface and the molecule. Initially, the gas phase molecule is located at an infinite distance from the surface (all the way to the right). As it approaches the surface it experiences long range attractive van der Waals (dispersion) forces that pull the molecule closer decreasing the distance to the surface and the total energy of the system. As the molecule moves even closer it will experience short range repulsive forces due to overlapping of the electron orbitals (Pauli repulsion), the energy of the system will start to increase again. Therefore, the molecule will halt the approach and settle at an equilibrium distance at the bottom of the potential well.
Some molecules, such as oxygen on a ruthenium surface, dissociate when adsorbed; the intramolecular bonds of the gas-phase molecule are broken, resulting in an atomic species or molecule fragments on the surface [22]. This effect is illustrated by the potential in Figure 1b where the orange line represents the potential for a dissociated species and the blue line represents the molecular potential. At large distance from the surface the molecular potential is lower in energy than the dissociated potential and thus the gas phase species is molecular. As the molecule moves along the molecular potential it meets an shallow well at some distance from the surface indicating that some weakly bound molecule-surface state can be formed. As the molecule moves further along the molecular potential it crosses the dissociated potential. The intersection of the two curves is denoted the transition state, the point where the molecular and dissociate species have the same energy. If this intersection lies below the gas phase energy, molecules can move into the dissociated potential and dissociate, forming two atomic species on the surface spontaneously. If the intersection lies above the gas phase energy as drawn in Figure 1b, some additional (activation) energy is required for the gas phase molecule to dissociate. Of course this one dimensional potential showing a single molecule adsorbing on an infinitely flat surface is a simplification, but it can be used to qualitatively comprehend adsorption. However, it is important to keep in mind that the adsorption energetics are in reality much more complex. A surface often consists of

Figure 1: Lennard-Jones potential energy diagram of a gas phase molecule approaching the surface and adsorbing for (a) molecular adsorption and (b) dissociative adsorption.
different adsorption sites, each with its own adsorption energy and potential well which depends on multiple spatial coordinates.

One can view the energy landscape that an adsorbate experiences on the surface as a potential parallel to the surface as illustrated in Figure 2a [20, 21]. Each surface site is represented by its own potential well and sites are separated by an energy barrier. In this picture we assume that each surface site has the same surface-adsorbate interaction strength, and thus each potential well has the same shape and depth. At low temperatures an adsorbate will remain on the initial site of adsorption since it cannot overcome the energy barrier for diffusion to another site. With increased temperature the adsorbate can gain enough thermal energy to overcome the energy barrier for diffusion and move across the surface to other (more favourable) adsorption sites.

Figure 2: Illustration of a potential energy diagram of the energy landscape parallel to the surface, each well represents a surface adsorption site. (a) Assuming a surface with equidistant surface sites and identical adsorption energies for each site. (b) Including energy variations that can occur due to adsorbate interactions and varying adsorption strength for different adsorption sites.

Additional complications in the adsorption arise from the adsorbates themselves, both because of adsorbate-adsorbate attractive or repulsive interactions and because adsorbates occupy adsorption sites effectively blocking these sites for further adsorption by other gas phase molecules. Figure 2b illustrates the changes in the 1D parallel potential that can occur due to such effects and the increase of complexity of the energy landscape. To the left of Figure 2b the difference in adsorption energy between two possible adsorption sites \(\Delta E_{\text{site}}\) is illustrated. One adsorption site has a lower adsorption energy for the adsorbate and is thus more favourable. Which adsorption site is favoured depends on the adsorbate, what atoms make up the surface and what crystal structure the surface has. To the right of Figure 2b the effect of interaction between adsorbates \(E_{\text{int}}\) on the surface is illustrated.
This interaction can be repulsive or attractive and change the adsorption energy for adjacent sites. If adsorbate-adsorbate interactions are repulsive it will be more difficult for an adsorbate to diffuse to a surface site adjacent another adsorbate since the energy barrier will be higher as illustrated in Figure 2b. Oppositely, if the interaction between adsorbates is attractive the energy barrier to move to an adjacent site will be lower.

If enough molecules adsorb on the surface we can speak of an adsorbate layer. The adsorbate layer can be disordered or have an ordered structure based on structure of the surface underneath. On a macroscopic scale the adsorbate layer can consist of patches or islands of different structures. The adsorbate-adsorbate interactions also result in a coverage dependence of the adsorption energy which typically decreases with increased coverage. Coverage is often discussed in terms of monolayers (ML), however different definitions of monolayer exist. One common definition is that 1 ML coverage equals a system where there is one adsorbate for every surface atom. The word monolayer is also used as a synonym for first layer, where multilayer refers to second, third and fourth layers. The first adsorbate layer can be either chemisorbed or physisorbed, the second and third layers are usually physisorbed due to the increased distance to the surface that impedes the overlap of surface and adsorbate electron densities needed to form a chemical bond. Due to their weak bond to the surface multilayers often desorb before reaction takes place. This is the case for the multilayers of naphthalene on Ni(111) in papers I-III, and the multilayers of ethanol on Cu$_2$O(100) in paper IV.

2.2 Surface catalysis

In general we differentiate between surface reactions that involve adsorbed reactants only and reactions that involve both adsorbed reactants and reactants in the gas or liquid phase above the catalyst surface. The first type of reaction follows the Langmuir-Hinshelwood (LH) mechanism [21, 23, 24] and the second is considered to follow the Eley-Rideal mechanism [25], since the present work involves reactions under conditions where there is no gas or liquid phase (UHV) only the LH mechanism will play a role.

Once the reactants are adsorbed on the surface, reactions can occur. Any successful catalytic reaction on a surface will start with the adsorption of reactant(s) and end with desorption of the products because without adsorption of reactants on the surface no catalysis will occur and if no products desorb, we will have difficulty isolating the product and the catalyst will lose efficiency due to poisoning.
What happens in-between adsorption of reactants and desorption of products can be a simple one step association or dissociation, or it can be a combination of several reaction steps including but not limited to: dissociation, association, translation (diffusion), or geometrical changes as illustrated in Figure 3. In principle any adsorbate will eventually desorb at non-zero temperatures, practically however, the residence time of adsorbates varies from (almost) infinity to rather short (<s). Only adsorbates with enough residence time on the surface will undergo reaction, thus desorption of reactants or intermediates can be competing mechanisms. This situation is encountered for example in paper VI and VII, where CO oxidation and CO desorption both are possible pathways.

**Figure 3: Schematic illustration of some possible reaction steps of a molecule upon adsorption on a metal surface. Adsorption, dissociation, diffusion, association, and desorption.**

Some reactions occur readily when molecules encounter each other, but most reactions require the input of energy in the form of heat or work [1, 2]. The energy required to drive a reaction is called the activation energy ($E_a$). The principal purpose of a catalyst is lowering this activation energy. This effect is depicted in Figure 4, where the potential energy of the system is plotted as a function of a chosen reaction coordinate [20, 21]. The solid line represents the energy pathway of the surface (catalysed) reaction and the dotted line represents the equivalent gas phase pathway. The surface pathway has an additional reaction step which involves the adsorption of the reactants, and the resultant adsorbates are considered reaction intermediates. An intermediate species can be either short lived or quite stable and represents a local minimum of potential energy. A (local) maximum in the potential energy surface is an energy barrier and indicates that the reaction has an activation energy. A transition state represents a molecular configuration along the reaction coordinate at such a maximum of energy. Transition states are
extremely short-lived and, unlike an intermediate species, cannot be isolated. In the figure both reaction pathways have an energy barrier, but the energy barrier for the surface pathway is significantly lower indicating that less energy is required to drive the surface reaction. This decrease of reaction costs can be the result of simply providing a means by which reactants can more easily meet, or can be caused by more complicated mechanisms. For example, interaction between the surface and the adsorbate can decrease the intramolecular bond strength of the adsorbate molecule, making it easier to dissociate the adsorbate. As another example, the presence of the surface can stabilize certain intermediates which would not exist in the gas phase. The latter is the case for the dehydrogenation reactions discussed in papers IV and V, where hydrogen atoms are broken off the alcohol adsorbate and “stored” on the surface oxygen of the Cu$_2$O surface as an OH species. Besides lowering the activation energy a catalyst can also promote a specific reaction path, favouring one specific product from a set of possible products, or even open up reaction pathways that are inaccessible for gas phase molecules.

**Figure 4:** Schematic of an energy landscape of a reaction path from reactants to product. The dotted line shows the gas phase energy curve, whereas the solid curve shows the energy pathway in the presence of a catalyst. The energy barrier for the reaction is lower when the catalyst is present and the reaction pathway has changed.
The lowering of the activation energy \((E_a)\) increases the rate of the reaction \((k)\) which can be expressed as a function of temperature and activation energy using the Arrhenius equation:

\[
k = A \cdot N^x e^{-\frac{E_a}{RT}}
\]

where \(A\) is the pre-exponential factor which is typically in the range \(10^{12}-10^{14}\), \(N\) is the surface coverage, \(x\) is the kinetic order of the reaction which can be zeroth, first or second order, \(E_a\) is the activation energy, \(T\) is the temperature and \(R\) is the gas constant.

A way to estimate the efficiency of a catalyst for a certain reaction is the Sabatier volcano plot. According to Sabatier’s principle [20, 26], the interactions of the surface with the reactants, intermediates and products should be of intermediate strength. If the interaction is too weak, fewer or no reactants will adsorb and the activation energy for the reaction will be high, therefore, the rate of the reaction will be low. If the interaction is too strong, products will not desorb and block the surface for new adsorbates, quenching the reaction rate, a process referred to as poisoning. Poisoning of the surface can reduce reaction efficiency, or even stop the reaction entirely and is thus a major challenge for industrial catalysis [2, 27]. In papers I-III we will see that poisoning occurs on Ni(111), where after the dehydrogenation of naphthalene, carbon atoms left behind on the surface block the adsorption of new naphthalene reactants.

Sabatier’s principle is commonly illustrated by the volcano plot, called so due to its shape, as shown in Figure 5. The reaction rate is displayed as a function of the heat of adsorption, which is the change in enthalpy \((\Delta H)\) that the system undergoes upon adsorption, and is a measure of the surface-adsorbate bond strength. The rate of reaction increases as the heat of adsorption for the reactants increases (green line), but as the heat of adsorption for the product increases the reaction rate decreases (red line). This results in an averaged reaction rate (blue line) where the top indicates the heat of adsorption for the ideal catalyst. Volcano plots are widely used to predict which materials give the highest reaction rate for a specific reaction [28-30].
2.3 Activating and controlling surface reactions

As seen in the previous section a reaction generally has an activation energy which needs to be overcome in order for the reaction to occur. This means that energy must be introduced into the system. The most straightforward and common way to do this is via thermal heating of the sample. As the sample heats up the thermal energy is distributed over the electron and phonon bath of the substrate and both baths can couple to the adsorbate and induce a reaction. Phonons can drive the reaction by increasing the vibrational energy of the adsorbates within the electronic ground state of the system until the activation energy is overcome. The electron bath is described using a Fermi-Dirac distribution as is illustrated in Figure 6 and electrons in the high energy tail of this distribution can transiently populate unoccupied states and induce a reaction [31, 32]. The coupling between substrate and adsorbate is discussed in more detail in section 2.3.3.

Thermal heating is slow, and therefore the electron and phonon baths are in equilibrium, making it impossible to distinguish between the phonon and electron energy pathways. Another way of depositing energy in the system is excitation by bombardment with photons, specifically photons from an ultrafast laser. Laser excitation with a femtosecond laser creates a nonequilibrium between the electron and phonon bath, since the laser pulse used to deposit energy is shorter than the electron-phonon equilibration time. This allows for investigation of the separate phonon and electron coupling processes.

Studying thermally activated reactions provides us with a plethora of useful information with regard to the catalytic process, but it is difficult to control the outcome of a thermally driven reaction. Laser driven reactions
however, do allow for a certain amount of control. By varying the photon energy of the laser pulse, we can activate different energy pathways within the substrate, favouring a certain product. This is the case for example in paper VI, where, upon laser excitation, CO oxidation occurs on a CO and oxygen covered ruthenium (0001) surface. When the reaction is driven through thermal heating instead, the CO molecules desorb before the energy barrier for the oxidation reaction is overcome and no CO oxidation occurs [31].

As mentioned in the introduction, the principle of ultrafast laser driven reactions was coined “femtochemistry” by Zewail, who mainly did experiments on gas phase molecules. In practice one can apply the concept of femtochemistry to surface adsorbate systems, but one needs to keep in mind that the excitation mechanism is intrinsically different from direct excitation as occurs in the gas phase. The majority of the laser energy is deposited in the substrate and the likelihood of direct excitation of adsorbates is considered negligible in a surface-adsorbate system. The surface will adsorb the photon energy and only by coupling of the surface to the adsorbate will the adsorbate be driven to react. Therefore, an additional framework is required to interpret the results of laser-controlled surface reactions, which will be presented in the following sections.

2.3.1 Optical excitation and thermalization

A laser pulse deposits energy into the electron bath of the surface and in the underlying bulk layers. The depth that the laser reaches in the material is usually expressed as the penetration depth ($\lambda$), which is defined as the depth inside the material at which the intensity of the light falls to $1/e$ of the intensity it had at the surface [33]. This property depends on both the surface and bulk material as well as the laser wavelength.

