Doctoral Thesis

Strategies for intact laser desorption

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Strategies for Intact Laser Desorption

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Abstract

Laser volatilization techniques are widely used in fields ranging from thin film deposition, materials processing to mass spectrometric and gas phase spectroscopic analysis of macromolecular compounds in chemistry, biology, environmental and materials sciences, medicine and pharmacy. However, despite the success of these techniques the underlying volatilization processes are not fully understood. In this dissertation, studies on laser volatilization of molecules are presented which address fundamental mechanistic questions. The work focuses on elucidation of the mechanisms which allow intact desorption of large molecules. The experiments include analysis of laser-induced thermal desorption of submonolayer films of aniline and poly-(ethylene glycol) (PEG) oligomers from various substrates as well as investigations on laser vaporization of molecular films with a thickness of hundreds of nanometers.

First, a complete study on nanosecond laser-induced thermal desorption (LITD) of aniline submonolayers from silica as well as nanosecond and picosecond laser desorption from glassy graphite is presented. The measurements include determination of equilibrium desorption kinetic parameters, time-resolved studies on the surface temperature during laser heating, and investigation of translational, vibrational, and rotational temperatures of laser-desorbed molecules. For determination of the temporal evolution of the surface coverage of submonolayer films during nanosecond LITD a novel two-laser experiment was developed. The experimental findings are that LITD of aniline up to heating rates of $10^{10}$ K/s is consistent with complete thermalization of the molecules during fast desorption. At $10^{13}$ K/s, only the kinetic energy of the desorbed molecules agrees well with a thermal desorption model whereas the internal degrees of freedom are not fully equilibrated.

Second, a systematic study on the desorption and dissociation kinetics of submonolayers of ethylene glycol and PEG oligomers with masses ranging from 62 to 35000 Da from a silica surface was carried out. The PEG - silica adsorption system was characterized by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Translational energy distributions
following nanosecond and picosecond laser desorption were determined and compared to simulations based on thermal equilibrium desorption and dissociation parameters. Desorption and dissociation of the PEGs was again found to be well described by thermal equilibrium kinetics in this case even for heating rates exceeding $10^{13}$ K/s. The experiments show that for intact desorption of ultra thin PEG films fast laser heating is less efficient than classical heating.

The third part of this dissertation describes a comparative study on matrix assisted laser desorption (MALD) at UV wavelengths, laser-induced thermal desorption, IR laser ablation, and volatilization of molecular films via electrical substrate heating. In order to determine to what extend material is desorbed as individual molecules or ejected as particles, respectively, the ablated material was intercepted by a trapping plate and the particle size distribution was analyzed by atomic force microscopy. The ratio of ejected particles to free molecules is strongly dependent on the laser volatilization technique used. High energy densities in the sample, as occurring for example in UV MALD, favor molecular desorption leading to very smooth films on the trapping plate. In contrast, IR ablation is dominated by ejection of large clusters and particulates. Volatization by an electrically heated flash filament is not significantly different from laser-induced thermal desorption. Therefore, it offers the potential to miniaturize and simplify devices used for volatilization of macromolecular compounds.

In summary, this dissertation provides comprehensive data on laser-induced thermal desorption of thin films as well as laser volatilization of molecules from mixtures with matrices. The results allow fundamental mechanistic questions to be answered and also serve as a basis for deriving strategies for optimizing laser volatilization techniques.
Zusammenfassung


Hieran schliesst sich eine systematische Untersuchung der Desorption- und Dissoziationskinetik von Poly- (Ethylenglykol) (PEG) Submonolagen von einem Quarzsubstrat an. Die Massen der untersuchten Oligomere erstreckten sich hierbei von 62 bis 35000 Da. Die Desorptionssysteme wurden mittels Röntgen-Photoelektronen-Spektroskopie und
Rasterkraftmikroskopie charakterisiert. Darüberhinaus wurden translatorische Energieverteilungen desorbiert Moleküle bestimmt und mit Simulationen, die auf thermischen Gleichgewichtsparametern basieren, verglichen. Die Messungen zeigen, dass die Desorption und Dissoziation der PEG Oligomere bis in den Heizratenbereich von $10^{13}$ K/s gut mittels der Gleichgewichtsparameter beschrieben werden kann. Im Fall ultradünner PEG Filme ist schnelles Laserheizen weniger geeignet als klassisches Heizen.

1 Introduction

Within the last three decades the developments in laser technology have been revolutionary. Equally important has been the impact of laser applications on numerous technology-driven industries. Lasers are presently used in fields as diverse as material processing [1-3], communication [4, 5], and medicine [6, 7].

Laser volatilization of molecules from the solid phase has proven invaluable for a variety of applications - from thin film deposition [8-11] to probing the spectroscopy and reactivity of biological molecules in the gas phase. In mass spectrometric applications liberation of the molecules which are to be analyzed from a solid sample, as either neutrals or ions, is essential. Compared to alternative techniques like plasma desorption [12], secondary ion mass spectrometry (SIMS) [13-15], and fast atom bombardment (FAB) [16], laser desorption (LD) is by far the most successful desorption technique available. It provides access to intact gas-phase molecules from high molecular weight, polar, nonvolatile, and thermally labile molecules [17-21]. Therefore, lasers are being used more and more in mass spectrometry, performing either desorption/ionization in one step (laser desorption mass spectrometry, LDMS [21, 22]), or a two-step combination of desorption and photoionization (two-step laser mass spectrometry, L2MS [18, 20, 23-28]). These techniques are now widely applied for analysis of macromolecular compounds in chemistry, biology, environmental and materials sciences, medicine, and pharmacy.
Laser desorption can be performed in many different experimental configurations. The essence of these methods relies on rapid energy deposition into a condensed phase system. With respect to the way how energy is coupled into the sample, two fundamental mechanisms can be distinguished: in laser-induced thermal desorption (LITD) the volatilization of adsorbate layers from a substrate is induced indirectly by laser heating of the substrate [18-20, 29], whereas in resonant laser desorption (RLD) the molecules are directly excited by pulsed laser radiation [30-33].

LITD is used as a standard technique for desorption of unknown analytes and analyte mixtures [20, 21]. Typically, nanosecond laser pulses are used to heat the substrate at heating rates on the order of $10^5$ to $10^{13}$ K/s [34, 35]. Depending on the laser wavelength and the electronic and vibrational properties of the substrate material, the laser radiation either leads to a direct excitation of phonons in the substrate, or to excitation of electrons which relax on a picosecond timescale and transfer their energy to the lattice. Volatilization of molecules which are adsorbed at the substrate surface is induced by energy transfer from the heated substrate to the molecules.

The most successful technique for mass spectrometric analysis of macromolecules is matrix-assisted laser desorption/ionization (MALDI), which is a variation of RLD [36-39]. Using MALDI techniques, intact molecules with masses above 1 MDa have been detected in mass spectrometric analysis [40]. In MALDI, analyte molecules are incorporated into a solid matrix to enhance both the sample volatilization and ion formation. Resonant excitation of the matrix molecules by UV laser pulses (UV MALDI) or IR laser pulses (IR MALDI) leads to intact desorption and charging of the analytes by (photo-) chemical ionization processes [41].

Numerous mechanisms have been proposed in the literature to explain intact desorption of nonvolatile molecules induced by laser techniques. The mechanisms range from kinetic [42, 43], restricted energy transfer [44-49], and collisional cooling models [19, 32, 50-54] to photothermal [52, 55-58], photomechanical [59-62], and photochemical [33, 62, 63] processes. However, despite the great success of laser volatilization methods, the underlying processes are not fully clarified.

The aim of this dissertation is to gain a better understanding of the mechanisms involved in laser volatilization, and to generate a basis on
which rational strategies for an optimization of the commonly applied
techniques can be derived. The central elements of this dissertation are
studies on laser-induced thermal desorption of submonolayer films from
substrates, investigations on laser volatilization of films with a thickness of
some hundreds of nanometers, and volatilization of mixtures of
macromolecules with various matrices.
In chapter 2, experiments on classical and laser-induced thermal desorption
of aniline submonolayer films from silica and glassy graphite are presented.
Thermal desorption of individual molecules from a surface is one of the
elementary processes in surface science. Understanding the underlying
mechanisms is a valuable prerequisite for elucidating reaction processes in
fields such as catalysis and surface chemistry. Therefore, within the last
decades, much effort has been put on experimental and theoretical
investigations on the desorption of thin films [46, 64-70]. However, up to now
it has not been clarified whether fast LITD of thin adsorbate layers is a
thermal or nonthermal process [45, 71-74]. The aim of the study presented in
chapter 2 is to contribute to the elucidation of the on the nature of LITD
processes. The experiments focus on elucidating the mechanism of energy
transfer from the heated substrate to the adsorbate molecules and on
determination of the desorption kinetics at substrate heating rates ranging
from 0.05 to $10^{13}$ K/s. The questions which are addressed are the following:

- At what heating rates do thermal desorption models collapse?
- Are restrictions in the energy flow from the heated substrate to the
  adsorbed molecules responsible for desorption of internally cold
  species?

In chapter 3, the mass range of the molecules which were analyzed was
systematically increased to the regime where dissociation becomes a
reaction channel that competes with intact desorption. Poly-(ethylene glycol)
oligomers with masses ranging from 62 to 30,000 Da desorbed from silica
were studied with respect to the question:

- Does fast laser substrate heating promote intact desorption of
  submonolayers of large molecules?
These results are important in order to identify the major pathways that lead to intact desorption of macromolecules. The findings on desorption of submonolayer adsorbate layers are complemented by the experiments presented in chapter 4. Here a comparative study of the techniques that are commonly applied for volatilization of macromolecules is presented. The samples were either multilayer macromolecular films or mixtures of macromolecules with matrices. UV matrix-assisted laser desorption, laser-induced thermal desorption, IR laser ablation, and volatilization of molecular films from an electrically heated filament were analyzed. The aim was to determine to what extend material is desorbed as individual molecules or ejected in the form of particles. In our experiments ablated material was collected on a trapping plate and the particle size distribution was analyzed by atomic force microscopy (AFM). The ratio of individual molecules and particles is relevant for applications since particle ejection reduces reproducibility and sensitivity in desorption experiments and makes deposition of homogeneous thin films impossible. Additionally, knowledge of the particle size distributions allows to draw conclusions on the ejection mechanisms that are involved in the various techniques. In these experiments, we were guided by the following questions:

- What are the mechanistic differences between the various techniques?

- Which heating method is best suited for intact molecular desorption of macromolecular compounds?
2 Laser-Induced Thermal Desorption of Aniline Submonolayers

2.1 Introduction and Background

Three mechanisms have been proposed in the literature that suggest that thin adsorbate layers of thermally labile, polar, and nonvolatile compounds can be desorbed without fragmentation by LITD whereas they dissociate under slower heating conditions. These effects are either based on a restricted energy flow from the heated substrate to the adsorbed molecules [44-46], on the ratio of desorption and dissociation rates at high temperatures [42, 43], or on collisional cooling in the desorption plume [19, 32, 50-54]. Whereas collisional cooling has been proven experimentally and is theoretically understood, the two other mechanisms are still rather speculative and are discussed controversially in the literature.

Bottleneck for Energy Flow

Various authors [44-46] suggested that internally cold molecules desorb if a "bottleneck" exists for energy flow from a rapidly heated surface through the surface-adsorbate bond into the internal modes of the desorbing molecules. Molecules are expected to desorb internally cold if their residence time on
the heated substrate is lower than the timescale for vibrational energy transfer (figure 2.1). The authors attribute the bottleneck for energy flow to the frequency mismatch between the low-frequency surface adsorbate mode and the high-frequency internal vibrational modes of the adsorbed molecules.

![Diagram](image)

**Fig. 2.1:** Schematic of the laser-induced thermal desorption process. The microscopic mechanism of heating involves creation of phonons and the inelastic scattering of these phonons from adsorbed molecules. This scattering imparts energy to the adsorbed molecule via vibrational excitation. According to the bottleneck model the excitation of the adsorbate is delayed due to the frequency mismatch of the substrate-adsorbate mode and the internal modes of the adsorbate. If the residence time of the adsorbed molecules on the surface is less than the timescale for vibrational energy transfer, adsorbed molecules are expected to desorb internally cold.

In order to quantify the bottleneck model, Zare and Levine [45] introduced an adiabaticity parameter $\zeta$. For energy transfer from the surface adsorbate
bond with a frequency $v$ to an internal vibration in the adsorbate with a frequency $v'$ this parameter is defined as

$$\zeta = 2\pi \frac{v}{v'}.$$ 

The kinetic equation for determination of the amount of energy which is transferred through the surface adsorbate bond can be written as

$$\frac{dE}{dt} = \frac{dE_0(t)}{dt} - k \cdot E(t).$$

In this equation $E_0(t)$ is the initial energy in the surface adsorbate bond, $k \cdot E(t)$ is the quantity of energy flowing into the adsorbate's internal vibrational mode and $\frac{dE}{dt}$ is the quantity of energy remaining in the surface adsorbate bond. The rate constant for energy flow into the vibrational mode of the adsorbate is given by

$$k = v \cdot \exp(-\zeta).$$

Integration of the kinetic equation allows determination of the amount of energy remaining in the surface-adsorbate bond if a time $\tau$ is allowed for energy transfer. It is given by the equation

$$E(\tau) = E_0(1 - k\tau)$$

where $E_0$ has been set to the bond dissociation energy $E_d$. If $k\tau < 1$, no energy is transferred into the internal modes of the adsorbate. Therefore, the criterion for desorption of internally cold molecules is

$$v\tau < \exp(\zeta).$$

Little energy is expected to flow into the internal modes of the adsorbate if the product of the surface adsorbate bond frequency $v$ and the
characteristic time $\tau$ is smaller than the quantity $\exp(\zeta)$. For typical frequencies of vibrational modes (surface-adsorbate mode $\approx 200 \ldots 500$ cm$^{-1}$; internal vibrational modes of the adsorbate $\approx 1000 \ldots 2000$ cm$^{-1}$) this model delivers transfer times for one quantum of vibrational energy of the adsorbate through the substrate-adsorbate bond on the order of 10 ns. Therefore, for laser desorption proceeding on a faster timescale, nonthermal effects are expected. Intact desorption was predicted especially for small, loosely bond, physisorbed species where the difference between $v$ and $\nu'$ is large [75].

Beuhler and coworkers [76] argued that large molecules often form multiple bonds to the surfaces. Their total adsorption energy can largely exceed the energy necessary for breaking one of the intramolecular bonds. Intact desorption should only occur if all the surface-adsorbate bonds are ruptured almost simultaneously, which requires a high excess energy to be delivered to the surface-adsorbate complex. Consistent with the proposed bottleneck effect, these authors suggested that fast surface heating could prevent excitation of internal degrees of freedom of the adsorbates and therefore promote intact desorption.

**Rate Crossover at High Temperatures**

Hall and De Santolo [42] as well as Deckert and George [43] suggested that fast laser heating can lead to enhanced yields of intact desorption even at a thermal equilibrium. Under thermal equilibrium conditions the desorption rate is given by the Polanyi-Wigner rate equation

\[
\frac{d\Theta}{dt} = \Theta^n \cdot \nu \cdot \exp \left( \frac{-E_A}{k \cdot T(t)} \right)
\]

which is also known as the Arrhenius equation. $\Theta$ is the surface coverage, $T(t)$ the time dependent surface temperature, $\nu$ the preexponential factor and $E_A$ the activation energy of the desorption process which corresponds to the depth of the potential curve in figure 2.2. The reaction order $n$ is zero in the case of multilayer films and one in the case of submonolayers.
The suggested mechanism is based on competing desorption and decomposition channels. According to Arrhenius kinetics increased heating rates shift the temperature range at which thermal processes occur to higher values. At high temperatures the process with the highest preexponential factor becomes the major reaction channel, regardless of the activation energy. If the substrate heating rate is sufficiently high, predominantly intact desorption is expected for systems where the preexponential factor for intact desorption exceeds the one for dissociation in the high temperature regime.

Fig. 2.2: Qualitative Lennard-Jones potential curve for an adsorbate physisorbed onto a surface with a well depth $E_A$ and a distance $r$ from the surface.

