Laser studies of energy- 
and charge-transfer dynamics

A thesis presented

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Abstract

This thesis presents the results of three experiments which use lasers to investigate energy-transfer and charge-transfer dynamics. The dynamical processes studied include nanosecond vibrational energy transfer in molecules, subpicosecond electron relaxation in semiconductors, and subpicosecond initiation of surface bimolecular reactions on a metal crystal.

In experiments using time-resolved coherent Raman spectroscopy to probe infrared multiphoton excited molecules, we study CO$_2$-laser excited SO$_2$ and SF$_6$. In SO$_2$ we observe direct $\nu_1$-mode excitation and distinguish between this process and excitation of the nearly resonant $\nu_2$-mode overtone. In SF$_6$, we directly observe $\nu_3$-mode excitation followed by collisional energy redistribution to a heat bath of non-pumped modes. Quantitative modeling of the SF$_6$ spectra yields excited vibrational population distributions and resolves some long-standing inconsistencies between different previously published reports.

In an experiment using time-resolved photoelectron spectroscopy, we observe the subpicosecond evolution of an optically-excited nonequilibrium electron distribution in silicon. We observe an electron thermalization time of less than 120 fs, electron equilibration with the lattice in 1 ps, and an energy-dependent electron cooling rate consistent with published calculations of the electron-phonon scattering rate. The results indicate the formation, in 1 ps, of a surface space-charge electron layer with an electron density two orders of magnitude greater than the bulk electron density.
In an experiment using 100-fs laser pulses to induce desorption of O$_2$ and reaction of O$_2$+CO to form CO$_2$ on a Pt(111) surface, we present desorption and reaction data obtained over an absorbed fluence range of 1–20 mJ/cm$^2$ at wavelengths of 800, 400, and 266 nm. We observe a highly nonlinear desorption and reaction yield fluence dependence; the data are fit by a power law model in which the yield is proportional to fluence to the power $p = 5.9$ and 3.8 for the 800 nm and 400 nm data respectively. The ratio of O$_2$ to CO$_2$ desorption is found to be 14:1, 12:1 and 3:1 at 800, 400, and 266 nm respectively. At 800 nm, the desorption and reaction are independent of laser pulsewidth in the range 100 fs to 3.6 ps.

Finally, this thesis describes the design, development and operation of new equipment used for the surface reaction experiment: a state-of-the-art amplified femtosecond Ti:sapphire laser, and an ultrahigh-vacuum surface-science chamber.
Acknowledgments

First and foremost, I thank my advisor, Prof. Eric Mazur. Eric accepted me into the QEMP group early in my first year of graduate school, jump-starting my education as an experimentalist. Throughout the past six years, Eric created a lab group environment favorable for experimental science. Independent thought, planning, and effort were stimulated; at the same time, he taught us to value efficient teamwork and an enjoyable social atmosphere. He also taught me much about the proper manner for presenting the results of one’s work by assisting in preparing talks and forcing my writing to be as clear and concise as I could manage. He encouraged us to propose our experiments, and generated the considerable funding required to undertake the resulting efforts described in Chapters 4–6. I feel very fortunate that I had the opportunity to work in his group; these past years had a profoundly positive impact on my personal and professional development.

Great thanks must go to Dr. Judy Prybyla, who invited me to work with her at AT&T Bell Labs. She provided a working experiment, gave me the run of her lab, and worked together with me every day during my final weeks there; the results of that experience provided the topic of Chapter 3 of this thesis. Perhaps more importantly, she gave me the opportunity to experience life and experimental science in one of the world’s great scientific institutions, a place where incredible resources can be brought to bear on a problem. I was able to learn a number of valuable skills at AT&T which were useful later for the desorption experiments performed at Harvard. I should note that these desorption and reaction experiments were inspired in part by her earlier experiments on femtosecond desorption at AT&T. I also had the opportunity to meet a number of friendly people at Bell
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It is in the nature of the Mazur group that much collaboration and discussion goes on between the various sub-groups, and I have benefited greatly from everyone's help and camaraderie. A generation of previous QEMP-ers, now graduated, welcomed me into the group and offered advice and friendship during my first few years at Harvard: Drs. Doo Soo Chung, Ka Yee Lee, Peter Saeta, and Juen-Kai Wang. A knowledgeable, helpful, and fun generation has succeeded them. Dr. Yakir Siegal provided expertise and useful insights during analysis of the photoemission experiment and preparation of my thesis. He also was a great advisor during my consulting job search and interviewing process. Eli Glezer frequently answered science questions and kept me in shape on the basketball court. Dr. Qing Yu Wang studied at the desk next to mine during the writing of this thesis and initiated many cheery conversations and diversions. Aryeh Feder drew me into many hours of enjoyable philosophical discussions. Li Huang offered many smiles and a sharp wit. Mei Shibata and Wendy Zhang inspire us with their zeal and zest for learning physics, and they generate fresh perspectives and new ideas for group outings, along with our newest group member, Glenn Wong.

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There is a tide in the affairs of men,
Which, taken at the flood, leads on to fortune;
Omitted, all the voyage of their life
Is bound in shallows and in miseries.
On such a full sea are we now afloat,
And we must take the current when it serves,
Or lose our ventures.

Shakespeare, *Julius Caesar*

Don’t ask what the world needs, ask of yourself what makes you come alive and go do that.
Because what the world needs is people who are alive.   Howard Thurman
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PART TWO: Laser and UHV Apparatus-- Design, Construction, Methodology

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Part One: Experiments -- Motivations, Approaches and Results

Chapter 1

Introduction

This thesis presents the results of three experiments. The purpose of this introduction is to provide a general context for the experiments. While the three experiments are different, they fit together as important pieces of a larger experimental goal, namely, to time-resolve and state-resolve the transient intermediate states of a surface bimolecular reaction. It is this larger goal, observing ‘the birth of a surface molecule,’ which provides much of the motivation for this thesis. The experiments described in Chapters 2–4 have laid the ground-work for planned experiments which will use time-resolved spectroscopy for identifying the intermediate states of a laser-induced surface reaction.

The results presented in this thesis fall within the following fields of research: (1) gas-phase molecular spectroscopy and vibrational energy transfer, (2) laser photoemission study of semiconductor electron dynamics, and (3) laser-induced reactions on atomically-clean metal surfaces. The experiments are described in separate chapters, each of which
provides an introduction to these topics, including the motivation for each experiment, and

descriptions of previous work in the field. The next section of this introduction describes

the relationships between the experiments described here and other related work in these
currently active fields of research.

1.1 Overview

Time-resolved spectroscopy of energy and charge transfer dynamics in molecular and

condensed matter systems is of current experimental and theoretical interest. In general, the
goal of this research is to obtain a detailed picture of a sequence of events triggered by a
sudden excitation, such as the absorption of a laser pulse. For example, time-resolved
experiments can reveal the dynamics of charge or vibrational energy transfer between
molecules during a reaction, or the rapid thermalization of a non-equilibrium electron
distribution.

Continuing technological improvements in the generation of ever shorter laser pulses
have driven the focus of time-resolved experiments into the femtosecond (10^{-15} sec) time-
domain. On this timescale, which is shorter than the vibrational period of a molecule, a
reaction can exhibit previously unidentified transient excited molecular states as
intermediate steps of the process. The opening of this window in time offers the possibility
of precise characterization, and possibly control, of subpicosecond events.

As discussed in Chapter 2, early experimental efforts to use short laser pulses for
selective control of molecular reactions were unsuccessful. However, more recent
experimental advances have rekindled interest in this goal. A series of experiments by
Zewail et al., and others [1-4] have had a particularly strong impact. These experiments
demonstrated the first use of time-resolved spectroscopy to drive and probe a gas-phase
dissociation reaction with 100-fs time-resolution. These results demonstrated that new
ultrashort pulse techniques can characterize transient intermediate states of a reaction.
Subpicosecond spectroscopy of molecular adsorbates on atomically clean crystal surfaces has also been investigated by several research groups. Direct spectroscopic measurement of vibrational relaxation and dephasing of adsorbate vibrations on metals and semiconductors was demonstrated \[5, 6\]. Furthermore, femtosecond pulse laser-induced desorption of an adsorbate was directly observed in the subpicosecond time domain \[7, 8\]. At the time of these new developments, we were performing experiments using time-resolved gas-phase vibrational spectroscopy, the subject of Chapter 2 of this thesis. Upon completion of that work, our group set out to extend our experience with molecular spectroscopy into the area of subpicosecond surface reaction dynamics.

Experiments in surface reaction dynamics have numerous features unavailable in gas-phase studies. In particular, the presence of a surface provides a catalytic agent on which a laser-induced reaction between two different adsorbed molecular species can be initiated. One goal of studying such a system is to observe the evolution of a surface reaction in time. Direct observation of the ‘birth’ of a new molecule on a surface is a first step towards finding new approaches for controlling the outcome of a surface reaction.

The study of the interactions between molecule, crystal substrate, and laser photons in a surface reaction provides impetus for new experimental and theoretical work. Figure 1.1 schematically illustrates the interconnections of research in time-resolved spectroscopy, ultrashort pulse laser technology, surface dynamical theory, and surface science required for the observation of the birth of a molecule on a surface.
**Fig. 1.1** Schematic illustration of interconnections between various fields and the goal of state-sensitive time-resolved detection of molecular reactions on a crystal surface. See text below for details.

*Time-resolved spectroscopy:* A challenge remains to develop a state-resolved and time-resolved probe with a sensitivity sufficient to detect changes in a single layer of molecules. Techniques such as coherent Raman spectroscopy (CARS, *cf.* Ch. 2), electron photoemission (*cf.* Ch. 3) infrared absorption and upconversion spectroscopy, second-harmonic and sum-frequency generation, and laser-induced fluorescence are leading candidates for this task.

*Laser technology:* To achieve the required time-resolution, advances over existing ultrashort pulse laser technology are needed. Most importantly, new methods of ultrashort pulse generation and amplification (*cf.* Ch. 5), ultrashort pulse shaping [9], and generation of ultrashort pulses at previously inaccessible wavelengths are required for the success of the above-mentioned spectroscopic techniques.

*Model systems:* To study the birth of a molecule on a surface, appropriate model systems need to be identified and characterized. The results of work in surface science, photochemistry,
ultrafast reaction dynamics in the gas and liquid phase, and ultrafast surface reaction
dynamics *(cf. Ch. 4)* all play a role in identifying suitable candidate systems.

**Reaction mechanisms:** Initiating a surface reaction requires different approaches for different
model systems. Each unique reaction mechanism involves various surface-molecule and
light-substrate interactions. For example, coherent control of reactions using frequency- and
amplitude-tailored light pulses may be possible if a time-varying frequency pulse can be
created to produce a desired excitation within the electronic levels of an adsorbate. A
different approach is to utilize a substrate-electron-mediated reaction channel initiated by
substrate light absorption. This initial excitation can lead to molecular dissociation or
activated molecular reactions driven by substrate electron interaction with adsorbates (see
Ch. 4 for a discussion of reaction mechanisms).

**Theory:** Finally, theoretical developments will play an important role. New models of
substrate electron dynamics, adsorbate-substrate charge and vibrational energy transfer, and
intramolecular vibrational energy relaxation on a surface need to be developed in order to
interpret the results of present and future experiments.

### 1.2 Content and Organization of this Thesis

The work described in this thesis represents contributions to several key parts of the
overall goal of Fig. 1.1. Part one of this thesis describes three experiments that represent
advances in time-resolved spectroscopy, and advances in the understanding of substrate
electron dynamics and surface reaction dynamics. Chapter 2 deals with time-resolved studies
of intramolecular vibrational energy relaxation. In particular, we show how time-resolved
coherent Raman spectroscopy can be used to obtain a detailed picture of the vibrational
relaxation dynamics in molecules excited by an intense infrared laser pulse. In Chapter 3, we
describe the use of time-resolved photoemission spectroscopy to study non-equilibrium substrate electron dynamics in a semiconductor. This work directly reveals the equilibration of excited conduction band electrons with the lattice on a picosecond timescale. In Chapter 4, we present the results of an experiment using 100-fs laser pulses to initiate surface reactions. We demonstrate the use of a 100-fs laser pulse to drive the reaction $\text{O}_2 + \text{CO} \rightarrow \text{CO}_2$ on a platinum crystal surface; the results indicate that this system is a suitable candidate for future time-resolved surface reaction experiments.

Part two of the thesis describes the development of a femtosecond pulse laser system and an ultrahigh vacuum (UHV) apparatus. In Chapter 5, we detail original contributions to the development of a femtosecond pulse Titanium-doped sapphire (Ti:sapphire) laser system. The system consists of a self-mode-locked oscillator and a high-repetition rate regenerative amplifier; this represents the state-of-the-art in ultrashort pulse laser technology. Chapter 6 discusses the design and construction of a UHV chamber used for surface reaction experiments. This chamber has unique design features that make it especially well suited for optical studies of laser-induced surface reactions.

Finally in Chapter 7, we conclude the thesis with a brief summary of the work presented, and discuss how the results of this thesis contribute to the ultimate goal of directly observing the birth of a molecule on a crystal surface.
References:

Chapter 2

Coherent anti-Stokes Raman Spectroscopy of Infrared Multiphoton Excited Molecules

2.1 Introduction

2.1.1 Motivation

The experiments described in this chapter lie at the intersection of two areas of research: infrared excitation of polyatomic molecules, and nonlinear laser spectroscopy. Early studies of infrared-excited molecules were in part motivated by the goal of achieving state-selective laser chemistry. Because infrared lasers can be tuned in resonance with a particular vibrational mode of a molecule, researchers hoped to use a laser as an ‘optical scissors’ to selectively break a specific molecular bond. However, in reaching the high level of excitation required to dissociate a molecule, other vibrational modes are also excited due to intermode coupling which increases with higher vibrational excitation. As a result, a continuum of modes is excited and selective laser chemistry cannot be realized in general since the energy
is redistributed among all the modes. More recently, advances in ultrafast laser pulse-shaping and the study of laser-induced surface reactions (see Chapter 4) have re-opened the possibility of achieving selective laser chemistry.