The substrate is described as having two heat baths, the phonon (lattice vibrations) bath and the electron bath. Both baths can be characterized by the temperatures of the respective distributions denoted by $T_{\text{ph}}$ and $T_{\text{el}}$. In thermal equilibrium, the temperatures of both heat baths are equal, and in most cases the equilibration by electron-phonon coupling is so fast that, even upon thermal heating, both heat baths are in equilibrium. A femtosecond laser pulse, however, is much shorter than the coupling time-constant (ps), and thus pushes the system out of equilibrium as illustrated in Figure 6 [32, 34]. Before irradiation, the electrons in the metal substrate can be described with a Fermi-Dirac distribution with a temperature $T_0$. As the substrate is irradiated, energy is transferred to the electron bath. This optical excitation excites part of the distribution of the electrons above the Fermi level as shown in Figure 6. This
distribution is not thermal, which means that it cannot be described by a distribution with a temperature $T_{el}$. Rapidly, on a time scale comparable to the laser pulse length, the electrons thermalize due to electron scattering and the system can now be described by a Fermi-Dirac distribution with a temperature $T_{el} > T_0$. One can see in Figure 6 that after thermalization there is a high-energy tail of hot electrons in the Fermi-Dirac distribution. These hot electrons, as we will see later, can transiently transfer to unoccupied adsorbate orbitals.

![Figure 6: Schematic electron distribution before and after laser excitation. Part of the electron distribution is excited above the Fermi level creating non-thermalized electrons. Only after thermalization can we describe the electron distribution as an electron distribution with a hot electron temperature $T_{el}$.](image)

### 2.3.2 Electron-phonon coupling

After thermalization, the hot electrons can relax either by heat diffusion into the bulk, or by coupling to the phonon system. Coupling of the electron bath to the phonon bath raises the phonon temperature $T_{ph}$, but on a slower time scale (several picoseconds) than the electronic response (femtoseconds). Both the hot electrons and the phonons can transfer energy to the adsorbate. If the total energy transferred to the adsorbates is high enough to overcome the reaction barrier, the adsorbates can undergo desorption or reaction. Figure 7 illustrates the various energy paths and the accompanying timescales [32, 35, 36].
Figure 7: Schematic of the energy flow within a metal-adsorbate system upon laser excitation. Direct optical excitation of the adsorbate is negligible. The majority of the laser pulse energy is deposited in the electron bath which can transfer to the adsorbate molecules with a timescale of 0.1-1 ps. In a timescale of 1-2 ps the electron bath can also couple non-adiabatically to the phonon bath. The phonon bath can transfer energy to the adsorbate on a slightly longer timescale. The coupling between the heat baths is described with the 2T-model while the coupling of the two baths to the adsorbate is described by the friction model.

The time evolution of the electron and phonon temperatures upon the laser irradiation of the surface can be evaluated using the two-temperature (2T) model by Anisimov and Kaganov [37, 38]:

\[ C_{el} \frac{\partial}{\partial t} T_{el} = \nabla (\kappa \nabla T_{el}) - g(T_{el} - T_{ph}) + S(z,t) \] (2)

\[ C_{ph} \frac{\partial}{\partial t} T_{ph} = g(T_{el} - T_{ph}) \] (3)

where \( C_{el} = \gamma T_{el} \) is the electron heat capacity, \( \gamma \) is the specific heat, \( C_{ph} \) is the phonon heat capacity, \( \kappa \) is the thermal conductivity and \( g \) is the electron-phonon coupling constant. The temperature dependence of the thermal diffusion can be given by \( k = k_0 (T_{el} / T_{ph}) \). Since the laser beam diameter is much larger than the electron diffusion length we only need to consider diffusion along the surface normal \( (z) \). Equation 2 shows that the time evolution of the phonon temperature \( T_{ph} \), depends on the electron phonon coupling only. The time evolution of the electron temperature, \( T_{el} \), depends on three terms. The first term \( (\kappa \nabla T_{el}) \) describes the thermal diffusion, the second describes the coupling to the phonon bath \( (g(T_{el} - T_{ph})) \) and the third describes the energy deposited by the laser pulse \( S(z,t) \) [32, 36]

\[ S(z,t) = (1 - R_{metal}) I(t) \lambda^{-1} e^{-z/\lambda} \] (4)
where $R$ is the reflectivity of the metal, $I(t)$ is the time profile of the laser intensity, $\lambda$ is the optical penetration depth and $z$ is the distance along the surface normal.

### 2.3.3 Substrate adsorbate coupling

In an attempt to reach equilibrium the electron and phonon heat baths will transfer energy to the adsorbate. The phonons can perform this transfer adiabatically (without heat transfer) in a stepwise manner where the substrate atoms couple their vibrations to the adsorbate and the adsorbate gains vibrational energy within its electronic ground state as is visualized in Figure 8a. When enough kinetic energy is transferred, the adsorbate reaches the top of the ground state potential and can overcome the barrier towards desorption or reaction. The hot electrons transfer the energy non-adiabatically to the adsorbates and two theoretical frameworks can be used to describe this process. The first framework is DI(M)ET, Desorption Induced by (Multiple) Electronic Transitions [39, 40]. This theory assumes that the desorption happens due to one or multiple electronic transitions, illustrated in Figure 8b. Hot electrons from the substrate scatter and move the substrate-adsorbate system from the ground state to an excited state, where it remains for several femtoseconds. During this time, the system moves along the excited-state potential energy surface (PES) after which de-excitation takes place and the adsorbate returns to the electronic ground state, but with some gained vibrational energy. This process can repeat itself until the adsorbate has gained sufficient energy to desorb. The downside of this model is that it describes only the electronic mediated desorption and that the excited state to which the electrons scatter is unknown, so only a qualitative and no quantitative description can be given.
A different commonly used model for the substrate-adsorbate coupling is the friction model [40, 41], which describes both the electronic and the phonon contribution to the coupling. It involves coupling of the heat baths to the adsorbate vibrational degrees of freedom within the ground state of the adsorbate via electronic friction. Adsorbate vibrations result in a movement along the reaction coordinate, and thus the resonance frequency shifts with respect to the Fermi level. Therefore, this coupling allows the hot electrons from the heat bath to exert fluctuating forces on the nuclear coordinates. The frictional coefficients $\eta_{el} = 1/\tau_{el}$ and $\eta_{ph} = 1/\tau_{ph}$ determine how fast the energy flows to the adsorbate. The vibrational levels of the adsorbate can be represented as a harmonic oscillator and we can express the average energy of the adsorbate as [40, 41]:

$$\frac{d}{dt} U_{ads} = \eta_{el}(U_{el} - U_{ads}) + \eta_{ph}(U_{ph} - U_{ads})$$

(5)

$U_x$ is the mean vibrational energy of a specific heat bath with temperature $T_x$ which can be calculated using a Bose-Einstein distribution:

$$U_x = \frac{\hbar \nu_{ads}}{\exp \left( \frac{\hbar \nu_{ads}}{k_B T_x} \right) - 1}$$

(6)

where $\nu_{ads}$ is the frequency of the vibration along the reaction coordinate. If we consider the adsorbate motion classically, we can express Equation 4 using the classical limit for the energy $U_x$, which is $T_x$, the temperature of the corresponding heat bath [40, 42]:
\[
\frac{d}{dt} T_{ads} = \eta_{el} (T_{el} - T_{ads}) + \eta_{ph} (T_{ph} - T_{ads}) \tag{7}
\]

It is possible to determine \( T_{ads} \) by using the above equation and a value for \( T_{ph} \) and \( T_{el} \) calculated according to the two-temperature model. Using the obtained adsorbate temperature the reaction rate \( (R) \) can be computed according to:

\[
R = \frac{d}{dt} N^n = N k_b e^\frac{E_a}{k_b T_{ads}} \tag{8}
\]

where \( N \) is the surface coverage, \( n \) is the reaction order and \( T_{ads} \) is the adsorbate temperature.
3. Experimental equipment and methods

3.1 Some general remarks
The present chapter describes the experimental setups and methods used to produce the results presented in Chapter 4 of this thesis. All experiments concern adsorbates on a single crystal surface mounted in UHV. The first part of this chapter is dedicated to a description of the UHV system at Stockholm university. For beamline experiments we made use of the local end stations and UHV systems and I defer to the respective papers for details on the UHV setups at BESSYII, MAX IV, LCLS and for the system employed at KTH.

Much of the experimental work involves the use of photons produced either by a femtosecond laser (visible range) or by a synchrotron or free electron laser (FEL) (X-ray range). The second part of this chapter describes the methods and setups for photon generation.

This will be followed by descriptions of the different experimental methods used to produce the results in the presented papers. The number of different techniques featuring in the various papers is large, therefore I choose to present the methods that I was principally responsible for in more detail than the other methods, which I will only describe summarily.

The chapter will be concluded by touching upon the basics of the theoretical calculations of surface adsorbate systems since almost every paper included in this thesis also contains computational results. It is important to note that these calculations were performed by skilled theoreticians and not by the author of the present thesis.
3.2 Ultra-High Vacuum (UHV) equipment
All experiments in the present thesis were performed in UHV. For the X-ray based experiments which need to take place at beamline facilities, locally provided end stations were used. For the SFG, TPD and laser based pump probe measurements as well as for the preparation of beamtimes, the local surface science UHV system was used. This system consists of a stainless-steel UHV chamber, pumped down to \(1 \cdot 10^{-10}\) torr by an ion pump and a turbo pump which is backed by a ruffling pump. Both pump lines can be opened and closed using gate valves. The base pressure in the chamber is continuously monitored using an ion gauge. In addition to the ion-pump and turbo pump, the system is equipped with a titanium sublimation pump (TSP).

With regard to analysis the chamber is equipped with a Low Energy Electron Diffraction (LEED) system for checking surface ordering and quality. A Quadrupole Mass Spectrometer (QMS) is mounted to check the chamber for contamination, check the purity of gases used in the experiments and most importantly for the recording of TPD and Time-of-Flight (TOF) measurements. For sample preparation the chamber is furnished with an ion-gun for sample cleaning by sputtering and a total of three leak valves and one pinhole doser that allow for controlled dosing of molecules into the chamber. All dosers are supplied with gas via a gas system that is kept at low pressure (\(< 1 \cdot 10^{-3}\) torr) by a turbo pump in combination with a backing pump.

The sample is mounted on a sample holder which is in turn mounted on a manipulator arm allowing for translational \((x,y,z)\) and rotational \((\theta)\) movement. The sample temperature is continuously monitored using a thermocouple spot-welded to the side of the sample. Cooling of the sample down to 104 K is achieved using a nitrogen cooled cryostat through the manipulator arm. The sample can be heated through a filament which is mounted underneath the sample, if high temperatures are required the filament can be biased allowing for electron bombardment through which temperatures over 1500 K can be reached. As an alternative to filament heating the sample can also be heated though resistive heating, which is more controlled, but cannot reach as high temperatures.

3.2.1 Sample mounting and preparation
In the present thesis results of experiments on four different surfaces are presented, Ru(0001), and Cu$_2$O(100) and (111) and Ni(111). During experiments the samples are cleaned on a daily basis as a minimum. The cleaning and preparation procedures vary for each sample and the effectivity of the procedure is checked using LEED. Below a short description of each
sample cleaning process is given. Note that for the sample preparation, gases are dosed in units of Langmuirs ($L$) where $1L = 1 \cdot 10^{-6}$ torr·s.

Noble gas ion bombardment sputtering is a common method in surface science to obtain nominally clean surfaces. During the sputtering process an electron impact ion source, ionizes the noble gas in the chamber and the sample is bombarded with noble gas ions which remove atoms in the top layer of the surface. This leaves a clean surface with surface defects. To remove these defects often annealing to high temperatures is needed [43].

The Ru(0001) crystal was cleaned by argon ion sputtering at room temperature and an argon pressure of $1.0 \cdot 10^{-6}$ torr for five minutes to remove contaminants. Since sputtering can expose carbon on the surface, the surface was annealed in an oxygen atmosphere at 1200 K for 5 minutes, allowing the carbon on the surface to react to CO and desorb. Finally, to remove the residual oxygen from the surface the surface was flash heated to 1530 K at which molecular oxygen completely desorbs. After cleaning, the sample is cooled to 104 K and capped with 4 L of CO to preserve sample cleanness. CO can be easily desorbed just before use by flashing to 600 K. The cleanness of the sample can be checked by running CO TPD or by LEED.

The Cu$_2$O(111) surface was sputtered for 15 minutes at room temperature with an argon pressure of $1.0 \cdot 10^{-6}$ torr. Subsequently the sample was annealed in an O$_2$ atmosphere at 870 K for 20 minutes after which it is annealed in vacuum at 780 K for another 20 minutes. After cleaning the sample is cooled to 104 K where it is kept for the duration of the measurements. Cleanness of the sample can be checked with LEED. To prepare the methanol covered surface 4.8 Langmuir of methanol was dosed over a period of 5 minutes.

The Cu$_2$O(100) surface was sputtered for 10 min at room temperature with an argon pressure of $1.0 \cdot 10^{-6}$ torr. After sputtering the sample was annealed in an oxygen atmosphere with a pressure of $2.0 \cdot 10^{-7}$ torr to 900 K for 5 minutes. After 5 minutes the oxygen was pumped out and the sample was subjected to another 5 min of annealing in vacuum at 900 K. The clean sample was cooled down to 110 K where it was kept for the duration of the experiments.

The Ni(111) surface was cleaned by a 5 min sputter session at room temperature and an argon pressure of $8.0 \cdot 10^{-7}$. After sputtering the sample was annealed to 1100 K using the biased filament. The clean sample was cooled down to 110 K where it was kept for the duration of the experiments.
3.3 Photon generation

The majority of the experiments described in the present thesis employ photons in one way or another, some as a probe of the adsorbate-surface system and some as a pump to drive the reaction. These photons need to be generated and the current section describes the laser system that produces the photons for the SFG and femtochemistry experiments and the synchrotron and FEL systems that are generally used to produce the X-ray photons for XPS measurements.

3.3.1 The ultrafast laser system

The laser system is illustrated in Figure 9 and consists of an oscillator, a regenerative amplifier and two pump lasers to pump the oscillator and the amplifier. The system produces a pulsed beam of 1kHz repetition rate with pulses at a central wavelength of 800 nm, a pulse duration of 40 fs and an average power output of 3.8 W.