According to transition state theory the preexponential factor in the Arrhenius equation is proportional to the ratio of the partition functions in the initial state $Q$ and the transition state $Q^*$. It is given by

$$v = \frac{kT}{h} \cdot \frac{Q^*}{Q}$$

[77-80]. $h$ and $k$ are the Planck and the Boltzmann constant, respectively, and $m$ denotes the molecule’s mass. The term $\frac{kT}{h}$ corresponds to an
attempt frequency \( \frac{kT}{h} = 6 \times 10^{12} \text{ s}^{-1} \) at 300 K. The partition functions \( Q \) and \( Q^* \) are given by the following sum over all states \( i \) of the system

\[
Q = \sum_i g_i \cdot \exp \left( -\frac{E_i}{kT} \right),
\]

where the term \( g_i \cdot \exp \left( -\frac{E_i}{kT} \right) \) is proportional to the probability that one molecule among many at thermal equilibrium is in a particular state \( i \) with the statistical weight \( g_i \) [79]. A detailed overview of the partition functions for translational, vibrational and rotational degrees of freedom is given in ref. [79]. Introducing thermodynamic quantities, the equation describing the preexponential factor can be transformed to

\[
v = \frac{kT}{h} \exp \left( \frac{\Delta S}{k} \right),
\]

where \( \Delta S \) denotes the change in entropy from the reactants to the transition state [70, 81, 82]. This entropic concept is commonly used to account for large preexponential factors for desorption and dissociation processes. Since desorption is typically expected to involve a transition state where the molecule is less constrained, the entropy and thus the preexponential factor for the desorption channel are assumed to be greater than those for a reaction channel where the transition state remains bound to the surface. The desorption of methanol from nickel is an example where the frequency factor for intact desorption exceeds the one for dissociation on the surface. Slow heating leads to dissociation whereas intact desorption can be obtained by fast laser heating of the substrate [42]. For this system it is expected that the transition state for decomposition is likely to have specific steric requirements. In contrast, methanol binds to metal surfaces through the O atom with the methyl group sticking up and it can be argued that decomposition may require the H atom proximal to the surface. This would lower the degrees of freedom in the transition state relative to the reactants.
and reduce the preexponential factor with respect to the one characterizing intact desorption.

**Collisional Cooling in the Desorption Plume**

The third mechanism involves postdesorption collisions. Both experimental and theoretical evidence suggests that postdesorption collisions serve to cool the internal energy and increase the translational energy as well as sharpen the angular distribution of the desorption products [51-53, 83]. Effective collisional cooling is dependent on a sufficient density of molecules in the desorption plume. Significant changes of the velocity distributions are already reported for 3 collisions [50] whereas typically 5 to 1000 collisions are required for cooling of rotational and vibrational degrees of freedom [19]. Zhang et al. obtained very impressive results on jet cooling and supersonic jet formation under MALDI conditions [54]. By performing laser postionization analysis of MALDI desorption plumes they showed that the internal temperatures of the desorbed species are significantly lower than the initial temperature of the sample, which can only be explained by a postdesorption cooling mechanism. However, for very low surface coverages on the order of submonolayers or some few multilayers, jet cooling cannot be the explanation for intact desorption since the number of collisions does not suffice for efficient cooling [50]. For example, Elam and Levy [32] performed calculations on the effect of collisional cooling for UV laser desorption of indole. According to their work, typically 2 ... 7 collisions per molecule occur after desorption of ≈ 2 monolayers per shot of a 10 ns laser, resulting in only minor vibrational cooling (< 10 %).

For applications such as high resolution electronic and fluorescence excitation spectroscopy of gas phase peptides, entrainment of laser desorbed species in supersonic helium or argon beams is used successfully [27, 84-89]. This combination of laser volatilization and molecular beam techniques allows further reduction of the internal temperatures of the desorbed molecules even in cases where the desorption flux is low.
Desorption of Aniline Submonolayers

With respect to elucidating LITD processes the Zare group [71] as well as our group [72, 73] analyzed the energy partitioning on the various degrees of freedom of aniline which was laser desorbed from sapphire and silica substrates by nanosecond CO₂ laser pulses. The analyzed surface coverages were low enough that jet cooling effects could be ruled out. Direct information on the energy transfer from the heated substrate to the adsorbed molecules could thus be obtained. In both studies, aniline was used not because it is chemically more interesting than other moderate-sized molecules but rather because the spectroscopy is well known and manageable [90-93]. Both groups found that the temperatures describing translation, vibration and rotation of aniline desorbed from either substrate at heating rates on the order of 10⁸ to 10¹⁰ K/s do not differ significantly. This alone can be interpreted as a result of thermal equilibrium during desorption [71].

In addition, Voumard carried out simulations to estimate the surface temperature at which desorption occurs [72, 73] by extrapolation of temperature programmed desorption data obtained at much lower heating rates (< 1 K/s). A surface temperature of around 600 K at the time of desorption was estimated, ≈ 150 ... 200 K higher than the translational and internal temperatures of the desorbed aniline. This would be consistent with a bottleneck for energy flow during LITD. However, the extrapolation of temperature programmed desorption (TPD) data to the regime of laser heating rates is difficult and very sensitive to the exact shapes of the TPD curves. Therefore, we repeated the TPD experiments on the aniline/silica system with an improved experimental setup where the sample preparation procedure and the detection of desorbed species were optimized. These new results lead to a simpler interpretation of the earlier data on nanosecond laser desorption of aniline from silica [72, 73] that does not require a “bottleneck”. Furthermore, we systematically extended the previous studies on laser desorption of aniline, which allows to derive general conclusions on LITD mechanisms and kinetics. The work described in this chapter also includes analysis of the desorption of aniline from glassy graphite, which, in contrast to sapphire and silica, is a nonpolar substrate. Since glassy graphite absorbs at 1064 nm, laser desorption experiments
using the fundamental of a picosecond mode-locked Nd:YAG laser can be performed. For the first time, all important kinetic parameters of one desorption system were determined experimentally: For nanosecond CO$_2$ laser-induced thermal desorption of aniline from glassy graphite we measured the surface temperature transient and followed the temporal evolution of the surface coverage during the desorption process [94]. The translational energy was obtained from time-of-flight distributions of the desorbing molecules. Vibrational and rotational temperatures were derived from resonance-enhanced multiphoton ionization spectra (REMPI). All these data are compared to simulations based on measured thermal equilibrium kinetic parameters. It is the aim of this study to provide an experimental foundation that allows to conclude the controversy on the desorption mechanism of aniline. The questions which are to be answered are the following:

- At what heating rates do thermal equilibrium kinetics collapse and bottleneck effects start to play a major role?
- Does a bottleneck for energy flow, which might occur at fast heating rates, lead to desorption of molecules that are internally colder than those obtained at lower heating rates?

2.2 Experiment

UHV Chamber and Sample Preparation

The experiments were performed in the ultrahigh vacuum chamber which is depicted schematically in figure 2.3 and described in detail in refs. [72, 95]. During the experiments the background pressure was typically on the order of $1 \times 10^{-10}$ Torr, which is one of the experimental prerequisites for surface science investigations on submonolayer films.
Fig. 2.3: Schematic sketch of the UHV chamber. The sample is mounted on a manipulator which allows to translate and rotate the sample to different ports on two height levels in the chamber. On the upper level laser beams for desorption and ionization of molecules can enter the chamber. The various directions of desorption laser beams and ionization laser beams are indicated as solid and dashed arrows, respectively (upper panel). The quadrupole mass spectrometer (QMS) was used for TPD measurements and determination of time-of-flight distributions of laser desorbed molecules. In photoionization spectroscopic experiments desorbed molecules were ionized using UV laser pulses mass selected in the time-of-flight tube (TOF tube) which is equipped with a microchannel plate (MCP) detector. On the lower level the instrumentation for x-ray photoelectron spectroscopy and Auger spectroscopy (x-ray source, electron source, and electron energy analyzer) is installed (lower panel).
The substrates, either a 20 mm x 10 mm, 3 mm thick piece of glassy graphite (Goodfellow, Cambridge, U.K.) or a 19 mm diameter, 2 mm thick disc of fused silica, both with surfaces polished to optical quality, were mounted on a manipulator to translate and rotate the sample to different ports in the UHV chamber. The substrates were in thermal contact with a liquid nitrogen reservoir for cooling. The graphite disc was heated by passing a current through the disc whereas the silica disc was heated by an electrical current in a thin gold film, vapor-deposited onto the back of the disc. The temperature of the substrate surfaces was measured by thermocouples cemented into holes that had been laser-drilled into the edge of the samples. Before each measurement the surfaces were cleaned by annealing at 700 K for 20 minutes. Under the influence of this thermal treatment the silica surface was dehydroxylated, forming a siloxane terminated surface [96].

Aniline (Fluka AG, Buchs, Switzerland, specified purity ≥ 99.5 %) was transferred into glass flasks connected to the gas handling system and degassed. The surface was dosed by leaking vapor into the chamber through a dosing system. Exposures were determined from the pressure measured by a nude ion gauge and were controlled by the exposure time (for temperature programmed desorption experiments) or the laser repetition rate (for LITD experiments). Surface coverages of 0.05 monolayers (ML) or lower were used in the time-of-flight and gas phase spectroscopic experiments.

**Temperature Programmed Desorption**

For characterization of the desorption systems temperature programmed desorption experiments were performed. The substrates were heated at a linear temperature rates in the range of 0.02 to 2 K/s and the partial pressure of the aniline parent ion at 93 Da was recorded on a quadrupole mass spectrometer (QMS) (Spectra Multi-Quad, Leda Mass, Stoke-on-Trent, U.K.) simultaneously with the substrate temperature. The rate of desorption per unit area of the adsorbent is determined from the expression [66, 97, 98]

\[
\frac{d\Theta}{dt} = \frac{V}{AkT_s} \left( \frac{dP}{dt} + \frac{S}{V} P \right)
\]
where $\Theta$ is the surface coverage (molecules cm$^2$), $P$ is the pressure increase above the background, $V$ is the volume of the desorption chamber, $S$ is the system pumping speed, $A$ is the adsorbent area, and $T_g$ is the gas phase temperature. If the pumping speed to volume ratio is large and the heating rate $\beta = \frac{dT}{dt}$ is low, then $\frac{dP}{dt} \ll \frac{S}{V} P$, and the desorption rate is to first order proportional to the pressure increase. Under these conditions the activation energy $E_a$ and the frequency factor $\nu$ can easily be obtained by fitting the measured pressure signal using the Polanyi-Wigner rate equation

$$\frac{d\Theta}{dt} = \Theta^n \cdot \nu \cdot \exp \left( \frac{-E_a}{k \cdot T(t)} \right)$$

where $\Theta$ is the surface coverage, $T(t)$ the time dependent surface temperature, and $n$ the reaction order [78, 99-103].

With respect to previous TPD measurements of aniline desorbing from silica [73], the experimental setup was optimized. A micro-structured dosing head was used to prevent deposition on the sample holder. Furthermore, a “Feulner cup” [104] which had previously been placed around the QMS was removed. Both steps lead to a significant reduction of the width of the TPD peaks: decay times of TPD signals were on the order of 20 s, approximately 5 times smaller than before. TPD signals recorded with the improved QMS agree well with pressure signals which were measured using an ion gauge. This shows that broadening of the TPD signal due to the QMS is now negligible.

**Desorption Lasers**

Two different lasers were used to induce desorption: a 70 nanosecond CO$_2$ laser (Allmark 853, Alltec, Lübeck, Germany) [105] and a 35 picosecond Nd:YAG laser (PY61, Continuum, Santa Clara, CA, USA) [106]. The desorption pulses were directed onto the surface at an angle of 45°. Using apertures we only passed the central parts of the beams onto the substrate.
surface which lead to spatial laser profiles that were homogeneous within
$\approx 15\%$. The pulse profiles on the sample had an elliptical shape with a full
width at half maximum (FWHM) of 4 mm in the horizontal direction and 3 mm
in the vertical direction. The CO$_2$ laser fluence at the surface was determined
to be 1 J/cm$^2$. Picosecond LITD using the Nd:YAG laser was performed at a
fluence of 16 mJ/cm$^2$.

**Time-of-Flight Distributions**

Information on kinetic energy of laser-desorbed neutral molecules was
obtained by measuring time-of-flight distributions. In the experiment
desorbing molecules and fragments were detected in the direction of the
surface normal with the quadrupole mass spectrometer which was also used
for the TPD experiments and their flight time from the substrate to the
detector was determined. The flight distance from the surface to the
ionization volume of the mass spectrometer was 7 cm.

Commercial quadrupole mass spectrometers are generally used for high
precision and high sensitivity residual gas analysis and are not optimized for
the detection of TOF distributions with a time resolution of some
microseconds. Only if the time response and the drift time through the
instrument is known the transient ion signals can be interpreted correctly
[107]. For determining the time response of the mass spectrometer, we
applied a 130 V, 4 $\mu$s voltage pulse to the extraction plate of the QMS ion
source while a background pressure of $\approx 10^{-8}$ mbar of the molecules to be
investigated was present in the chamber. For all molecules studied the
overall time response of the instrument was accurately determined in this
way. All response times were between 60 and 80 $\mu$s, approximately five
times smaller than typical flight times of the neutrals from surface to QMS
ionizer. Once the QMS temporal characteristics were known, the
experimental velocity distributions could be fitted with Maxwell Boltzmann
distributions convoluted with the time response of the instrument.
Resonance-Enhanced Multiphoton Spectroscopy

Internal energies of laser desorbed aniline were investigated by resonance-enhanced multiphoton spectroscopy (REMPI) [71-73, 108]. As shown in figure 2.4 a first photon excites the molecule from its ground state, $S_0$, to the lowest electronically excited state, $S_1$, and a second photon excites the molecule to the ionization continuum. The process is called (1+1) REMPI when the two photons that are involved have the same energy. Efficient ionization yields are only obtained if the first photon excites the molecule to a real intermediate state because the absorption cross section of virtual states is much smaller. This characteristic of the process allows one to extract information on the population of individual vibrational levels of desorbing molecules by tuning a UV ionization light source to the various vibrational levels of a molecule.

![Schematic of the (1+1) resonance-enhanced multiphoton ionization process.](image)

In the experiment, molecules were desorbed either by the nanosecond CO$_2$ laser or the picosecond Nd:YAG laser and laser postionized in the direction of the surface normal, at the maximum of the velocity distribution. The radiation of an optical parametric oscillator (MOPO-730D20, Spectra Physics
Lasers Inc., Mountain View, CA, USA) [109, 110] pumped by the third harmonic of a pulsed Nd:YAG laser (GRC-230) [111] was used for recording the REMPI spectra. Saturation was avoided by using laser fluences around $10^4$ W/cm$^2$. A pyroelectrical detector (ED-100, Gentec, Québec, Canada) was placed behind the ionization source to measure the energy of each UV pulse. The ions created in the REMPI process were extracted by electrical fields, mass-separated in a linear time-of-flight tube, and detected with a pair of microchannel plates. This ion signal as well as the laser pulse energy were integrated and averaged over 100 laser shots with two identical Boxcar averagers (SR 250, Stanford Research Systems, Palo Alto, CA, USA). The output at each wavelength was digitized and calibrated by dividing the ion signal by the square of the laser pulse energy.

Surface Temperature Transients Induced by Pulsed Laser Radiation

Laser-induced temperature transients on the substrate surface were either calculated or determined experimentally.

Calculations

Calculations of the surface temperature transients induced by laser heating were performed by integrating the one dimensional heat diffusion equation

$$\rho \cdot C_p \cdot \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(k \frac{\partial T(x,t)}{\partial x}\right) + Q(x,t)$$

where the source term $Q$ represents the laser heating which takes the absorption coefficient $\alpha$ and the reflectivity of the substrate into account. $k$ denotes the thermal conductivity, $\rho$ the density and $C_p$ the heat capacity. In the experiments the dimension of the laser beam impinging on the surface was several orders of magnitude larger than the thermal diffusion length $d$. $d$ is given by $d = 2\sqrt{\kappa \cdot \tau}$, where $\tau$ is the time interval considered and $\kappa$ is the thermal diffusion coefficient given by $\kappa = k / (\rho \cdot C_p)$. Therefore the lateral
heat diffusion is negligible and it is justified to reduce the problem to one dimension. At the beginning of each simulation the initial condition was

\[ T(x, t = 0) = T_o \]

For the integration of the diffusion equation the following boundary conditions were used:

\[ \frac{dT}{dx} \bigg|_{x=0} = 0 \text{ and } T(x = \infty, t) = T_b \]

Since the temperature dependence of \( C_v \) and \( k \) was explicitly included in the simulations, numerical methods had to be used for solving the heat diffusion equation [34]. This was done by slicing the semi-finite solid into thin slabs of thickness \( \Delta x \) and assuming a constant temperature within each slab. A forward-time finite difference formulation was chosen, where the energy balance for each slab can be written as

\[
k \frac{T_{m+1}^p - 2T_m^p + T_{m-1}^p}{\Delta x} \Delta t + I_m^p \left[ 1 - \exp(-\alpha \cdot \Delta x) \right] \Delta t = \rho c_p \Delta x \left[ T_{m+1}^{p+1} - T_m^p \right]
\]

where \( T_m^p \) is the temperature of the node \( m \) (at the center of the slab \( m \)) at the time \( p \), \( T_{m+1}^{p+1} \) is the temperature at the same position one time interval \( \Delta t \) later, \( I_m^p \) is the heating power incident on the slab \( m \) and \( \alpha \) is the optical absorption coefficient [34]. Measured laser pulse profiles were used as an input for the source term. The energy balance is used to calculate the temperature of each node. The surface itself is a node (\( m = 0 \)) of a slab with a thickness \( \Delta x/2 \). The numerical solution is stable if the coefficient \( T_m^p \) is positive. By reducing \( \Delta x \) and \( \Delta t \) the solution could be made as precise as desired.

**Measurements**

In addition to the calculations, the temperature transient of laser irradiated substrates was also followed by detection of black-body radiation emitted
from the surfaces. This technique allows non-contact and high precision
determination of the surface temperature of non-transparent substrates on a
nanosecond timescale [35].