In the work described in this chapter the goal is not to initiate laser control of a molecular excitation, but rather to use time-resolved nonlinear spectroscopy to characterize a laser-excited molecular ensemble. Following resonant excitation by a laser pulse, we directly observe energy transfer among the vibrational and rotational degrees of freedom of the molecule.

The method used to observe energy transfer dynamics is time-resolved coherent Raman spectroscopy. Analysis of time-resolved coherent Raman spectra yields time-resolved molecular vibrational state distributions. The analysis presented here involves modeling each molecule as a system of coupled anharmonic oscillators [1]. This approach yields a detailed picture of the excitation and subsequent flow of vibrational energy between oscillator modes, as well as intramode and collisional relaxation rates, and self- and cross-anharmonicities.

2.1.2 Description of experiment

In the experiments described here, we excite a molecular ensemble using a pulsed CO₂-laser and probe the resulting vibrational distribution using time- and energy-resolved nonlinear Raman spectroscopy. The CO₂-laser is tuned to the ground-state frequency of an infrared active mode; it excites a broad distribution of vibrational modes via a process called infrared multiphoton excitation [5-7]. The highly-excited ensemble is probed using multiplex coherent anti-Stokes Raman spectroscopy, or M-CARS [8, 9]. With this technique one obtains the complete vibrational spectrum of the excited molecular ensemble in a single laser shot. A single-shot spectral measurement ensures that relative spectral intensities are

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1This work done at Harvard in collaboration with S. Deliwala, Dr. C. Z. Lü, Dr. K. H. Chen, and Prof. E. Mazur. We have published these results in Refs. [2-4].
reproducible, independent of shot-to-shot probe-laser energy fluctuations. Compared to spontaneous Raman or absorption spectroscopy, coherent Raman spectroscopy offers better noise rejection owing to directional separation of the signal from background scattered light and high spatial resolution. With nanosecond-pulse lasers and a sample at a pressure of 1 torr, the coherent Raman signal is typically orders of magnitude larger than the spontaneous Raman or absorption signal [8, 10].

To determine the role of collisional energy redistribution we probe the molecules at various positions in a free jet expansion and compare these results to spectra obtained in a static gas cell. This allows the study of energy relaxation in adiabatically cooled, nearly collision-free conditions, or alternatively at relatively high collision-rate, room-temperature conditions.

### 2.1.3 Summary of results

This chapter presents the results of experiments on CO2-laser excited sulfur hexafluoride (SF6) and sulfur dioxide (SO2). In SO2 [3] we observe direct excitation. We are able to distinguish between laser-excitation of the $\nu_1$-mode and excitation of the nearly resonant $\nu_2$-mode overtone. The CARS spectra of infrared excited SO2 exhibit discrete peaks characteristic of low-level coherent excitation in a small molecule with few vibrational modes. In contrast, SF6 has a broad, nearly continuous CARS spectrum, revealing direct $\nu_3$-mode pumping followed by rapid collisional energy redistribution to the non-pumped modes [4]. Varying the collision rate of the molecular ensemble in a free jet expansion, we observe collision-rate dependent effects on the excitation and relaxation processes for both molecules.

The chapter is organized as follows. Section 2.2 presents a brief theoretical description of multiplex coherent anti-Stokes Raman spectroscopy and the infrared multiphoton excitation process in polyatomic molecules. Section 2.3 details the experimental apparatus and technique. In Section 2.4, we present the results for SO2 and SF6. These results illustrate
Chapter 2  
CARS spectroscopy of IRMPE molecules

how infrared multiphoton excitation and vibrational relaxation proceed in these systems, and what role collisions play in redistributing vibrational energy during and following excitation. They also demonstrate the utility of multiplex coherent anti-Stokes Raman spectroscopy for directly determining time-resolved excited state distributions.

2.2 Theory

2.2.1 Multiplex coherent anti-Stokes Raman spectroscopy

Previous theses from our research group by K.H. Chen [11] and J.K. Wang [12] extensively review the theoretical and practical descriptions of nonlinear optics and coherent Raman spectroscopy. Here we briefly review pertinent issues useful for interpreting the data presented in Section 2.4.

The goal of this experiment is to time-resolve an evolving ‘rovibrational’ population distribution \( N_{\{v,J\}} \), where \( \{v,J\} \) labels a molecular rotational and vibrational state (\( v \) and \( J \) are the vibrational and rotational quantum numbers, respectively). This population distribution \( N_{\{v,J\}} \) is deduced from the spectrum of a Raman-active vibrational mode.

For infrared excitation of a polyatomic molecule well below the dissociation threshold, a normal mode description is appropriate. As alluded to above, a polyatomic molecule is a good example of a system of coupled anharmonic oscillators. The normal mode frequency of each molecular vibration, \( \omega_i \), is shifted by \( \Delta \omega_i \) when the molecule is excited vibrationally into a state \( \{v\} \). The shifts \( \Delta \omega_i \) are given by [1]:

\[
\Delta \omega_i = (v_i + \frac{g_i}{2}) x_{ii} + \frac{1}{2} \sum_{j=1}^{n} (v_i + \frac{g_i}{2})(v_j + \frac{g_j}{2}) x_{ij} + ..., \tag{2.1}
\]

where \( v_i \) are the vibrational quantum numbers for each of the \( n \) normal modes, \( x_{ii} \) is a self-anharmonicity, \( x_{ij} \) is a cross-anharmonicity, and \( g_j \) is the degeneracy of each mode. Note that
for the molecules discussed here, both self- and cross-anharmonicities are negative. The
shifted frequency $\omega'_i$ of each rovibrational mode is then:

$$
\omega'_i = \omega_i + \Delta \omega_i + \frac{\mathcal{H}(J)}{\hbar}
$$

(2.2)

where $E(J)$ is the energy of rotational state $J$. Inspection of Eq. (2.2) shows that the
rovibrational spectrum of a probed mode can exhibit many peaks. Each spectral peak will be
shifted from the normal mode frequency by an amount proportional to the anharmonic
coupling between the probed mode and an excited rovibrational mode. Figure 2.1
schematically illustrates the resulting spectrum in the case of SF$_6$, where we pump the $\nu_3$-
mode and probe the $\nu_1$-mode.

Coherent anti-Stokes Raman scattering is a third-order nonlinear Raman process, in
which two laser beams of frequency $\omega_1$ are mixed with a beam at $\omega_2$ to produce an output
signal at $2\omega_1 - \omega_2$. The frequency difference $\omega_1 - \omega_2$ is chosen to be resonant with a single
rovibrational transition $\omega'_i$ (see Figure 2.2 (a)) [8]. Multiplex coherent anti-Stokes Raman
spectroscopy (multiplex CARS [8]) incorporates a broadband $\omega_2$ beam with a spectral width
that allows $\omega_1 - \omega_2$ to cover the entire energy range of anharmonically-shifted levels $\omega'_i$. This is schematically illustrated in Fig. 2.2 (b). In this way, the entire rovibrational spectrum
containing all the $\omega'_i$ peaks is obtained in a single laser shot.
Fig. 2.1 Schematic of the multiplex-CARS spectrum in the SF$_6$ experiment. In this experiment, we pump the $\nu_3$-mode and probe the $\nu_1$-mode. The CARS spectrum of the $\nu_1$-mode then exhibits spectral peaks due to the anharmonic coupling between these two modes, characterized by $x_{13}$, and due to the self-anharmonicity of the probe mode, characterized by $x_{11}$. (a) shows the vibrational levels of the probe and pump modes. Excited population in the $\nu_3$-mode produces CARS peaks down-shifted by $x_{13}$ from the main (tallest) CARS peak in (b). Excited population in the $\nu_1$-mode produces CARS peaks down-shifted by multiples of $x_{11}$. A possible resulting spectrum is shown in (b), assuming negative values of $x_{11}$ and $x_{13}$.

If intra-mode relaxation leads to equilibration among the vibrational levels of each molecular vibrational mode in the excited ensemble, then the vibrational distribution is characterized by a single temperature. The assumption of intra-mode equilibrium for the spectra analyzed here is justified because our time-resolution (10 ns) is greater than the time scale for intra-mode equilibration [13]. The intensity of the multiplex CARS signal $I_{\text{CARS}}$ is then proportional to:
Fig. 2.2 Multiplex CARS spectroscopy scheme. (a) shows the three probe photons at $\omega_1$ and $\omega_2$ producing the CARS signal $\omega_c$, with $\omega_1 - \omega_2 = \omega'_i$. (b) shows the broadband $\omega_2$ beam, and how the CARS spectral peaks $\omega_c$ fit within the $\omega_2$ spectral width.

$$I_{\text{CARS}}(2\omega_1 - \omega_2) \propto \sum_{\{v, J\}} \Delta N_{\psi, J} \frac{d\sigma}{d\Omega} \frac{1}{\omega_1 - \omega_2 - \omega'_i - i\Gamma} \left| \frac{I^2(\omega_1)}{\sum I^2(\omega_2)} \right|^2$$

(2.3)

where $d\sigma/d\Omega$ is the Raman cross-section of the mode, $\Gamma$ is the effective linewidth of the transition which in general is a function of vibrational excitation, and $\Delta N_{\psi, J}$ is the vibrational population difference between the lower and upper levels of the probed Raman-active transition, with $N_{\psi, J}$ given by:

$$N_{\psi, J} = \frac{g_{\psi, J} \exp \left( -\sum \beta_v \hbar (\omega_j + \Delta\omega_j) \right) g_j \exp \left( -\sum \beta_J E(J) \right)}{\sum_{\psi, J} N_{\psi, J}}.$$  

(2.4)

Here $\beta_v = 1/\hbar T_{\text{vibrational}}$ and $\beta_J = 1/\hbar T_{\text{rotational}}$. The vibrational distribution, $N_{\psi, J}$, is obtained in practice by a numerical fitting procedure in which the vibrational and rotational temperatures $T_{\text{vibrational}}$ and $T_{\text{rotational}}$ are adjustable parameters, as discussed below.
When analyzing multiplex CARS spectra, one finds that the simplest experiment to interpret is one in which multiplex CARS probes one mode, while the CO\textsubscript{2}-laser excites a different mode. This is in fact the case for the SF\textsubscript{6} results presented in Section 2.4.2. This situation is easiest to interpret because peaks corresponding to self-anharmonicity terms are absent. In this case assuming also that our multiplex CARS spectral resolution is narrower than the anharmonic shifts, the multiplex CARS ensemble spectrum appears as a sequence of discrete peaks as follows: (i) a molecular ground state peak (labeled \(a\) --- cf. Fig. 2.6 (b)) at the probed mode normal frequency; (ii) a ‘primary’ series of peaks (labeled \(b\)) downshifted from \((a)\) by multiples of the cross-anharmonicity between excited and probed modes. These peaks correspond to rovibrational excitation in the pumped mode; (iii) a set of ‘satellite’ peaks \((c)\) downshifted from each of the primary peaks \((a)\) and \((b)\) corresponding to rovibrational excitation in non-laser-excited modes. In the more general case where the same mode is both excited and probed, as with SO\textsubscript{2}, a series of \(b\) and \(c\) peaks is observed multiple times (cf. Fig. 2.6 (b)), once for each vibrationally excited level of the probed mode, with each sequence shifted in proportion to the self-anharmonicity of the probed mode.

\textbf{2.2.2 Infrared Multiphoton Excitation (IRMPE)}

Intense laser beams are capable of exciting polyatomic molecules beyond the dissociation threshold, via a process known as infrared multiphoton excitation (IRMPE). This is true even though at low excitation intensities, vibrational excitation to highly excited states using a monochromatic pulsed laser is hindered by the anharmonic nature of each vibrational mode. In other words, if the pump laser wavelength is resonant with the ground state vibration of an infrared-active mode, each successive transition upwards in energy to higher vibrational levels is increasingly out of resonance with the pump laser.

Many models of infrared multiphoton excitation have been published [7, 14-17]. Essentially, multiphoton excitation in polyatomic molecules by an intense infrared laser pulse proceeds through two distinct stages. Initially, the nearly-resonant pulse excites the low-lying
levels of the infrared-active mode, overcoming the relatively small anharmonicity of the vibrational levels via power broadening, collisional broadening, and rotational compensation. This stage of excitation is a coherent, stepwise process with the rate of each step proportional to the laser pulse intensity. At higher levels of excitation, the high density of states in all vibrational modes and increased intermode coupling to this dense manifold of levels leads to fast dephasing rates. The excitation then proceeds incoherently, proportional to the energy in each laser pulse. At the highest levels of excitation the process is no longer mode-specific. This regime of level mixing and fast energy redistribution is often called the incoherent, or ‘quasicontinuum’ regime.