![Figure 9: Schematic drawing of the laser system. The pump laser pumps the oscillator. The pulsed signal from the oscillator is amplified using the second pump laser light in the amplifier. Before amplification the oscillator light is stretched and after amplification it is recompressed to achieve femtosecond pulses.](image)

3.3.2 Laser pulse generation

The oscillator is a passively mode-locked Ti:Sapphire laser. Mode-locking is the process that converts the continuous wave into pulses with a fixed phase
relationship and separated by some time equivalent to the interval cavity round trip time. The presently used passive mode-locking system is based on the Kerr effect. A Kerr medium’s refractive index can be influenced by the presence of a high electric field such as a laser. For a Gaussian beam the centre, which has the higher energy, is refracted more than the edges of the beam which have lower energy. Because of this an active Kerr medium focuses the high intensity part of a light beam. In the oscillator, the Ti:Sapphire crystal functions as the Kerr medium. Placing an (adjustable) aperture behind the Kerr medium allows us to block the low energies and let the focused high energies through therefore “locking” onto the high-energy modes (Figure 10). The resulting group velocity dispersion is compensated by a set of prisms. The oscillator outputs pulses at a repetition rate of 78 MHz and a power of 700 mW which are sent to the regenerative amplifier for amplification.

![Figure 10: Schematic of the Kerr-mode locking. The Kerr medium focuses the higher power centre-part of the beam. Subsequently an aperture blocks the low power and lets the high-power through selecting the high-energy modes of the laser light.](image)

### 3.3.3 Laser pulse amplification

A schematic of the amplifier is found in the lower part of Figure 9. The first part of the amplifier is the stretcher; here the laser pulses are stretched from femtoseconds to picoseconds. After that, the light wave reaches the amplifier cavity which is pumped by a Nd:YLF pump laser, with a wavelength of 527 nm. Regenerative amplification is a process used to create short laser pulses of high intensities. The light wave from the oscillator is trapped in a resonator where it stays until it has gained enough intensity. This trapping, as well as the releasing of the pulse is done using Pockels cells, which act like on-demand quarter-wave-plates. When activated, a double pass through the Pockels cell will change vertical polarisation to horizontal polarisation. Polarisation dependent mirrors cause light of a specific polarisation to be captured inside the cavity of the resonator. The pulse can stay in the cavity until it reaches saturation or until it extracts most of the energy stored in the gain medium. When the pulse achieves a high amplification, the second
Pockels cell is activated in order to change the polarisation of the light so that it will be released from the resonator. After the light wave is amplified it passes a grating compressor to regain femtosecond pulse length.

3.3.4 X-ray generation: Synchrotrons and free electron lasers

A synchrotron is based on the principle that charged particles such as electrons emit photons when accelerated. In a synchrotron, electrons are forced to travel in a loop (storage ring) using bending magnets. These magnets apply a Lorentz force perpendicular to the electron’s traveling direction. This force causes a centripetal acceleration that changes the traveling direction of the electrons and causes the emission of photons in the X-ray range. Thus, two goals are met; the electron is kept inside the storage ring and synchrotron light is generated. More modern synchrotrons do not rely on the bending magnets but use undulators to generate the X-rays. An undulator consists of a series of magnetic dipoles causing an alternating magnetic field which forces electrons traveling through the undulator to oscillate. These oscillations are accompanied by the emission of photons and the wavelength range of these photons can be controlled by changing the magnetic field that causes the oscillations. The emitted radiation is collimated, has a larger brightness and a narrower spectrum then if a bending magnet was used.

Figure 11 shows a schematic view of a synchrotron and its vital components with to the right an enlargement of a straight segment showing an undulator in more detail. The electrons stored in the storage ring are initially produced using an electron gun and transferred to a linear accelerator and a booster ring where their energy is “boosted” using a radio-frequency (RF)-cavity. From the booster ring the electrons are then injected into the synchrotron ring where they can be stored for several hours. The synchrotron ring is equipped with the earlier mentioned bending magnets and undulators as well as sets of focusing and defocusing mirrors (not shown in the figure) and an additional RF-cavity that compensates for the energy loss that the electrons experience due to the X-ray emission. The X-rays are emitted tangentially to the electron pathway and coupled out after each undulator and led to a beamline and an end station. The beamline is equipped with a monochromator to select the specific X-ray wavelength needed for the experiment conducted at the end station.
Electrons are created by the electron gun and in the linac and booster ring their energy is increased. From the booster ring they are injected into the synchrotron ring where they are made to travel in circles by bending magnets. When the electrons travel through the undulator X-rays are generated.

Another way of generating X-rays is the X-ray Free Electron Laser, (X-FEL) where the X-rays are generated using optical amplification rather than using spontaneous emission as in synchrotrons. The main advantage of X-FEL X-rays compared to regular undulator radiation in a synchrotron is a much higher intensity due to the fact that a large number of electrons radiate coherently. The main component of an X-FEL is a very long undulator. In a regular undulator the electrons emit radiation without any correlation to each other which means that the light is not coherent and intensity scales with the number of electrons in a bunch $N$. In an X-FEL the electrons radiate coherently and the intensity is proportional to $N^2$. This coherence is the result of microbunching which is illustrated in Figure 12 the electron bunch enters the very long undulator at a speed close to the speed of light the electrons start undulating and they emit non-coherent radiation. This radiation in return interacts with the electrons in the bunch in such a way that a longitudinal Lorentz force is produced which moves the electrons within the bunch. This force is zero at the nodes of the light wave and thus electrons collect at the nodes, this way the bunch becomes a collection of equally spaced micro bunches with a period equal to the radiation wavelength. These micro bunches
radiate like a single particle of high charge producing coherent radiation. This strong radiation again enhances the microbunching until a saturation limit is reached. This way the initial wave that started the microbunching is optically amplified.

Figure 12: Schematic image of the generation of coherent radiation through microbunching in an undulator.
3.4 Sum Frequency Generation (SFG) Spectroscopy

Infrared-visible sum frequency generation spectroscopy is an interface specific, second order nonlinear optical method that provides vibrational spectra of molecules located at surfaces and interfaces [44, 45]. In SFG spectroscopy two light waves with different frequencies interact in a medium characterised by a second order nonlinear susceptibility tensor [13, 46-49]. As a result, a new light wave with a frequency at the sum of the two initial waves is generated. In this section, the basics of nonlinear optics will be introduced followed by a more practical description of SFG as a vibrational spectroscopy.

3.4.1 Nonlinear optics

In linear optics, the polarisation $P$ can be expressed as:

$$ P = \epsilon_0 \chi^{(1)} E $$  \hspace{1cm} (9)

where $\epsilon_0$ is the dielectric constant, $\chi^{(1)}$ is the first order susceptibility and $E$ is the electric field strength. In the strong electric fields of pulsed lasers this linear approximation is no longer applicable and nonlinear contributions need to be taken into account, which leads to the following expression:

$$ P = p^{(1)} + p^{(2)} + p^{(3)} + \ldots $$
$$ = \epsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots) $$  \hspace{1cm} (10)

where $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order susceptibilities respectively [13, 46]. From this equation, we can extract the expression for the second order nonlinear polarisation:

$$ p^{(2)} = \epsilon_0 \chi^{(2)} E^2 $$  \hspace{1cm} (11)

Since sum frequency generation explicitly uses two different electric input fields we can write an expression for the electric field $E$ as a function of two incoming fields:

$$ E = E_1 \cos \omega_1 t + E_2 \cos \omega_2 t $$  \hspace{1cm} (12)

Substituting this expression for $E$ in Equation 11 leads to four cross terms that each represent a different second order nonlinear response. If we isolate the term that describes sum frequency generation we find:

$$ p_{SFG}^{(2)} = p^{(2)}(\omega_1 + \omega_2) = \chi^{(2)} E_1(\omega_1) E_2(\omega_2) $$  \hspace{1cm} (13)
The polarisation $P_{\text{SFG}}$ causes an electric field at the sum of the frequencies of the input fields $E_1$ and $E_2$, which induces a light wave.

In centrosymmetric media such as gases, liquids and some crystals, $\chi^{(2)}=0$ in the dipole approximation, which means that second order nonlinear processes do not occur. Only in media with a broken inversion symmetry, such as a crystal surface-vacuum interface, is $\chi^{(2)}$ nonzero and can second order nonlinear processes take place. Thus, SFG is a surface sensitive method and vibrational spectra of adsorbates on the surface can be recorded without contributions from the crystal bulk [44, 50].

### 3.4.2 SFG as a vibrational spectroscopy

In practice we employ a broadband mid-IR pulse and a spectrally narrow 800 nm pulse as the two incident light waves $E_1$ and $E_2$ from Equation 13. When both these pulses are spatially and temporally overlapped on the surface sum frequency generation can occur and produce photons in the visible range [44]. Figure 13a shows a schematic illustration of this light generation. The outgoing light is separated according to wavelength using a spectrometer and recorded using a charge coupled device (CCD) camera. CCD cameras generally work optimally in the visible range, which makes SFG an advantageous method as information can be obtained on vibrational frequencies in the IR range, by recording light in the visible range [50].

Figure 13c depicts a schematic of the SFG excitation process. The incoming IR light can induce a polarisation from the ground state to an excited vibrational state, simultaneously the 800 nm light up-converts the system to a virtual state. When this virtual state relaxes, light at a frequency that is the sum of the frequencies of the two incident optical fields is emitted. Thus SFG is a combination of an IR-active process and a Raman anti-Stokes process.

In the present work we use broadband IR pulses with a width of about 300 cm$^{-1}$ (FWHM). Any resonant vibrational transition covered by the IR bandwidth will be excited and upconverted. This allows for the observation of resonance shifts and of multiple resonances simultaneously without the need for scanning the IR spectrum.
Figure 13: Sum frequency generation. a) two incoming beams with variable frequency hit the surface and the resulting SFG signal is measured with a spectrometer. b) Schematic of the spectral shapes of the vibrational resonance and non-resonant response of the surface, the latter having the same spectral shape as the incoming IR light. c) SFG energy diagram, the IR and visible photons cause an excitation to a higher energy virtual state. When the virtual state relaxes a photon with a summed-frequency is released.

In the case of SFG at a surface-adsorbate interface the second order susceptibility \( \chi^{(2)} \) from Equation 13 can be separated into a resonant \( \chi_R^{(2)} \) contribution from the adsorbate layer and a non-resonant \( \chi_{NR}^{(2)} \) contribution from the surface [45]:

\[
\chi^{(2)} = \chi_R^{(2)} + \chi_{NR}^{(2)}
\]  

(14)

When the broadband IR does not match any of the vibrational excitations of the adsorbates or if there are no adsorbates, \( \chi_R^{(2)} = 0 \) and only the non-resonant contribution \( \chi_{NR}^{(2)} \) remains. The resonant adsorbate contribution can be expressed as a sum over all resonances according to:

\[
\chi_R^{(2)} = \sum_n \frac{A_n e^{i\varphi_n}}{\omega_{IR} - \omega_n + i\Gamma_n}
\]  

(15)

where \( A_n, \varphi_n, \omega_n \) and \( \Gamma_n \) are the amplitude, relative phase, frequency and half width of the nth resonance, respectively. A recorded spectrum will contain both the resonant and non-resonant signal (Figure 13b) since it is physically unpractical to separate the two. This is usually dealt with by recording a spectrum from a clean surface prior to adsorption of the reactants, which can be used as a measure for the non-resonant background during the experiment.
The intensity of the emitted SFG light, $I_{SFG}$, is proportional to the second order susceptibility and thus has resonant and non-resonant contributions:

$$I_{SFG} \propto \left| \chi^{(2)}_{NR} + \chi^{(2)}_R \right|^2 = \left| |A_{NR}| + \sum_n \frac{A_n e^{i\varphi_n}}{\omega_{IR} - \omega_n + i\Gamma_n} \right|^2 I_{IR} \quad (16)$$

$\chi^{(2)}_R$ is proportional to the amount of vibrating molecules (oscillators) on the surface, i.e. the surface coverage ($N$). Thus, $I_{SFG}$ is proportional to the square of the coverage ($N^2$). This means that the SFG intensity can, to some extent, be used as a measure of surface coverage, but also that measuring SFG for systems with low coverages can be rather difficult since the signal will be low.

For surfaces containing free electrons, such as metal surfaces, an additional selection rule for SFG exists which has an influence on $I_{SFG}$. Free electrons in the surface interact with the electric field of the laser creating an image dipole in the surface as illustrated in Figure 14. The image dipole enhances the SFG signal if the dynamic dipole moment is perpendicular (or has a perpendicular component) with respect to the surface. If the dynamic dipole moment of an oscillator is parallel to the surface the image dipole cancels out the molecule’s dipole and the vibrations will in general be invisible in SFG.

![Figure 14](image.png)

Figure 14: Illustration of the selection rule for SFG on conducting surfaces. The surface will mirror the dipole moment and oscillators with a dynamic dipole moment perpendicular to the surface have an enhanced SFG intensity, while oscillators with a parallel dynamic dipole moment are cancelled out and are thus not active.

There are two different measurement modes used in the SFG experiments in the present thesis. Figure 15 illustrates the typical result of both these methods, in this case for Naphthalene on Ni(111). The first measuring mode (Figure 15a) is static: a sample is prepared and kept at constant temperature while spectra are accumulated until an acceptable signal-to-noise ratio is reached. The second measuring mode (Figure 15b) is kinetic: the sample is
undergoing a change and spectra are recorded as a function of the change parameter such as coverage or temperature. The data is accumulated during certain time intervals and for each time interval a new spectrum is recorded. The changing parameter is recorded as a function of time and we can correlate each new spectrum with a certain coverage or temperature. This is presented as a two dimensional false colour plot as depicted in Figure 15b. The second measuring mode results in noisier data, since there is a trade of between statistics, ramping rate and thermal (or other) resolution. Thus, kinetic mode measurements are mainly useful for systems producing large SFG intensities, so that reasonable signal-to-noise ratios can be reached within short amount of times. When a decent SFG signal can be obtained the kinetic mode can be very insightful. It is a way to visualize changes such as the appearance and disappearance of resonances or more subtle changes such as shifts and intensity variations as a function of temperature. This information can aid the understanding of reaction mechanisms and possibly corresponding reaction rates.