In the experiment black-body radiation in the 1-2 µm range was detected by
a fast infrared InGaAs-PIN photodiode (Hamamatsu, mod. G3476-03) in the
direction of the surface normal. A micro lens objective was used to image a
spot of 0.9 mm diameter of the surface to the sensitive part of the detector.
Care was taken to keep the imaged part of the surface much smaller than the
laser heated area. The desired base temperature of the sample was
stabilized by resistively heating the sample and the use of a temperature
controller. The rise time was limited to 2 ns by the electric bandwidth of our
preamplifier which was based on a 500 MHz operational amplifier (Burr-
Brown, OPA621).

Since the emissivity of samples is not well known the total black body
radiation was calibrated over a temperature range of ≈ 500 K to ≈ 800 K and
fitted by an analytical expression that contains the transmission of the whole
optical system. The functional form of the calibration curve is obtained by
integration of Planck’s law in the spectral range where the detector is
sensitive

\[
P(T,[v_1, v_2]) \propto \int_{v_1}^{v_2} \frac{1}{v} \exp \left( \frac{h v}{kT} \right) - 1 \exp(-n \beta) \left( \frac{v_1^3}{n \beta} + \frac{3 v_1^2}{n^2 \beta^2} + \frac{6 v_1}{n^3 \beta^3} + \frac{6}{n^4 \beta^4} \right) \mid _{v_1}^{v_2}
\]

with \( \beta = \frac{h}{kT} \), where \( h \) and \( k \) are the Planck and Boltzmann constant,
respectively. The emissivity of the sample and the detector response are
assumed to be constant between the frequencies \( v_1 \) and \( v_2 \) and independent
of temperature. For temperatures where the maximum of the emission lies on
the long wavelength side of the detector response curve, the fitting curve
predicts a stronger increase of the detected radiation with temperature than
given by the well known \( T^4 \) law describing the collection of the radiation over
the whole spectrum.

Calibration of the emitted radiation versus temperature was performed by
resistive heating of the sample. The detector signal was recorded for
different sample temperatures. In figure 2.5 the recorded radiation signal of a glassy graphite substrate is depicted. The curve confirms that the emissivity of the sample is constant for the given temperature and wavelength range, so that the equation for the calibration curve which is given above can be applied. Once the calibration curve was recorded it allowed us to transform the measured intensities of black body radiation signals to temperatures in a straightforward and accurate way.

Fig. 2.5: Static calibration of the electric detector signal for different temperatures (triangles) of a glassy graphite substrate. The full line represents the emitted calibration curve derived from Plank's law.
2.3 Desorption of Aniline from Silica

Thermal Equilibrium Desorption Kinetics

In figure 2.6 TPD traces of aniline desorbing from silica are depicted. Thermal equilibrium desorption kinetics were determined by fitting TPD traces using the Polanyi-Wigner differential rate equation. In the fits the broadening of the signal due to the finite pumping rate of the vacuum chamber is included.

![Figure 2.6: TPD signal of aniline adsorbate layers of various thickness desorbing from silica at a heating rate of 0.3 K/s (solid lines) and fitted desorption rates (dotted lines).](image)

At surface coverages ≤ 1 ML the TPD signal consists of a single, relatively broad peak. If the surface coverage exceeds 1 ML, a second desorption peak is observed at temperatures lower than the (sub-) monolayer peak. It can be attributed to desorption of molecules which do not have any direct contact to the silica substrate. When fitting TPD signals of multilayer surface coverages we considered the contributions of both, monolayer and multilayer desorption. The TPD peak stemming from multilayer desorption
Desorption of Aniline could be fitted well using zero order kinetics with an activation energy of $59 \pm 1$ kJ/mol and a frequency factor of $(1 \pm 0.5) \times 10^{16}$ Hz. For submonolayer coverages best fits were obtained using first order desorption kinetics with activation energies in the range of 70 to 73 kJ/mol and frequency factors of $(1 \pm 0.5) \times 10^{16}$ Hz. Frequency factors on this order are typical for molecular desorption from surfaces [66, 112]. At all heating rates applied we found the shape and position of the submonolayer peak to be dependent on the initial coverage. At higher coverages the peak maximum is shifted to lower temperatures. This phenomenon might be explained by repulsive intermolecular interactions or heterogeneity of the substrate. Since the position of the desorption peak showed hardly any coverage dependence in the case of glassy graphite, we attribute the peak shift on silica to the heterogeneity of the silica binding site, which might stem from partial hydroxylation of the surface. The differences in activation energies for submonolayer and multilayer surface coverages can be attributed to distinct attractive interactions. IR spectra recorded of aniline submonolayers on silica suggest that two types of interactions are involved in the binding: the amine group is hydrogen bonded to the surface or the $\pi$ system of the aromatic ring binds to surface oxygen [113]. In the case of multilayer films, intermolecular attraction between neighboring molecules is either due to van der Waals forces or due to intermolecular hydrogen bonds. Since nitrogen is less electronegative than oxygen, the attractive interactions between neighboring aniline molecules can be assumed to be weaker than the binding forces to the silica substrate.

In a previous study on the desorption of benzene derivatives from silica [104] Voumard et al. reported that TPD traces of aniline have long tails which expand up to high temperatures. Our recent data which was recorded after improving the experimental setup - removal of the “Feulner cup” which had surrounded the QMS head and utilization of a novel dosing head - these tails did not occur any more. We interpret the tails as an experimental artifact originating from molecules which are trapped by and redesorbed from the walls of the Feulner cup before being detected by the QMS. Based on the data reported here, the previous findings on the equilibrium desorption kinetics of aniline from silica [104] have to be revised: the absence of the
high temperature tails in the TPD data leads to a reduction in the desorption activation energy and a concomitant lowering of the extrapolated desorption temperatures at laser heating rates.

Simulations of Laser Desorption

Previous studies on laser-induced thermal desorption of aniline surface adlayers from silica were performed at surface coverages on the order of 0.05 ML [72, 73]. Based on the kinetic parameters given above we can extrapolate the surface temperature at which molecular desorption would be expected to occur if a purely thermal mechanism was operational under fast laser heating conditions.

![Fig. 2.7](image)

Fig. 2.7: Measured CO$_2$ laser pulse profile as a function of time (dashed line), calculated surface temperature rise of the silica disc (solid line), and desorption flux of a 0.05 ML thick aniline adsorbate layer calculated on the basis of equilibrium desorption parameters ($E_A = 73$ kJ/mol; $v = 1.0 \times 10^{16}$ Hz) (gray shaded area).

The laser-induced temperature transient on the silica surface is depicted in figure 2.7. It was calculated by numerically integrating the one-dimensional heat diffusion equation. For comparison with the previous studies, these
calculations were done for the laser heating conditions applied in refs. [72, 73] (laser wavelength = 9.27 \mu m, fluence = 500 mJ/cm²). In the case of silica the density $\rho$ is 2.4 g/cm³ at 300 K. In the simulations the thermal dependence of the heat capacity $C_p$ and the thermal conductivity $k$ as given in refs. [114-116] was used. The source term $Q$ takes the absorption coefficient of $3.0 \times 10^4$ cm⁻¹ [117] of silica at 9.27 \mu m and a reflectivity of 40 % into account. Our calculations yield that the maximum surface temperature and the heating rate are $690 \pm 50$ K and $5 \times 10^9 \pm 1 \times 10^9$ K/s, respectively. The simulated trace of the desorption flux of aniline molecules which is depicted in figure 2 was calculated by integration of the Polanyi-Wigner differential rate equation for an adsorbate layer of 0.05 ML. The calculated laser induced temperature and the equilibrium desorption kinetic parameters were used in the calculations. Considering the ranges of the activation energy and the preexponential factor, simulations predict that thermal desorption of aniline should occur in the temperature range between 400 and 510 K using CO₂ laser heating, i.e., during the rising edge of the surface temperature transient. This is about 200 K lower than previous estimates of the desorption temperature [72, 73] for the same system. An estimated desorption temperature of 400 to 510 K agrees well with the previously determined translational temperature of laser desorbed aniline ($T_{\text{kin}} = 360 - 480$ K) [72, 73]. The ranges of the vibrational and rotational temperature ($T_{\text{vib}} = 300 - 420$ K; $T_{\text{rot}} = 250 - 450$ K) [72, 73] also overlap with the calculated temperature interval, however, they are shifted towards slightly lower temperatures.

2.4 Desorption of Aniline from Glassy Graphite

The use of graphite as a substrate has two reasons: First, graphite absorbs well at 10.6 \mu m and at 1064 nm, which allows to use either a CO₂ laser or the Nd:YAG laser fundamental to induce thermal desorption. Second, since graphite is nonpolar, its interaction with adsorbed aniline molecules is weaker than in the case of the silica substrate. Bottleneck effects for energy
flow from the heated substrate to the adsorbates are more likely for weakly bound adsorbates [45, 75].

**Thermal Equilibrium Desorption Kinetics**

For the aniline/glassy graphite system equilibrium desorption kinetic parameters were also determined by fitting TPD traces with the Polanyi-Wigner equation (figure 2.8).

![TPD signal](image)

**Fig. 2.8:** TPD signal of aniline adsorbate layers of various thickness desorbing from glassy graphite at a heating rate of 0.3 K/s (solid lines) and fitted desorption rates (dotted lines).

For this desorption system the monolayer and multilayer desorption peaks in the TPD traces overlap completely. Monolayer and multilayer desorption can therefore not be distinguished by the position of the TPD peaks but only by their shapes. At low surface coverages the TPD peak is symmetric, which clearly indicates a first order desorption process. If the surface coverage is increased the peaks become asymmetric with a steeper slope on the high temperature side. This peak asymmetry is typical for zero order multilayer desorption. Best fits for submonolayer coverages were obtained using first order desorption kinetics with activation energies in the range of 58 to 59
kJ/mol and a frequency factor of (1±0.2)×10^{16} Hz. As for aniline on silica, desorption of multilayers is best described by zero order kinetics, with an activation energy of 59 ±1 kJ/mol and a frequency factor of (1±0.5)×10^{16} Hz.

Simulations of Laser Desorption

Laser-induced temperature transients on the graphite surface were calculated for nanosecond CO\textsubscript{2} as well as picosecond Nd:YAG laser heating by integration of the one dimensional heat diffusion equation (figure 2.9). In the simulations, we used the thermal dependence of the heat capacity \( C_p \) and the thermal conductivity \( k \). The heat capacity was extracted from ref. [118] by fitting the data with the Debye equation. The thermal conductivity of glassy graphite is given by \( k = 3.2 \times 10^{-3} T^{1.33} \) W/(K·m), where \( T \) is the temperature in Kelvin [119, 120]. The density \( \rho \) of glassy graphite is 1.42 g/cm\(^3\) at 300 K. For the source term \( Q \) the absorption coefficient of 4.1×10\(^4\) cm\(^{-1}\) of glassy graphite at 10.6 \( \mu \)m and a reflectivity of 50 % were taken into account [121]. The maximum surface temperature and the heating rate under CO\textsubscript{2} laser heating conditions were found to be 770 ± 30 K and (1±0.2)×10\(^{10}\) K/s, respectively. The calculated temperature transient agrees well with experimental data obtained from black body radiation measurements.

For picosecond Nd:YAG laser the temperature profile was calculated using the optical properties of glassy graphite at 1064 nm (reflectivity = 20 %; absorption coefficient of 1.3×10\(^5\) cm\(^{-1}\)) [121]. The simulations gave a maximum surface temperature of 740 ± 50 K and a heating rate of (1±0.3)×10\(^{13}\) K/s. For both laser heating scenarios the desorption flux based on thermal equilibrium desorption kinetics was calculated by integration of the Polanyi-Wigner equation (figure 2.9). Calculations that took the ranges of the activation energy and the preexponential factor into account predict that desorption should occur in the temperature range of 380 to 450 K for nanosecond laser heating and 550 to 670 K for picosecond heating.
Fig. 2.9: (a) Measured CO$_2$ laser pulse profile as a function of time (dashed line), calculated (solid line) and measured (dotted line) surface temperature rise of the silica disc, and desorption flux of a 0.05 ML thick aniline adsorbate layer calculated on basis of equilibrium desorption parameters ($E_a= 58$ kJ/mol; $v = 1.0 \times 10^{16}$ Hz) (gray shaded area). (b) Nd:YAG laser profile (dashed line), calculated surface temperature on glassy graphite (solid line) and calculated desorption flux (gray shaded area).
This “overheating” is due to a competition between desorption and surface heating: the higher the heating rate, the higher the temperature at which desorption (or other thermal processes) will occur \([100, 122]\). Figure 2.10 visualizes this effect of the substrate heating rate on the desorption temperatures which are expected on basis of pure thermal equilibrium desorption kinetics.

![Graph showing desorption temperatures vs. heating rate](image)

Fig. 2.10: Calculated desorption temperatures of a 0.05 ML thick aniline adlayer desorbing from glassy graphite heated at various linear ramps. The crosses indicate the substrate temperature at which the maximum desorption flux occurs. The simulations for all heating rates were performed on basis of pure thermal equilibrium desorption kinetics.

**Temporal Evolution of the Surface Coverage During Laser Desorption**

In order to investigate the temporal evolution of the aniline surface coverage during nanosecond laser desorption, a novel two laser pulse experiment was developed as part of this thesis. In the experiment the desorption process initiated by a 70 nanosecond CO\(_2\) laser pulse was probed by a 10 nanosecond pulse of a Nd:YAG laser (GCR 230, Spectra Physics, Mountain View, CA; wavelength 1064 nm). Information on the temporal evolution of the
surface coverage was extracted from time-of-flight distributions of the desorbing molecules which were recorded by the QMS as a function of delay time between the two laser pulses which were overlapped at the surface. This technique allows to transform the desorption process occurring on a nanosecond timescale into TOF distributions which can be measured easily on the microsecond timescale. The experimental setup is shown schematically in figure 2.11.

The fluences of the CO₂ laser and the Nd:YAG laser were 1 J/cm² and 120 mJ/cm², respectively. Under these conditions a single pulse of either laser suffices to desorb the whole aniline layer completely. The substrate heating rate obtained by the CO₂ laser was ≈ 10¹⁰ K/s whereas the one induced by the Nd:YAG laser was more than ten times higher. Due to the different heating rates, the TOF distributions of aniline desorbed by the CO₂ and the Nd:YAG laser differ significantly (figure 2.12).

The surface temperature induced in the two laser experiment follows a complex profile that depends on the time delay of the lasers. Hence, their relative timing influences the shape of the TOF distributions. Two simple limiting cases can be identified. The TOF distribution is fast if the YAG laser pulse arrives first, because it is determined by a faster heating rate and a higher peak temperature obtained by the Nd:YAG laser. Conversely, the TOF distribution is slow if the YAG pulse arrives after the CO₂ laser pulse has completely desorbed the whole aniline layer, due to the lower heating rate of the latter. In figure 2.13 time-of-flight distributions obtained at various delay times between the CO₂ laser pulse and the Nd:YAG laser pulse are depicted.

The mean velocities extracted from the TOF distributions recorded at various delay times are plotted in figure 2.14 c. The error bars are obtained from the temporal laser jitter and pulse to pulse fluctuations in laser energy. For each delay time five sets of TOF distributions were recorded which were obtained by averaging over 100 laser shots. Mean velocities were determined by fitting Maxwell Boltzmann distributions to the TOF traces. The error bars are given by the maximum scatter of the velocities extracted from the independent sets.
Fig. 2.11: Sketch of the experimental apparatus used for time-resolved analysis of the surface coverage during LITD: Time-of-flight distributions of desorbed molecules were recorded by a quadrupole mass spectrometer (QMS) as a function of delay time between pulses of a 70 ns CO\textsubscript{2} laser and a 10 ns Nd:YAG laser. The TOF distributions were displayed and stored on scope 2 on a microsecond timescale. The two lasers were triggered externally by a delay/trigger unit. The output of both lasers was recorded with fast photodetectors. Their signals were displayed on scope 1 to visualize the time delay between the lasers on a nanosecond timescale.
Fig. 2.12: Time-of-flight distributions of aniline desorbing from glassy graphite under CO$_2$ laser (solid line) and Nd:YAG laser (dotted line) heating conditions. The TOF distributions were obtained by averaging over 100 shots. The mean velocities of the desorbed molecules are 315 m/s and 340 m/s for desorption by the CO$_2$ laser and the Nd:YAG laser, respectively.

At a delay time of $\approx 50$ ns after the onset of the CO$_2$ laser pulse the mean velocity of desorbed molecules drops sharply from values typical for the Nd:YAG laser to values characteristic for CO$_2$ laser desorption. In fact, at delay times greater than 50 ns the TOF distributions are identical with the ones obtained by the CO$_2$ laser only, indicating that desorption induced by the CO$_2$ laser is complete after 50 ns. For the experimental conditions used, aniline completely desorbs during the rising edge of the surface temperature transient, at a surface temperature of $\approx 400$ K.