To understand the details of infrared multiphoton excitation in a particular molecule, many parameters need to be determined. Of significant interest is whether a characteristic level of vibrational excitation can be identified at which a given molecule makes the transition from the coherent stage of excitation to the incoherent regime. While this transition may not be distinct in all systems, such information can be used in a given experiment to estimate the average number of laser quanta absorbed per molecule, or to predict properties of the relaxation process depending on pump-laser intensity. Also it is interesting to compare the onset of quasicontinuum excitation for different molecules. In general, larger polyatomics have more vibrational modes and hence a relatively higher density of states at a given energy, leading to an earlier onset of incoherent excitation [16, 18, 19]. CARS spectra may indicate a transition to incoherent excitation when discrete spectra of a given excited molecule become broad or continuous at higher levels of excitation, corresponding to level mixing due to strong vibrational coupling. It is also important to be able to determine whether a transition to quasicontinuum excitation can ever be reached for a given system. Intense excitation resonant with a single rovibrational transition in the coherent regime can saturate the transition in the ensemble. If so, a rovibrational population ‘hole’ will result which prevents further absorption of photons [13, 20, 21]. Multiphoton excitation will be inefficient in systems that cannot unsaturate or ‘fill’ such a hole at a
sufficient rate. One mechanism for hole filling is provided by collisions; collisions therefore enhance the infrared multiphoton excitation for some molecules [21]. Collisions when present are also an important mechanism for redistribution of excitation to non-pumped modes\(^2\). For these two reasons, collisions can play a significant role in infrared multiphoton excitation, possibly affecting the transition from the coherent to the incoherent excitation regime. Obtaining multiplex CARS spectra under variable collision-rate conditions allows us to test the role of collisions in the excitation process, and in the subsequent relaxation processes as well.

2.3 Experimental Apparatus

The experimental layout for the experiments discussed here is shown in Fig. 2.3. The infrared excitation source was a pulsed TEA CO\(_2\)-laser providing 200-ns pulses with a low intensity microsecond ‘tail’. The pulses were truncated with a plasma shutter to produce pulses typically 40 ns in duration. The CO\(_2\)-laser beam was focused using a 0.15-m focal length cylindrical ZnSe lens to an elliptical cigar-shaped focus with 100-\(\mu\)m cross-sectional diameter centered over the smaller 80-\(\mu\)m CARS overlap region. Typical fluences (energy per laser pulse per unit area in the interaction region) were \(\geq 3\, \text{J/cm}^2\) at \(\lambda = 10\, \text{\mu m}\) (corresponding to 0.12-eV, or 1000-cm\(^{-1}\) photon energy). Careful efforts were made to ensure that the multiplex CARS probe region was entirely enclosed within the infrared excited sample volume. The optical probe beams were generated by a Nd:YAG laser and custom-built dye-laser oscillator-amplifier setup.

\(^2\)A ‘non-pumped mode’ refers to a vibrational mode not in resonance with the pump laser frequency.
A Quantel YG471 frequency-doubled Nd:YAG laser produced linearly polarized, 300-mJ, 10-ns pulses at 532 nm. This green beam was split in three parts to produce two $\omega_1$ beams, and an $\omega_2$ beam with approximately 60-cm$^{-1}$ bandwidth. This broadband beam was generated in a prism-tuned dye-laser oscillator-amplifier, using Fluorescein 548 dye. As explained in Sect. 2.2, the $\omega_2$ beam was tuned so that $\omega_1 - \omega_2$ covered the full spectrum of the rovibrational frequencies $\omega'_i$ of a given Raman-active mode.

To satisfy momentum conservation for the incident laser beams while at the same time achieving spatial separation of the probe and signal beams, we used a BOXCARS phase matching geometry [8], shown in Figure 2.4.
The three incident beams were aligned parallel to each other, then focused into the sample chamber with a 0.3-m lens. The multiplex CARS signal was generated in the focal overlap region, which had an 80-µm beam waist. To align the detection optics, a HeNe laser beam was aligned parallel to the input beams through an appropriately placed pinhole so that the HeNe beam emerged at the phase matched angle collinear with the signal (CARS) beam. A second 0.3-m lens after the sample chamber recollimated all four beams. This geometry ensured a high rejection of background noise from the sample chamber windows and non-pumped portions of the gas sample, as well as rejection of scattered light from the probe beams. A 1-m spectrograph (Jarrell-Ash) was used to spectrally disperse the multiplex CARS signal. Following dispersion by the monochromator grating, the multiplex CARS signal was
diverted out a side port of the monochromator instead of passing through an output slit. As schematically illustrated in Figure 2.5, the entire spectrum was analyzed at once using a Hamamatsu C1587 streak camera and vidicon video camera detector. The output was collected by a personal computer. The effective spectral resolution of the apparatus was \( \leq 0.1 \text{ cm}^{-1} \).

In order to obtain time-resolved spectra, we varied the temporal delay \( \tau \) between the excitation-laser (CO\(_2\)) and probe-laser pulses. To obtain spectra with \( \leq 40\)-ns time resolution, we desired synchronization of the lasers and streak camera to \( \leq 1 \) ns. For our commercial CO\(_2\)-laser however, we typically observed a \( \pm 30\)-ns time-jitter between the electrical trigger signal and the laser pulse output. We effectively eliminated this timing jitter from our measurement as follows. A custom-built fast pyroelectric detector and RF-amplifier circuit was used to optically trigger the streak camera from the CO\(_2\)-laser pulse. This triggering scheme provided \( \leq 1 \) ns timing jitter between the streak camera and the CO\(_2\)-laser pulse. We then took advantage of the unavoidable timing jitter between the YAG-laser pulse and the streak camera sweep, obtaining time-resolved spectra by collecting several hundred shots with random pump-probe delays \( \tau \) over a \( \pm 30\)-ns interval and superposing them electronically in the streak camera. An advantage of collecting data in this way is that the entire time evolution of the spectrum can be obtained in a single streak camera video image which is then analyzed on a personal computer. This technique ensures precision referenced time delays, signal intensities and spectral frequencies. Data analysis was performed on a personal computer using digital image-analysis software which extracted multiple narrow time-delay ‘slices’ from each streak camera image. Each ‘slice’ is a multiplex CARS spectrum for a given time delay \( \tau \).
Fig. 2.5  Data acquisition for the experiment. A streak camera collects the time and frequency resolved spectrum image. The image is digitized by computer into time ‘slices’, each of which is a multiplex CARS spectrum.

The gas samples were either static gas samples held at pressures from 1 – 100 torr, or pulsed free jet samples. Our pulsed jet is a modified Toyota fuel injector nozzle with an output diameter $D = 0.94 \text{ mm}$. It is arranged in a vertical geometry and outputs gas pulses 1–10 ms in duration along the $z$-direction, synchronized with the laser pulses. The jet is mounted on a $xyz$-translation stage in a vacuum chamber maintained at $10^{-3} \text{ torr}$ by a roughing pump. Adjusting the translation stage allowed probing of the center of the molecular beam at various vertical distances $z$ downstream from the nozzle. The reservoir gas pressure behind the nozzle and the ratio $z/D$ were varied to obtain variable collision rates of ca. 10 collisions
per 100 ns at \( z/D = 2 \) to \textit{ca}. 1 collision per 100 ns at \( z/D = 4 \) [22-24]. Rotationally and vibrationally cooled samples are obtained due to the adiabatic cooling which occurs in the free jet expansion. For SF\(_6\), typical vibrational temperatures were 160 K at \( z/D = 2 \) and 100 K at \( z/D = 4 \), as determined from fits of the multiplex CARS ground state linewidths and from published data [24, 25]. For smaller molecules cooling is more efficient [26]; for N\(_2\), rotational temperatures as low as 10 K were obtained.

### 2.4 Results and Discussion

#### 2.4.1 SO\(_2\): Direct observation of \( \nu_1 \)-mode excitation

##### 2.4.1.1 Overview

Small polyatomic molecules like SO\(_2\) are difficult to excite via infrared multiphoton excitation. Early studies of infrared multiphoton excitation in SO\(_2\) were motivated by the discovery of inverse electronic excitation in this molecule [27, 28]. In this process, excitation of electronic states occurs when highly excited vibrational states are populated via infrared pumping with intense 9-\(\mu\)m CO\(_2\)-laser lines. Our interest in this molecule arose because two possible pathways for the excitation are possible; excitation might proceed either via levels of the symmetric \( \nu_1 \)-mode at 1151 cm\(^{-1}\), or via even overtone transitions in the \( \nu_2 \)-mode with 1035 cm\(^{-1}\) steps. Both modes are Raman and infrared-active (see Table 2.1). Using time-resolved M-CARS we found that \( \nu_1 \)-mode excitation is much more efficient, and is the dominant infrared multiphoton excitation pathway [3]. We also found that collisional enhancement of the infrared multiphoton excitation is critical for this molecule.

\(^3\)For SF\(_6\) at a reservoir pressure \( \rho_{\text{res}} = 30 \) psi.
### Table 2.1 Vibrational frequencies for SO$_2$ (Refs. [29, 30]) and CO$_2$-laser lines used in this experiment. R and IR: Raman- and infrared- active modes, respectively.

<table>
<thead>
<tr>
<th>SO$_2$ mode</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>activity</th>
<th>CO$_2$ line</th>
<th>$\nu$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>1151.3</td>
<td>R, IR</td>
<td>9R(32)</td>
<td>1085.8</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>517.6</td>
<td>R, IR</td>
<td>9R(22)</td>
<td>1079.8</td>
</tr>
<tr>
<td>2$\nu_2$</td>
<td>1035.2</td>
<td>IR</td>
<td>9P(32)</td>
<td>1035.5</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1361.7</td>
<td>R, IR</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The SO$_2$ molecule is an asymmetric top ($C_{2v}$ symmetry) having three vibrational modes (Table 2.1). Since the $\nu_1$-mode is Raman active, we can pump any infrared active mode while simultaneously observing the $\nu_1$ CARS spectrum. As discussed in Sect. 2.2.1 the CARS signal contains three main features: (1) a ground state peak ($a$) at the resonant frequency of the Raman probed mode, (2) peaks ($b$) shifted by multiples of $2\nu_{ij}$ cm$^{-1}$ from the ground state which correspond to excited levels of the Raman probed mode $i$, and (3) peaks ($c$) shifted by multiples of $\nu_{ij}$ cm$^{-1}$ from each of the peaks in (1) and (2) corresponding to population in any other vibrational mode $j \neq i$ (see Table 2.2).

Ambiguity in previous infrared multiphoton excitation experiments on SO$_2$ arose primarily because there is no available CO$_2$-laser line resonant to the $\nu_1$-mode. The 9R(32) line is a strong CO$_2$-laser line close to $\nu_1$-mode resonance (see Table 2.1); the 9P(32) line is resonant with the first overtone of the $\nu_2$-mode; and the 9R(22) line, one of the more intense CO$_2$ lines in the 9-$\mu$m region, lies between these two bands (71 cm$^{-1}$ detuned from $\nu_1$ and 44 cm$^{-1}$ from 2$\nu_2$). Because infrared multiphoton excitation is intensity dependent for a small molecule like SO$_2$ [5, 13] the strong 9R(22) line is historically the one most often utilized in the literature. It is not immediately clear, however, which of the two aforementioned modes undergoes infrared multiphoton excitation when this line is used.
2.4.1.2 Results

We directly monitored the infrared multiphoton excitation in SO\textsubscript{2} by observing the intensity of the ground state CARS peak of SO\textsubscript{2} in gas cell and free jet samples following excitation with various CO\textsubscript{2}-laser lines at fluences of about 2 J/cm\textsuperscript{2}. Figures 2.6 (a) and (b) show spectra obtained in gas cell samples. In Fig. 2.6 (a) the large peak at 1151 cm\textsuperscript{-1} is the ground state peak of the unexcited molecules at the resonant frequency of the probed \(\nu_1\)-mode. Following pumping with the 9R(22) line, a number of excited peaks with a distinct, repeating pattern appear (see Fig. 2.6 (b)). The strongest of these new peaks (\(b\)) appear at positions shifted by a multiple of \(-7.3\) cm\textsuperscript{-1} from the ground state peak (\(a\)). Furthermore, smaller peaks (\(c\)) are visible at a shift of \(-3.3\) cm\textsuperscript{-1} from each of the peaks \(a\) and \(b\).

Spectra obtained in a supersonic jet appear much cleaner and exhibit fewer peaks compared to the bulk data, see Figs. 2.7 (a) & (b). In general, excitation is less efficient in the jet than in bulk samples. Figure 2.7 (a) shows a ground state spectrum taken close to the nozzle (\(z/D = 2.0\)), with the intensity scale expanded.

Thermal vibrational population of the excited states is visible. These peaks lie at the same spacing as before, \(-7.3\) (\(b\)) and \(-3.3\) cm\textsuperscript{-1} (\(c\)), but now only one of each type of peak is visible. Following 9R(22) excitation (Fig. 2.7 (b)), peak \(b\) dramatically grows and the ground state peak \(a\) diminishes, while peak \(c\) is unchanged. Spectra taken far from the nozzle (\(z/D = 10\)) show only a ground state peak. We did not observe any depletion of this peak under these circumstances, not even at the maximum available laser fluence of 2.5 J/cm\textsuperscript{2}. 
Fig. 2.6 Vibrational CARS spectra of SO$_2$ in gas cell samples at room temperature and 13 kPa (100 torr). (a) Ground state (no excitation) spectrum. The large peak at 1151 cm$^{-1}$ corresponds to the $\nu_1$-mode. (b) An excited spectrum, 1.2 $\mu$s after 2 J/cm$^2$ excitation with 9R(22), showing excited states $b$ and $c$ (from Ref. [3]).
Fig. 2.7 Vibrational CARS spectra of SO$_2$ in a free jet (for $z/D=2.0$). Intensity scale is expanded to show small shifted peaks. (a) Ground state spectrum. (b) Excited spectrum, 200 ns after 1 J/cm$^2$ excitation with 9R(22). As a result of excitation, peak $b$ grows (from Ref. [3]).