Figure 15: Example of a typical SFG measurement, a non-resonant background from a clean Ni(111) surface (black), measured signal from naphthalene multilayer on Ni(111) (red), showing a resonance at 3057 cm\(^{-1}\). Example of an SFG kinetic measurement, in this case naphthalene on Ni(111), measured with a ramping rate of 3 K/min. To the left a false colour plot of spectra recorded as a function of temperature. Adapted from paper II.
3.4.3 SFG instrumentation and optical set-up

Figure 16 depicts a schematic of the set-up used for the SFG experiments. The setup consists of two beam paths, one for the generation of the broadband IR light and one for the narrowing of the 800 nm light. This narrowing is necessary since the IR spectrum is broad (300 cm$^{-1}$ FWHM) in order to cover a wide range of possible vibrational frequencies, and it is thus the width of the 800 nm pulse that determines resolution of the experiment.

The 800-nm light from the laser system is led into an optical parametric amplifier (TOPAS). Here a nonlinear crystal is used to convert one incoming photon into two photons which have a total sum energy equal to the energy of the incoming photon. The two generated laser pulses are called the signal and the idler. The wavelength of each of these pulses is determined by the phase matching condition, which can be changed to produce different wavelengths. This way a laser pulse of 800 nm can be used to create two pulses in the near-IR region. The TOPAS we use is fully tuneable using pc software. The output of the TOPAS is split into two parts, the (unconverted) 800 nm light is directed in the towards the pulse shaper and the newly created IR light is directed towards the non-collinear difference frequency generator (nDFG). In simplified terms the nDFG creates broad mid-IR pulses via difference frequency generation. Difference frequency generation is a second order
nonlinear process in which photons are created, their frequency is the difference between the frequencies of the two incoming light beams:

\[ \omega_{dfg} = \omega_1 - \omega_2 \]  

(17)

In essence the process is quite similar to sum frequency generation, but there is one important difference. Conservation of energy requires that the input photon with higher energy be destroyed in the process and thus an extra photon at the lower input energy must be created. This means that the field of the lower input frequency is amplified by the nDFG. The nDFG generates mid-IR light (tuneable within 2.6 to 11 \( \mu \)m). The produced mid-IR light is directed through the barium fluoride (\( \text{BaF}_2 \)) viewport on the UHV chamber and onto the sample by gold mirrors that are set such that the beam path of the mid-IR and the 800 nm have a similar length.

The residual 800 nm light coming from the TOPAS is redirected to a pulse shaper so that it can be spectrally narrowed, usually to about 12 cm\(^{-1}\) which consequently increases the pulse length of the light to picosecond scales. A delay stage facilitates temporal overlapping of the beams on the sample. To assist in finding spatial and temporal overlap there is a reference beam path set up that couples out the light towards a lithium niobate (\( \text{LiNbO}_3 \)) crystal in an equivalent plane of the sample outside the vacuum. The light enters the chamber through an IR transparent \( \text{BaF}_2 \) viewport and the generated SFG light from the sample leaves through a fused silica viewport and is directed towards a spectrometer. A filter is placed to block the 800 nm light from entering the spectrometer to protect the CCD camera, which records the SFG spectrum as the light exits the spectrometer.
3.5 X-ray Photoelectron Spectroscopy (XPS)

XPS [51, 52] is a versatile surface sensitive technique that uses the adsorption of a photon and resultant emission of an electron to identify the type and chemical environment of atoms at the surface of a sample. Figure 17a shows a schematic energy diagram of the photoemission process on which XPS is based.

![Schematic diagram of XPS process]

Figure 17: Schematic illustration of the X-ray photoelectron emission process. a) An X-ray with energy $h \nu$ is adsorbed and an electron of binding energy $E_B$ is ejected from a core level to the continuum. The ejected electron has a kinetic energy $E_K$ which is measured by the spectrometer. b) X-rays excite electrons from different atoms in a system, only electrons from surface layers or adsorbate layers manage to escape the system. Electrons from bulk layers or from surface layers underneath adsorbates are stopped within the material due to inelastic scattering and other processes.

An incoming photon of energy ($h \nu$) in the X-ray range (100 eV-1.5keV) excites an electron from the core orbital of an atom to the continuum, leaving behind a core hole. Emission of the electron only occurs if the photon energy $h \nu > E_B$, where $E_B$ is the binding energy of the electron. If $h \nu$ is too low no emission will occur regardless of the intensity of the X-ray radiation. If the energy of the photons exceeds $E_B$ the number of emitted electrons will be proportional to the intensity of the X-rays. The kinetic energy of the ejected electron ($E_K$) can be measured with an electron spectrometer and is linearly proportional to the energy of the incoming photons. It can be expressed according to:

$$E_K = h \nu - E_B - \Phi_{sp}$$  \hspace{1cm} (18)
where \( \Phi_{sp} \) is the spectrometer work function which is a combination of the sample work function \( \Phi_s \) and the work function of the analyser \( \Phi_a \). The work function usually can be compensated for by putting the sample and the spectrometer on the same bias, so that \( \Phi_{sp} \) can be eliminated from Equation 18. The binding energy is defined as the minimal energy required to completely free an electron from an atom and can be expressed as a function of the energy of the incoming photon and the measured kinetic energy:

\[
E_B = h\nu - E_K
\]  

(19)

Due to the short mean free path of electrons, only electrons emitted from the first few surface layers stand a chance of actually escaping the material. The electrons excited from deeper layers have a longer path through the material and therefore an increased chance of undergoing inelastic collisions, recombination and other processes that will prevent them from reaching the continuum (see Figure 17b). It is this surface specificity that makes this method extremely suited to study surface chemistry.

3.5.1 Chemical shift

The binding energy is unique to the element from which the electron is ejected and depends on the electronic structure of that element. Changes of the electron distribution of an atom, for example due to the creation of a bond with another atom, produce a shift of the binding energy. This shift is usually referred to as the chemical shift. For example, the carbon in the CO molecule is bound to an electron-drawing oxygen which causes the carbon to be slightly more electropositive. The interaction between the nucleus and the electrons of the carbon atom is therefore stronger and more energy is required to free a core electron, thus the binding energy of a carbon in a CO molecule is higher than that of a single carbon atom. In addition to chemical bonds, the electron distribution of an atom can also be influenced by the oxidation state of the atom or its lattice adsorption site. Thus, the binding energy not only provides information on which chemical element is on the surface but also on the chemical environment of that element.

The chemical shift is usually thought of as the result of initial state effects, which involve anything that affects the ground state of the atom before the photoemission process, the initial state. However, technically both initial and final state effects determine the binding energy. Final state effects are those effects that influence the state of the atom after the photon has been absorbed or that influence the ejected electron while it is leaving. For example, when an electron is ejected, the other electrons in the atom, or even the
electrons in nearby atoms can rearrange in such a way that the energy of the ionized atom is shielded or minimized. This reorganization causes a relaxation and results in a lower binding energy. In general, the binding energy can be expressed as the difference between the energy of the final state $E_f$ and the energy of the initial state $E_i$ of an atom with $n$ electrons:

$$E_B = E_f(n-1) - E_i(n)$$

(20)

In practice it is the kinetic energy that is measured and the binding energy is calculated based on this measurement. A spectrometer registers how many ejected electrons with a particular kinetic energy reach the detector and the counts are plotted as a function of the binding energy. This results in a spectrum consisting of one or more peaks. The position of the peak is the binding energy of the electrons from a specific surface species. The surface area under the peak is a measure for the number of atoms of that species. The peak width is largely determined by the life time of the created core hole and the resolution of the equipment used. A deeper core-hole has a shorter lifetime as there are more possible mechanisms of relaxation. A shorter lifetime means a larger width of the XPS peak as peak width ($\Gamma$) and core hole lifetime ($\tau$) are related according to $\Gamma = h/\tau$. There are several mechanisms that can cause broadening of the peaks such as the energy spread of the incoming X-rays and the resolution of the spectrometer. Another broadening effect is caused by the vibrational structure which has strong influence on the width of the C1s spectra for hydrocarbons as we encounter in paper II for naphthalene on Ni(111). For nonconducting materials such as the cuprous oxide in paper IV and V, additional broadening can occur, since charge compensating is required to prevent charging of the surface as a result of the loss of electrons. Such charge compensation can be done by flooding with low energy electrons which can cause additional broadening.

Even with optimal resolution chemical shifts can be small and many and peaks are rarely completely separated. Therefore, it is necessary to perform peak fitting to resolve peaks and subpeaks in order to be able to determine the exact binding energies and identify all the different surface species.
3.6 Temperature Programmed Desorption (TPD)

TPD is a surface science method used to investigate the kinetic behaviour of adsorbates on the surface. It is a simple but insightful method. The temperature of the surface sample is increased with a linear heating rate and based on the strength of the surface-adsorbate interaction, the adsorbates desorb from the surface at a certain temperature. The number of desorbed molecules of a certain mass are measured as a function of temperature using a mass spectrometer. Figure 18 shows a schematic of the TPD setup used and an enlargement of the quadrapole mass spectrometer. The heating is done using resistive heating, which allows for the most stable ramping of the temperature in our setup.

![Figure 18: Schematic of the TPD-MS setup (left) and enlargement of the quadrapole mass spectrometer (right).](image)

Mass Spectrometry is based on the principle of the ionization of incoming molecules and the subsequent filtering of the ions based on their mass-to-charge ratio. In the present experiments this filtering is done by a quadrapole system. The quadrapole consists of four rods, arranged according to Figure 18, that have applied potentials of \( \pm (U + V\cos(\omega t)) \) where \( U \) is a DC voltage, \( V \) is an AC voltage and \( \omega \) is the angular frequency. Based on the potential the rods generate an electric field that influences the trajectory of the ions through the spectrometer. Only particles with a selected charge-to-mass ratio have a
so called resonant trajectory and can reach the detector. Particles with a different charge-to-mass ratio will have a non-resonant trajectory and will not reach the detector. By changing the potential on the rods the quadrupole mass spectrometer (QMS) can change which mass-to-charge ratio has a resonant trajectory and thus which masses are measured. This change of potential is fast enough to allow for several masses to be measured “simultaneously”, within some ms of each other, which is often the case when we do TPD measurements. For experiments with a higher time resolution, only one mass-to-charge ratio will be measured as we will see in the section on Time-of-Flight measurements.

The result of a TPD measurement is a graph showing intensity as a function of temperature, where the intensity is a measure for the desorption rate. In this plot, the area under the graph is proportional to the total amount of desorbed molecules. The position of the peak on the temperature axes can be a measure of the strength of the adsorption of the molecules to the surface. Stronger molecule-surface interactions will cause desorption to occur at higher temperatures. Since an increase in temperature can also induce reaction the desorbates that are observed might also be reaction products. Thus, TPD allows us to identify products and estimate activation energies. Multiple peaks in a TPD spectrum can correspond to adsorption on different surface sites, where the sites have different interaction strength or to different mechanisms leading to the same product or multilayer adsorption. Figure 19 illustrates a typical TPD spectrum for the desorption of physisorbed multilayers of naphthalene on Ni(111) at 220 K as was recorded for paper I.

![Figure 19: Example of a typical TPD for Naphthalene on Ni(111) measuring mass-to-charge ratio of 128 amu with a heating rate of 50 K/min. Adapted from paper I.](image-url)
The shape and position of a TPD peak can be described using the surface coverage and the desorption energy. The desorption rate \( k_{\text{des}} \) can often be expressed using an Arrhenius expression:

\[
k_{\text{des}} = A \cdot N^x e^{-\frac{E_a}{RT}}
\]  

(21)

Where \( A \) is the pre-exponential factor, \( N \) is the surface coverage, \( x \) is the kinetic order of the desorption \((0,1,2)\), \( E_a \) is the adsorption energy, \( T \) is the temperature and \( R \) is the gas constant. The signal intensity \( (I) \), as a function of temperature is then proportional to the decrease in surface coverage:

\[
I(T) \propto -\frac{dN}{dT} = \frac{A \cdot N^x}{\beta} e^{-\frac{E_a}{RT}}
\]  

(22)
3.7 Femtochemistry

Femtochemistry is in principle a term describing any science that monitors the dynamics of reactions, in our group however we use it to refer to experiments involving the measurement of the time-of-flight (TOF) of desorbing molecules. For these measurements we use mass spectrometry as described in a previous section in a time-dependent manner to follow the time evolution of the desorption of a certain mass. These measurements are used in two types of schemes, one where the laser fluence is varied to obtain a fluence dependence, and one where two laser pulses that are delayed with respect to each other are used to measure a two-pulse correlation. Both schemes are explained in detail below including the experimental specifics used to obtain the results in papers VI and VII.

3.7.1 Time-of-flight and first shot yield

The number of particles with a certain mass/charge ratio as detected by the QMS are recorded as a function of time, where the moment that the laser pulse hits the surface is defined as the time-zero. This results in a time-of-arrival distribution as depicted in Figure 20a. Both the desorption process and the flight from the surface to the QMS take time, therefore the first signal is observed several µs after the laser pulse hits.

The total yield of the reaction can be retrieved by integrating the time-of-flight distribution over time. As we record the time-of-flight for each laser pulse we can compute the yield for each shot individually. The yield is largest at the first shot and less for each consecutive shot, since depletion of the reactants occurs. The resultant plot of yield per laser shot can be fitted with a decay function and is called yield decay or decay curve (Figure 20b). Extrapolating this decay function to the first shot delivers the first shot yield.