The finding is fully consistent with the desorption temperature calculated from Arrhenius type first order desorption kinetics on basis of equilibrium kinetic parameters (figure 2.14 b). It lends support to the notion that desorption temperatures at laser heating rates can be obtained by extrapolation of TPD data.
Fig. 2.13: Time-of-flight distributions obtained at various delay times between the CO$_2$ laser pulse and the Nd:YAG laser pulse (solid line) and TOF distribution obtained by the CO$_2$ laser only (dotted line). The delay times refer to the time axis used in figure 2.14. Time zero corresponds to the onset of CO$_2$ laser heating. Negative delay times indicate that the Nd-YAG laser pulse impinges on the substrate before the CO$_2$ laser whereas positive times characterize situations where the substrate heating induced by the CO$_2$ laser has already started before the Nd:YAG pulse hits the surface.
Fig. 2.14: (a) Temporal profile of the CO$_2$ laser pulse (dotted line) and surface temperature transient induced on the glassy graphite substrate (solid line). The origin of the time axis refers to the onset of CO$_2$ laser heating. (b) Calculated temporal evolution of the surface coverage assuming thermal equilibrium kinetics for the desorption of aniline from glassy graphite under CO$_2$ laser heating conditions. (c) Mean velocities of desorbed molecules extracted from TOF distributions recorded at various delay times between the CO$_2$ and the Nd:YAG laser pulses. The error bars are due to the temporal laser jitter and pulse to pulse fluctuations in laser energy.
Kinetic Energies of Laser Desorbed Molecules

Translational temperatures of laser desorbed molecules were obtained by fitting TOF distributions with Maxwell-Boltzmann (MB) distributions convoluted with the time response of the quadrupole mass spectrometer. For surface coverages of 0.05 ML the desorption plume is virtually collision-free [50, 51] and no stream velocity needs to be included in the MB fits. We proved that the influence of jet effects on the TOF distributions are negligible at coverages of 0.05 ML by showing that TOF distributions within the coverage range from 0.01 to 0.1 ML have the same shape.

For the fits, Maxwell Boltzmann time distributions of the following form were used

\[ g(t) = c \cdot t^4 \cdot \exp \left( -\frac{m \cdot v^2}{2kT} \right) \]
\( t \) is the flight time, \( m \) the molecular mass, \( T \) the temperature, \( k \) the Boltzmann constant and \( c \) a constant for adjustment of the signal amplitude. These distributions describe the movement of molecules in the half space directed away from the sample surface. The factor \( r^{-4} \) also takes into account that the ionization probability of the QMS is proportional to the residence time of the molecules in the ionization volume [107].

In figure 2.15 TOF distributions of aniline desorbed from glassy graphite by either the nanosecond laser or the picosecond laser are depicted together with the corresponding Maxwell-Boltzmann distributions. The translational temperature of molecules desorbed by the nanosecond CO\(_2\) laser is 440 ± 50 K. Picosecond Nd:YAG laser desorption leads to kinetic temperatures of 640 ± 50 K.

**Vibrational and Rotational Energies of Laser Desorbed Molecules**

In the case of aniline the absorption cross section for photoexcitation from the S\(_0\) state to the S\(_1\) state is four times smaller than for excitation from the S\(_1\) state to the ionization continuum [71]. Therefore, the spectral shape of the REMPI ion signal is dominated by the absorption of the first photon and the vibrational and rotational structure reflects the population in the electronic ground state of aniline. This is the prerequisite for its use as a spectroscopic probe for internal excitation.

Vibrational and rotational excitation of the desorbed aniline molecules was studied using the the 0\(_{0}^{0}\) origin transition and the 10\(_{0}^{1}\) hot band [71] (figure 2.16). In figure 2.17 the 10\(_{0}^{1}\) vibration is visualized schematically, it can be described as flexing of the amino group and the carbon skeleton of the ring [71, 89].
In general, the relative intensity of two vibrational bands originating from levels $m$ and $n$ of the electronic ground state is given by

$$\frac{I_m}{I_n} = \frac{F_{i-m} g_m}{F_{j-n} g_n} \exp \left( -\frac{E_m - E_n}{kT} \right)$$
where $E_m$ and $E_n$ are the energies of the vibrational levels considered, $T$ is the vibrational temperature, $F_{i-m}$ and $F_{j-n}$ are the Franck-Condon factors of the vibronic states $i$ and $j$, respectively. In the case of aniline, the 10b normal mode is nondegenerate ($g_m = g_n = 1$) [123]. Since the Franck-Condon factor is independent of temperature, the intensity ratio of two transitions at two temperatures, $T_1$ and $T_2$, can be expressed by

$$\ln \left( \frac{I_m(T_1)}{I_n(T_1)} \frac{I_m(T_2)}{I_n(T_2)} \right) = \frac{\Delta E}{k} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where $\Delta E$ is the difference of the energy levels, $E_m - E_n$. In the case of the vibrational ground state and the 10b state, $\Delta E$ is 177±3 cm$^{-1}$ [71]. Therefore, based on a calibration spectrum which we recorded at $T_1 = 300$ K, the vibrational temperature $T_2$ of laser desorbed molecules can be determined simply by comparing the intensity ratio of the $0^0_0$ and $10b^1_1$ vibrational bands. Rotational temperatures were determined by comparing the spectra with simulated rotational bands contours. Since the rotational envelopes obtained for the $0^0_0$ and $10b^1_1$ transitions are almost identical [74], only the rotational band structure of the $0^0_0$ transition was used for fitting the data throughout. The simulations were performed according to the calculations derived and executed by Voumard and Zenobi [73, 74, 95, 124]. A detailed description of the procedure and listings of the programs can be found in ref. [124]. In a first step the rotational eigenstates and eigenfunctions and in the $S_0$ and $S_1$ state were determined by diagonalization of the rotational Hamiltonian of aniline

$$H = AJ_x^2 + BJ_y^2 + CJ_z^2$$

where $A$, $B$, $C$ are the rotational constants given in table 2.1 [125] and $J_x^2$ are the squares of the kinetic moments. For the calculations the Born-Oppenheimer and the rigid rotor approximation were applied.
Table 2.1: Rotational constants (in cm⁻¹) for the 0⁰ transition of aniline [125].

<table>
<thead>
<tr>
<th>ground state S₀</th>
<th>excited state S₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 0.01838</td>
<td>0.1762</td>
</tr>
<tr>
<td>B 0.08652</td>
<td>0.08788</td>
</tr>
<tr>
<td>B 0.05938</td>
<td>0.05869</td>
</tr>
</tbody>
</table>

In a second step, the spectra were calculated. The resolution of the laser Δλ was introduced by assuming a Gaussian spectral profile. Each point of the spectrum is given by a sum over all transitions considered:

\[
I(E) = \sum_{\tau} p \cdot \exp\left(-\frac{(E - E_{\tau})^2}{2 \cdot \Delta \lambda}\right)
\]

where the probability p is given by

\[
p = S(J'\tau'; J''\tau'') \exp(-E_{J'\tau'} / kT)
\]

The Boltzmann term \(\exp(-E_{J'\tau'} / kT)\) considers the occupation of the initial state at a given temperature T. \(S(J'\tau'; J''\tau'')\) is the Hönl-London factor between the initial and final state of the transitions which are characterized by the rotational quantum number J and the index τ which marks the various rotational states belonging to a given J [126]. A total number of 300,000 transitions were taken into account for the calculations which was necessary at higher temperatures. In figure 2.18 aniline spectra are depicted which were calculated for vibrational and rotational temperatures in the range of 100 K to 1000 K. They clearly visualize the temperature dependence of the intensity ratio and the spectral shape of the 0⁰ and 10⁰ transitions.

Figure 2.19 shows a the calibration spectrum recorded at 300 K and spectra of aniline molecules which were laser desorbed with either the nanosecond CO₂ laser or the picosecond Nd:YAG laser together with the corresponding fitted rotational contours. The relative contribution of the background signal from residual aniline was found to be = 2 % and was subtracted from the spectra. The vibrational and rotational temperatures resulting from the fits
are inserted for each trace. To account for the spectral overlap of the two bands, the following fitting procedure was used: First the $0^0$ band was fitted using the main feature of only 30 cm$^{-1}$ of the data. This fit was subtracted from the measurement over the whole range, giving the deconvoluted $10^{b_1}$ band, which was in turn fitted using the same, spectrally shifted band structure. The free parameter was always the relative band intensity; an arbitrary baseline was also subtracted from the data as part of the fitting procedure. A good agreement of the fitted rotational shapes and the experimental data was obtained using rotational temperatures between 250 and 450 K for nanosecond and between 400 and 600 K for picosecond laser desorption, respectively.

At room temperature the ratio obtained from the areas of the $10^{b_1}$ band and the $0^0$ band is $0.41 \pm 0.02$. Based on the fits, the intensity ratio in the spectra was found to be in the range of 0.41 to 0.52 for nanosecond and 0.46 to 0.61 for picosecond laser desorption, corresponding to vibrational temperatures of 300 to 450 K and 350 to 600 K, respectively.

![Fig. 2.18: Computer simulations of the rotational band contour of the $0^0$ and $10^{b_1}$ transitions at various temperatures. A spectral resolution of 0.5 cm$^{-1}$ was used in the calculations.](image)
Fig. 2.19: (a) Calibration spectrum of aniline vapor at 300 K, and spectra of (b) nanosecond CO₂ laser-desorbed and (c) picosecond Nd:YAG laser-desorbed aniline. Superimposed on the spectra are simulations of the rotational envelopes for the temperatures indicated next to the traces.

2.5 Discussion

In table 2.2 all the data from IR laser-induced thermal desorption of aniline are summarized. With nanosecond laser heating, the temperature ranges characterizing translation, vibration, and rotation of the desorbed molecules all overlap well. These temperatures are also consistent with the calculated desorption temperatures based on equilibrium desorption kinetics.

If a bottleneck for energy flow from the heated substrate to the adsorbate molecules occurred it would be expected to be more pronounced for graphite than for silica due to the weaker substrate-adsorbate bond. However, the experimental results on nanosecond CO₂ laser desorption from graphite show that all the temperature ranges of all degrees of freedom overlap well with the calculated desorption temperature. Also, the experimentally determined surface temperature range at the time of desorption fits well into the picture of a thermal equilibrium process. Based
on these findings, we conclude that laser-induced thermal desorption of aniline submonolayers at heating rates up to $10^{10}$ K/s can be fully characterized by pure thermal equilibrium. Pronounced bottleneck effects in the energy partitioning can certainly be ruled out on a timescale of tens of nanoseconds.

The picture is somewhat different on the timescale of tens of picoseconds. The translational temperature of aniline desorbed by the picosecond Nd:YAG laser still agrees well with the desorption temperatures extrapolated from TPD data obtained at much lower heating rates. However, the temperature ranges that characterize the vibrational and rotational excitation of the molecules are shifted towards lower temperatures.

Can collisions account for this temperature difference? For the very low surface coverages ($\approx 0.05$ ML) investigated here, an influence of collisional cooling in the desorption plume is very unlikely. Our TOF data are described well by Maxwell-Boltzmann distributions without an additional stream velocity term, a strong indication that postdesorption collisions are negligible. Typically 5 to 1000 collisions are required for cooling of rotational and vibrational degrees of freedom [19] whereas significant changes of the velocity distributions are already reported for 3 collisions [50]. Calculations performed on the effect of collisional cooling for UV laser desorption of $\approx 2$ monolayers of indole showed that postdesorption collisions result in only minor vibrational cooling < 10 %. Therefore, the discrepancy between translational and internal temperatures found for picosecond laser heating is an indication that thermalization is not complete. These findings are consistent with the results of Heilweil et al. [127, 128] on the energy flow in the other direction. These authors found that relaxation times of vibrationally excited, chemisorbed molecules are typically $\leq$ 100 ps.

As shown in table 2.2, the vibrational and rotational temperatures of aniline molecules which are desorbed under picosecond LITD conditions exceed those of molecules desorbed on a nanosecond timescale. This finding clearly shows that the bottleneck which occurs on a picosecond timescale is not strong enough to compensate for the increase in desorption temperature resulting from faster substrate heating.

For femtosecond laser desorption, nonthermal desorption mechanisms have been proposed in the literature. For example, femtosecond desorption of
submonolayer films from semiconductor surfaces is typically explained by multiple electronic scattering (DIMET: desorption induced by multiple electronic transitions) [82, 129]. However, internal temperatures of small molecules desorbed by femtosecond laser radiation are reported to be much higher than those obtained under nanosecond laser heating conditions [129]. Therefore, reduction of the pulse length to the sub-picosecond time regime cannot be regarded as rational strategy for obtaining internally cold gas phase species.

Table 2.2: Summary of calculated (calc.) and measured (meas.) temperatures for different degrees of freedom, obtained by nanosecond and picosecond laser induced desorption of aniline from various substrates. The calculated substrate temperatures at the time of desorption refer to thermal equilibrium desorption kinetics.

<table>
<thead>
<tr>
<th></th>
<th>ns LITD from silica</th>
<th>ns LITD from sapphire ref. [71]</th>
<th>ns LITD from graphite</th>
<th>ps LITD from graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate heating rate</td>
<td>$5 \times 10^9$ K/s (calc.)</td>
<td>$10^9$ K/s (calc.)</td>
<td>$10^{10}$ K/s (calc. &amp; meas.)</td>
<td>$10^{13}$ K/s (calc.)</td>
</tr>
<tr>
<td>surface temperature at the time of desorption</td>
<td>400 - 510 K (calc.)</td>
<td>-</td>
<td>380 - 450 K (calc.)</td>
<td>550 - 670K (calc.)</td>
</tr>
<tr>
<td>translational energy (meas.)</td>
<td>360 - 480 K ref. [73]</td>
<td>= 400 K</td>
<td>380 - 500 K</td>
<td>580 - 700 K</td>
</tr>
<tr>
<td>vibrational energy (meas.)</td>
<td>300 - 420 K ref. [73]</td>
<td>350 - 550 K</td>
<td>300 - 450 K</td>
<td>350 - 600 K</td>
</tr>
<tr>
<td>rotational energy (meas.)</td>
<td>250 - 450 K ref. [73]</td>
<td>-</td>
<td>250 - 450K</td>
<td>400 - 600 K</td>
</tr>
</tbody>
</table>
2.6 Summary

This study on classical as well as laser-induced thermal desorption of aniline submonolayers from silica and glassy graphite sheds light on the desorption kinetics and the energy transfer from the heated substrate to the adsorbed molecules. The conclusions of the experiments are the following:

- Nanosecond LITD of aniline from both substrates at heating rates as high as $10^{10}$ K/s is fully consistent with a thermal mechanism, i.e. the various degrees of freedom of desorbing molecules are fully thermalized and consistent with the desorption temperature.

- At $10^{13}$ K/s only the kinetic energy of desorbed molecules agrees well with simulations based on equilibrium desorption kinetics whereas the internal degrees of freedom are not fully equilibrated. However, the bottleneck for energy flow is not strong enough to compensate for the “overheating” associated with higher heating rates.
3 Laser-Induced Thermal Desorption of Poly- (Ethylene Glycol) Submonolayers

3.1 Introduction

In order to obtain an understanding of laser-induced thermal desorption of higher mass species where dissociation starts to compete with intact desorption, a systematic investigation of the desorption and dissociation kinetics of ethylene glycol and poly- (ethylene glycol) (PEG) oligomers (OH- [CH₂-CH₂-O]-ₙ H ; n= 1...900) was performed. The study includes analysis of oligomers within the mass range from 62 to 35000 Da under slow surface heating and LITD conditions. PEG molecules are typical representatives of a class of compounds characterized by a linear backbone, moderate polarity, and multiple noncovalent interactions to surfaces and neighboring molecules. With increasing chain length the adhesion of the PEG molecules to the surface, as well as the intermolecular polar and van der Waals interactions are strengthened. PEG molecules therefore mimic the desorption characteristics of biopolymers and a large range of synthetic polymers. In this study, we used silica substrates which are typically employed in LITD experiments.

In this work, quasi-equilibrium desorption and dissociation kinetics of the various oligomers were determined by temperature programmed desorption measurements at heating rates between 0.02 and 0.5 K/s. Kinetic parameters for dissociative desorption differ from those found for intact
desorption so that these two competing desorption channels can be clearly distinguished. Additionally, atomic force microscopic investigations and x-ray photoelectron spectroscopy were performed to characterize the growth and thermal degradation of the ultra thin PEG 1500 films on silica under slow heating conditions. Time-of-flight distributions of PEGs desorbed under nanosecond and picosecond laser heating conditions at heating rates of $10^9$ K/s and $10^{13}$ K/s, respectively, were recorded. We compare these measurements to simulations based on the results in the slow heating regime. This gives valuable insight in desorption and dissociation kinetics under fast heating conditions. The central question which is to be answered in this study on the desorption of PEG submonolayer films is the following:

- Is intact desorption of macromolecular species favored at fast heating rates either due to a bottleneck for energy flow or due to a favorable rate crossover of desorption and dissociation rates?