When we tuned to the 9R(32) line, which is closer to resonance with the $v_1$-mode, a maximum fluence of only 1 J/cm$^2$ was attainable. Yet even at this reduced fluence identical excitation to the 9R(22) data was observed in the bulk, indicating a much higher pumping efficiency at this wavelength.
Finally, we attempted to pump the SO$_2$ $v_2$ first overtone band with the 9P(32) line. However, even with as much as 3 J/cm$^2$ of infrared fluence in bulk and beam samples no excitation beyond the thermal excitation shown in Fig. 2.6 (a) was observed.

2.4.1.3 Discussion and Conclusions

The above sequence of observations suggests that the CO$_2$-laser excites the $v_1$-mode. This is substantiated by the higher efficiency of the 9R(32) excitation, since 9R(32) is closer to resonance with $v_1$ than with $2v_2$, and by the fact that 9P(32), in resonance with the $2v_2$ overtone, produces no observable excitation at all. There are no other overtone or combination bands in this frequency range with significant absorption [29, 30]. Hence we are led to the conclusion that Figs. 2.7 (a) and (b) must be a direct observation of infrared multiphoton excitation in the $v_1$-mode.

Table 2.2 lists the anharmonic shifts of all possible peaks that might appear in the SO$_2$ CARS spectrum. To establish the identity of the $b$ and $c$ peaks we first note the absence of both peaks far from the nozzle without CO$_2$-laser excitation. This proves that these peaks must be hot bands with detectable room temperature population that disappear when the ensemble is vibrationally cooled by adiabatic expansion in the jet. From the dramatic growth of the $b$ peak in Fig. 2.7 (b) it then follows that the $b$ peaks correspond to the $v_1$-mode; the two $b$ peaks in Fig. 2.6 (b) are the $v_1$-mode $\nu=1$ and $\nu=2$ levels. The satellite peaks $c$ then correspond to thermal (unpumped) population in the $\nu=1$ level of another mode.
Table 2.2 Coherent anti-Stokes Raman peaks and their anharmonic shifts for SO2. The first three columns show the two $v_1$-mode levels involved in the CARS probe, the corresponding anharmonic shift and the literature value for this shift. The next column indicates how intensity of peak changes after IR-pumping, and the last two columns give the assignment and observed shift.

The location of the $b$ peaks yields a value for the $v_1$ self-anharmonicity of $\chi_{11} = -3.65 \pm 0.06 \text{ cm}^{-1}$, in close agreement with published values around $-3.7 \text{ cm}^{-1}$ (Table 2.3). The $c$ peaks can be assigned to the $010 \rightarrow 110$ and $110 \rightarrow 210$ Raman transitions based on their positions relative to the $a$ and $b$ peaks and the observation that their intensities are unaffected by IR pumping. Thus the $c$ peaks represent thermal $v_2$ population, and yield a value for $\chi_{12}$ of $-3.3 \pm 0.3 \text{ cm}^{-1}$.

A comparison of the peak intensities in Figs. 2.6 (b) and 2.7 (b), after correction for the spectral profile of the broadband dye-laser, shows that the vibrational temperatures following excitation in the bulk and in the beam are $1200 \pm 100 \text{ K}$ and $700 \pm 100 \text{ K}$, respectively. There are two possible reasons for the much less efficient excitation of the $v_1$-mode in the molecular beam. First, since the collision rate in the beam is much lower,
Table 2.3 Values of the anharmonic constants $\chi_{11}$ and $\chi_{12}$ in cm$^{-1}$ as reported in this work and in the literature.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{11}$</td>
<td>$-3.65 \pm 0.06$</td>
<td>$-3.99$</td>
<td>$-3.71$</td>
<td>$-3.711$</td>
<td>$-3.655$</td>
</tr>
<tr>
<td>$X_{12}$</td>
<td>$-3.3 \pm 0.3$</td>
<td>$-2.05$</td>
<td>$-3.03$</td>
<td>$-4.236$</td>
<td>$-3.129$</td>
</tr>
</tbody>
</table>

collisionally assisted excitation may be reduced. Second, rotational cooling due to adiabatic expansion limits the spectral overlap with the CO$_2$-laser line. To estimate the importance of this effect, we first assume that SO$_2$ can be approximated as a prolate symmetric top molecule [32]. For such a molecule, $v_1$ and $2v_2$ are categorized as type-$B$ bands [32], whose infrared absorption spectra are characterized by a number of overlapping $Q$-branches. From the expression for the rotational energy of a symmetric top [31],

$$E_{J,K} = BJ(J + 1) + (A - B)K^2,$$

where $A$ and $B$ are rotational constants related to the molecular moments of inertia, we see that the $Q$-branch lines ($\Delta J = 0, \Delta K = \pm 1$) occur at frequencies given by:

$$v = v_0 + (A' - B) \pm 2(A' - B')K + [(A' - B') - (A'' - B'')]K^2$$

$$\approx v_0 + (A' - B') \pm 2(A' - B')K,$$

where the single and double primes refer to the final and initial states, respectively. Thus, the $Q$-branch lines are separated approximately by $2(A - B)$ cm$^{-1}$. For the SO$_2$ $v_1$-band one has $2(A - B) = 3.4$ cm$^{-1}$ [30], so the 71-cm$^{-1}$ detuning from band center for the 9R(22) CO$_2$-laser line overlaps with the rotational band around $K = 21$. At room temperature the rotational distribution for SO$_2$ peaks at $J = 17$, so pumping by 9R(22) at a nominal detuning of 71 cm$^{-1}$ is not surprising.
Far from the nozzle in a supersonic jet, after the adiabatic expansion, the rotational distribution is greatly cooled to low $J$-value, as evidenced by narrowing of the ground state peak in the spectrum. As a result of this, the overlap between the CO$_2$ line and the rotational bands is reduced and the pumping becomes less efficient to the point where it is not observed at all.

The absence of $v_2$ first overtone excitation is probably due to an extremely small cross section for this excitation [34]. While it is an allowed transition, it is not observed in absorption spectra [34], nor in collisional energy transfer experiments [33].

Based on these results we can conclude that the laser intensities in this experiment are below the incoherent excitation regime for SO$_2$. This conclusion is supported by the lack of laser-induced excitation of any modes except for the laser-pumped mode, including the more highly excited gas-cell samples. This means that even in the case of gas cell samples where collisions assist excitation, too few photons are absorbed per molecule to achieve strong coupling between laser-pumped and non-pumped molecular modes. As we show shortly, this is in marked contrast to the results for SF$_6$, where significant intra- and inter-molecular population redistribution is evident.

Our results unambiguously show that 9R(22) and 9R(32) pumping of SO$_2$ lead to excitation of the $v_1$-mode at 1151.3 cm$^{-1}$. While these lines are significantly detuned from the band head, they fall near the peak of the rotational $Q$-branch of the $v_1$-mode at room temperature. The data presented here also illustrate the utility of the multiplex BOXCARS technique for direct observation of low-energy mode-selective excitation.

2.4.2 SF$_6$: A two-ensemble picture

For a larger polyatomic molecule like SF$_6$, the density of states (and hence inter-mode coupling) increases rapidly as a function of increasing vibrational quantum number $v$. The resulting increase in excitation efficiency compared to SO$_2$ leads to high vibrational excitation in both the laser-excited and non-pumped modes. Since strong coupling between
laser-excited and non-pumped modes produces efficient energy redistribution, multiplex CARS spectra of excited SF₆ tend to be complex and difficult to interpret compared to SO₂ spectra. The results presented here clarify contradicting reports in previously published work on SF₆. We find that collisional energy redistribution dominates the dynamics observed on a 100-ns time scale. We also report a new model for interpretation of the spectra. Analysis using these new results resolves the contradictions in the literature and provides a qualitatively simpler interpretation of the experiments described here and in the literature.

2.4.2.1 Previous Work

Early studies of infrared multiphoton excitation in SF₆ were motivated by the discovery of efficient dissociation in samples pumped by a high-power CO₂-laser [35-39]. The molecule’s similarity to UF₆ [40] led to further research which produced applications in laser isotope separation. SF₆ has six normal modes; the ν₃-mode is strongly infrared active and resonant with several 10-µm branch CO₂-laser lines [41].

Coherent anti-Stokes Raman and other Raman probes have been used to investigate infrared multiphoton excitation in SF₆. The high efficiency of excitation produces markedly different results from those obtained for SO₂. Using spontaneous Raman scattering, Bagratashvili et al. [42] observed a dual spectral distribution of broad ‘hot’ and ‘cold’ ensembles created by 10P(20) excitation; following excitation, the two ensembles appeared to dynamically equilibrate to a single distribution. Scanning-CARS gas cell-sample studies [43] show selective low-energy ν₃-mode excitation under low collision-rate conditions; multimode excitation occurs at higher collision rates producing nearly continuous, more highly excited spectra [44-46]. These authors conclude that their results support the existence of an energy threshold marking the onset of excitation into ‘quasicontinuum’ states. Furthermore the authors suggest that the nearly continuous spectral features at higher energies correspond to quasicontinuum states. These experiments place an estimate on the excitation threshold to quasicontinuum states at 6000 cm⁻¹, which is equivalent to an
average absorption of about six $10P(20)$ photons per molecule [44]. On the other hand, a different series of CARS experiments with infrared excited SF$_6$ by Schweitzer et al. [47] yielded quite different results; while ground-state depletion was observed following $10P(20)$ pumping, no excited state peaks or broad continuous features as seen by the previous two groups were observed.

2.4.2.2 Results

The results of our measurements with variable collision rates in a jet explain the disparity between previous results, and show that, depending on excitation and collisional parameters, spectra consistent with the results of either group of researchers can be achieved. Furthermore, we find that collisions dominate the energy redistribution following laser excitation of the ensemble.

\[ \nu_1 \quad 775 \text{ cm}^{-1} \]

\[ \nu_3 \quad 948 \text{ cm}^{-1} \]

Fig. 2.8 Pump and probe normal mode vibrations. The probed $\nu_1$-mode is a symmetric stretch at 775 cm$^{-1}$. The pumped $\nu_3$-mode is an infrared-active vibration at 948 cm$^{-1}$.
We performed multiplex CARS on the SF$_6$ symmetric $\nu_1$-mode at 775 cm$^{-1}$ while pumping the infrared-active $\nu_3$-mode with truncated 300-mJ/cm$^2$ 10$P$(20) CO$_2$-laser pulses in free jet samples [2, 4]. Figure 2.8 schematically illustrates these two normal modes. By varying the collision rate and pump-probe delay, we obtained spectra that qualitatively reproduce both previous low and high collision rate measurements in which a continuum feature appears. Furthermore, the multiplex method yields accurate relative intensities of the evolving spectra at different collision rates or pump-probe delays. This allows quantitative

![Vibrational CARS spectra of IR-excited (10$P$(20) line at 300 mJ/cm$^2$) SF$_6$ at various pump-probe delays for high and low collision rates. (a) High collision rate ($z/D=2.0$, 0.14 collisions/ns). (b) Low collision rate ($z/D=4.1$, 0.014 collisions/ns). Note change in vertical scale for different delays.](data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAABAAAAAQA...)

Fig. 2.9  Vibrational CARS spectra of IR-excited (10$P$(20) line at 300 mJ/cm$^2$) SF$_6$ at various pump-probe delays for high and low collision rates. (a) High collision rate ($z/D=2.0$, 0.14 collisions/ns). (b) Low collision rate ($z/D=4.1$, 0.014 collisions/ns). Note change in vertical scale for different delays.
modeling of the spectra, revealing (1) a ‘two-ensemble’ population distribution produced via infrared multiphoton excitation, and (2) collision-rate-dependent energy transfer from the laser-pumped mode to the non-pumped modes after excitation.

Time-resolved spectra for both high and low collision rates are shown in Figure 2.9. In both cases, one sees the intensity of the ground state at 775 cm\(^{-1}\) decrease from the onset of infrared pumping (note change in vertical scale). Under high collision rates \((\zeta/D = 2.0; 0.14 \text{ collisions/ns})\), we observe rapid formation of a high-excitation broad spectral continuum within 50 ns (Fig. 2.9 (a)). At 70-ns delay, this continuum peaks at about 770 cm\(^{-1}\), but then shifts towards higher excitation as time elapses. After several hundred nanoseconds (see Figure 2.10) the peak of the continuum reaches 750 cm\(^{-1}\); this 25-cm\(^{-1}\) shift corresponds to the absorption of about five infrared photons in the \(v_3\)-mode. The overall intensity of the continuum drops below detectable levels after 500 ns. In contrast, results obtained at low collision rate \((\zeta/D = 4.1; 0.014 \text{ collisions/ns})\) exhibit selective \(v_3\)-mode excitation up to only the \(v = 3\) level, as shown by the individual peaks at a 50-ns delay in Fig. 2.9 (b). A barely detectable broad continuum does arise at about 70 ns, with a peak around 765 cm\(^{-1}\). The entire low-collision rate spectrum drops in intensity below detectable levels within 150 ns following excitation.