*Figure 20: Time-of-flight distribution retrieved with QMS (a) and the corresponding yield decay for consecutive laser shots (b).*
3.7.2 Fluence dependence and yield weighted fluence

The recorded first shot yield varies with the fluence of the laser pulse used to excite the surface-adsorbate system. If the yield is recorded as a function of the laser fluence, a so called fluence dependence, it shows a nonlinear relation that can typically be fitted using a power law $Y = F^n$. Reactions induced with femtosecond lasers typically show such nonlinearity. A consequence is that we must account for the spatial non-uniform distribution of the energy in the beam profile. This can be done by introducing yield-weighted fluence. It is defined as the laser pulse energy ($J$) per effective focal spot area ($cm^2$). The focal spot area can be recorded as a beam profile using the CCD camera and the fluence ($F$) can be weighed according to:

$$\langle F \rangle = \frac{\sum Y_i F_i}{\sum Y_i} = \frac{\sum F_i^{n+i}}{\sum F_i^n}$$  \hspace{1cm} (23)

where $n$ is determined by fitting to the measured fluence dependence and $i$ represents each CCD pixel.

3.7.3 Move-stop measuring mode

For the femtochemistry experiments a so-called move-stop measuring mode is used. Only the adsorbates on the surface in the direct area of the focused laser beam react. This means that if we move the laser to a different sample spot we can measure a new ‘fresh’ sample. If this is not done each subsequent measurement depletes the adsorbate layer even more and the reaction conditions are not the same for each measurement.

In general, a surface adsorbate layer is prepared before the experiment and during the experiment the sample is scanned in steps. For each measurement at a new spot, the surface is irradiated for a certain time (usually 1s) such that multiple laser pulses (depending on laser frequency) reach the surface spot, and the time-of-flight is recorded for each pulse. Then the sample is moved and a new spot is irradiated, this way the maximum amount of data is retrieved for one preparation.

3.7.4 Two-pulse correlation

Two pulse correlation is a method that is used to get insight in the dynamics of a reaction, giving an indication of the energy pathways involved in the laser induced reaction. In two pulse correlation, two laser pulses of similar intensity with a known and variable delay are spatially overlapped on the sample to drive the reaction. The yield as retrieved by integration of TOF measurements is recorded as a function of the time delay between the two laser pulses. Figure
21a, b and c show the temperature of the surface heat baths for electrons ($T_e$) and phonons ($T_{ph}$), as a function of time, calculated using the two-temperature model for three different pulse delays. When the delay between the pulses is long (20 ps), the phononic and electronic systems have time to equilibrate between pulses and the time profile for both electron bath temperatures is the same for both pulses. As the delay between pulses decreases (Figure 21b and c) the second pulse arrives when the system is still at raised temperature therefore the energy of the second pulse is added to the pre-existing excitation. When the two pulses exactly overlap, the electron temperature is greatly enhanced.

Figure 21: a,b,c) Electron and phonon temperatures for two-pulse-correlation schemes as calculated using the 2T model for pulses of 50 fs and 400 nm, with three different delays, 20 ps, 1 ps and 0 ps respectively. d) Calculated two-pulse correlations illustrating the difference in FWHM for phonon and electron mediated excitations.

Figure 21d depicts the calculated two-pulse correlation for a phonon (p) and an electron (e) driven reaction, the yield shows a maximum close to a delay of 0, when both beams exactly overlap in time and the electron temperature that is reached is the highest. Towards longer and shorter delays, the yield decreases nonlinearly and the width (FWHM) of the yield peak depends on the reaction activation pathway. A narrow FWHM of a few picoseconds is an
indication of an electron mediated reaction since it implies that the time delay between the pulses is shorter than the electron-phonon equilibration time. A wider FWHM is harder to interpret because it can have various causes. Phonon mediated processes are slower, since the energy has to be transferred from the electron bath to the phonon bath with an equilibration time of several picoseconds and the coupling time of the phonon bath to the adsorbate is longer as well. Thus, where a broader FWHM in two-pulse correlation can imply involvement of the phonon system, it does not, exclude involvement of the electron system. Additionally, if the coupling of the electrons to the adsorbate is weak, the FWHM can be broad even though the process is electron mediated only.

3.7.5 Optical setup for femtochemistry
A schematic of the optical setup for the femtochemistry experiments is shown in Figure 22. The light from the laser system, as described previously, is sent through a $\lambda/2$ waveplate, which in combination with a polarizer, can be used to attenuate the energy of the laser beam. A telescope is used for adjustment of the beam size. The 800-nm light is then frequency doubled by a BBO (β-Barium borate) crystal to 400 nm. For experiments that require 800 nm, the BBO crystal is simply removed. A chopper chops the 1kHz beam to lower frequencies, in these experiments we use 50 Hz. A shutter is placed between the beam and the sample so that the irradiation time of the sample can be controlled. For two-pulse correlation experiments an additional beam splitter and delay stage are needed. The beam splitter splits the light in two beams of equal energy and the delay stage is used to scan the time delay between the two beams by changing the path length of one of the beams.

The laser can be coupled out in front of the chamber into a reference beam path with a CCD camera at the same distance as the sample in the chamber. The reference path allows characterisation of the spatial beam profile and determination of temporal overlap. The laser is aligned to travel straight through the chamber, entering by a fused silica window, so that it is possible to precisely align the sample at an angle with respect to the beam.
Figure 22: Schematic of the femtochemistry optical set-up.
3.8 Spatially resolved techniques

3.8.1 Low Energy Electron Diffraction (LEED)
Low Energy Electron Diffraction (LEED) is a common technique in surface science. It is a quick and easy method to check the structure and quality of the surface and its adsorbate layers. This technique uses de Broglie’s postulate that electrons can be viewed as electromagnetic waves moving at a speed \( v \) and a wavelength \( \lambda \). The surface is bombarded with low energy electrons which are scattered upon hitting an area of high electron density, such as the atoms in the sample crystal lattice.

![Figure 23: Schematic representation of the scattering process, where an incident electron beam is scattered at an angle \( \theta \) by atoms in a crystal lattice at distance \( d \) from each other.](image)

Figure 23 shows a schematic representation of the scatter process. The incoming electrons are scattered under an angle \( (\theta) \) and the path difference between two electrons scattered by neighbouring atoms at a distance \( d \) is \( d \times sin(\theta) \). If this path difference is equal to or a multiple of the wavelength \( \lambda \) of the electrons we will get constructive interference. This produces a diffraction pattern.

\[
d \times sin(\theta) = n\lambda
\]

(24)

Because the penetration depth of low energy electrons (20-200 eV) is only several Ångström due to energy losses via inelastic scattering, we can view the observed elastic scattering as produced by the first few atomic layers only. In other words, the use of low energy electrons makes this technique surface sensitive. The diffraction pattern, which is observed by accelerating the elastically scattered electrons onto a phosphorus screen, is a representation of the reciprocal lattice of the surface structure. For example, the ruthenium crystal we use in paper VI and VII has a hexagonal close packed structure and
is cut on the 001 plane, in LEED it looks like Figure 24a. One can also investigate the ordering of a layer of adsorbates with respect to the metal crystal lattice. Figure 24b shows the LEED pattern of (2x2) CO adsorbed on Ru(0001). For the purpose of the present thesis LEED is used to check the cleanliness and structure of prepared samples.

Figure 24: a) LEED pattern as recorded for a clean Ru(0001) sample, b) LEED pattern as recorded for a CO covered Ru(0001) surface.
3.8.2 Scanning tunnelling microscopy (STM)

Scanning Tunnelling Microscopy (STM) [53-55] is a non-optical type of microscopy able to produce real space images with atomic resolution. In STM an (atomically) sharp tip is scanned across a surface in a highly controlled fashion. A bias is applied between the tip and the surface and when the tip approaches the surface close enough a tunnel current ($I_T$) can flow from tip to surface or vice versa depending on the applied bias.

The observed tunnel current is one of the fundamental principles of STM. Tunnelling is the movement of electrons through a barrier that they in classical terms should not be able to move through. In quantum mechanics electrons have wavelike properties and the wave function does not stop directly at any barrier, but instead decays rapidly with distance. If the barrier is thin enough the wave function might extend into the next region before it has completely abated, which means that there is a probability that some electrons move or “tunnel” through the barrier.

Because of the rapid decay of the wave functions through the barrier, the actual number of electrons that will tunnel, i.e. the tunnel current, will depend exponentially on the thickness of the barrier (roughly one order of magnitude per Ångström). Thus measuring the tunnel current between two objects can be a measure of the distance between the two objects, such as the tip and a sample surface.

In general STM is considered to have two different measuring modes, “constant current” and “constant height”. In the constant current mode, the position of the tip is adjusted during the scan such that the tunnel current (and thus the distance to the sample) is kept constant. The changes in tip position are recorded during the scan and a topographical image of the surface can be obtained. In the constant height mode the z-position of the tip is kept constant during the scan and the changes in tunnel current are recorded. This mode is only recommended if the surface does not have any large protrusions that the tip can crash into. The resulting image of a constant height scan is not a true topographical image, but an image of the electron density of states at the surface. For metal surfaces the electron density does resemble the topography reasonably well.

Figure 25 shows a schematic of a STM setup. As mentioned before a bias is applied either to the tip or the sample, this is necessary to ensure that there are available empty states on the other side of the barrier that any tunnelling electrons can occupy. As one can imagine when studying systems on the atomic level, the position of the tip needs to be controlled very precisely in all three dimensions, for STM to be useful. This high level of control is most often achieved using a holder of piezoelectric material. During the scans
both the position of the tip according to the piezoelectric holder and the tunnel current are recorded. For the constant current mode a feedback loop is required that adjust tip position in such a way that the tunnel current is kept constant. Because of the extremely small distances involved in STM measurements the system is usually isolated from external vibrations.

Figure 25: Schematic of an STM setup showing tip and sample connected to a bias. The tip position is controlled by a piezoelectric holder. Tip position and tunnelling current are measured simultaneously and if necessary a feedback loop is used to keep the tunnel current constant by adjusting tip position.

The resolution of STM measurements is affected by several factors. One very important factor is the tip. Since the obtained image is a convolution of the tip and the sample, resolution decreases with tip size. Fortunately, it is not difficult to produce tips with a single atom at the tip. However, it is possible that the tip deteriorates during a scan for example due to sticking of atoms onto the tip, or crashing of the tip into the sample. In general a horizontal resolution of 10Å and a vertical resolution of 0.01Å is achieved. Vertical resolution is influenced by the stability of the instrument and the effectiveness of the feedback electronics.

For catalytic systems STM is often employed to investigate the surface structure of the catalyst as well as the structure of the adsorbate layer including adsorbate orientation and adsorption site.
3.9 Theoretic calculations of surface adsorbate systems

Although the present thesis is a report on experimental work, most papers presented contain a combination of both experimental and theoretical work. Thus, it is useful to devote a few words to the basic principles of computational chemistry.

In surface science computations are commonly used to predict adsorbate geometries, adsorption energies, potential energy surfaces of reactions, vibrational frequencies and spectra. Surface adsorbate systems, which are large many-particle systems, are usually described within framework of density functional theory (DFT) [56]. DFT uses the electron density ($\rho$) to obtain electronic structure properties by using certain approximations to maximize accuracy while minimizing computational time. The basis of DFT was formulated by Hohenberg and Kohn [18] and later made applicable by Kohn and Sham [19], leading to the following expression of the energy as a functional of the electron density:

$$E[\rho] = T_s[\rho] + \int \rho(r)V_{ext}(r)dr + J[\rho] + E_{xc}[\rho]$$  \hspace{1cm} (25)

Where $T_s[\rho]$ is the kinetic energy functional, the integral describes the potential energy arising from interaction with an external potential, $J[\rho]$ is the classical Coulomb energy, and $E_{xc}[\rho]$ is the exchange correlation functional.

Of these terms it is the exchange correlation functional that is unknown and needs to be approximated in order to make accurate predictions. Various schemes for the approximation of the exchange correlation functional exist with increasing amounts of accuracy and complexity, which approach is used depends on the purpose of the calculation (bond lengths, adsorption energies, potential energy surface etc.) and the appropriate balance of accuracy and computational cost. The simplest (and least accurate) version is the local density approximation (LDA) which only uses the electron density of a homogeneous electron gas [56]. The calculations in the presented papers all make use of the generalized gradient approximation (GGA) which uses the derivative (gradient) of the electron density in addition to the electron density to compose the exchange correlation functional. LDA functionals tend to overestimate the binding between atoms, which may lead to the underestimation of bond lengths. GGA functionals correct for this, but may underestimate the bonding and lead to slightly longer bond lengths instead. Other, more complicated, functionals exist using the second derivatives and/or intermixing Hartree-Fock (HF) exchange, though often the increase in accuracy is not worth the computational cost. The Perdew-Burke-Ernzerhof (PBE) functional [57] is one commonly used GGA functional recommended
for studies of molecules interacting with metal surfaces, and is used in papers I-V. For papers VI and VII the revised PBE (RPBE) functional designed by Hammer et al. [58] to improve the description of metallic surfaces was used.

No functional is perfect since they are all based on approximations and often additional correction terms are added to improve the quality of predictions or compensate for errors. One drawback of GGA functionals is that they do not include the long-range electron correlations that cause the van der Waals dispersion forces which play a role in, for example, the orientation of molecules on a surface. Dispersion effects are therefore often corrected for using one of the schemes by Grimme (+D1,3) [59-61] (papers I-V) or BEEF-vdW [62] functionals (papers VI and VII) among others. For transition metal oxides a common problem is the assignment of conducting properties to semi-conducting or insulating materials due to an erroneous promotion of electron delocalization in GGA functionals. This issue is remedied by the addition of a so-called Hubbard correction (+U) [63] to the localized states, as was done for papers IV and V which concern cuprous oxide surfaces.