3.2 Experiment

Sample Preparation

The experiments were performed in the UHV chamber which was also used in the study on aniline (see chapter 2.2). For classical heating as well as nanosecond laser heating a 19 mm diameter, 2 mm thick disc of fused silica, polished to optical quality was used as a substrate. The picosecond LITD experiments were performed using a 20 mm x 8 mm, 0.8 mm thick tungsten plate which had been polished to optical quality and on which a 5 nm silica layer had been evaporated. Before each measurement the surfaces were cleaned by annealing at 700 K for 20 minutes which leads to dehydroxylation and formation of a siloxane termination [96]. Ethylene glycol (puriss, 99.5 %, Fluka, Buchs, Switzerland) and diethylene glycol (Dihydroxyethyl ether 99 %, Arcos, Geel, Belgium) were transferred into glass flasks connected to the gas handling system and degassed. The surface was dosed by leaking vapor into the chamber. Surface coverages were estimated by comparing peak intensities of the C 1s, Si 2s and Si 2p peaks in the XPS spectra. Surface coverages in the range of a tenth of a monolayer to one monolayer were investigated.
For PEG 300, 600, 1000, 1500, 20000, and 35000 (all from Fluka) the name refers to the average mass of the oligomer distribution. The total mass distribution spans a width of approximately ±15 % of the central mass, as measured by MALDI MS in our laboratory. Due to their small vapor pressures the larger PEG oligomers could not be dosed in situ. For their preparation the chamber was opened and a drop of solution in water or tetrahydrofuran (THF) was dragged over the sample surface. The chamber was then evacuated and experiments were performed as soon as the chamber pressure had reached 5·10⁻⁹ mbar or better. The surface coverages obtained with this dosing method were determined by XPS and AFM measurements to be on the order of 0.3 monolayers.

Temperature Programmed Desorption
TPD experiments at various heating rates were performed using the quadrupole mass spectrometer described in chapter 2. Electron impact ionization of PEGs yields fragments at mass 45 and 89 Da, corresponding to the protonated monomer and dimer, respectively. The dominating intensities of these ions in the cracking patterns is neither influenced by the desorption method, nor by the PEG molecular mass. Fragmentation to monomer units is also reported to be the dominant reaction channel during pyrolysis of PEGs [130]. Intact desorption can therefore not be discriminated from dissociative desorption from the fragmentation pattern observed with the QMS. As TPD curves at mass 45 and mass 89 were highly correlated, we took the signal at m/z = 45 as a measure for the PEG molecules desorbing from the silica surface.

Time-of-Flight Distributions
Thermal desorption was induced using the 70 ns FWHM pulses of the CO₂ laser and the 35 ps FWHM pulses of the Nd-YAG laser which were also used in the aniline study. The beam of either laser was focused onto the surface at an angle of 45°. The pulse profile of the CO₂ laser on the sample had an elliptical gaussian shape with a FWHM of 4.2 mm in the horizontal direction and 2.4 mm in the vertical direction. The pulse energy at the surface was determined to be 0.25 J. In the case of the ps laser, the homogeneous central part of the laser profile was selected using a 4 mm diameter aperture. The profile on the sample was elliptical with an extension of 6 mm in the
horizontal direction and 4 mm in the vertical direction. Pulse energies of 6
and 12 mJ, corresponding to fluences of 30 mJ/cm² and 60 mJ/cm²,
measured at the sample position, were applied. The laser radiation at 1064
nm is absorbed effectively by tungsten whereas absorption by the SiO₂
layer is negligible. Since the radiation of both lasers is not absorbed by the PEG
molecules, laser desorption in this case is a purely nonresonant effect
induced by heating of the surface.

TOF distributions of the desorbing species were measured in the direction of
the surface normal using the quadrupole mass spectrometer. The flight
distance from the surface to the ionization volume of the mass spectrometer
was 7 cm and 9 cm in the case of nanosecond and picosecond laser
heating, respectively. We determined the time response of the mass
spectrometer, which is important for correct interpretation of experimental
time-of-flight distributions by pulsed extraction of a background pressure of
≈ 10⁻⁶ mbar of ethylene glycol monomer or dimer as described in chapter
2.2.

**X-Ray Photoelectron Spectroscopy**

For complementary chemical analysis of the surfaces XPS was used. XPS
analysis was performed by irradiating the sample with x-rays from a dual
anode 600 W X-ray source which could be operated on the Al-Kα line
(E(Kα) = 1486.6 eV, ΔE = 0.85 eV) or the Mg-Kα line (E(Kα) = 1253.6 eV,
ΔE = 0.7 eV). The photoelectrons emitted from a 6 mm diameter region of
the sample were collected and analyzed by a 100 mm mean radius
hemispherical analyzer fitted with a channeltron detector (DAX 600 & HSA
100; VSI GmbH, Bad Schwalbach, Germany). In XPS analysis the measured
kinetic energy \( E_{\text{kin}} \) of the electrons is given by

\[
E_{\text{kin}} = h\nu - E_b - \Phi,
\]

where \( h\nu \) is the photon energy, \( E_b \) is the binding energy of the atomic orbital
from which the electron originates, and \( \Phi \) is the sample work function. Due
to the unique set of binding energies of each element, XPS can be used as a tool for identification and determination of the concentration of elements. Variations in the binding energies (chemical shifts) arise from differences in the oxidation state and molecular environment of the compounds. These chemical shifts allow identification of the chemical state of the materials which are analyzed [131].

XPS is commonly believed to require rather long acquisition times for the collection of spectra of reasonable quality. Hence, only few studies report real time XPS to probe chemical variations of adsorbed layers during reaction time [132]. We showed that it is possible to follow temperature programmed thermal desorption spectra at moderate heating rates by XPS in real time for processes that proceed on a timescale of some minutes. To follow the desorption and surface decomposition of PEG 1500 on silica, the surface temperature was ramped at 0.1 K/s. Simultaneously, the sample was irradiated with the Al Kα line of the X-ray gun operated at 400 W. The emitted photoelectrons were collected in the energy windows of the O 1s, the C 1s and the Si 2p peaks using a resolution of 1.3 eV for the hemispherical analyzer. The position of the silicon peak did not shift during the experiments so that surface charging effects that sometimes complicate XPS measurements on insulating samples could be ruled out.

Atomic Force Microscopy

Atomic force microscopy was used to investigate the topography of PEG 1500 films on silica during their growth and thermal degradation at low heating rates. AFM is a scanning probe techniques where the height profile of a surface is analyzed by moving a sharp tip over it. Mechanical (attractive or repulsive) forces between the surface and the tip are the fundamental interactions on which the technique is based [133-137]. In the study an atomic force microscope (Lumina, Topometrix, St. Barbara, CA, USA) was used, which was operated in "non-contact mode" mode (also called "tapping mode") to minimize tip sample interactions. In “non-contact” mode the tip is kept several nanometers away from the sample. At this distance it is pulled towards the surface primarily by capillary forces on contaminated samples (covered with a water film) and van der Waals forces on clean samples. In
“contact” mode, the tip is closer to the surface, in the repulsive force region, and the cantilever is pushed away from the sample. In “non-contact” mode the cantilever is oscillating perpendicular to the surface at its resonance frequency (typically 230 kHz, Q-factor 500). If the tip comes close to the surface, the oscillation is damped and the resonance frequency is shifted. This damping is used as a feedback for keeping the average tip-sample distance constant. The topographic data is derived from the tip height at 50% damping. Silicon cantilevers with spring constants between 24 and 85 N/m, tip radii smaller than 20 nm and an aspect ratio of 3:1 were used throughout the experiments. Stable imaging conditions were obtained at a scan speed of 1 line/s.

For imaging at variable temperatures a small heating stage was added to the instrument. A rectangular ceramic frame was used to mount the silica substrate, which minimized the thermal drift and heat conduction to the piezo table. The silica substrate was resistively heated by a thin metal film deposited on its back side. The temperature was monitored by a thermocouple cemented into a hole that was laser drilled in the side of the sample. In air, the accessible temperatures range of the heating stage lied between 300 K and 600 K. Scanning without loosing feedback was only possible up to 360 K. Therefore the polymer films that were heated above 360 K were cooled down to room temperature before the image was recorded.

### 3.3 PEG 1500 Layer Formation

In the bulk, PEG crystallizes in a lamellar form. The unit cell is defined by the vectors a, b, c and the angle \( \beta \) (see figure 3.1) [138, 139]. The polymer chains are helices of symmetry D7. The average oligomer length is calculated as \( \lambda = (M/44) \times \lambda_0 \) where \( \lambda_0 = c/7 = 2.783 \text{ Å} \) is the length of one monomer unit in the crystal unit cell and \( M \) the average molecular weight. For a PEG 1500 oligomer containing 40 repetitive units, \( \lambda \) equals 95 Å. On a silica substrate at low coverage, the mutual alignment of the PEG 1500 molecules found in the lamellas of the bulk polymer is conserved. If a thin
film of THF containing a low concentration of PEG is dried on a clean silica surface, the timescale of solvent evaporation is much too short to allow an equilibrium crystallization process. Instead, one observes the nucleation and growth of highly branched, 2-dimensional structures that can be imaged using AFM. The structure depicted in figure 3.2 displays a cluster formed immediately after evaporation of the solvent at room temperature. An hour later the submonolayer film has relaxed, and a typical randomly ramified pattern covers the whole surface (same sample, figure 3.3).

![Structural model of a PEG repeating unit](image)

**Fig. 3.1:** Structural model of a PEG repeating unit (carbon: light; oxygen: dark) compiled from the x-ray diffraction data given in [138, 139]. The bulk polymer crystallizes in lamellar form with the unit cell parameters given as $a = 8.05$ Å, $b = 13.04$ Å, $c = 19.48$ Å and $\beta = 125.4^\circ$. 
Fig. 3.2: AFM image of a disordered polymer cluster scanned directly after deposition and drying of the dilute PEG/THF solution. The height range is 16 nm, the scan area 1.6 x 1.6 \( \mu m^2 \).

Fig. 3.3: AFM image: Overview of 50 x 50 \( \mu m^2 \) of a submonolayer of PEG 1500 molecules at \( T = 300 \) K (same sample/coverage as in figure 3.2). The fractal pattern exhibits a constant height of 10 nm.
Fig. 3.4: AFM image: The same surface area depicted in figure 3.3 imaged at 355 K. Smooth 10 nm terraces appear while the fine structure of the room temperature pattern is coarsening. The height range is 40 nm (see figure 3.5). The scan area is 50 x 50 μm².

Fig. 3.5: The line scan across the central part of the pattern depicted in figure 3.4 yields discrete steps of 10 nm height and terraces of high average smoothness.
Although the lateral scale on which the pattern can be observed does not need a very high resolution, the additional height information included in the pictures allows a remarkable conclusion. The pattern consist exclusively of smooth terraces with a constant height of 10±1 nm which exactly matches the length of a single PEG 1500 polymer chain (figure 3.4 and 3.5). This height indicates a vertical orientation of the molecules, each occupying ~ 100 Å^2. The density of an adsorbed monolayer of vertically oriented molecules will thus be about 10^{14} molecules/cm^2. The residual microscopic roughness of the terraces reflects the polydispersity of the PEG, the nonuniformity of the substrate and the acoustic noise coupled into the scanning stage. The absolute overall surface coverage can also be deduced from the AFM images. Point defects and rosetta structures typical for fused silica surfaces can be resolved on the polymer free areas and help to distinguish between covered and uncovered surface. Since PEG thin films are very soft compared to the glass substrate we also found a pronounced difference in the force distance curves on the terraces and on the silica substrate. Therefore it can be excluded that the silica surface is covered with multilayers. One can surmise that the loose aggregation in two dimensions (figure 3.2) is established on a fast timescale, comparable to that of the solvent vaporization. The vertical unfolding and in-plane self-assembly (figure 3.3) of these loosely clustered polymer molecules needs about an hour at room temperature.

One possibility to systematically study the assembly process is to determine the fractal dimension of the observed patterns by analyzing its scaling properties. The approach we used to determine the fractal dimension D of the structure was the box counting method [140]. A grid of boxes of dimension ε was placed on the pattern and the number of boxes fully or at least partially filled by the pattern was counted. The smallest size of ε is typically the size of a pixel in the digital image. For a homogenous, self-similar fractal the number of partially covered boxes scales as

\[ N(\varepsilon) \sim \varepsilon^{-D}. \]

By plotting \( \log(N(\varepsilon)) \) versus \( \log(\varepsilon) \), the fractal dimension D can be obtained from the slope of the graph.
Fig. 3.6: A log-log plot of the scale dependent polymer covered surface of the pattern depicted in figure 3.3 yields a fractal dimension of $D=1.7\pm0.1$.

Figure 3.6 demonstrates that such an analysis of the data depicted in figure 3 yields a linear relation over more than 2 orders of magnitude. The resulting fractal dimension is $D=1.7\pm0.1$. At constant image size of 300 x 300 pixels the scan range of the AFM was varied between 50 $\mu$m (167 nm/pixel) and 10 $\mu$m (33 nm/pixel). The same power law was found to hold for over three orders of magnitude, which is a good indicator for true self similarity. Apparently the two-dimensional fractal structure of figures 3.3 and 3.4 closely resembles patterns obtained from the diffusion limited aggregation model introduced by Witten and Sander [141]. Also, the fractal dimension obtained is typical for diffusion controlled growth processes. This value is not affected by the fact that in the early stages of growth the sticking coefficient of the mobile polymer species to the contour of the pattern is below unity [142]. The amorphous substrate structure leads to completely isotropic diffusion processes and no preferential symmetry of the pattern can be recognized. Despite this good qualitative interpretation, the AFM images cannot fully unravel the kinetics of the aggregation process. The problem lies mainly in the lack of process control during pattern formation. Neither does the polymer concentration in the solvent remain constant, nor can the surface
mobility and sticking coefficient be predicted with reasonable accuracy during the drying process of the thin film.

3.4 Thermal Desorption

In order to get information on the behavior of the polymeric thin film during slow heating we recorded a series of AFM images at exactly the same location on the surface (figures 3.4, 3.7 and 3.8) after exposing the sample to various temperatures between room temperature and 405 K. The obvious structural change at 355 K reveals that first a rearrangement in two dimensions takes place. The flat terraces grow without changing their step height. The contours of the resulting pattern are smoothed out although the fractal nature is conserved. At 375 K surface dewetting takes place, the fractal structure collapses, and the discrete steps disappear. Above 400 K the compact three-dimensional droplets start to shrink due to partial desorption. Finally at 600 K the flat and clean silica surface is recovered (data not shown).

Fig. 3.7: AFM image recorded after heating the sample to 375 K. Surface dewetting takes place and the molten polymer forms 3 dimensional islands. The image has a total height range of 190 nm. The scan was performed at room temperature. The scan area is 50 x 50 μm².
Fig. 3.8: AFM image recorded after heating the sample to 405 K. Due to surface dewetting small micro droplets and rim-like structures appear (small white spots). The larger islands start to shrink due to partial desorption and redistribution of mobile species over the silica surface at 405 K. The image has a total height range of 140 nm. The scan was performed at room temperature. The scan area is 50 x 50 μm².

The desorption onset at 405 K observed by the AFM investigation is no artifact of the tip that moves the PEG micro droplets on the surface since the data presented in figure 3.7 and 3.8 were taken after cooling down to room temperature. A strong influence of the tip on the polymer film can also be excluded by scanning a small (e.g. 5x5 μm²) square of the sample surface and then switching back to a larger scan area: no topographic modification stemming from the first scan was observed.

**XPS Analysis**

In figure 3.9 XPS data on the thermal degradation and desorption of a submonolayer PEG 1500 film under ultrahigh vacuum conditions is shown. Heated with 0.1 K/s the carbon 1s peak is depleted until it completely vanishes at 600 K. Within the limits of the relatively low energy resolution of the real time XPS measurement, no chemical shift in the C 1s or the O 1s
binding energy was found. Transient formation of new chemical species on the surface can therefore be ruled out.

Fig. 3.9: Temperature evolution of the C 1 s peak measured with XPS (count rate plotted vs. binding energy and surface temperature). The heating rate in this experiment was 0.1 K/s.