Figure 2.11 shows an extensive set of data in which we examined the spectra at fixed pump-probe delays in the range 100 to 400 ns for variable collision rates \((0.10–0.70 \text{ collisions/ns})\). In these data, the low collision-rate spectra \((\zeta/0.14 \text{ ns}^{-1} \text{ data in 2.11 (a) and (b)})\) exhibit discrete peaks as in Fig 2.9 (a), and the high collision-rate spectra exhibit the continuous features of Fig 2.9 (b). Qualitatively, similar spectral evolution is observed either as a function of the pump-probe delay (as in Fig. 2.9) or as a function of collision rate at fixed pump-probe delay (Fig. 2.11).
2.4.2.3 Analysis

To extract the time-resolved population distribution $N_{\{\nu,j\}}$ we need to quantitatively model the multiplex CARS spectra. A spectral fitting procedure that computes the ensemble distribution for each of the six normal modes is not helpful for an intuitive interpretation; a six parameter model that assigns a vibrational temperature to each normal mode will not produce a unique fit. Instead we tested the assumption that the degrees of freedom might be reduced by computing the temperatures of only two Boltzmann ensembles, using one temperature for the laser-pumped mode and another temperature for the remaining non-pumped modes. This assumption essentially treats the non-pumped modes as a heat bath, similar to the description used in theoretical work by several authors [5, 7, 19]. The assumption of a heat bath is consistent with strong inter-mode coupling driven either by a high collision rate or fast intramolecular processes.
Fig. 2.11 Vibrational CARS spectra of IR-excited (10P(20) line at 300 mJ/cm²) SF₆ at fixed pump-probe delays for variable collision rates. (a) 160-ns pump probe delay (b) 300-ns pump-probe delay. All spectra are plotted on same vertical scale. Spectral intensities are corrected for the change in density of the jet as a function of \( z/D \).

We wish to emphasize that multiplex CARS spectra require careful analysis for quantitative interpretation: when computing a spectrum with overlapping peaks, one needs to correctly add the real and imaginary parts of the lineshapes of each peak (cf. denominator in Eq. 2.3), as well as properly normalize each spectrum using the partition function. We performed this fitting procedure for the data shown in Fig. 2.9, but found that the spectral shape and intensity of the infrared excited spectra could not be fit using the aforementioned two-temperature model. One finds, for example, that a spectrum such as that obtained at 70-
ns delay (Fig. 2.9 (a)) cannot exhibit both a broad continuum and a small ground state peak in a two-temperature model.

Instead, we divided each of the two distributions, the pumped and non-pumped modes, into two ‘hot’ and ‘cold’ ensembles. Thus we have four parameters that describe the spectra: two temperatures (‘hot’ and ‘cold’) for the pumped mode and two temperatures for the non-pumped modes. The motivation behind this model is the concept of a threshold in the multiphoton excitation process, as discussed in Section 2.2.2. If a threshold exists, and the CO₂-laser fluence is near the threshold value, one would expect that some fraction of the laser-excited molecules will be excited above threshold. The multiplex CARS spectrum from the excited molecules will then be a convolution of signals from a highly excited above-threshold fraction (‘hot ensemble’) and from a cooler below-threshold fraction (‘cold ensemble’).

Spectra from the four-temperature model are shown in Fig. 2.12 for the data of Fig. 2.9 using published values for the normal mode frequencies and anharmonic coupling constants of SF₆ [48, 49], and adjusting the temperatures for optimal fit to the data. Comparison of the two figures shows that the model produces curves that match both the spectral shape and the relative intensities of the spectra. Similar agreement was found for the data obtained as a function of collision rate. Table 2.4 summarizes the pumped-mode parameters for the calculated spectra in Fig. 2.12.⁴

At high collision rates (Fig. 2.12 (a)), the temperature of the ν₃-mode hot ensemble increases from 900 K at a 10-ns delay to a high of 2500 K at 70 ns, with the hot ensemble containing 90% of the molecules. The ν₃-mode cold ensemble peaks at 600 K. At low collision rates (Fig. 2.12 (b)), the ν₃-mode hot ensemble increases from 1000 K at a 25-ns

⁴The fits are obtained by eye, without the use of any quantitative error minimization. We find that the double requirement of spectral overlap and magnitude overlap constrain the parameters of Tables 2.4 and 2.5 to within ± 100 K of the values shown.
Fig. 2.12 Computed CARS spectra of SF$_6$ for the data of Fig. 2.9. Data are plotted for various pump probe delays (a) 0.14 collisions/ns (b) 0.014 collisions/ns. See text for explanation of computation algorithm. Temperature parameters obtained for these computed spectra are shown in Table 2.4.

delay to a high temperature of 3500 K at 70 ns, with the hot ensemble containing 80% of the molecules. The $\nu_3$-mode cold ensemble peaks at 800 K. The non-pumped, or heat bath, modes in both cases do not get as hot, nor is there much variation between the heat bath hot and cold ensembles. Typically the heat bath temperatures range from 300–500 K. The difference in peak temperatures reached in the high and low collision rate cases is attributed to a difference in CO$_2$-laser fluence.
Table 2.4 Parameters for the SF$_6$ calculated spectra in Figs. 2.12 (a) (0.14 collisions/ns) and 2.12 (b) (0.014 collisions/ns). $\tau$ is the pump-probe delay. $T(\nu_3)_{\text{hot}}$ and $T(\nu_3)_{\text{cold}}$ refer to the $\nu_3$-mode hot and cold ensemble temperatures respectively, with $F_{\text{hot}}$ equal to the fraction of the molecules in the hot ensemble.

<table>
<thead>
<tr>
<th>$\tau$ (ns)</th>
<th>$T(\nu_3)_{\text{hot}}$ (K)</th>
<th>$T(\nu_3)_{\text{cold}}$ (K)</th>
<th>$F_{\text{hot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>900</td>
<td>350</td>
<td>0.30</td>
</tr>
<tr>
<td>30</td>
<td>1900</td>
<td>450</td>
<td>0.69</td>
</tr>
<tr>
<td>50</td>
<td>2300</td>
<td>600</td>
<td>0.81</td>
</tr>
<tr>
<td>70</td>
<td>2500</td>
<td>600</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>n/a</td>
<td>500</td>
<td>0.70</td>
</tr>
<tr>
<td>25</td>
<td>1000</td>
<td>740</td>
<td>0.71</td>
</tr>
<tr>
<td>50</td>
<td>2500</td>
<td>780</td>
<td>0.71</td>
</tr>
<tr>
<td>70</td>
<td>3500</td>
<td>800</td>
<td>0.81</td>
</tr>
</tbody>
</table>

As noted above, the spectral evolution observed as a function of pump-probe delay is qualitatively the same as the evolution observed as a function of collision rate at a fixed pump-probe delay. Table 2.5 summarizes the results of fitting the two ensemble model to the data of Fig 2.11. As a function of collision rate at 160 ns pump-probe delay, the $\nu_3$-mode hot ensemble increases from 1150 K at 0.14 collisions/ns to 2000 K at 0.69 collisions/ns. The hot ensemble grows from 50% of the molecules to 80% in the same collision rate range. Similar to the data from the pump-probe delay experiment, the $\nu_3$-mode cold ensemble rises to 500 K while the heat bath temperatures range from 300–500 K.

The model curves of Fig. 2.12 directly yield the population distribution function $N_{\{\nu, j\}}$ (cf. Eq. 2.3). Vibrational population distributions for the $\nu_3$-mode spectra in Fig. 2.12 (a) are shown in Figure 2.13. These distributions are obtained by plotting the sum of the two Boltzmann distributions (the hot and cold ensembles) weighted by the computed fractions.
Table 2.5 Parameters for the SF$_6$ spectra in Figs. 2.11 (a) (160-ns delay) and 2.11 (b) (300-ns delay) as a function of collision rate. $T(\nu_3)_{\text{hot}}$ and $T(\nu_3)_{\text{cold}}$ refer to the $\nu_3$-mode hot and cold ensemble temperatures respectively, with $F_{\text{hot}}$ equal to the fraction of the molecules in the hot ensemble. Fits were corrected for the change in CARS signal as a function of density of molecules in the jet at each collision rate.

<table>
<thead>
<tr>
<th>coll. rate (ns$^{-1}$)</th>
<th>$T(\nu_3)_{\text{hot}}$ (K)</th>
<th>$T(\nu_3)_{\text{cold}}$ (K)</th>
<th>$F_{\text{hot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>1150</td>
<td>400</td>
<td>0.50</td>
</tr>
<tr>
<td>0.22</td>
<td>1250</td>
<td>330</td>
<td>0.66</td>
</tr>
<tr>
<td>0.35</td>
<td>1750</td>
<td>500</td>
<td>0.74</td>
</tr>
<tr>
<td>0.47</td>
<td>1900</td>
<td>500</td>
<td>0.76</td>
</tr>
<tr>
<td>0.67</td>
<td>2000</td>
<td>500</td>
<td>0.79</td>
</tr>
</tbody>
</table>

The resulting nonequilibrium distributions show the evolution of the pumped mode population from its initial ground state condition to a highly excited state within 70 ns. Note that a single rotational temperature (70 K) is adequate for all the data included in Fig. 2.13; thus we have assumed no evolution of the rotational part of $N\{v, J\}$ in producing the vibrational distributions.

From the distribution function $N\{v, J\}$ we also determine the number of photons absorbed per molecule. As expected, we find that the number of photons absorbed is a constant for pump-probe delays greater than the laser pulsewidth. For the data obtained at a CO$_2$-laser fluence of 300 mJ/cm$^2$, the modeling yields a range of 3–5 photons absorbed per molecule. While the computed number of absorbed photons is constant within a few percent for a given data set it varies in the above range between different data sets. This is so even though we monitored the fluence from shot to shot and even though we took special
care to ensure that the probed volume was uniformly pumped by the CO2-laser, with no ‘hot spots’ in the focal volume. The variability in the number of photons absorbed most likely arises from the 10% shot-to-shot intensity fluctuations in the CO2-laser fluence. Because of the threshold in the excitation process, small fluctuations in the fluence lead to different ratios of hot-to-cold fractions. We note here that without quantitative modeling, these variations would have gone unnoticed.

![Image](image_url)

**Fig. 2.13** Nonequilibrium vibrational population distributions $N(v)$ for the $v_3$-mode of SF$_6$ at various pump-probe delays for the high collision rate computed spectra of Fig. 2.12 (a).

### 2.4.2.4 Discussion

Using a simple two-ensemble picture, we can successfully model the multiplex CARS spectra of laser-excited SF$_6$. We find that individual, resolved peaks in the spectra of less-excited molecules correspond to excited levels of the laser-pumped ($v_3$) mode, while the broad spectral continuum observed in more highly-excited spectra corresponds to excited
levels of the non-pumped modes. These non-pumped modes can essentially be treated as a single temperature heat bath. We also find that even for pump-probe delays much longer than the laser pulse excitation: (1) two ensembles persist, each with different heat bath and laser-excited-mode temperatures, and (2) the spectral evolution as a function of either pump-probe delay or collision rate is qualitatively the same.

These results imply that SF₆ does not reach intra-mode equilibrium within 100 ns of the infrared excitation in these experiments, and that this nonequilibrium condition can persist as long as 500 ns. Furthermore, the results show that collisional vibrational energy redistribution dominates all the dynamics observed.

A nonequilibrium distribution is observed when the multiphoton excitation produces two ensembles of excited molecules, one hotter than the other. In each single molecule, intramolecular energy relaxation will redistribute vibrational energy within a few nanoseconds (assuming an average of 3–5 photons absorbed per molecule [13]). Thus an equilibrium distribution is rapidly reached within each ensemble of molecules. The multiplex CARS spectra show the convolution of these two overlapping ensembles, and the redistribution dynamics between them as they equilibrate to a single temperature. Because we observe these dynamics to be similar either as time progresses, or as the collision rate increases at a fixed time, we clearly see that these dynamics are dominated by intermolecular, or collisional, energy transfer.

The observed two-ensemble distribution supports the hypothesis that infrared multiphoton excitation can produce two distinct ensembles, as originally suggested by Letokhov [19]. The observation of (1) two distinct ensembles, and (2) high variation in the average number of photons absorbed per molecule, point to the existence of a threshold to incoherent excitation. For SO₂ the average number of photons absorbed per molecule is

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We note that spatially inhomogeneous laser pumping might lead to the production of two or more distinct ensembles. However, we ensured that the probed volume was well within the infrared-pump volume, ensuring a homogeneously pumped volume.
below the predicted threshold, but for SF$_6$, with an average of 3–5 infrared photons absorbed per molecule (3000–5000 cm$^{-1}$), we excite close to the predicted threshold (5000–6000 cm$^{-1}$) [18].

The broad continuum observed in the spectra consists of overlapping peaks of the non-pumped modes, populated predominantly by collisional energy transfer from the laser-pumped mode. This contrasts with the interpretation of Ref. [46], in which intramolecular redistribution is considered to be the dominant energy transfer mechanism in infrared multiphoton excitation of SF$_6$. Our interpretation furthermore shows that the broad highly excited feature in the SF$_6$ spectra does not, as previously stated [44, 46], correspond to ‘quasicontinuum’, or above-threshold, states directly populated by the laser. Instead, this broad feature is formed by rapid population of a heat bath of non-pumped modes via intermolecular energy transfer in collisions. Hence, collisions significantly enhance the overall excitation process.

In summary, we find that while the spectra of infrared excited SF$_6$ are more complex than the spectra of the smaller polyatomic SO$_2$, this system can nevertheless be simplified and quantitatively modeled within the context of the coupled anharmonic oscillator picture. The simplifications we use incorporate the concept of a threshold in the infrared multiphoton excitation. The resulting model fits to the data indicate that IR-excitation creates (1) a two-ensemble vibrational distribution and (2) a heat bath of non-pumped modes in molecules excited above threshold. These results are consistent with the experimental interpretation of Bagratashvilli et al. [50] in spontaneous Raman experiments, and with the theoretical work of Letokhov [16] and others. The model yields dynamic population distributions $N_{\{n,j\}}$ and provides useful qualitative and quantitative insight into the excitation and energy redistribution process.
2.5 Conclusion

2.5.1 Summary of Results

In this chapter we discuss multiplex CARS measurements of infrared multiphoton excited molecules. Analysis of the resulting spectra generate detailed qualitative and quantitative information about the vibrational population of an excited polyatomic, and the evolution of this population as inter- and intra-molecular processes redistribute the energy. In SO$_2$ we observe direct $\nu_1$-mode excitation and distinguish between this process and excitation of the nearly resonant $\nu_2$-mode overtone. In SF$_6$, we directly observe $\nu_3$-mode excitation followed by collisional energy redistribution to a heat bath of non-pumped modes. Quantitative modeling of the SF$_6$ spectra resolves some long-standing inconsistencies between different published reports and supports the concept of a threshold for infrared multiphoton excitation. In the sequence of presentation (SO$_2$, SF$_6$) we see an increasing complexity in the infrared multiphoton excitation and the vibrational relaxation process as higher levels of excitation are produced in molecules with successively more vibrational modes.