For the identification of transition states and the determination of (minimum) energy pathways of a surface reaction, interpolation methods such as the nudged elastic band (NEB) [64] method are used. For this method the initial and final geometries are locked and a series of intermediate structures are generated using linear interpolation. These structures are connected to each other by springs with a spring constant $k$ ensuring that their geometry is constrained between the preceding and following geometries, and function as an initial guess of the energy pathway. Optimization is carried out using a force projection of the forces parallel and perpendicular to the reaction pathway. Accuracy of the resulting PES increases with the amount of intermediate geometries used, but this will come at the cost of optimization efficiency. In both paper II and paper VI NEB was employed to find the activation energies of reaction steps.

For further and detailed specifics on the computations complementing the individual experiments I refer to the "Computational Details" sections of the respective papers.
4. Results and discussion summary

This chapter summarizes the results presented in the papers in appendix I-VII. The papers are grouped according to the three main projects: Studies of naphthalene on Ni(111) (Paper I-III), studies of alcohols on Cu$_2$O (Paper IV-V) and studies of CO oxidation on Ru(0001) (Paper VI-VII).

4.1 Studies of naphthalene on Ni(111)

4.1.1 Introduction

Biomass gasification is a process in which various sources of biomass such as food waste, wood or corn are converted into useful products. One main product is syngas, a mixture of H$_2$ and CO, that can be used for the production of renewable energy. Unfortunately, biomass gasification also results in unwanted by-products in the form of tar that mainly consists of heavy hydrocarbons and polyaromatic hydrocarbons (PAHs) [65-67]. The tars prevent the implementation and upscaling of biomass gasification to industrial levels because of a downstream clogging of pipes and catalyst poisoning. It is thus no surprise that there is interest in the development of methods that mitigate the negative effects of the tar. One promising method is the catalytic reforming of tar to useful gases such as CO and H$_2$. In catalytic steam reforming nickel-based catalysts are common and they are considered a viable option for biomass gasification [68, 69]. One needs to note however that nickel is also a good catalyst for graphite formation which can result in poisoning of the catalyst [70]. As a main component in most tars and a decomposition intermediate for larger PAHs, naphthalene is an ideal
candidate as a model molecule for the decomposition of tar. Therefore, we studied the adsorption and temperature dependent dehydrogenation of naphthalene on Ni(111) as a first step towards understanding catalytic steam reforming of tars on a molecular level. The results of this project, which consists of TPD, SFG, STM, and XPS measurements paired with DFT calculations, are presented in papers I, II and III (manuscript). The present chapter is an integrated summary of the main results from these papers. Naphthalene is a planar molecule consisting of ten sp²-hybridized carbon atoms organized in two adjacent aromatic rings as is illustrated in Figure 26.

The intermixing of the carbon 1s, 2px and 2py orbitals creates the sp² molecular orbitals that are responsible for the bonding within the molecule. The 2pz orbitals are perpendicular to the sp² plane (Figure 26) and not involved in the formation of the molecular orbitals. Because of this the electrons in the 2pz orbitals are delocalized (can move around between 2pz orbitals of different carbons) which gives rise to an additional stabilization within the molecule through the formation of π-bonds. This stabilization of cyclic alkenes through delocalization of electrons is called aromaticity and will play a role in the dehydrogenation reaction of...
naphthalene on Ni(111). It is important to note that when the 2p\textsubscript{z} orbitals are involved in the formation of molecular orbitals (sp\textsuperscript{3}-hybridization), the molecule can no longer be aromatic. The eight hydrogen atoms of naphthalene can be divided into two groups of equivalent hydrogens, alpha (\(\alpha\)) and beta (\(\beta\)) based on their position in the molecule. Alpha hydrogens are bound to a carbon atom that has only one neighbouring C-H whereas the beta hydrogens are bound to a carbon with two neighbouring C-H moieties.

4.1.2 Adsorption and dehydrogenation

The adsorption geometry of naphthalene on Ni(111) was investigated using STM and DFT as presented in paper I. The naphthalene molecules adsorb flat on the smooth terraces of the Ni(111) surface in a geometry in which the aromatic rings are positioned over Ni-bridge sites. The carbon atoms in the molecule bind to the metal atoms of the surface (chemisorption) and as a result the hybridization of the atoms changes from sp\textsuperscript{2} to sp\textsuperscript{3}, which results in a pronounced de-aromatization of the aromatic rings. This is observed also in the SFG measurements in paper II where the monolayer naphthalene exhibits C-H stretching vibrations in the aliphatic region rather than in the aromatic region (Figure 27b 300K).

Higher doses result in physisorbed multilayers that do not exhibit the same de-aromatization upon adsorption as the monolayer, since the interaction of the multilayer molecule with the surface is much weaker. In the SFG measurements multilayer naphthalene indeed exhibits strong C-H stretching vibrations in the aromatic region of the spectrum (Figure 27b 150K), close to the vibrational frequencies observed for gas phase naphthalene [71].

Both the TPD measurements from paper I (Figure 28a) and the SFG measurements from paper II (Figure 27) show desorption of the physisorbed multilayer around 200 K, at which point no reaction has taken place yet. Dosing at temperatures above 200 K results in monolayer adsorption only, it is thus reasonable to assume that only the chemisorbed naphthalene undergoes dehydrogenation. Besides the desorption of molecular naphthalene (m/e=128) from the multilayers, only one other product is observed to desorb from the surface in the TPD experiments: hydrogen gas (H\textsubscript{2}). Hydrogen desorption starts around 380 K and shows two desorption peaks in the TPD spectra, one feature peaking at 440 K and one broader feature around 550 K. This implies that there are two different pathways for hydrogen formation with a peak is mainly due to dehydrogenation of beta positions. Assuming that complete dehydrogenation occurs, the integrated area under the hydrogen TPD peaks
suggests that the first peak is the result of the breaking off of two hydrogen atoms and the second peak is the result of abstraction of the other six.

Figure 27: (a) False colour plot of the SFG spectra as a function of temperature recorded with a ramping rate of 3K/min. (b) Selected slices from (a) to illustrate the observed resonances. Adapted from paper II.

Figure 28b shows evolution of the amplitudes of both the resonances observed in the temperature dependent SFG measurements in Figure 27a, fitted according to equation 16. As the multilayer desorbs, the (aromatic) multilayer resonance at 3057 cm\(^{-1}\) disappears, and the (aliphatic) monolayer resonance at 3003 cm\(^{-1}\) appears, since the monolayer vibrations are no longer suppressed by the multilayer molecules on top. Heating further to 360 K, close to where according to the TPD measurements H\(_2\) production starts, the aliphatic resonance starts to disappear and a new resonance appears, very close to where we previously observed the aromatic multilayer signal. This implies that upon dehydrogenation the monolayer molecules regain their aromaticity. A similar effect is observed in the XPS measurements from paper II, where the spectrum at 380 K is shifted towards lower binding energies which is indicative of an increase in sp\(^2\) character of the carbon and thus an increase in aromaticity.
The recovery of aromaticity is interpreted as a tilting of the initially flat-lying monolayer molecules. As the molecules start dehydrogenating the carbon atoms that lose their hydrogens bind more strongly to the metal atoms in the surface. As a consequence, the molecule starts to tilt and the carbon atoms on the other side of the molecule are lifted, increasing their distance to the surface and decreasing their bond to the surface nickel atoms. This in turn increases the sp$^2$ character of the lifted carbon atoms. This explanation is supported by the DFT calculations and STM measurements as presented in paper II. The DFT calculations show a tilting of 7 degrees of the carbon backbone of the naphthalene molecule with respect to the surface and the STM measurements show an increase in average height of the adsorbate layer after flashing to 360 K. An additional argument for the tilting of the molecules can be found in the TPD measurements in Figure 28. When dosing naphthalene at 470 K instead of 110 K, we not only observe the disappearance of the first H$_2$ desorption peak as expected, but also observe that the total area under the second peak increases by 60%. This implies that more naphthalene molecules are packed on the surface, which is possible if the molecules no longer lie flat but stand up at some angle with respect to the surface.

The SFG resonance attributed to the tilted molecule appears at 360 K, peaks at 400 K and is gone by 480 K. When we fit the temperature evolution of this resonance assuming a 1$^{st}$ order reaction and an Arrhenius pre-factor of $10^{13\pm1}$ s$^{-1}$ we calculate an energy barrier of 27 ±2 kcal/mol which is in the
range of the energy barriers of 23 and 30 kcal/mol found for hydrogen abstraction using DFT from alpha and beta position respectively.

Above 500 K all signal in the SFG measurements disappears, although in the TPD measurements hydrogen production is observed up to 680 K. According to the STM measurements from paper I the adsorbate layer becomes disordered at 520 K which can explain why the SFG resonances are invisible even though C-H bonds are still present. When, at 700 K, all the naphthalene has dehydrogenated neither TPD nor SFG measurements contain (resonant) signal.

4.1.3 Graphite/Graphene formation and Passivation
Since the TPD measurements show that the only product desorbing from a prepared monolayer of naphthalene is hydrogen gas, it is reasonable to assume that after dehydrogenation the surface is covered with carbon atoms. This is indeed observed in the STM measurements in paper I and the XPS measurements from paper II. Figure 29 shows the results of these XPS and STM measurements. In the STM measurements we initially observe ordered patches of naphthalene, heating causes the patches to disappear, and after annealing to 570 K the naphthalene fragments form chains of 1.5 Å high and 20 Å wide. At 650 K the chains have merged into a graphite-like network.

![Figure 29: (a) XPS C1s spectra recorded for naphthalene on Ni(111) during stepwise heating of the sample, the red lines are indicators for the position of the two observed peaks. (b-e) STM images of the formation of a graphite-like network on Ni(111) during the dehydrogenation of naphthalene. (Adapted from paper I and II)](image-url)
In the C1s XPS measurements in Figure 29a we observe two main features. The first is a broad feature at 284.6 eV that with increasing temperature narrows and shifts towards higher binding energies. The narrowing is due to a decrease of C-H vibrational broadening of the peak as C-H bonds are broken. And the shift is due to the growth of graphitic carbon, both the observations are in line with dehydrogenation of the naphthalene molecules. The second feature in the XPS spectra appears around 465 K at 283.6 eV, and is attributed to carbidic carbon which has been suggested as a precursor for graphene growth.

As mentioned in the introduction, surface carbon can poison the nickel catalyst rendering it inactive. Thus, the growth of graphene-like layers on the surface is not desired in a catalytic sense. Additional TPD measurements from paper I illustrate that catalyst poisoning is a problem for this system. Several TPD measurements were run in series without any cleaning of the surface in-between measurements. The total hydrogen yield goes down for each subsequent cycle indicating that each cycle less naphthalene is able to adsorb on the surface, presumably because the carbon blocks the naphthalene adsorption sites. After seven cycles the surface is inert with respect to hydrogen production and desorption. This has implications for the catalytic process on industrial scale where cleaning after each run is not cost-effective.

4.1.4 Naphthalene on oxygen precovered Ni(111)
Under catalytic conditions the presence of oxygen or water in the reaction chamber can lead to varieties of surface oxygen which can potentially oxidize surface carbon producing CO or CO₂, decreasing the level of poisoning of the catalyst. Therefore, we investigated the effect of oxygen pre-coverage on the decomposition reaction pathway of naphthalene on Ni(111) and its consequences for catalysis, the results of which are presented in paper III.

The different oxygen doses were chosen such that the prepared surfaces resembled the three different stages of oxidation of a transition metal [72, 73]; chemisorbed p(2x2) oxygen atoms on a Ni(111) surface, a nickel oxide of 3-4 layer thickness and an intermediate version with patches of both p(2x2) and NiO. The results of temperature dependent SFG experiments of naphthalene dosed on top of each of these three preparations is shown in Figure 30.
Figure 30: Selected spectra from the temperature dependent SFG measurements for the three oxygen precovered surfaces; chemisorbed p(2x2)(a), mixed(b) and 3-4 layer thick NiO (c). The black vertical line is used to indicate the position of the resonance at 3052 cm\(^{-1}\) (a) and 3057 cm\(^{-1}\) (b, c). Adapted from paper III.

All oxygen predosed surfaces exhibit a single resonance in the aromatic region. For the chemisorbed p(2x2) preparation (Figure 30a) a fir places the resonance at 3052 cm\(^{-1}\) and for the mixed preparation and NiO preparation the resonance is at 3057 cm\(^{-1}\). At temperatures below 220 K this resonance is ascribed to the physisorbed multilayers, analogous to the results for naphthalene on Ni(111). When the multilayers desorb at 220 K the difference between the systems with and without oxygen becomes clear. For the two preparation containing chemisorbed oxygen (a, b), there is no resonance in the SFG signal above 220K. However, chemisorbed naphthalene must still be present since the TPD measurements do show naphthalene decomposition products (H\(_2\) and CO) at higher temperatures. We suggest that the presence of the chemisorbed oxygen in-between the naphthalene adsorbates and the nickel surface decreases the interaction between the naphthalene molecules allowing for the hydrogen atoms to no longer point away from the surface, but be parallel to the surface. This could explain why the chemisorbed naphthalene is invisible in SFG, since the C-H stretching vibration would then no longer have a dynamic dipole moment out of the surface plane.
For the 3-4 layers of NiO preparation the SFG temperature dependence looks very different. The resonance at 3057 cm\(^{-1}\) does decrease at 220 K indicating that some physisorbed naphthalene desorbs, but the resonance never disappears completely and even grows in the region 300-600 K. Additionally, the resonance in the aliphatic region that was attributed to the dearomaticized chemisorbed naphthalene on clean Ni(111) (Figure 27) is not observed. This implies that either the interaction between NiO and naphthalene is weaker allowing naphthalene to retain aromatic character upon adsorption, or, that naphthalene adsorbs in a tilted geometry on NiO already at low temperatures. The fact that the 3057 cm\(^{-1}\) resonance remains present up to much higher temperatures for naphthalene on the NiO preparation (620 K) than on the not-oxygen dosed Ni(111) (500 K), is an indication that the adsorbed naphthalene is indeed more stable on NiO. This would fit with the suggestion that the naphthalene is not dearomaticized upon adsorption on NiO since the aromaticity provides stability and stronger bonds within the molecule. Thus NiO seems to have higher activation energies for C-H and C-C bond breaking, which is confirmed in the TPD measurements where for all oxygen prepared surfaces CO is a desorption product, but for the NiO preparation CO desorption occurs at higher temperatures (above 600 K).