Fig. 3.10: The surface coverage measured with XPS (full line) does not follow the surface depletion (dotted line) expected from the desorption signal (gray shaded area). For determining the desorption rate, the protonated monomer at m/z=45 was recorded.
In figure 3.10 the temperature dependent decrease of the XPS signal is compared to the TPD data. Surprisingly, the XPS signal does not reflect the decrease of the surface coverage \( \theta \) calculated by integrating the measured desorption rate according to the formula

\[
\theta = \theta_0 - \beta^{-1} \int_{T_0}^{T} \dot{\theta} \, dT
\]

where \( \theta_0 \) is the initial surface coverage, \( \beta \) is the heating rate and \( \dot{\theta} \) is assumed to be proportional to the ion current in the mass spectrometer. Above 350 K the XPS signal starts to decrease whereas no desorption is detected. We interpret this early drop in the XPS signal as a dewetting transition of the polymer film. At the onset of desorption the XPS signal continues to falls progressively. At \( T = 560 \) K, when the desorption rate reaches a maximum, the decrease of the XPS signal does not follow as quickly. Even at temperatures where desorption is almost complete some surface coverage can still be detected with the XPS. This conflict of the XPS surface coverage signal and the depletion of the surface by desorption of PEG fragments is resolved by the variable temperature AFM images. The decrease of the C 1s XPS signal prior to the onset of desorption is a natural consequence of the structural changes in the PEG layer. Due to the narrow escape depth (=10 Å) of the photoelectrons the XPS signal accounts only for the topmost layer of the polymer film. Only those molecules from which photoelectrons can be emitted contribute to the C 1s peak. Therefore the surface sensitivity of the emitted photoelectrons leads to an underestimation of the total amount of polymer on the surface if three-dimensional clusters are formed. Opposite to this trend, if the surface coverage has fallen below a critical value the vertical molecular orientation is not stabilized any more. Some mobile PEG fragments oriented parallel to the surface will contribute with a higher relative intensity to the photoemission signal. The fact that at 600 K some polymer fragments are still detected on the surface by XPS, whereas the mass spectrometer hardly detects any desorption, can also be explained. At low temperatures each PEG molecules that is removed from the surface contributes with 40 monomer units to the ion signal of the QMS,
but only liberates approximately 100 Å² of the silica surface. At high temperatures the surface coverage consists of smaller fragments which can desorb, but they induce a lower ion current in the mass spectrometer than would an intact polymer chain. Total disappearance of the C 1s XPS signal at 680 K indicates that the polymer film is fully desorbed without formation of residual graphitic carbon contamination on the silica surface.

**Determination of Equilibrium Reaction Kinetics**

The desorption temperature of PEG molecules under slow heating conditions rises with increasing molecular mass as shown in figure 3.11. With respect to the mass dependence of the desorption temperature one can distinguish two regimes. In the regime below 1500 Da each additional monomer unit shifts the desorption temperature up by approximately 10 K. In contrast, the desorption temperature rises by less than 0.5 K per monomer unit in the range from 1500 Da to 35000 Da.

In figure 3.12 TPD traces of PEG 300, PEG 1500 and PEG 20000 recorded at heating rates of 0.02 and 0.5 K/s as well as fitted desorption rates calculated from the Polanyi-Wigner differential equation for first order kinetics are depicted. The broader shape of the desorption curves is partly due to experimental effects, like the finite pump rate and thermal gradients across the sample surface, and partly due to the width of the oligomer distribution of the investigated PEG molecules (figure 3.13).

The TPD traces do not show a distinct multi-peak structure. This is the reason why we did not consider different kinetic parameters for isolated molecules, lateral aggregates, or three-dimensional clusters, and also neglected the influence of diffusion effects on the kinetics in the fits. This is perhaps not entirely justified. However, it proved to be a simple way to fit all our data reasonably well. The corresponding kinetic parameters shown in table 3.1 are therefore given with generous error bars. The equilibrium desorption kinetics depend significantly on the molecular weight. Submonolayer desorption of low mass molecules (≤ 600 Da) is characterized by first order Arrhenius kinetics, with frequency factors on the order of 2·10¹⁶ Hz. The corresponding activation energies rise linearly from 70 kJ/mol for the monomer to 145 kJ/mol for PEG 600. PEG 300 shows a
slight deviation from the linear dependence of the activation energy on the molecular weight. This effect is due to the finite vapor pressure of this compound resulting in a fractionation or "distillation" of the PEG 300 oligomers in vacuum: lower mass oligomers are pumped away preferentially, resulting in a relative accumulation of higher mass oligomers. In the high mass regime (> 1500 Da) the kinetics are characterized by preexponential factors on the order of \(2 \cdot 10^{21}\) Hz. The corresponding activation energies are on the order of 265 kJ/mol. They increase only slightly towards higher mass. Desorption of PEG molecules between the two regimes (1000 < m < 1500 Da) is described by intermediate parameters, frequency factors on the order of \(5 \cdot 10^{18}\) Hz and activation energies ranging from 175 to 220 kJ/mol.

Fig. 3.11: Desorption temperatures of PEG oligomers at a heating rate 0.5 K/s. The maximum of the desorption peak determined by TPD measurements is displayed versus molecular mass. Error bars for desorption temperatures are ± 10 K. For the error of the molecular mass the relative width of the oligomer mass distribution is indicated.
Fig. 3.12: TPD signal of PEG 300, PEG 1500, and PEG 20000 desorbing from silica at heating rates of 0.02 and 0.5 K/s (dotted lines) and fitted desorption rates based on first order kinetics (solid lines). The corresponding fit parameters are given in table 3.1. The broader shape of the experimental curves is mainly due to the width of the oligomer distribution of the PEG molecules investigated (compare to figure 3.13).
Fig. 3.13: Recorded TPD trace of PEG 600 desorbed at a heating rate of 0.5 K/s (thick solid line), calculated desorption traces for the various oligomers within the oligomer distribution of "PEG 600" (thin dotted lines) and sum of the calculated contributions of the various oligomers to the TPD signal (thin solid line).

Table 3.1: Experimentally determined parameters describing PEG desorption and dissociation kinetics at slow heating rates (compare to figure 3.12).

<table>
<thead>
<tr>
<th>molecule</th>
<th>activation energy [kJ/mol]</th>
<th>preexponential factor [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG monomer</td>
<td>70 ± 2</td>
<td>5·10^{16} ± 2·10^{16}</td>
</tr>
<tr>
<td>PEG dimer</td>
<td>76 ± 2</td>
<td>5·10^{16} ± 2·10^{16}</td>
</tr>
<tr>
<td>PEG 300</td>
<td>132 ± 3</td>
<td>5·10^{16} ± 2·10^{16}</td>
</tr>
<tr>
<td>PEG 600</td>
<td>145 ± 3</td>
<td>5·10^{16} ± 2·10^{16}</td>
</tr>
<tr>
<td>PEG 1000</td>
<td>176 ± 3</td>
<td>5·10^{18} ± 1·10^{18}</td>
</tr>
<tr>
<td>PEG 1500</td>
<td>220 ± 5</td>
<td>1·10^{19} ± 0.5·10^{19}</td>
</tr>
<tr>
<td>PEG 20000</td>
<td>265 ± 5</td>
<td>5·10^{21} ± 2·10^{21}</td>
</tr>
<tr>
<td>PEG 35000</td>
<td>270 ± 5</td>
<td>5·10^{21} ± 2·10^{21}</td>
</tr>
</tbody>
</table>
The differences in the desorption kinetics of PEG molecules in the low and high mass regimes are strong indications for different processes during surface heating. The activation energies determined for PEG molecules with masses greater than 1500 Da agree with dissociation energies of PEGs and other polymers [115, 130]. Frequency factors on the order of $10^{21}$ Hz also are consistent with those reported for the dissociation of biomolecules [79, 81]. In the low mass regime frequency factors do not depend on the molecular mass, whereas each additional monomer unit leads to an increase of the activation energy by 8 kJ/mol. In the whole regime from monomer to PEG 600, frequency factors are 5 orders of magnitude smaller than those found for the dissociation of the large PEG molecules, another indication that a different mechanism prevails in the low mass regime. The characteristic dependence of the activation energy on the molecular size in this mass regime is consistent with the idea that the PEG molecules desorb intact. The mass dependence of the temperature at which maximum desorption is obtained, as well as the kinetic parameters found support the interpretation that under slow heating conditions the regime of intact desorption is overtaken by dissociative desorption at a molecular mass of $\approx 1000$ Da.

### 3.5 Nanosecond Laser-Induced Thermal Desorption

The spatial profile of the CO$_2$ laser pulses used for surface heating in this study was not a "top hat" but rather a Gaussian. Therefore, the surface temperature varies with the distance from the center of the beam spot. In figure 3.14, temperature transients determined by integration of the one-dimensional heat diffusion equation using the parameters of silica given in chapter 2.3 are depicted. The upper trace is the temporal evolution of the temperature for maximum power density in the center of the beam, whereas the lower one represents the result expected for 50 % of the maximum power density. In the central region of the laser spot, temperatures of about 1000 K are reached at a rate of $4 \times 10^9$ K/s. In the following discussion temperature transients within the half width of the gaussian profile are considered.
Time-of-flight distributions were measured for the different PEGs, and were fitted with Maxwell Boltzmann (MB) distributions (figure 3.15). No stream velocity was used for the fits since surface coverages were kept low enough to avoid the formation of a Knudsen layer, and no effect of an additional velocity compound to the quality of the fits was observed. The fact that variation of the surface coverage did not lead to significant changes of the TOF distributions also indicates that major influence of postdesorption collisions on the velocity distributions at the low surface coverages used can be ruled out. For the fits, we first excluded the possibility of dissociative desorption and assumed the mean PEG molecular mass to be the mass entering into the Maxwell Boltzmann distributions. The velocity distributions of PEG molecules with masses less or equal than 600 Da can be fitted well with Maxwell Boltzmann distributions using the average molecular weights
and temperatures less or equal to the maximum surface temperature. This simple fitting of the data completely fails for PEGs ≥ 1000 Da: the temperatures necessary for a tolerable MB fit exceed the maximum surface temperature by far.

Fig. 3.15: Time-of-flight distributions of laser desorbed PEG oligomers (dots) are depicted together with the corresponding fitted Maxwell Boltzmann distributions (solid lines). The Maxwell Boltzmann temperature $T_{MB}$ resulting from the fits and the average PEG molecular weights are inserted for each trace.
If the MB temperature entering into the fits for the large PEGs is kept constant and set to the maximum surface temperature, but the fragment mass is allowed to vary, the upper limit of the fragment mass is estimated to lie at ≈ 800 Da. This shows that the transition from desorption to dissociation cannot be shifted towards higher mass using nanosecond laser heating instead of classical heating. Since jet effects can be ruled out as a reason for increased velocities of desorbed species when working at low surface coverages and low desorption flux, we interpret the fast TOF distributions of the large PEGs as fragmentation of the parent molecules originally present on the surface. The data for large PEGs also exhibits some deviation from pure MB behavior: some fast particles are detected, which can be interpreted as a contribution of small fragments to the signal.

In addition to the temperatures obtained from the MB fits, the surface temperature at which the desorption rate reaches a maximum under LITD conditions was calculated by numerical integration of the Polanyi-Wigner equation. In these calculations we assumed that first order equilibrium kinetics still apply at heating rates of ≈ 10⁹ K/s. To account for the gaussian profile of the laser pulse, desorption rates were calculated for the two temperature transients depicted in figure 3.14, corresponding to the maximum power density and half the maximum power density in the laser profile. Even though the choice of the two temperature transients represents a fairly conservative estimate for the uncertainty of the heating rate, the variation in desorption temperatures is rather small. For direct comparison, temperatures from the MB fits and from the desorption simulations are compiled in table 3.2. The TOF results of PEG 600 agree well with equilibrium kinetics, whereas TOF temperatures of the monomer and the dimer fall slightly short of the ones predicted by equilibrium calculations. These small deviations do not necessarily involve strong nonequilibrium effects but can be explained by a weak physisorption well in the desorption channel [143]. An additional potential well of only 10 meV (= 1 kJ/mol) is sufficient to shift the TOF temperatures down by 50 K.
Table 3.2: Maxwell Boltzmann temperatures \( (T_{MB}) \) extracted from the best fit to the measured time-of-flight distributions. For comparison the surface temperatures of maximum desorption rate \( (T_{Des}) \) calculated assuming first order equilibrium kinetics for LITD conditions is given in the second column. Desorption temperatures for the highest and lowest surface temperature transients depicted in figure 5 representing the temperature at the center of the laser beam and at the half width, respectively, were determined. The corresponding temperature values are identified as "high power limit" and "low power limit".

<table>
<thead>
<tr>
<th>molecule</th>
<th>( T_{MB} [K] )</th>
<th>( T_{Des} [K] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-monomer</td>
<td>360</td>
<td>420 high power limit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>410 low power limit</td>
</tr>
<tr>
<td>PEG dimer</td>
<td>370</td>
<td>460 high power limit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440 low power limit</td>
</tr>
<tr>
<td>PEG 600</td>
<td>790</td>
<td>840 high power limit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>660 low power limit</td>
</tr>
</tbody>
</table>

3.6 Picosecond Laser-Induced Thermal Desorption

In figure 3.16 temperature transients following picosecond laser irradiation are depicted. The traces were determined by integration of the one-dimensional heat diffusion equation for the silica/tungsten substrate. In the case of tungsten at 300 K the heat capacity is 24.1 \( J/(K\cdot mol) \) and the thermal conductivity is 1.38 \( W/(K\cdot cm) \). The temperature dependence of the heat capacity and the thermal conductivity as given in refs. [115, 116, 144] was used. In the source term the absorption coefficient of \( 4.6\cdot 10^5 \ cm^{-1} \) of tungsten and the measured reflectivity of 60 % of the SiO\(_2\)/W substrate were taken into account. Since the SiO\(_2\) layer does not absorb the laser light, it does not enter the source term but was considered in the heat diffusion term. The simulations show that the SiO\(_2\) surface equilibrates quickly and that the temperature transients on the surface of the SiO\(_2\) layer are very close to those at the SiO\(_2\)/W interface. The upper trace in figure 3.16 characterizes the temporal evolution for pulses with a fluence of 60 mJ/cm\(^2\) whereas the lower one represents the result for 30 mJ/cm\(^2\). The maximum surface temperatures are 1500 and 900 K, the heating rates \( 3\cdot 10^{13} \ K/s \) and \( 1.5\cdot 10^{13} \)
K/s, respectively. Due to the large thermal conductivity of tungsten the surface temperature declines rapidly with a decay time on the order of a few hundred picoseconds.

![Graph showing the evolution of surface temperature](image)

Fig. 3.16: Calculated evolution of the surface temperature of a SiO₂ surface irradiated by a 35 ps FWHM Nd-YAG laser pulse at 1064 nm (dotted line). The upper solid trace is for a fluence of 60 mJ/cm² whereas the lower one represents the result for 30 mJ/cm².

Time-of-flight distributions of the different molecules and corresponding Maxwell Boltzmann distributions are shown in figure 3.17. Only the velocity distributions of ethylene glycol can be fitted well with Maxwell Boltzmann distributions using the correct molecular mass and a temperature less than the maximum surface temperature. Already for the desorption of PEG 600 and PEG 1500, the fits yield temperatures far higher than the maximum surface temperatures. Maxwell Boltzmann temperatures at or below the maximum surface temperature are only obtained for PEGs ≤ 300 Da. This can be interpreted as evidence that PEGs with masses > 300 Da desorb dissociatively if picosecond laser heating is applied.
Fig. 3.17: Measured time-of-flight distributions of submonolayer coverages of PEG oligomers (dots) following picosecond laser surface heating and fitted Maxwell Boltzmann distributions (solid lines). The Maxwell Boltzmann temperatures $T_{MB}$ indicated were obtained by using a mass equal to the average molecular weight of the PEG samples used. For each molecule the upper trace represents the TOF distribution for a fluence of 30 mJ/cm$^2$, whereas the lower one is for 60 mJ/cm$^2$.

In addition to the temperatures obtained from the MB fits, the surface temperature at maximum desorption rate under LITD conditions was calculated for ethylene glycol by numerical integration of the first order Polanyi-Wigner differential rate equation. In these calculations we assumed that first order equilibrium kinetics still apply at heating rates of $\approx 10^{13}$ K/s.
The calculations yield that for both laser fluences employed, ethylene glycol desorbs completely during the rising edge of the temperature transient. Maximum desorption was determined to occur at 730 K in the high fluence case and at 700 K in the low fluence case. These temperatures agree very well with the Maxwell Boltzmann temperatures determined from the TOF distributions, 740 K and 700 K, respectively. This finding strongly suggests that no major deviations from thermal equilibrium have to be postulated, even at a heating rate of $10^{13}$ K/s.

### 3.7 Discussion

The comparison of the kinetic energies of intact desorbed molecules and simulated desorption temperatures show that even desorption induced by fast picosecond laser heating fits well into a thermal equilibrium kinetic model. The mass at which intact desorption is taken over by dissociation is reduced with faster heating. Therefore, for PEG submonolayers on silica fast laser heating is less suitable than classical heating to induce intact desorption.

In figure 3.18 dissociation and desorption rates of various PEGs are plotted as a function of temperature. The desorption rates of ethylene glycol, PEG 600, and PEG 1500 were calculated from the thermal equilibrium kinetic parameters determined in the TPD experiments (table 3.1). The black area indicates a range of rates which is expected to comprise the dissociation rates of the various PEGs. It covers activation energies of 250 ... 270 kJ/mol and frequency factors from $1 \cdot 10^{19}$ to $5 \cdot 10^{21}$ Hz. The ratio of the depicted rates is strongly temperature dependent. The kinetics of the monomer, a typical representant of a weakly adsorbed molecule, are dominated by intact desorption in the whole temperature regime relevant to this study. PEG 600 is bound more strongly to the surface and to neighboring molecules than the monomer. Due to the increased activation energy the desorption rates are shifted to lower values. They cross the dissociation rates of the large oligomers at $\approx 1000$ K. This rate crossover, even though the dissociation rates were not determined explicitly for PEG 600, reflects the experimental
findings: Under classical and nanosecond laser heating conditions intact desorption is observed in the experiments. The corresponding calculated desorption temperatures are below 1000 K. Picosecond laser heating is expected to shift the temperature to the range where the dissociation rates dominate. This is consistent with the experimental finding that PEG 600 dissociates under picosecond laser heating conditions. The rates for intact desorption of PEG 1500 and larger PEGs oligomers, representing strongly bound molecules, are shifted even further downwards. According to our experimental findings they are of vanishing importance compared to dissociation rates over the whole temperature range.