2.5.2 Future Work

Current experimental effort in the area of molecular energy transfer has moved from the nanosecond timescale to the subpicosecond regime. Using ultrashort pulse excitation one can excite specific vibrational or electronic states on a timescale much faster than competing energy transfer processes. This fact eliminates the problem of having the laser-excitation timescale overlap with energy redistribution timescales. Subpicosecond excitation and probing also avoids the effect of collisional energy redistribution. Therefore extension of the work described in this chapter to the ultrashort pulse regime would provide a clearer picture of the vibrational relaxation dynamics. Given the fact that the excitation rate using femtosecond pulses can exceed the rate of energy relaxation and redistribution, a study in the
femtosecond domain may reveal excitation and reaction channels which are only accessible via femtosecond pulse excitation [15, 16].

Extending the M-CARS technique to the ultrafast time domain is of current theoretical and experimental concern as well. Experiments are now planned in our laboratory that will test the applicability of ultrashort pulse CARS for detecting time- and state-resolved molecular states excited by a 100-fs laser pulse. The study of ultrashort pulse initiation of molecular reactions is the subject of Chapter 4. Chapter 7 describes how ultrashort pulse CARS might be used in conjunction with the results of Chapter 4 to realize the goal of time-resolving the birth of a molecule on a catalytic surface.

References:

Chapter 3

Ultrafast time- and energy-resolved relaxation of laser-excited electron energy distributions in silicon

3.1 Motivation for the experiment

3.1.1 Ultrafast dynamics of semiconductors

The timescale for electron-phonon equilibration in a semiconductor is $10^{-12}$ s (1 ps); this timescale is determined by the electron-phonon scattering rate [2]. The timescale for carrier-carrier equilibration is on the order of tens of femtoseconds [3, 4]. Given the two orders of magnitude difference between these timescales, the absorption of a 100-fs laser pulse, with photon energy greater than the bandgap, produces a highly excited conduction band electron distribution, and a corresponding excited valence band hole distribution, without initial heating of the lattice [5]. On a 1–10 picosecond timescale, electron-phonon scattering equilibrates the carriers with the lattice [6]. On a nanosecond timescale, diffusion transports

\[^{1}\text{The work described here is published in Ref. [1]}\]
Chapter 3 Ultrafast time- and energy resolved electron distributions

heat into the bulk, away from the excited region [7]. Also on this timescale, for a clean
surface, the charge distribution relaxes via electron-hole surface recombination [8]. As long
as no structural change has occurred such as lattice melting [9], the system returns to its
initial unexcited state.

Since the advent of ultrashort pulse lasers, the study of ultrashort pulse interactions with
semiconductors has been of great theoretical and experimental interest. The study of
ultrafast electronic relaxation in semiconductors offers the opportunity to directly observe in
the time domain processes that previously had only been assumed theoretically. Measuring
the timescales of carrier-carrier and electron-phonon interactions is important for modern
semiconductor device design [10]. These timescales are required as parameters for a variety
of semiconductor physics calculations, including Monte Carlo scattering rate calculations and
surface-state dynamical simulations [2, 11].

3.1.2 Electron energy distributions in Si

Ultrashort pulse lasers have been applied extensively to the study of electron dynamics in
direct gap semiconductors, especially GaAs and InP [12-14]. In contrast, prior to this work
there had not been a study with subpicosecond time resolution performed on Si. The main
reason for this appears to be that Si, with its indirect gap, is more difficult to study using the
standard approaches that work well with direct-gap materials. These techniques include
reflectivity/transmission-type [15, 16], and nonlinear-optical-type probes [17, 18]. For
example, in order to study electron relaxation in GaAs, Shank et al. [15] used a hole-burning
technique where the change in transmission of their sample at the probe wavelength is
measured following a pump pulse. Because the pump and probe photons induce direct
transitions of known energy across a direct gap, the electron dynamics can be inferred from
the experiment directly. However, with an indirect gap material, a wide range of indirect
transitions involving a phonon will occur. This fact makes it difficult to interpret changes in
Si reflectivity or transmission as due to a decrease or increase in electron population at a
particular energy and wavevector, because the specific indirect pump transitions that occur are difficult to identify.²

Ideally then, to study an indirect gap material one desires a technique which directly yields the entire electron energy distribution created by the pump laser pulse. Direct time-resolved measurement of the electron energy distribution unambiguously reveals the electron dynamics. The most common approach for obtaining such a distribution is electron photoemission. In photoemission, a probe laser pulse with energy $E_{\text{photon}}$ causes emission of electrons out of the sample and into the surrounding vacuum (cf. Fig. 3.1). The portion of the electron distribution in the sample which lies within $E_{\text{photon}}$ of the vacuum level $E_{\text{vac}}$ are photoemitted. If the photoemitted electrons experience no scattering with the lattice during emission, and no distortion of the distribution occurs due to electron-electron interactions outside the sample [19], then the photoemitted electron energy distribution will be the same as the distribution inside the sample, shifted in energy by an amount $E_{\text{photon}} - \phi$, where $\phi$ is the sample work function. The electron energy distribution is measured using either time-of-flight spectroscopy (Sect. 3.3.2) or retarding-field spectroscopy [20]. If the probe pulse follows an exciting (pump) laser pulse in time, and has 100-fs duration, then the evolution of the substrate electron energy distribution created by the pump pulse can be observed with 100-fs time resolution. Furthermore, if the spatial angular distribution of the electron photoemission is measured, these angle-resolved distributions can be used to determine the momentum distribution of the electrons in the bulk band structure as well [21], yielding a more complete dynamical picture of electron relaxation.

²It is also important to note that while Si does have a direct gap at for photon energies above 3.5 eV, the conduction and valence bands are nearly parallel over a large region of $(E,k)$ space around the direct gap, making reflectivity/transmission techniques equally difficult to interpret for the direct gap.
In a photoemission experiment from a crystal surface, the probe photon photoemits electrons only from a thin region limited by the penetration depth of the high energy photons required to produce photoemission. Ultraviolet pulses with $E_{\text{photon}} \geq 4 \text{ eV}$ have penetration depths $\leq 10 \text{ nm}$. This fact can be used to one’s advantage by choosing a probe wavelength with maximum penetration depth for the study of primarily bulk effects, or with a minimum penetration depth for studying surface effects. In general, photoemission is a valuable tool for distinguishing between surface and bulk semiconductor electron dynamics, particularly in the case of surface recombination [22].

\footnote{For example a penetration depth of $\leq 1 \text{ nm}$ will probe the first few atomic layers of Si (lattice constant $= 0.54 \text{ nm}$ [7]).}
3.2 Description of Experiment, and Previous Work

3.2.1 Overview

In the experiment described here, we performed the first subpicosecond (100-fs) time-resolved measurement of the energy relaxation of optically excited electrons in Si [1]. This is accomplished in a pump-probe experiment by analyzing the photoelectron spectrum generated by an ultrashort ultraviolet (4-eV, 310-nm) probe pulse, as a function of the delay time from a visible (2-eV, 620-nm) pump pulse. The photoelectron spectrum is measured using a time-of-flight technique. Analysis of the resulting electron energy distributions shows electron-electron thermalization in under 120 fs, followed by fast electron cooling and equilibration with the lattice in 1 ps.

In addition, we report a new approach for probing hot electron distributions, using two-photon probe photoemission in a high probe-intensity regime. Unlike the standard approach which directly photoemits excited conduction band electrons via one-photon probe transitions, the two-photon approach detects the conduction band electron population indirectly by measuring the decrease in two-photon photoemission of valence band electrons following the pump pulse. A decrease occurs because the excited conduction band electrons block intermediate states of the two-photon probe transitions from the valence band. Using this approach we observe surface and bulk electron dynamics for long pump-probe delays, from 1 ps to 1 ns.

3.2.2 Si band structure, and choice of pump and probe photon energies

Silicon has an indirect gap of 1.0 eV at room temperature, and a direct gap of 3.5 eV along the \( \Gamma \) direction [8] (see Figure 3.1). The work function \( \phi \) is the energy required to promote an electron from the valence band maximum (labeled ‘vbm’ in Fig. 3.1) to the

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4Work done in collaboration with J.A. Prybyla at AT&T Bell Labs, Holmdel, NJ.
vacuum energy $E_{\text{vac}}$. We hereafter use the notation $E_{\text{vbm}}$ and $E_{\text{cbm}}$ to refer to the valence band minimum and conduction band maximum energies, respectively, measured referenced to $E_{\text{vac}} = 0$ eV. Typical values for $\phi$ lie between 4.4–5.1 eV depending on crystallographic face and surface preparation [8]. For our Si(100) surface we measure $\phi = 4.7$ eV (see Sect. 3.3.1 for sample preparation technique, and Sect. 3.4.2 for the method of measuring $\phi$). The Si(100) surface forms a $2\times1$ reconstruction [23, 24]. Calculations for the Si(100)$2\times1$ surface [24, 25] indicate that dangling bond states extend into the gap, with one state ($\pi_1^*$) extending from near the conduction band minimum to 0.4 eV above the valence band maximum. The $\pi_1^*$ state is believed responsible for pinning the Fermi level [26] at the surface at 0.2 eV above the valence band maximum [20]. The doping of the sample used here (doped with boron to $1\Omega\text{-cm}$ resistivity) fixes the bulk Fermi level at also 0.2 eV above the valence band maximum [8], which means that there is no significant band-bending in the surface region [20].

The 100-fs, 2-eV pump photons will excite electrons via indirect transitions from the valence band into the conduction band, shown schematically by the vertical arrow (labeled ‘pump’) in Fig. 3.1. Surface states can also be populated directly by the pump, or indirectly through electron relaxation from excited conduction band states. Given the photon and band gap energies, one expects a maximum excess electron energy of 1 eV above the conduction band minimum. The actual conduction band electron distribution that results from pumping will be proportional to the product of the initial and final electronic density of states.

The probe photon energy of 4 eV is ideal because 4 eV is insufficient energy to directly photoemit valence band electrons via one-photon transitions. Photoemission from the
valence band is undesirable, because valence band photoemission will mask out the orders of magnitude smaller conduction band photoemission signal.\(^\text{5}\)

The 4-eV probe promotes conduction band electrons (and some electrons near and slightly below the conduction band minimum in gap states) to energies above the vacuum level \(E_{\text{vac}}\). Measured from the conduction band minimum, the electron energy in the conduction band, \(E_{\text{cb}}\), can reach a maximum of 1 eV. The ionization potential, \(\chi\), the energy difference between \(E_{\text{vac}}\) and the conduction band minimum, is about 3.7 eV (cf. Fig. 3.1) [27]. Therefore, the photoemitted electrons will have a kinetic energy spectrum, \(E_{\text{KE}}\), which extends from near zero energy to a maximum of about 1 eV, with \(E_{\text{KE}}\) given by:

\[
E_{\text{KE}} = E_{\text{cb}} + E_{\text{photon}} - \chi + \Delta\phi_d, \tag{3.1}
\]

where \(\chi = E_{\text{vac}} - E_{\text{cbm}},\) and \(\Delta\phi_d\) is the contact potential difference between the sample and the electron detector.

The kinetic energy given by Eq. 3.1 includes the approximation that photoemission by the 4-eV probe exactly preserves the initial conduction band electron distribution. This approximation is valid if (1) no significant interaction arises between a photoemitting electron and the sample after irradiation, and (2) the number of photoemitted electrons is well below the electron density at which electron interactions outside the sample can distort the photoemitted electron distribution. Point (1) above is a conventional approximation for photoemission measurements [28, 29], and is justified when the photoemitted electron’s mean free path in the sample lattice is greater than the penetration depth of the probe pulse. According to the universal mean free path curve [26], electrons with less than 1-eV kinetic energy have mean free paths exceeding 20 nm, and this value is further corroborated by Monte Carlo simulations of the electron dynamics [2]. Since the mean escape distance for our photoemitted electrons is given by the 10-nm penetration depth of the 4-eV probe light,

\(^\text{5}\)We performed some earlier measurements with a 6-eV probe, which has some advantages if one desires to obtain gap state electron distributions via one-photon photoemission. However the small conduction band signal that results is swamped by the four orders of magnitude greater valence band photoemission.
the effect of scattering on the measured distributions should be minimal. We avoid electron interactions outside the sample, point (2) above, by using a probe-beam intensity that emits fewer than 10 electrons per laser shot. We verified that the photoemission spectra presented here were reproducible over a range of probe intensities less than and greater than the probe intensities we used when collecting data, and furthermore verified that at a factor of 5–10 × higher intensities, distortion of the photoemission could in fact be observed. All the data presented here are collected in a probe intensity regime where no distortion occurs.

We note that 4-eV probe photoemission of conduction band electrons is assumed to occur via indirect transitions, since there are no final states in the bulk Si band structure 4 eV above the conduction band minimum. The lowest energy direct transitions lie 10 eV above the conduction band minimum as determined by x-ray photoemission measurements [30]. Because spectral assignment can be determined by identifying bulk band structure features in the electron photoemission spectra (see Sect. 3.4.2), detailed knowledge of the photoemitting electron transitions is not required for interpretation of the results.