The CO desorption yield increases with increased oxygen exposure, presumably because there is an excess of carbon on the surface when the naphthalene decomposes. The production of CO shows that the presence of oxygen indeed removes carbon from the surface which will decrease catalyst poisoning. Unfortunately increased amounts of oxygen substantially decrease the hydrogen production and, as was discussed before, very large amounts of oxygen (NiO preparation) increases the activation energy for naphthalene decomposition. Thus Ni(111) is the preferred catalyst for H\(_2\) production and suggest that catalytic activity and catalyst lifetime can be improved by addition of a small amount of oxygen, enough to reduce catalyst poisoning, but small enough to keep hydrogen production ongoing.
4.2 Studies of alcohols on Cu₂O

4.2.1 Introduction
The oxidation (or dehydrogenation) reaction of alcohols can be exploited to benefit the production of clean green energy by fuel cells in two ways. In a hydrogen fuel cell, hydrogen gas reacts with oxygen in the presence of a catalyst to form water and electricity without any harmful side products. The dehydrogenation reaction can be used to produce the hydrogen gas that fuels these fuel cells [74]. However, hydrogen gas storage and infrastructure still pose challenges. Liquid alcohols are much easier and safer to store and transport, which has led to the development of direct alcohol fuel cells (DAFC) where alcohol molecules are oxidized directly in the fuel cell to produce electricity [75, 76]. Methanol (CH₃OH) and ethanol (CH₃CH₂OH) can both function as a source of hydrogen atoms for hydrogen gas production or as a fuel in direct alcohol fuel cells. Of these two alcohols ethanol is the “greener” choice since it is less toxic than methanol, has a greater energy potential, and is readily available from renewable resources [66]. Methanol is however still relevant since it is more easily produced than ethanol. A comparison of the two species can be interesting since the smaller methanol only has C-O and C-H bonds whereas ethanol consists of two carbon atoms which makes C-C cleavage a necessary step for the full oxidation of ethanol. Copper based catalysts are considered to be better and cheaper alternatives to the rare earth metal catalysts currently used for driving alcohol chemistry[77, 78]. Under reaction conditions copper is susceptible to corrosion and its main corrosion product is Cu₂O. Therefore, we studied the decomposition of methanol and ethanol on two different Cu₂O single crystal surfaces, (100) and (111), using the surface science techniques XPS, SFG, TPD and DFT. The results of these investigations are presented in paper IV and V which are summarized in the following sections.

It is good to note that metal oxides in general have more complex surface structures than transition metals which often complicates the interpretation of surface science experiments. This is no different from cuprous oxide where the (111) surface is a collection of coordinatively saturated and unsaturated Cu and O atoms and the presence and absence of the different atom types is still under debate. For this surface the (√3x√3)R30° surface reconstruction is the most observed under UHV conditions [79] and Figure 31 shows this surface structure with and without undercoordinated copper vacancies. These unsaturated surface atoms are believed to play an important role in the catalytic activity of Cu₂O [80].
For the Cu$_2$O(100) surface a Cu terminated structure is expected under oxygen lean conditions, while the O terminated structure will occur under oxygen pressures. The (100) surface facet reconstructs under reaction conditions and the (3,1;0,0) structure as depicted in Figure 31 is considered the most stable [81]. However, this structure is also observed to reconstruct to the c(2x2) reconstruction upon adsorption of reactants such as methanol as discussed in paper V.

![Figure 31: Illustrations of the two most relevant surface structures for both the (111) and (100) surface structures of Cu$_2$O. Adapted from paper IV.](image)

### 4.2.2 Adsorption and decomposition of ethanol on Cu$_2$O

Paper IV reports the investigation into the adsorption, desorption and decomposition of ethanol on Cu$_2$O(100) and (111) surfaces. The core of the paper consists of XPS experiments which are complimented with SFG and TPD experiments and DFT calculations. In the adsorption experiments both the (111) and (100) single crystal surfaces are exposed stepwise to increasing amounts of ethanol up to 8 L. To investigate the reactivity of the system the samples with the highest dose were heated in steps up to 455 K to induce reaction. For each step during the dosing and heating XPS O1s and C1s spectra were recorded. Selected spectra were numerically fitted to identify the various O1s and C1s components.

The O1s spectra of clean and ethanol dosed Cu$_2$O(100) and (111) are shown in Figure 32. The clean surface spectra have 3 components. The
component with the highest intensity, B, represents the oxygen atoms in the bulk of the crystal, due to problems with charging effects, which are common for the Cu$_2$O surface, the bulk peak has been positioned at 0 eV and all other binding energies are given relative to the bulk signal. The components S1 and S2, represent coordinated unsaturated oxygen atoms in the top layer and second surface layer.

Adsorption of ethanol at 120 K removes the S1 and S2 components and generates two new components to more positive binding energies, one representing a chemisorbed ethoxy species (A1) and the other representing physisorbed ethanol (A2). On Cu$_2$O (100) the evolution of A1 and A2 is sequential, first the ethoxy peak grows, implying that the first layer adsorption is dissociative. When the first layer is complete, the second layer consisting of physisorbed ethanol starts to grow. On Cu$_2$O(111) A1 and A2 increase in intensity simultaneously, implying that the first layer on this surface facet is mixed ethanol and ethoxy.

![O1s spectra of ethanol dosed (a, b) and clean (b, d) Cu$_2$O(100) and (111), showing the experimental data and the fit components. All binding energies are plotted relative to the bulk peak B. S1 and S2 originate from surface oxygen, A1 and A2 originate from adsorbed ethoxy and ethanol species, respectively. Adapted from paper IV.](image)

Similar adsorption trends are observed in the C1s spectra, of which Figure 33 shows a selected set to illustrate the main conclusions of paper IV. Upon adsorption, the two carbon atoms in both the ethoxy (OCH$_2$CH$_3$) and ethanol
(HOCH$_2$CH$_3$) adsorbates give rise to double C1s peaks. On the Cu$_2$O(100) surface (Figure 33c, d) we observe initial adsorption of ethoxy followed by additional ethanol peaks at higher doses. For the Cu$_2$O(111) surface the C1s spectra after adsorption (Figure 33g, h) not only contain ethoxy and ethanol components but also the products of C-C cleavage, CH$_x$ and OCH$_x$. This means that C-C cleavage occurs already upon adsorption on this surface facet.

Figure 33: C1s spectra of ethanol on (left) Cu$_2$O(100) and (right) Cu$_2$O(111) for two selected doses at 120 K, and two selected heating temperatures after a total dose of 8L to illustrate the most important observations in paper V. (Adapted from paper IV)
Heating of the prepared samples leads to desorption of the physisorbed ethanol in the second layer around 150-165 K for the (100) surface and between 180 and 220 K on the (111) surface. On the Cu$_2$O(111) surface an OCH species is observed to grow and disappear between 120 and 200 K which indicates low temperature dehydrogenation of the OCH$_x$ fragments leading to CO desorption. Further heating of both surfaces leads to decomposition of the monolayer through both C-C cleavage with products OCH$_x$, and CH$_x$ species, and C-O cleavage with as products CH$_x$-CH$_x$ species. At temperatures above 300 K acetate species (O-CH$_x$O) are formed, most likely as a result of diffusion of OCH$_x$ species and formation of a bond between this species and surface oxygen atoms. On the Cu$_2$O(111) surface C-C cleavage is dominant while C-O cleavage occurs more on the (100) surface. This means that to achieve full oxidation of the ethanol, for which C-C cleavage is necessary, Cu$_2$O(111) is the preferred catalyst.

The SFG spectra recorded for the Cu$_2$O(100) surface as depicted in Figure 34 largely follow the conclusions based on the XPS experiments. At low temperatures two resonances are observed at 2910 and 2950 cm$^{-1}$ which are contributed to the symmetric and asymmetric C-H stretching vibrations of the ethanol and ethoxy methyl groups. The spectrum at 400 K is rather featureless, but its shape is different from the non-resonant background and from the XPS measurements we know that at these temperatures adsorbates are still present on the surface. It is suggested that the absence of resonances is the result of bending of the adsorbate to facilitate C-C cleavage that causes a decrease of the perpendicular component of the dynamic dipole moment of the C-H stretching vibrations rendering them invisible to SFG. After heating to even higher temperatures a new feature appears at a similar frequency but with a clearly different phase as the resonances at low temperatures. This resonance is attributed to decomposition products such as an acetate species as was identified in the C1s spectra. At temperatures of 550 K and above the SFG spectrum resembles the non-resonant background and the XPS C1s spectra show only background, indicating that all surface species have disappeared, presumably through desorption.
Figure 34: SFG spectra for ethanol on Cu₂O(100) at increasing temperatures. The black dots represent the experimental data, the red line is the fit. The top spectrum shows the non-resonant background. From paper IV.

4.2.3 Methanol on Cu₂O

Paper V presents investigations into the adsorption and dehydrogenation of methanol (CH₃OH) on Cu₂O(111) and (100) combining XPS, DFT and SFG studies. The experiments for methanol on Cu₂O (111) and (100) were conducted in a similar way as for ethanol, employing stepwise dosing and heating and recording O1s and C1s spectra for each step. The results of the XPS experiments are shown in Figure 35.

The O1s spectra of methanol on Cu₂O look similar to those for ethanol on the same surface. Thus, similar to ethanol, methanol adsorption at 120 K on the (100) surface, is dissociative, resulting in a methoxy species and adsorbed hydrogen. The (100) surface initially exhibits a (3,0;1,1) reconstruction [81] which, upon adsorption of methanol, reconstructs to a Cu-dimer structure where, methoxy and atomic hydrogen adsorb on Cu-bridge sites. Adsorption of methanol on the (111) surface results in a mixed layer of methanol and methoxy. Opposed to ethanol, no low temperature dissociation is observed for methanol on Cu₂O(111), which makes sense since it was the C-C bond of ethanol that was dissociated at low temperatures and methanol does not have a C-C bond.
The C1 spectra for methanol contain only one peak which contains contributions from methanol, methoxy and at higher temperatures their dehydrogenation products. Unfortunately the individual peaks overlap so that the dehydrogenation is only observed as a shift towards lower binding energies. Dehydrogenation is the main reaction pathway upon heating for both surfaces, but it occurs at lower temperatures and is more complete on the (111) surface, where it leads to OCH surface species. On the (100) surface the methoxy species reacts towards formaldehyde (CH₂O) which is stabilized and does not react further. This difference in reactivity can be explained by the great variety of adsorption sites on the (111) surface, which contains oxygen vacancies, copper vacancies, and un-coordinated surface oxygen, the latter of which can function as a hydrogen storage for the hydrogen atoms that detach during the dehydrogenation of the adsorbed methanol.

**Figure 35**: O1s and C1s spectra recorded for methanol on Cu₂O(100) and (111) for increased doses and heating. Adapted from paper V.
4.3 Studies of CO oxidation on Ru(0001)

4.3.1 Introduction
All experiments described in the previous sections concerned investigations into thermally driven catalytic reactions. However, the product of thermally driven reactions is difficult to control. Thermal energy is distributed over the available degrees of freedom and the ratio of reaction products is based on the energy barrier of the various reaction pathways. Thus, if multiple pathways exist, the result will be a mixture of products. Ideally one would want to maximize the output of the one desired pathway and to minimize the effort needed to separate products. One way to (to some extent) control or manipulate the selectivity of a catalytic reaction is to use a non-thermal instead of a thermal excitation mechanism such as photons in the visible range of the spectrum as we do in paper VI. Another means of non-thermal excitation is through atom-specific activation by photons in the X-ray range interacting with the core electrons as is explored in paper VII.

Both papers that are discussed in the current section concern the CO oxidation on ruthenium from a mixed layer of CO and O adsorbates. CO oxidation on ruthenium is not only a logical choice of reaction for this type of studies because it is a well understood model system, but also because in UHV ordinary thermal excitation does not lead to the oxidation reaction [83] while it does when the system is non-thermally activated [31]. We can thus show that a degree of control of the reaction yield is possible when using these excitation methods.

4.3.2 Laser induced CO oxidation
In paper VI we study CO oxidation from co-adsorbed carbon monoxide and oxygen on a Ru(0001) surface with 400 and 800 nm light. Upon laser excitation two reaction pathways can occur for this system: one results in the desorption of CO molecules, while the other results in CO oxidation that produces CO\textsubscript{2} which then desorbs from the surface. The fluence dependence and two-pulse correlation (2PC) was measured for both CO desorption and CO oxidation pathways. Both reactions were modelled using a kinetic model combining the two-temperature model [37] for laser excitation of the substrate and the friction model [42] to describe substrate-adsorbate interactions. DFT calculations were performed to determine the relevant parameters needed in the kinetic model.

Experimental results show that the yield and power law exponent for the desorption of CO are higher than for the oxidation reaction. Additionally, a higher yield is obtained for both reaction pathways with 400 nm light than
with 800 nm. This is explained by the shorter penetration depth of 400 nm light which increases the temperature at the surface and thus the reactivity of the system. The branching ratios found for oxidation with respect to desorption are 1:31 for 800 nm and 1:9 for 400 nm light. This implies that the oxidation reaction pathway is more efficient when 400 nm light is used to induce reactivity. The difference between the branching ratios for the two wavelengths cannot be explained by the penetration depth since penetration depth should affect both reaction pathways equally. The result of the 2PC measurement is presented in Figure 36a, and shows a high background which is indicative of a weak dependence on the laser fluence. The FWHM of the two-pulse correlation is 2.4 ps which indicates an electron mediated mechanism and is consistent with experiments by Bonn. et al. [31].