Fig. 3.18: Desorption and dissociation rates of various PEG oligomers depicted as a function of temperature. The black area represents the range of dissociation rates which was determined for the large PEG oligomers.

Our findings unambiguously show that fast laser heating is not a universal technique to induce intact desorption of thin surface coverages of nonvolatile species. The experimental results do not provide any indication that a bottleneck for energy flow plays any role. Furthermore, based on the equilibrium desorption kinetics found, a rate crossover which would lead to
intact desorption of the PEGs at high temperatures can be ruled out. For biomolecules a behaviour similar to the one of the PEGs can be expected. Even if our experiments clearly indicate limitations of fast laser heating at very low surface coverages, they do not contradict the general consensus that fast laser volatilization techniques can be used successfully for intact volatilization of macromolecular species. However, the positive effect of fast laser heating on intact desorption is limited to cases where either thicker films or mixtures with an excess of smaller matrix molecules are volatilized. Laser volatilization of such systems is addressed in the next chapter.

3.8 Summary

The most important findings of this systematic analysis of laser-induced thermal desorption of PEG submonolayers from silica are the following:

- The translational temperatures of PEG oligomers desorbed by nanosecond and picosecond LITD agree with calculated desorption temperatures based on equilibrium desorption kinetics.

- The highest mass PEG oligomer that can be desorbed intact from silica is smaller under picosecond heating conditions than under classical heating conditions, which is consistent with a thermal equilibrium kinetic model for desorption and dissociation.
4 Laser-Induced Molecular Desorption and Particle Ejection from Organic Films

4.1 Introduction and Background

Presently, the most successful concept for intact desorption of macromolecules is to volatilize them from a mixture with an excess of matrix molecules. The function of the matrix molecules for the success of these techniques is manifold: Solid-phase solvation or co-crystallization of the large molecules with smaller matrix species reduces the heat of sublimation of the desorption system. Co-desorption of the matrix contributes to collisional cooling in the gas phase. In practical applications laser-induced thermal desorption and resonant laser desorption techniques are both used. Due to different energy deposition schemes they require different absorption characteristics of the matrix molecules: Whereas in MALD volatilization is induced by resonant absorption of the matrix molecules [145], LITD is induced by laser excitation of the substrate and absorption of the matrix is therefore not desired. For MALDI mass spectrometric analysis it is further essential that the matrix molecules, typically organic acids, contribute to the ionization of the analyte species [41, 146, 147].

In the following an overview of the models which have been proposed for laser ejection of macromolecules from matrices is presented. These range from photothermal [52] to photomechanical [60-62, 148] and photochemical [33] models.
Matrix-Assisted Laser Desorption

With respect to elucidating volatilization in UV MALDI Hillenkamp and coworkers [149] investigated the fluence dependence of the yield of individual neutral molecules and ions. They did not find any discontinuities in the increase of the yield of individual molecules and ions as a function of laser fluence and argue that the amount of neutral and ionized molecules can be well described by a quasi-thermal desorption model which is based on an Arrhenius description of thermal equilibrium processes.

To account for high velocities and forward peaked angular distributions of ejected UV MALDI plumes [53, 54, 150-156] the authors suggest a two step model for desorption under UV MALDI conditions: in an essential instantaneous step the ablated volume disintegrates into a large number of small particles with a large surface area. These particles are expected to contain enough energy to melt and to evaporate neutrals in a second step. The idea of a thermal equilibrium desorption process is supported by the finding that the fluence needed to obtain a reasonable signal-to-noise ratio of the MALDI mass spectra linearly increases with decreasing initial sample temperature [157]. Electron microscopy of 2,5 dihydroxybenzoic acid (DHB) and sinapic acid single crystals yielded that cones with a base ranging from 2 to 20 nm are formed at the laser focus [158]. However, these investigations did not unambiguously prove that particulates are generated and ejected in the UV MALD process.

Molecular dynamics simulations of laser ablation and desorption of organic solids by Garrison and coworkers [58, 159, 160] yielded that a threshold fluence separates two mechanisms for the ejection of molecules: surface vaporization at low fluence and collective ejection and ablation at high fluence. The authors report that below the threshold fluence, primarily single molecules are desorbed from the surface due to thermal fluctuations in the energy. The calculations yield that the amount of ejected material rises sharply at the threshold fluence and that at fluences exceeding the threshold, large molecular clusters constitute a significant part of the laser-ejected plume. Consistent with the findings of the Hillenkamp group, the authors report a continuous increase of desorbed individual molecules with increasing fluence. The calculations yield that at fluences exceeding the threshold value, the laser pulses induce a high pressure in the irradiated
material and an explosive homogeneous phase transition that leads to the strongly forwarded emission of ablated material and high maximum velocities of the ejected plume expansion.

In IR MALDI, photons in the wavelength range from 1 to 10.6 μm are used for resonant vibrational excitation of the matrix molecules. In IR MALDI typical penetration depths of the laser radiation is on the order of ten to several tens of micrometers whereas they are ≈ 100 nm in UV MALDI. The laser fluences which are required for obtaining reasonable mass spectra are typically one order of magnitude higher for IR MALDI (≈ 600 J/m² [158]) than for UV MALDI (≈ 60 J/m² [149]) and therefore the energies density per unit volume at the MALDI threshold are 10-100 times smaller in IR MALDI than in UV MALDI. Under UV MALDI conditions the laser induced energy density is comparable to the sublimation energy of the matrix, however it does not suffice for sublimation under IR MALDI conditions. This simple energy consideration clearly suggests that different desorption processes are operative in IR and UV MALDI [158]. The Hillenkamp group reports [161], that the IR MALDI process for laser pulse durations of 100 ns or longer is dependent on the laser irradiance rather than the laser fluence. This finding is in contrast to the fact that for UV MALDI a fluence dependence of the MALDI signal was found in the typical pulse duration range of 0.5 to 20 ns. Based on these findings the authors favor a spallation model for IR MALDI according to which chunks of material are ablated due to mechanical stress [161]. Kampmeier et al. [158] showed that single pulses of a Er-YAG laser at a typical IR MALDI fluence of ≈ 700 J/m² lead to photodamage of DHB and sinapic acid single crystals that is clearly visible by scanning electron microscopy. Droplets at the ablation site indicate melting and resolidification of at least a part of the excited volume, whereas numerous cracks clearly indicate the impact of mechanical stress. The ablation depth of succinic acid single crystals under typical IR MALDI conditions was found to be 5 μm.

Valuable additional information on resonant IR ablation of multilayer films is provided in a study by Braun and Hess [31]. They performed TOF investigations on IR laser-induced resonant ablation of benzene layers condensed on cooled substrates. Their data on the dependence of the mean kinetic energy on the laser fluence suggests melting of the laser-irradiated
material prior to desorption. The authors argue that a transient pressure rise in the adsorbate of several orders of magnitude is obtained during laser excitation. The pressure difference between the adsorbate and its surrounding is believed to be the main driving force of the ablation process. The dynamics of the pressure release lead to an energy-momentum transfer from deeper layers to the ejected upper layers. Besides collisional cooling in the desorption plume, this ejection mechanism is expected to be a major source for the high kinetic energies observed in multilayer volatilization experiments.

IR Ablation of Polymer Films
Matrix molecules for optimization of volatilization of analyte molecules are not only restricted to relatively small organic molecules. Haefliger et al. have proposed to embed the analyte molecules in a smooth polymeric membrane (PVC) to reduce the heterogeneity of the sample [162]. In the experiment a thin 50 μm film was completely vaporized by a single IR laser shot and in a second step the analyte molecules entrained in the expanding plume were ionized by pulsed UV radiation. The progress that has been realized by this sample preparation technique is the high reproducibility for ablation at different locations on the sample and a high linearity with respect to the analyte concentration. One of the problems of the technique is that it is very sensitive to fluctuations of the desorption laser power and that the detection sensitivity is strongly reduced compared to pure analyte films desorbed from silica.

Laser-Induced Thermal Desorption
One of the most impressive results obtained by fast substrate heating is the volatilization of DNA fragments with masses up to \(400,000\) Da by pulsed laser ablation of frozen aqueous solutions deposited on a copper substrate by Williams and coworkers [61, 163]. The authors report two distinct volatilization processes: spallation of macroscopic chunks of ice and ablation. According to them spallation is dominant when thick films are used, whereas ablation is more readily detectable in the case of thin films. The
authors explain their findings by a shock-based spallation model. This model considers that the rapid heating of the substrate to many thousand degrees results in an instantaneous pressure of \( \approx 50 \text{ kbar} \) at the substrate/ice interface. This shock is expected to heat the ice and compress it. Relaxation of the compression finally results in an explosive spallation of the adsorbate film. Subsequent cooling in the molecules in the ablation plume is regarded as the essential process for intact transfer of the molecules into the gas phase.

**Analysis of Particle Size Distributions**

One of the major drawbacks of all volatilization techniques described above is the fact that shot-to-shot fluctuations make the reproducibility of the amount of sample which is volatilized per shot problematic. For example, in UV MALDI the high sensitivity of the signal intensity to laser power fluctuations and sample heterogeneity makes quantitative analysis very delicate. Not only the variations of the total amount of material that is ejected, but also the ratio of ejected particles to individually desorbed molecules is crucial for many applications since ejection of particles reduces the sensitivity of the technique. This ratio also has implications for mechanistic considerations: absolute ionization yields cannot be obtained by simply comparing the amount of ablated material to the measured ion current. Instead, the amount of individually desorbed molecules has to be considered. With regard to thin film deposition of supraconducting materials, metal alloys, semiconductors, dielectrics, and diamonds, numerous studies have been performed in which the composition and topography of deposited material was analyzed by spectroscopic and microscopic techniques [11, 164-168]. However, up to now no reliable data is available on the ratio of particles and individual molecules in the desorption plumes obtained by the various experimental configurations which are typically applied for volatilization of macromolecules.

With respect to this question, a direct investigation of the composition of material ejected in UV matrix-assisted laser desorption, IR laser ablation, laser-induced thermal desorption, and volatilized from electrically heated
filaments is presented. The central questions that are addressed are the following:

- What are the mechanisms involved in the various volatilization techniques?
- Which volatilization method is best suited for intact molecular desorption of macromolecular compounds?

4.2 Experiment

Sample Preparation

The samples for LITD and MALDI experiments were prepared by the dried droplet technique which is commonly used in MALDI applications [169]. Poly (ethylene glycol) PEG 3000 and 2,5 dihydroxybenzoic acid were dissolved in methanol at a molar ratio of 1: 100 and then dosed onto a clean silica support. In figure 4.1 the AFM image of a typical MALDI sample is shown, DHB/PEG 3000, prepared by the dried droplet technique. The characteristic polycrystalline morphology of such DHB films has been previously described by Allwood et al. [145]. If not indicated otherwise we always used DHB/PEG layers with a typical thickness of approximately 1 μm for our LITD and UV MALDI investigations.

Polymer matrices for IR ablation experiments were made from a solution of 3 g of high molecular weight polyvinyl chloride (PVC) powder (Fluka) in 40 ml tetrahydrofuran (THF) (Fluka). 2 ml of the solution were poured into a 5 cm diameter petri dish. A 50 μm thick membrane was obtained after the THF had evaporated, a process that requires at least one hour to ensure that the membrane is perfectly dry. The solid membrane was taken out of the petri dish and cut to pieces of about 1 cm².
Fig. 4.1: AFM image of a typical sample used for the IR LITD and UV ablation experiments: The DHB/PEG polycrystalline adlayer on silica was prepared by the dried droplet technique. (20 x 20 μm² scan; 800 nm height range)

**AFM Analysis of Deposited Material**

The transfer experiments were performed in a vacuum chamber which was pumped down to 10⁻⁶ Torr. AFM imaging of the deposited material was then performed ex situ.

The samples were irradiated with pulses from either the CO₂ laser which had also been used for the LITD studies presented in chapter 2 and 3, or from a N₂ laser (VSL-337ND-T, Laser Science Inc., Newton, MA, USA) at an angle of 45°. For laser heating of the substrate in the LITD experiments we applied single CO₂ laser pulses with a fluence of ≈ 2 J/cm². At 10.6 μm, the wavelength of the CO₂ laser laser, a DHB layer with a thickness of 1 μm absorbs only ≈ 10 % of the impinging laser energy [170]. We found that the DHB/analyte layer was volatilized completely by a single CO₂ laser shot if silica, which strongly absorbs the laser radiation, was used as a substrate, whereas only a small part of it was desorbed if reflecting materials such as metals were used. This clearly indicates that substrate heating is the dominating process in the case of CO₂ laser ablation of DHB adlayers from silica. These conditions are comparable to laser-induced back side heating
of MALDI substrates [62, 171]. The CO₂ laser-induced surface temperature transient can be calculated by numerical integration of the one-dimensional heat diffusion equation. The maximum temperature obtained in the calculations for laser heating of an uncovered silica plate is \( \approx 1100 \) K, with heating rates on the order of \( 10^9 \) K/s. If the silica surface is coated with a thin film of 1 \( \mu \text{m} \) of low absorption the maximum interface temperature and the heating rate will be reduced by less than 30%. In the flash filament experiments a polycrystalline DHB/PEG 3000 mixture was volatilized from a thin tungsten filament which was extracted from a 1.2 V light bulb. The filament was heated by 2 \( \mu \text{s} \), 70 V electrical pulses.

![Sample trapping plate](image)

**Fig. 4.2:** Schematic of the transfer experiment. Molecules were desorbed from the sample and the normal component of the ablation plume was collected on a trapping plate mounted at 30 mm working distance.

In all cases the normal component of the ablation plume was collected on the trapping plate (figure 4.2). Silica wavers with a roughness of less than 0.5 nm and highly oriented pyrolytic graphite (HOPG) substrates were used as trapping plates. The surface morphology of the deposited films was analyzed using an atomic force microscope (Lumina, Topometrix), which was operated in "non contact mode" mode as described in chapter 3.2. For a correct interpretation of the AFM images one has to consider that the deposited material can change in morphology and composition due to diffusion and desorption processes on the trapping plate. The interpretation of the data is further complicated because identical sticking probabilities on
the trapping plate cannot be assumed for particles of different energy and size. We therefore complemented our measurements with experiments where annealing of the deposited material was carried out to distinguish between volatile and mobile species and immobile macromolecules.

4.3 Laser-Induced Thermal Desorption

The AFM image shown in figure 4.3 proves that under LITD conditions large particles are transferred from the target to the trapping plate. The particles have a lateral extension of typically 2 μm and a height of typically 500 nm. Annealing of the deposited material for 1 h at 400 K leads to shrinking of the height of the particles from ≈ 400 nm to ≈ 20 nm whereas the lateral extension of the particles diminishes only slightly (fig. 4.4). PEG 3000 does not desorb at a temperature of 370 K. Therefore the observed volume reduction is due to the evaporation of the more volatile DHB. No significant lateral diffusion of the remaining PEG is observed during the annealing cycle. Each particle is surrounded by a halo of small clusters (diam. < 30 nm), probably originating from the impact of the large particles with the target plate (figure 4.4 b). These are also present in fig. 4.4 a but invisible because of the vastly different z-range of the AFM. The integrated volume of these clusters is much smaller than the volume of the large particles. If a film of reduced thickness (≈ 500 nm) is volatilized under equal laser heating conditions, the ejected clusters are much smaller (figure 4.5).

The cluster size distribution exhibits two main components: Microcrystallites of about 500 nm diameter and small clusters of less than 100 nm diameter (figure 4.5 b). The absence of a homogeneous molecular film on the trapping plate indicates that molecular desorption does not contribute significantly to the overall material transfer. The large fraction of particles in the ablation plume is a direct consequence of fast laser heating of the silica substrate. Only material close to the silica/matrix interface is efficiently heated (figure 4.6). The outer part of the film remains relatively cold during the process. In an interfacial layer of about 200 nm thickness temperatures exceeding 800 K
are reached. For DHB desorption rates as high as $10^{10}$ s$^{-1}$ are expected at these temperatures. These high desorption rates will induce a pressure pulse which leads to spallation of the whole matrix film. A similar mechanism has been proposed by Williams and Nelson [61, 163] to explain the intact volatilization of DNA molecules embedded in thin ice films.