### 3.2.3 Carrier-carrier and electron-phonon interactions

Typical incident pump fluences were 0.25 mJ/cm² in this experiment. This value was chosen to be well below the 100-mJ/cm² Si damage threshold [15] and below the threshold where photoemission is observed from the pump beam alone. With the 1-μm penetration depth of 2-eV light, and assuming 40% reflectivity, typical absorbed fluences were sufficient to excite 5×10¹⁸ carriers/cm³. Given the Si specific heat of 0.7 J/g°C [8], this absorbed fluence will heat the lattice by only 2 K. Assuming that the 2-eV photon energy is shared equally by electrons and holes, the average conduction band electron energy $E_{cb}$ will be 0.5 eV.

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6Photoemission from the pump alone is observable well below the Si damage threshold, and is assumed to result from two and three-photon valence band and gap state photoemission.
An electron temperature in the conduction band, $T_{cb}$, can be defined as the temperature of the thermalized conduction band electron distribution, taking the conduction band minimum as the zero of energy. This is appropriate for describing the conduction band electron temperature since these electrons are isolated from the valence band electrons and interact only among themselves on a sub-picosecond timescale. As discussed in greater detail in Sect. 3.4.3, the temperature $T_{cb}$ is a good average measure of the electron energy above the conduction band minimum for very high temperature distributions (i.e. for temperatures above the effective Fermi temperature). With this definition, an average electron energy $E_{cb}$ of 0.5 eV corresponds to a temperature $T_{cb} = 4000$ K.\(^7\)

At these carrier densities and energies, the initial electron and hole conduction band and valence band distributions are expected to equilibrate via carrier-carrier scattering in $10^{-13}$ to $10^{-14}$ s [6]. Note that this process does not cool the electron distribution; the average energy of carriers is not changed by carrier-carrier interactions. We note also that higher order interactions such as Auger recombination, which can significantly alter the electron distribution at carrier densities $\geq 10^{20}$/cm$^3$ [31] will be negligible at the carrier densities in our experiment. The primary channel for hot carrier cooling is electron-phonon scattering. The electron-phonon scattering rate in Si has been computed using pseudopotential methods that take into account the band structure [2, 11]. The results of this calculation at sample temperatures of 77 K and 300 K are shown in Figure 3.2 (a) and (b). The scattering rate varies with temperature due to changes in the phonon distribution, and is strongly dependent on electron energy. The scattering rate varies in the range $(0–0.7 \times 10^{14}$ s$^{-1}$) for electrons with energies $E_{cb}$ between 0–1 eV.

Figure 3.3 shows the electron cooling predicted by a simple model which assumes a linear scattering-rate dependence on electron energy, and an average phonon emission energy of 60 meV (zone-center LO and TO phonons in Si have 63-meV energy [7]). In the

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\(^7\)Computed by taking $3/2 k_B T_{cb} = 0.5$ eV.
model, each collision occurs in a time given by the energy-dependent scattering rate, and each collision reduces the electron energy by 60 meV. The calculation predicts that hot electrons will cool from the initial temperature $T_{cb} = 4000$ K to room temperature in 0.5 ps. This simple picture ignores the effect of heat transfer to the lattice and the role of other phonons beyond those at zone center, but it nevertheless provides a simple physical picture of the electron cooling process.

![Graph of computed conduction band electron phonon scattering rate $R_{e-p}$ from Ref. [11]. Results of calculations at sample temperatures of 77 K and 300 K are shown. The thin and thick solid lines are results of two different calculations. In the expanded view, two values for $R_{e-p}$ obtained in this work are plotted (see text for details).](image)

Fig. 3.2 Computed conduction band electron phonon scattering rate $R_{e-p}$ from Ref. [11]. Results of calculations at sample temperatures of 77 K and 300 K are shown. The thin and thick solid lines are results of two different calculations. In the expanded view, two values for $R_{e-p}$ obtained in this work are plotted (see text for details).

On nanosecond timescales, carrier diffusion and surface recombination are important. Electron diffusion transports heat away from the surface into the bulk, following the spatial conduction band electron density gradient created by the light pulse. A density gradient is established by the initial excitation since the pump pulse intensity drops exponentially with
depth on the length scale of the penetration depth. It is possible for diffusion to be important on sub-ns timescales. Using ultrashort ultraviolet pump pulses with \( \leq 5 \text{-nm} \) penetration depth, Rowe et al. showed [20] that on a ps timescale, sufficient diffusion can occur to significantly reduce the carrier density in the 5-nm surface region.

Surface recombination reduces the population of electrons and holes in the surface region. Surface recombination proceeds via relaxation of electrons and holes into gap (surface) states. Bulk recombination occurs on a microsecond timescale, so this process is not important in our experiment. The rate of surface recombination can be affected by surface states or defect states that preferentially capture either electrons or holes. In the presence of such states, surface charging may create a space-charge layer in the near-surface region hindering diffusion and/or surface recombination [22]. This possibility is discussed further in Sect. 3.4.4.3.

**Fig. 3.3** Simple conduction band electron cooling model. The model assumes an energy-dependent scattering rate from the calculation of Fig. 3.2, and takes a constant 60-meV energy drop per electron for each scattering event.
3.2.4 Previous photoemission experiments

Photoemission from Si was first studied in detail at Bell Labs in the early 1960’s in the seminal works of Allen and Gobeli [27, 32, 33], and described theoretically by Kane [28]. These researchers used intense ultraviolet arc lamps to induce photoemission, and measured the photoelectron yield as the current from sample to ground. In this way, they were able to measure the Si work function and the effect of surface adsorbates and contamination on the work function. They also evaluated methods for clean surface preparation in ultrahigh vacuum (10⁻¹⁰ torr). These experiments and others were pivotal in experimentally determining the bulk Si band structure and the electronic structure of Si surface states.

Time-resolved photoemission has been performed in a number of previous experiments which motivated the approach we use here. In metals, recent work demonstrated the use of ultrashort pulse photoemission to observe femtosecond image-potential dynamics [34]. Surprisingly long electron thermalization times (> 300-fs) were observed in a time-resolved photoemission study of gold films [35]. Angle-resolved and time-resolved photoemission with ultrashort pulses has been applied extensively by Haight, et al. [21, 36, 37] to study electron dynamics in GaAs, InP, and Ge.

The first photoemission spectra of laser-excited Si were measured using synchrotron radiation as the probe [38]. Two-photon photoemission from Si using 5-ns pulsed lasers was demonstrated by Benssoussan, et al. [39]. The first time-resolved observation of conduction band electrons was performed by Long, et al. with 65-ns resolution [29]. In this experiment, 2.33-eV pump pulses produced excited conduction band electrons that were photoemitted by 4.66-eV probe pulses. The photoelectron spectra were measured using retarding-field spectroscopy with a cylindrical mirror analyzer. Conduction band electrons, in equilibrium with the lattice, were found to have $T_{cb}$ exceeding 1100 K. The first application of a time-of-flight approach to obtain time-resolved photoelectron spectra in a pump-probe laser experiment was demonstrated by Bokor et al. at AT&T [22]. In these angle-resolved
experiments, normally-unoccupied Si(111) surface states, and near-surface conduction band minimum states were excited by 0.44-eV and 2.3-eV 60-ps pulses [22, 40]. The photoemission was produced by 4.68-eV or 10.5-eV probe pulses. Surface recombination was found to occur on a 200-ps timescale; space-charge layer formation had a significant effect on the recombination dynamics. While excited conduction band electrons were not directly observed, most likely due to the longer pulse durations, this experiment provided the impetus to try the same technique with ultrashort laser pulses. Rowe, et al. recently reported experiments on the Si(111) and Si(100) surfaces with 1–3 ps pulses [20, 41]. These experiments extensively characterized the one- and two-photon photoelectron spectra for 4.66-eV probe pulses for a variety of surfaces and surface preparations. Their time-resolved measurements were performed with identical 4.66-eV, 1.2-ps pulses in a cross-correlation type of measurement. These measurements were unable to measure an excited conduction band population; this fact was attributed to diffusion of conduction band electrons into the bulk, and to strong capture of photoelectrons by surface states. Compared to the work of Rowe, et al. [20], a primary advantage of our approach is that we used a 2-eV pump which has an orders of magnitude greater penetration depth (1µm, compared to 5 nm for 4.66-eV light). As a result of the greater depth at which excited carriers were generated, diffusion of carriers out of our 10-nm probe region is much slower, allowing hot electrons to be detected.

### 3.3 Experimental Technique

The primary experimental goal was to obtain subpicosecond time-resolved conduction band electron spectra from Si as a function of time delay between a 2-eV pump laser pulse and a 4-eV probe laser pulse. To obtain photoelectron spectra from an atomically clean sample, the measurements were carried out in ultrahigh vacuum (UHV). An amplified, high repetition-rate laser system was used to produce the pump and probe laser pulses. At a fixed
pump-probe delay, a photoelectron spectrum was generated by collecting and averaging
together time-of-flight electron photoemission spectra produced by several thousand probe
laser pulses. Pump-probe delays were varied from 120 fs to 1 ns.

### 3.3.1 UHV chamber and sample preparation

Our experiments were performed on a Si(100) sample in UHV (2 × 10⁻¹⁰ torr) at room
temperature. The 10 × 10-mm sample was cut from a wafer which had a clean, thermally
grown oxide layer on the surface. A clean Si(100) surface was obtained in UHV by removing
the oxide with a flash anneal to 1300 K. The sample was subsequently flash annealed to 1100
K every few hours during data collection to ensure a clean surface. This procedure led to
excellent reproducibility of the photoelectron spectra.

A similar approach to sample preparation was reported by Johansson et al. [25, 42], and it
was found that this cleaning method produces reproducible 2×1 low-energy electron
diffraction (LEED) patterns. Angle-resolved inverse photoemission studies of this surface
[25] indicate that the 2×1 reconstructed surface has regions of asymmetric dimers arranged
into local c(4×2) or p(2×2) periodicities. Two normally unoccupied surface states are
observed, consistent with electronic structure calculations of the Si(100) c(4×2) surface. They
arise from the two antibonding bands of the four dangling surface bonds in each c(4×2) unit
cell [24]. The π₁⁺ state lies entirely in the gap, starting at about 0.4 eV above the valence
band maximum at the Γ point in the surface Brillouin zone. The π₂⁺ state lies near the
conduction band minimum, at 1.3 eV above the valence band maximum at the Γ point in the
surface Brillouin zone.

Our photoemission spectra from this sample show no surface photovoltage shift [41]
following 2-eV excitation, consistent with photoemission results on the Si(100) surface
reported by Rowe, et al. [20]. As noted earlier, this is thought to occur because the Fermi

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[8] First theoretically proposed by Chadi [23].
level is pinned at the surface by the $\pi_{1}^*$ state coincident with the bulk Fermi level determined by the bulk doping. We performed earlier experiments with a highly doped ($3 \times 10^{15} \text{ cm}^{-3}$) p-type Si(100) sample using 6-eV probe light, and observed a surface photovoltage shift of 0.5 eV. This effect manifests itself in the data as a 0.5 eV shift of the entire two-photon valence band photoemission to higher energy following 2-eV pumping. The shift occurs because the bands, normally bent at the surface due to Fermi level pinning at an energy below the bulk Fermi level, ‘flatten out’ following 2-eV pumping [41]. The magnitude and direction of this shift were inconvenient for our experiments, so the sample was switched to one with which no surface photovoltage shift was observed.

The Si sample was mounted in direct thermal contact with a ‘button-type’ resistive heater (Spectra Mat), and could be electrically isolated from the UHV chamber, allowing application of a bias to the sample. For the experiments reported here, the sample/heater mount was kept grounded to the chamber. The photoemission spectra indicated that a + 0.3-eV contact potential $\Delta \phi_d$ existed between the sample and chamber ground. The sample was located directly facing, and 2.5 cm away from, the entrance to a time-of-flight analyzer for the photoemitted electrons. The time-of-flight tube was made of a copper tube (OFHC grade) 2.5-cm in diameter and 25-cm long, with a smooth graphite surface on the inside and a double magnetic shield on the outside. The graphite surface is designed to capture electrons that scatter off the inside of the tube, allowing only direct line-of-sight electrons to reach the electron detector. A one-inch diameter double-plate channel electron multiplier (Galileo), with a 50-Ω conical anode, was fixed at the end of the time-of-flight tube to collect the photoemitted electrons. In addition to the magnetic shielding of the time-of-flight tube itself, the UHV chamber was fabricated by Perkin-Elmer to include full magnetic shielding on the inside.
3.3.2 Time-of-flight detection

Combining the pump-probe laser technique with a time-of-flight analyzer is a powerful approach for determining the photoelectron spectrum. In principle, a single laser probe pulse can produce the entire photoelectron energy distribution at a given time delay following the pump pulse. In practice, for ultrashort pump-probe experiments, space charge effects \[19\] limit the total number of electrons that can be photoemitted before distortion of the time-of-flight distribution results. We find that limiting our probe intensity so that we collect \(< 10\) electrons per laser shot puts us 5–10 times below the regime where we observe space-charge distortion. Reproducible spectra are obtained by averaging together thousands of laser shots at a fixed pump-probe delay. The laser system (Sect. 3.3.3) is operated at a 100-Hz pulse repetition rate, and 12,000–30,000 shots are averaged depending on signal level, to generate a spectrum at a single pump-probe delay in about 5 minutes.