![Figure 36:](image)

Figure 36: (a) Oxidation 2PC for 400 nm. The crosses represent the experimental data. The blue curve represents the only thermal fit and the red curve shows the corrected fit after addition of a linear non-thermal component. (b) Density of states for CO and O on ruthenium paired with schematic non-thermal electron distributions for 800 and 400 nm wavelengths. Adapted from paper VI.

The kinetic model successfully reproduces the fluence dependence for 800 nm light for both the oxidation and the desorption. The modelled branching ratios are however significantly larger than the experimental ratios. Also, the FWHM of the computed 2PC are broader than the experimental values. We propose that these discrepancies between experiment and theory are caused by the involvement of non-thermal electrons, which the 2T-model does not account for. As described in more detail in section 2.3 of this thesis, the laser can deposit energy in the metal substrate and the substrate electrons are directly excited above the Fermi level producing “non-thermal electrons”. The
non-thermal electrons will thermalize within femtoseconds, but before thermalization takes place the electron distribution will be different depending on the excitation wavelength. The 2T model assumes immediate thermalization, which means that any effect due to or involvement of the non-thermal electrons is not included.

If we imitate the non-thermal contribution to our model by increasing the electron coupling to increase the number of hot electrons or to lower the effective activation energy for oxidation, we find the same branching ratio of 1:9 for 400 nm light as we did for the experiment. When the experimental data is fitted with a weighted sum of the thermal model and a linear component to imitate the non-thermal contribution this results in a much better agreement between model and experiment. This is illustrated in Figure 36a where the red curve represents the corrected fit. This means that we have found a strong indication that the non-thermal electrons indeed play a role in laser induced CO oxidation and that the excitation wavelength used can be used to control the branching ratio, and thus the selectivity, of a reaction.

4.3.3 X-ray induced CO oxidation

In paper VII we study CO oxidation from co-adsorbed carbon monoxide and oxygen on a Ru(0001) surface driven by resonant X-ray excitation of the oxygen 1s orbital. Similar to the experiments described in the previous section, excitation of the system can result in two reaction pathways; CO desorption or CO oxidation, the excitation mechanisms leading to these reactions are different.

The possible mechanisms of X-ray excitation are divided into two groups, the direct and indirect excitations. The direct excitations consider the adsorption of an X-ray photon by an oxygen atom. The indirect mechanisms cover all mechanisms following absorption of the X-rays by the ruthenium surface and the subsequent substrate heating. Although deposition of the X-rays into the surface creates hot electrons and phonons, like in optical laser-induced reactions the processes involved are different and more complex. Despite the fact that the X-ray substrate heating is complex, the yield of the reactions induced via indirect mechanisms will have a nonlinear fluence dependence.

In optical laser induced reactions we consider direct excitation by the visible laser photons to be negligible but, for X-ray photons there exists a probability of direct excitation. This direct excitation involves the excitation of an electron out of a core level and we will see that the changes in the electronic structure of the adsorbate as a result of the creation of the core hole can lead to nuclear motion which can cause a reaction to occur. The fluence
dependence as a result of direct excitation will be linear since each incident X-ray photon will excite exactly one electron from an oxygen atom.

Direct mechanisms only play a role when the incident X-ray light is on resonance with the oxygen core levels, while indirect mechanisms can occur even if the X-ray is off-resonance with respect to the adsorbed oxygen atom. Thus we can, if we measure the fluence dependence on resonance and just below resonance, separate the direct from the indirect contributions.

We measured the fluence dependence for this system, for both CO desorption and CO\(_2\) desorption (the result of the oxidation reaction), excited both on the resonance (530.8 eV) and just below the resonance (528 eV). The results of these measurements are presented in Figure 37 and show a clear fluence dependence for CO\(_2\) desorption indicating that we indeed induce CO oxidation. Now we need to show that at least part of this CO-oxidation is due to direct X-ray excitation.

The error bars in Figure 37 are given as 1\(\sigma\) counting statistics and are rather large for the higher fluence regime. This is because shots at high fluences are rare due to the relatively large intensity fluctuations of the multi-pulse operation mode used in the experiment. Two points in Figure 37c appear at a negative yield as the result of a background correction which was applied to all data. For both the resonant excitation and the excitation below resonance, CO desorption is the main reaction product, which is similar to what was seen for the 800 nm and 400 nm optical laser induced reactions in the previous section.

All curves show a nonlinear fluence dependence, but there is a difference in the linearity between curves. The fluence dependence of the below resonance measurements should be substrate mediated only and we indeed find a branching ratio for CO oxidation vs CO desorption of 1:35, similar to the branching ratio found for the 800 nm optical laser excitation. Additionally, the below resonance fluence dependencies can be fit with a similar power law exponent to the 800 nm experiments. For the on-resonance measurements, the CO desorption can be fit well with the same power law, but the CO\(_2\) yield, for which we expect direct excitation to play a role, cannot be well described by this power law (Figure 37b). In a similar way as for 400 nm excitation, the addition of a linear component to the power law allows for a good fit of the on-resonance measurements of both the CO and CO\(_2\) fluence dependence with the same power law exponent N=3. To confirm the statistical significance of this linear component, statistical hypothesis testing was performed giving a probability value of 0.115 for the hypotheses that an only exponential model describes the data better than an exponential plus linear model. The details of this hypothesis test are described in the supplementary...
The fact that we need this linear contribution to describe the data implies that direct 1s core-level excitation of the oxygen atoms occurs and induces CO oxidation.

It is not the created core hole itself that causes the activation of the oxygen atom for CO oxidation, but a doubly valence excited state that occurs after the core-hole decay. The core-hole decays mainly through Auger decay which results in a valence state with two localized valence holes that are screened by charge transfer from the surface. This Auger final state has a strongly repulsive character with respect to the ruthenium surface caused by two things: the first is existence of holes in the highest occupied oxygen orbital which has bonding character, and the second is the presence of screening electrons in the lowest unoccupied orbital which possesses anti-bonding character. Because of this repulsive character the distance between the oxygen atom and the surface increases and the oxygen atom gains kinetic energy.
this gained energy is larger than the CO oxidation reaction barrier and smaller than the oxygen-ruthenium bond, CO oxidation can occur. Thus, we show that CO oxidation occurs upon direct X-ray core hole excitation and rationalize the relaxation process that leads to CO oxidation.
5. Conclusions & Outlook

In the studies of naphthalene on Ni(111) in papers I, II and III we are able to combine various surface science techniques to understand both the adsorption and dehydrogenation of the naphthalene molecule. The goal of the naphthalene project was to better understand the catalytic reforming of tar in the presence of nickel catalysts. Our studies are in that respect a solid first step. We show that the Ni(111) catalyst efficiently dehydrogenates this aromatic molecule, leading to the desorption of hydrogen gas and formation of graphitic and carbidic surface carbon. Additionally, we show that the planar naphthalene molecule tilts with respect to the surface, a central step in the reaction pathway.

From the surface science perspective it would be interesting to further explore the observed tilting of the molecule. One could investigate whether such geometrical changes occur for other polyaromatic hydrocarbons and angle resolved techniques could be used to better quantify the angle and direction of the tilting. Additionally, studies with deuterated PAHs could help to better understand the reaction pathways of hydrogen production. Is there a preference between alpha and beta hydrogens for initial and secondary dehydrogenation? Is there a preference for inter or intra-molecular hydrogen recombination?

From the catalytic perspective it is important to remember that realistically, tar is a mixture and contains many other components such as water (H₂O), other hydrocarbons and PAHs, hydrogen sulfide (H₂S) and traces of HCN and NH₃ [68, 84]. A continuation of the project should broaden
the model system to include some of these other molecules and study the effects of co-adsorption of naphthalene with these species.

In the second section of the present thesis we explored the interactions of methanol and ethanol with Cu$_2$O (papers IV and V). We used XPS, SFG and DFT to successfully determine the main adsorption modes and surface intermediates of the decomposition reaction for both the (111) and (100) surfaces. Additionally, we show that alcohol decomposition is more effective and complete on the (111) surface and occurs at lower temperatures than the (100) surface. Such understanding of the differences in reactivity of different surface structure is vital when designing novel catalysts.

To improve on the interpretation of the XPS results and the more exact determinations of some surface species, it could be interesting to expand the SFG experiments to not only include the C-H but, for example, also the O-H stretching vibrations. In the case of the (111) surface this could allow us to better differentiate between the decomposition pathways of the ethoxy and ethanol molecules in the mixed first layer. One problem that rises when observing O-H stretching vibrations is the adsorption of the IR light by the water molecules in the air. Therefore, to perform such experiments, one would need a properly purged beam path.

In the last section, we used femtochemistry to show that, for a system consisting of co-adsorbed CO and oxygen on Ru(0001), we can, to some extent, control the branching ratios of competing mechanisms. Although CO desorption is the dominant reaction process, we can change the branching ratio in favour of CO oxidation by changing the wavelength of the laser used to excite the system. We were able to understand the role of non-thermal electrons in these excitation mechanisms.

It would be interesting to explore the wavelength dependence of the oxidation yield further. Experiments using other wavelengths in addition to the measurements done for 800 and 400 nm could uncover trends for oxidation yield and potential involvement of non-thermal electrons. This could be used to improve the level of control we have over the reaction products. Another interesting avenue of investigation would be to find and test other reaction pathways besides CO oxidation in which non-thermal electrons play a similar role. Can we use theoretically computed densities of states to predict non-thermal electron involvement?

In the second part of the last section, we also show that direct X-ray core hole excitation is feasible and that we can rationalize the relaxation process that leads to CO oxidation with the support of theoretical calculations. This is of course just the beginning of a whole new range of possible core hole excitation experiments. For example X-ray pump/X-ray probe schemes can
be employed to study new dimensions of reaction dynamics. It is good to realize that this next step in science would not be possible without the technical advancements of free electron lasers. So again, as so many times in the history of surface science, does scientific advancement go hand in hand with technological developments.

Finally, we show that there are many useful tools available for the study of surface reactions and that a combination of techniques, both experimental and theoretical, can create a more complete understanding of catalytic surface reactions. In all projects presented here, we were able to shed some new light on the reaction mechanisms involved in the catalytic surface reaction and we explored means of altering or manipulating the reaction outcome. Each study presented here is a building block in the bigger picture of understanding catalysis and catalytic design, on which we can continue building.
6. Acknowledgements

Although a PhD is officially a one-person project it is rarely concluded without the help and support from others. My work is no exception.

First and foremost, I would like to thank Henrik Öström, my supervisor. He has not only taught me so much, but also guided and supported me through these years. He has had my back, he has been shoulders to stand on, offered a keen eye of critique, had a nose for nifty projects, was a helping hand in the lab and maybe most importantly was my favorite and closest colleague. We have spent many hours working together in the lab, more than most PhD students get to do with their supervisors and I am thankful of it. It was fun.

Secondly, I would like to thank Tony Hansson my second supervisor, you came in when we were already halfway across the racetrack, but I’m am glad to have run the last miles with your support. Thank you for the talks and the critique that made think.

During my time as a PhD student I have had two official mentors that were required to listen to my whining at least twice a year. Åsa and Astrid, thanks for listening, thanks for telling me not to give up.

In particular I would like to thank Jerry LaRue who has been my unofficial third supervisor, unofficial mentor, official second-best colleague and friend. Working with you in the labs in California and Stockholm was always great fun. You are a patient teacher and your confidence in me has greatly contributed to my own confidence in myself. Next to fruitful work together I will remember the fun trips to places like the Sala mines, Santa Cruz and Joshua Tree National Park with fondness. Thank you.
Especially in the natural sciences work is done in collaborations, people with different specialties work together to approach a problem from different sides and turn a problem inside out and upside down. Experiments can get so big that they cannot be executed by one person and interpretation so complicated you can lose yourself in it. Therefore, I want to thank the people that have collaborated with me over the years and have in their own way contributed to the present thesis, whether it is by writing text for papers, doing experiments or calculations, discussing results, proofreading my work, or by keeping me awake during a tedious night shift, thank you.

Stressful work gets a lot easier with a good working environment, which is exactly what my colleagues and friends at the department of physics and the division of physical chemistry provided me with; A friendly and supportive working environment and fun diversions from research such as lunches, movies, board games, Fysikshow, karaoke, tea drinking, pub quizzing, pingpong, climbing and more. Thank you all!

I need to especially mention the best office mates one can wish for, Emelie and Jesper, our office with the green sofa, Friday music, Friday Llama, and infinite chats have made work into a place I wanted to be. Never change.

Thank you Cody for diligently reading my writings and nitpicking on all the little things.

Thank you Emma, Linda and Moa for always being there and always understanding.

I should not forget to thank all my friends in the Netherlands and in other parts of the world that did a more long-distance version of sane-keeping and to whom I need to apologize to for my sloppiness in keeping in touch. I love you all!

Two important people to thank are my parents, Hans and Resi, that raised me to be curious, appreciate the value of knowledge and the fun in learning. Together with my little sisters, Tove and Jitka, you let me lean on you and let me vent my stress, my doubts and frustrations, reciprocating with calm, confidence and pride. Without you I would not be here. Knowing that there was a loving and safe home to return to, made me dare to take the jump. Thanks for being my lifeline.

And finally, Gustav. He was my rock outside the lab. His calm quenched my stress. His unconditional trust fed my confidence. His cooking kept me fed on the long days leading up to the deadline and his love provided me with a stable home to compensate my unstable brain. Thank you for putting up with my antics.
7. References