![AFM image of laser deposited DHB/PEG particles on a silicon wafer. The material was volatilized from a sample similar to figure 4.1 by a single ns CO$_2$ laser pulse with a fluence of 0.25 J/cm$^2$ (20 x 20 $\mu$m$^2$ scan; 600 nm height range).](image)
Fig. 4.4: (a) Single trapped DHB/PEG particle (5 x 5 μm² scan; 400 nm height range). (b) After annealing at 400 K for 1 hour the particle has shrunk to a height of 20 nm and to less than 1/20 of its initial volume. DHB is completely vaporized and only PEG is left on the surface.
Fig. 4.5: (a) AFM image of laser deposited DHB/PEG particles on a silicon wafer. A DHB/PEG layer with a thickness of ≈ 500 nm was volatilized by a single ns CO₂ laser pulse with a fluence of 0.25 J/cm². (5 x 5 μm² scan; 350 nm height range). (b) Detail of figure 4.5 a (1.5 x 1.5 μm² scan; 300 nm height range).
Fig. 4.6: Calculated temperature profiles of an organic film adsorbed on a substrate heated at 1000 K/s (top panel) and at $10^9$ K/s (bottom panel). The one dimensional heat diffusion differential equation was numerically solved using a linear increase of the temperature at the substrate - adsorbate interface as boundary condition. For the organic film we used the thermal constants of nicotinic acid: specific heat = 150 J/mol·K; thermal conductivity = $2\times10^{-3}$ W/cm·K; molar volume = 84 cm$^3$/mol. These values are typical for commonly used MALDI matrices.
4.4 Flash Filament Volatilization Techniques

Electrical heating has previously been used to vaporize molecules of up to several kDa [172-177]. The fundamental idea in these experiments is to induce fast heating by applying fast electrical pulses to resistor devices with a small heat capacity. We volatilized a polycrystalline DHB/PEG 3000 adlayer from an electrically heated thin tungsten wire. The layer thickness we applied in the experiments was typically $\geq 5 \mu$m. The temporal evolution of the temperature of the heated filament was determined by blackbody radiation measurements using a fast photodiode, calibrated against a pyrometer (figure 4.7). A temperature jump of $\geq 900$ K and a maximum filament temperature of $\approx 1200$ K were found. The heating rate can be estimated to be $5 \times 10^8$ K/s, only slightly lower than the heating rates obtained by the CO$_2$ laser. As for LITD, a large majority of the material is ejected as particles with a size of some hundreds of nanometers (figure 4.8). During the transfer experiment, the left part of the trapping plate was shielded with a thin aluminum foil to avoid precipitation of material there. This lead to an edge in the deposited film, from which its thickness could be determined to be $\approx 120$ nm. The surface morphology did not change significantly after storing the trapping plate for 24 hours, indicating the absence of diffusion. Our AFM investigations did not indicate a large fraction of material desorbing molecularly. However, Karbach et al. [178] recently succeeded in detecting molecular ions, K$^+$ adducts and protonated species, using a similar set-up. They deposited the samples with an excess of glycerol onto a pulsed filament source which allowed stable and reproducible ion production of a variety of compounds, including biomolecules and synthetic polymers with masses up to 3000 Da.

Our findings lend support to the notion that electrical filaments have the potential to compete with LITD techniques. Advantages of flash filaments are their low cost, the small dimensions, and simplicity. This makes them very attractive with respect to future optimizations of volatilization devices.
Fig. 4.7: Blackbody radiation signal of the thin tungsten filament used in the fast flash desorption experiments.

Fig. 4.8: AFM image of a DHB/PEG mixtures deposited by flash desorption from an electrically heated filament (5 x 5 µm² scan; 120 nm height range). During deposition, the left part of the trapping plate was shielded with a thin aluminum foil to avoid precipitation of material there.
4.5 UV Matrix-Assisted Laser Desorption

At a fluence of 40 J/m² small particles of less than 200 nm diameter in addition to a thin molecular film of 1 nm thickness cover the trapping plate (fig. 4.9). The film thickness was measured after removing a 1 µm² square of the film by scanning the AFM tip at high contact force and determining the depth of the tip-induced pit (figure 4.10). This structure is thermally stable at 350 K for several hours and expected to consist mainly of PEG molecules. The smoothness of the film is a strong indication that PEG molecules have been deposited as molecules or as very small DHB/PEG clusters. In postionization experiments, contributions to the signal can be expected from both, individual molecules and small clusters.

If the laser intensity is increased to 120 J/m² the total amount of ablated material is much higher (figure 4.11). The trapping plate is covered with a film of ≈ 20 nm thickness speckled with clusters of ≈ 200 nm diameter and 30 nm height. The low roughness of the film can be explained again by deposition of individual molecules or small clusters. Diffusion after landing may also play a role, but it seems unlikely that the mobility of the PEG molecules at 300 K is sufficient to assemble to a smooth film spontaneously. Even though the plume may be hotter than 300 K, a molecule hitting the surface will be thermally quenched to the substrate temperature on a picosecond timescale and will stick at its initial landing position [127, 128, 179]. Diffusion controlled growth has been observed only if the surface mobility is enhanced by a solvent, in contrast to the dry deposition conditions used here. Considering that the analyte molecules are typically not uniformly distributed within the matrix crystals and that there are even crystallites in which no analyte molecules are incorporated [169], we interpret the holes in the deposited film as DHB clusters that were transferred from the sample to the target and that vaporized before the AFM images were taken.
Fig. 4.9: (a) AFM image of DHB/PEG deposited by 10,000 N₂ laser pulses with a fluence of 40 J/m² (5 x 5 µm² scan; 15 nm height range). (b) AFM image of DHB/PEG deposited under the same conditions as in fig. 4.9 a (5 x 5 µm² scan; 10 nm height range). In the center of the image a 1 µm² square of the film was removed by scanning the AFM tip using a strong contact force.
A comparison of the AFM images recorded at laser fluences of 120 and 40 J/m² unambiguously shows that much more material is desorbed as individual molecules if high fluences are applied. The fact that we were able to detect transferred sub-μm sized particles at fluences exceeding the volatilization threshold strongly supports the model by the Hillenkamp group [149, 157] according to which particles are expected to play an important role in the volatilization process under MALDI conditions. Our finding of increased molecular desorption and decreased particle ejection at higher laser fluences is also fully consistent with the results of the molecular dynamics calculations by Garrison and coworkers [58, 159, 160]. Besides the direct implication for mass spectrometry these results may also have consequences for the dry growth of ultra thin macromolecular films [10].
Fig. 4.11: (a) AFM image of DHB/PEG deposited by 10,000 $\text{N}_2$ laser pulses with a fluence of 120 J/m$^2$ (5 x 5 $\mu$m$^2$ scan; 40 nm height range). The silica surface is covered with a thin 20 nm film speckled with holes and particles. (b) Detail of figure 4.11 a (1.5 x 1.5 $\mu$m$^2$ scan; 40 nm height range).
4.6 Laser Ablation of Polymer Thin Films

For pulsed IR ablation the threshold for PVC volatilization is on the order of 2 J/cm². At 1.5 J/cm², the target membrane remained intact and no polymer ejecta were found on the trapping plate. If the laser fluence was increased to 3.5 J/cm² the target membrane was fully perforated and the trapping plate was covered with small micro droplets (figure 4.12). Micro droplets were also found at 6 J/cm² but additionally, a thin 10 nm polymeric film covers the trapping plate at this fluence. We interpret the characteristic shape of the droplets to originate from the impact of molten polymer with the target surface. The homogeneous film can be attributed to material which is transferred either as single molecules, polymer fragments, or small clusters. The fraction and size of the ejected particles varies strongly with the applied laser intensity. At a fluence of 6 J/cm² the ratio of material that stems from clusters <10 nm and species that have reached the target plate via larger clusters is about 1. The diameter of the microscopic droplets lies between 100 nm and 2 µm. The impact of the hot polymer micro droplets seems to melt the thin polymer film covering the whole trapping plate. This can be seen by the dewetted surface around each micro droplet (figure 4.12 b), which also implies that the molecular species have reached the trapping plate first. At lower laser intensities (3.5 J/cm²) less molecular species are desorbed and the micro droplets are larger (2-5 µm) (figure 4.13).

In the present case, IR volatilization is probably initiated by pyrolysis of some of the polymer. The polymer film absorbs about 2/3 of the IR laser energy and is heated to about 800 K (for a 6 J/cm² pulse). At this temperature pyrolytic decomposition of the PVC to HCl, benzene, and other low molecular weight compounds induces a sudden pressure pulse in the material which disintegrates the film [180] and leads to spallation of the particles found on the trapping plate. At 1.5 J/cm² the polymer film is only heated to about 430 K and remains thermally stable.
Fig. 4.12: (a) AFM image of laser deposited PVC particles on highly oriented pyrolytic graphite (HOPG). The PVC material was volatilized from a 50 μm PVC film by a single ns CO₂ laser pulse with a fluence of 6 J/cm² (20 x 20 μm² scan; 280 nm height range). Two terraces of the HOPG substrate are separated by a step edge running through the image. (b) Zoom of fig. 4.12 a (5 x 5 μm² scan; 60 nm height range).
Fig. 4.13: CO$_2$-Laser deposited PVC at a fluence of 3.5 J/cm$^2$ (20 x 20 µm$^2$ scan; 250 nm height range). The particles are significantly larger than the ones obtained at a fluence of 6 J/cm$^2$.

4.7 Discussion

Our AFM investigations show that the ratio of ejected particles and free molecules is strongly dependent on the laser volatilization technique. LITD and flash filament volatilization of $\approx$ 1 µm thick DHB/PEG polycrystalline films as well as IR volatilization of polymer films lead to the transfer of micrometer size particles from the target to the trapping plate. The energy density in the target material is not sufficient to induce a high degree of molecular vaporization. Rather, the sharp pressure rise and the thermal expansion of the sample material is the driving force for spallation and particle ejection. Under UV MALDI conditions, the energy densities are comparable with the sublimation energy of DHB (100 kJ/mol [158]). Therefore the contribution of individual molecules or small clusters dominates the ablation plume. Generally we observe that in all ablation experiments an increased laser fluence leads to a reduced particle size. However, the larger fraction of molecular desorption must be weighed against higher plume temperatures.
that may lead to dissociation of labile analyte molecules. Under MALDI conditions we expect the favorable situation that the highly volatile matrix molecules reach the molecular desorption regime already at moderate temperatures which are further reduced by collisional cooling in the expanding plume. However, if the laser induced energy density is too high, metastable decay of desorbed analyte molecules is possible [181].

In the case of IR laser ablation of polymer films, the energy densities that are induced in the material are comparable to UV MALDI but approximately one order of magnitude higher than in IR MALDI [158]. Compared to typical IR MALDI matrices the nonvolatile PVC film requires relatively high energy densities for disintegration. The pressure pulse driving the volatilization process therefore is not due to molecular desorption but stems from pyrolysis of the polymer. Jet cooling certainly also comes into play since the total amount of material that is ablated (and collected) per laser shot is very high. However the efficiency of gas phase cooling is reduced since a large fraction of the ablated material is ejected as large particles lagging behind the front of the expanding plume.

In addition to the experiments described here, AFM analysis of trapped species can be regarded as a valuable tool for characterizing new desorption concepts, for example the idea to desorb molecules from a solid sample by directing a hot molecular beam at the sample surface [182]. In this case investigation of ejected species may shed light on the underlying mechanisms and allow optimization of the technique.

4.8 Summary

The most important results of the systematic comparison of UV matrix assisted laser desorption, laser-induced thermal desorption, IR polymer ablation and electrical substrate heating techniques with respect to volatilization of individual molecules and particles are the following:

- The ratio of ejected particles and free molecules is strongly dependent on the laser volatilization technique. High energy densities in the sample, as
occurring for example in UV MALD, enhance the yield of individually desorbed molecules.

- Volatilization of molecular films from electrically heated flash filament is comparable to LITD with respect to the yield of individually desorbed molecules. Flash filaments can therefore be regarded as a simple and inexpensive alternative to desorption by lasers.
5 Summary and Outlook

Laser-Induced Thermal Desorption of Aniline Submonolayers
The study on laser-induced thermal desorption of aniline submonolayers from silica and glassy graphite shows that LITD of aniline up to heating rates of $10^{10}$ K/s is consistent with complete thermalization of the molecules during fast desorption. Under picosecond laser heating conditions at heating rates of $10^{13}$ K/s only the kinetic energy of the desorbed molecules agrees well with a thermal desorption model whereas the internal degrees of freedom are not fully equilibrated. This shows the onset of a bottleneck for energy flow from a rapidly heated substrate to the internal degrees of freedom of adsorbed species. However, rotational and vibrational temperatures of molecules desorbed by picosecond laser heating exceed those obtained under nanosecond laser heating conditions. Therefore, one can conclude that the bottleneck effect is not strong enough to compensate for the increase in desorption temperature associated with faster heating.

Desorption of PEG Submonolayers
The kinetic energies of intact desorbed PEG oligomers were found to agree well with simulated desorption temperatures based on thermal equilibrium desorption kinetics even under picosecond laser desorption conditions. We found that increased heating rates lead to stronger fragmentation of the PEGs. The mass of the largest oligomer that is desorbed intact becomes
smaller as the substrate is heated more rapidly. This is consistent with a
description based on thermal equilibrium desorption and dissociation
kinetics. These findings give support to the notion that in the case of
submonolayer surface coverages, where collisional cooling within the
desorption plume is negligible, fast laser pulses are not a universal tool to
induce intact desorption of macromolecules.

Laser-Induced Molecular Desorption Versus Particle Ablation
from Organic Films
The comparative study on UV matrix-assisted laser desorption, laser-
induced thermal desorption, IR laser ablation, and volatilization of molecular
films via electrical substrate heating showed that the ratio of ejected particles
to free molecules is strongly dependent on the (laser) volatilization
technique used. High energy densities in the sample, for example in UV
MALD, favor molecular desorption. In contrast, IR polymer ablation is
dominated by ejection of clusters and particulates. The experiments give
direct support to some of the ablation models which have been proposed for
UV MALDI [58, 149, 159, 160].

Strategies for Improved Desorption Devices
Our findings show that electrical heating is a potential substitute for laser-
induced thermal desorption/ablation techniques. Utilization of electrically
heated filaments might allow one to miniaturize and simplify volatilization
techniques. For example, in postionization mass spectrometry, the
desorption step may be carried out by a simple heating device. For practical
applications where many measurements have to be averaged the simple
thermal desorption technique can be refined. Instead of a single flash
filament a microstructured array of individually addressable heat sources
could be designed [183]. The advantages of pulsed filament desorption
sources are obvious: low cost, small dimensions, and simplicity. Possible
uses of the technique include miniaturized instruments for molecular
analysis, highly parallel volatilization devices using chips with arrays of
filament strips, instrumentation for remote sensing applications, and for thin film deposition. Flash filaments in combination with a novel sample preparation technique can be expected to result in tangible advantages with respect to reducing shot-to-shot fluctuations. We suggest to equip the filaments with a well defined ready-made matrix adlayer with a thickness on the order of 200 nm on which molecules which are to be volatilized can easily be deposited by adding a drop of liquid solution. Our experimental results suggest that by carefully adjusting the layer thickness of the matrix film and the substrate heating rate, molecular volatilization of the whole adsorbed film can be obtained resulting in a minimization of shot-to-shot fluctuations. Even if the amount of analyte molecules is minute, strong jet effects stemming from desorbed molecules from the matrix film will promote cooling of the desorption plume and support intact desorption. We propose to prepare the matrix layer by spin-casting or Langmuir-Blodgett techniques.

On the one hand our experiments unambiguously show that the volatilization techniques which are applied today have a definite potential for optimization, on the other hand the mechanistic knowledge obtained in this dissertation can be directly used to push the limits in applications further ahead. Let's seize the opportunity!
Literature

(21) R. Zenobi, Chimia, 48, 1994, 64.


(106) Continuum, Operation and Maintenance Manual PY61 Laser, **1991**.
(109) Spectra-Physics, Quanta-Ray MOPO-730 Optical Parametric Oscillator, Instruction Manual, **1995**.
(110) Spectra-Physics, FDO-900 Frequency Doubler Option, User's Manual, **1996**.
(114) C. L. Yaws, Library of Physico-Chemical Property Data: Handbook of Thermal Conductivity; Gulf Publishing Company, Houston, **1995**.
(117) E. E. Palik, Handbook of Optical Constants of Solids; Academic Press, Inc., Boston, **1985**.
(118) Landolt-Börnstein, New Series, Springer, Berlin, III/22a, **1987**.
(124) P. Voumard, Enveloppe rotationelle d''une transition électronique de l'aniline, Report EPFL Lausanne, **1994**.


(137) S. N. Mogonov and M. H. Whangbo, Surface Analysis with STM and AFM, VCH, Weinheim, 1996.


Abbreviations

List of frequently used abbreviations:

AFM        atomic force microscopy
DHB        2,5 dihydroxybenzoic acid
L2MS       two-step laser mass spectrometry
LD         laser desorption
LID        laser-induced desorption
LITD       laser-induced thermal desorption
MALDI      matrix-assisted laser desorption/ionization
MB         Maxwell Boltzmann
ML         monolayer
PEG        poly- (ethylene glycol)
QMS        quadrupole mass spectrometer
REMPI      resonance-enhanced multiphoton ionization
RLD        resonant laser desorption
TPD        temperature programmed desorption
TOF        time-of-flight
XPS        X-ray photoelectron spectroscopy = ESCA: electron spectroscopy for chemical analysis

$E_A$       activation energy
$\nu$       preexponential factor
Publications

Several publications based on the work described above have already appeared in the literature or have been submitted:


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