Figures 3.4 and 3.5 schematically illustrate the time-of-flight technique. When photoelectrons reach the electron multiplier plate, the number which arrive as a function of arrival time, \(N(t)\), must be accurately recorded to produce a time-of-flight spectrum. This is accomplished using a digitizing oscilloscope (Tektronix DSA #602) with a long record length (1 \(\mu\)s) and high time resolution (\(\leq 1\) ns). The electron multiplier voltage is \(-1.9\) kV, adjusted to produce low-noise output with clearly resolved 2-mV pulses for each detected electron. The output is fed into a 2\(\times\) Tektronix attenuator, which serves as a protective fuse on the input of a 500-MHz bandwidth RF amplifier. All BNC cables and connections from the electron multiplier to the output of the RF amplifier, including the case of the amplifier itself, are enclosed in a grounded copper braid shield. This is necessary to reduce RF-noise pickup from the laser electronics, primarily from the excimer-laser power supply.
Chapter 3 Ultrafast time- and energy resolved electron distributions

Fig. 3.4 Schematic of time-of-flight experimental configuration. Electrons are photoemitted by the probe beam into UHV. A portion of the emitted electrons travel by direct line-of-sight into the time-of-flight (TOF) tube.

The RF amplifier output, about 1-V peak amplitude, is coupled into a Tennelec constant fraction discriminator (CFD) through a 1-pF capacitor. The 1-pF capacitor, mounted in a shielded Pomona box, reduces noise and ringing from the signal, and produces 30-mV peak-peak, \( \leq 2.5 \)-ns pulses input to the CFD. The CFD produces one negative-going, square-shaped, symmetric 2-ns pulse, 800-mV in amplitude with zero offset, for each input electron pulse. The CFD output was directly compared to the electron multiplier signal on the oscilloscope, which showed that it was a faithful representation of the signal. The CFD output is collected and stored on the DSA 602 oscilloscope, set in averaging mode, which can collect and store a complete 1-\( \mu \)s data trace at up to a 100-Hz rate. The memory capacity of the oscilloscope limits us to a maximum of 4096 laser shots per spectrum. The resulting spectra are downloaded to a desktop computer (IBM 386 via GPIB), where multiple 4096-shot spectra are summed to obtain 12,000–30,000 shot spectra. The computer is also used for data manipulation including smoothing (cf. oscilloscope screen inset in Fig. 3.5) and conversion of the time-of-flight distribution \( N(t) \) to an energy distribution \( N(E_{cb}) \).
The zero time-of-travel point of the time-of-flight distribution has to be determined in order to accurately convert the time distribution to an energy distribution. This is achieved by rotating the sample to directly reflect the probe laser beam into the electron multiplier. Ultraviolet light from the probe produces a sharp output pulse from the multiplier which establishes zero time for the time-of-flight distribution.

The conversion of the time-of-flight distribution $N(t)$ to an energy distribution $N(E_{cb})$ is performed simply by inverting the formula for the kinetic energy. We assume each electron with mass $m$ arrives in time $t$ after traveling distance $L$ with energy:

$$E_{KE}(t) = \frac{1}{2} m (\frac{t}{L})^2. \quad (3.2)$$

This equation assumes that once the electron escapes from the sample, it experiences no forces which affect its path or energy. It then follows that:
\[ N(E_{\text{KE}}) = \frac{N(t)}{\frac{\partial E_{\text{KE}}}{\partial t}} = N(t) \frac{t^3}{mL^2}. \] (3.3)

Next one converts \( N(E_{\text{KE}}) \) to \( N(E_{\text{cb}}) \) by calibrating the energy axis from the spectral features in the data (for details, see Sect. 3.4.2).

One needs to consider the effect of the contact potential \( \Delta \phi_d \) on the transit time of the electron, and whether this distorts the time-of-flight spectrum. The contact potential in our case acts only on the electron over the 2.5-cm distance that it travels from the Si sample to the grounded and shielded time-of-flight tube. Once inside the tube, the electron encounters a field-free region. We computed the effect of a contact potential in the range 0–0.5 eV for our geometry. We find that since the field free region is significantly longer than the contact potential region (the distance ratio is 11:1), very minor changes in the time-of-flight distribution result, and the effects are only significant at low electron energies (i.e. for electrons that spend a longer time accelerating in the contact potential region). For \( \Delta \phi_d = 0.3 \) eV, assuming a uniform shift of the entire distribution implies a maximum error in energy of 5% for \( E_{\text{KE}} = 0.5 \)-eV electrons, with a corresponding 2% maximum error in the derivative \( \left( \frac{\partial E_{\text{KE}}}{\partial t} \right)^{-1} \). Therefore we make no correction due to \( \Delta \phi_d \) for the time-of-flight spectra presented here.

The energy resolution of this time-of-flight spectrometer is determined by the finite pulsewidth from the CFD for an electron count, the path length difference for electrons due to the finite size of the electron multiplier, the magnitude of the time-of-flight path, and the effects of contact potential fields or stray magnetic fields that may be present. We estimate our resolution to be 50 meV at \( E_{\text{KE}} = 1 \) eV. This corresponds to a time resolution of \( \Delta t = 10 \) ns, five times greater than the 2 ns pulses produced by the CFD.
3.3.3 Laser system

Because thousands of single-shot photoelectron spectra need to be averaged to produce a single time-delay $N(E)$ spectrum, this experiment is impractical without a high repetition rate laser system. The system used here, designed by Judy Prybyla, produces 100-fs, 500-$\mu$J pulses at 2-eV photon energy (620 nm), at a 100-Hz repetition rate. The system is schematically illustrated in Figure 3.6.

At the heart of this high repetition-rate system is a pulsed XeCl excimer laser (Lamda Physik LPX) that can run up to 400 Hz at 308 nm. The laser was optimized to provide 10-ns pulses at an average power of 1 W at 100 Hz.

The ultrashort pulses are generated in a colliding-pulse mode-locked dye laser oscillator (CPM) operating at 620 nm and 100-MHz pulse repetition rate, producing pulses < 100-fs duration. The output of the oscillator is amplified in two stages. The first is a six-pass dye amplifier pumped by the excimer laser, following the design of Knox, et al. [43]. This amplifier incorporates a saturable absorber jet which, along with the 10-ns excimer pulses and short gain lifetime of the amplifier dye jet, acts as a pulse selector as well as amplifier. The subnanosecond synchronization timing of the excimer pulse with the oscillator pulse train is achieved using a picosecond delay generator (SRS DG 535). The second amplifier stage is a double-passed Bethune-type prism dye cell [44], also pumped by the excimer laser. The prism cell is four inches long and two inches wide on each side, with a 1-cm diameter bore through which the dye and laser beam pass. Following amplification, ultrashort pulses are produced following compression by a double-passed two-prism compressor which compensates for dispersion in the amplifier.
To achieve the best laser energy stability during collection of data, the following additional procedures need to be performed. The excimer laser is most stable following a fresh gas fill and cavity optics cleaning. After 5–6 hours of continuous operation at 100-Hz, the cavity is purged, the optics cleaned, and a fresh gas fill applied. Additionally, the dyes in the Bethune cell amplifier are supplemented hourly, and replaced entirely whenever an
excimer fill is performed. The amplified laser output energy, stability, and pulse shape are continuously monitored with a photodiode and BOXCAR integrator. We find that adjusting the excimer trigger delay (on a 1-ns timescale) using the SRS delay generator improves the system stability. Therefore we adjust the SRS delay at approximately one minute intervals during data collection as necessary to provide optimum stability. Using this approach we routinely achieve $\leq 10\%$ energy stability during the course of an entire data run.

The amplified output is telescoped down to a 1-mm diameter and split into pump and time-delayed probe using a beam splitter and motorized 0.1-µm resolution translation stage (Klinger). A 150-µm thick BBO nonlinear doubling crystal is inserted in the probe beam path to generate the 4-eV probe. For the experiments in which a 6-eV probe is needed, a second BBO crystal is placed right after the first to generate third harmonic. Pump and probe beams are then relay-imaged through a UV-grade CaF$_2$ window on the UHV chamber and overlapped onto the sample. Both beams are $p$-polarized and incident at 30° to the sample normal, with a 2° angle between them in the vertical plane. The pump beam is more loosely focused than the probe to ensure that the probe beam is incident on a uniformly pumped spot. The probe beam makes two 45° reflections off 310-nm dichroic high reflecting mirrors, which transmit 620-nm. In this way, residual 2-eV light is reduced to < 1% of the energy in the 4-eV probe beam. The energy of the pump and probe beams is adjusted by inserting neutral density filters (Kodak Wratten) in the pump and probe beam paths.

To facilitate overlap of the pump and probe beams on the sample inside the UHV chamber in space and time, the following procedure is followed. We find that a strong two-photon photoemission signal, sharply peaked in time, can be detected by the electron multiplier when the pump and probe beams overlap in time and space on the sample. We

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9The dye reservoir is 5 l, which limits the dye lifetime at high repetition rates.
10Monitoring the pulse output with a photodiode ensures that there is no double-pulsing of the output due to improper excimer timing with respect to the oscillator pulse train.
11Similarly, 6-eV (200-nm) high reflectors are used in the 6-eV probe beam.
use this signal to optimize the spatial and temporal overlap on the sample. This is a very sensitive method since the overlap signal can be made to drop by an order of magnitude by changing the pump-probe delay by 150-fs. With zero time delay and spatial overlap obtained, a mirror on a precision kinematic mount is inserted in front of the CaF$_2$ window outside the UHV chamber, to establish an equivalent optical path outside the UHV chamber. In this equivalent path, a thin KDP crystal is precisely aligned at the overlap of the pump and probe beams by optimizing the sum-frequency signal at 6-eV generated by the 2-eV and 4-eV beams. Once this alignment is obtained, the crystal and equivalent path mirror are used to establish pump-probe overlap and pump-probe time zero on the sample each day. Using the 6-eV sum-frequency signal, we measured the FWHM of the cross-correlation between pump and probe at the sample to be 150-fs, which corresponds to a pulsewidth of 100-fs assuming equal width, Gaussian envelope, pump and probe beams. An identical cross-correlation is obtained on the sample using the two-photon photoemission signal measured directly from the sample by the electron multiplier.

3.4 Results and Discussion

3.4.1 Overview

In the following discussion, two sets of data are presented. One set is collected in a low probe intensity (10 MW/cm$^2$, or 0.1-mJ/cm$^2$ incident fluence) regime, in which the 4-eV probe intensity is insufficient to drive two-photon photoemission. In this case, the photoemission signal results from linear probe photoemission of excited conduction band electrons generated by the preceding 2-eV pump pulse. The second set of data is obtained in a high probe intensity (100 MW/cm$^2$) regime.

As we show in the following, collecting data in the high-intensity regime is a new approach to probing excited conduction band electrons. The 4-eV intensity in the high intensity case is sufficient to generate significant two-photon photoemission, and what we
observe is a *decrease* in the probe photoemission when the probe is preceded by the 2-eV pump beam. We show that this decrease occurs because excited conduction band electrons block intermediate states of the two-photon probe transitions. We show that by analyzing the reduction of the probe photoemission, one can obtain conduction band electron distributions.

The conclusions that arise from the data presented here are as follows. In the low probe intensity regime, we obtain excited conduction band electron energy distributions, which exhibit (1) fast electron thermalization within our 100-fs time resolution, and (2) electron-phonon scattering rates consistent with pseudo-potential scattering rate calculations. We observe electron-phonon thermalization in 1-ps. In the high-probe intensity regime, which is most sensitive to the longer pump-probe delay dynamics, we observe near-surface electron dynamics on a 1-ps to 1-ns timescale which indicate electron accumulation in the near-surface region.

### 3.4.2 Spectral Assignment

The energy axis of a time-of-flight spectrum converted to $N(E_{KE})$ using Eq. 3.3 represents the kinetic energy of a photoemitted electron. One needs to identify which spectral features correspond to conduction band electrons. We make our spectral assignment by examining two-photon 4-eV photoemission spectra.

Figure 3.7 shows a two-photon photoemission spectrum using only 4-eV light (no 2-eV pump). By collecting two-photon 4-eV spectra over a range of 4-eV beam intensities, we verified that the two-photon photoemission is quadratic in 4-eV laser beam intensity over the range $E_{KE} = 0.3–1.7$ eV in Fig. 3.7. A small linear contribution is present at very low energies and small higher order contributions are present above $E_{KE} = 2$-eV. As we discuss shortly, we only analyzed data which falls entirely in the quadratic region.
To interpret the spectrum of Fig. 3.7, we begin by pointing out that all quadratic photoemission that is observed must originate from normally occupied states (i.e. valence band states). Therefore the intermediate states of the two-photon 4-ev transitions for the photoelectrons in this spectrum are located either (1) in the conduction band, (2) at energies degenerate with conduction band states, or (3) at energies degenerate with surface (gap) states. One expects sharp features in the conduction band density of states, such as the conduction band minimum, to produce distinct features in the two-photon photoemission. The presence of surface states will produce spectral features as well [45]. We find that dosing the sample with oxygen, which is known to change the surface state electronic structure [45, 46], only affects the amplitude of spectral features in Fig. 3.7 below $E_{KE} = 0.55$ eV. Thus,
we conclude that the low energy spectral features ($E_{KE} < 0.55$ eV) arise from photoemission through intermediate states in the band gap.

We find that the 'shoulder' feature at $E_{KE} = 0.6$ eV, labeled by an arrow in Fig. 3.7, is unaffected by surface dosing with oxygen. This behavior is characteristic of a bulk band structure feature. We assign this feature to be at the conduction band minimum energy $E_{cbm}$. This assignment is consistent with many features of our data, and is identical to a previously reported assignment for two-photon 4.66-eV photoemission from this surface [20]. The low energy cutoff of our data is $E_{KE} = 0.3$ eV; this offset from zero energy arises due to a contact potential $\Delta \phi_d = 0.3$ eV. To define a new energy axis in which $E_{cbm} = 0.0$ eV, we take $E_{KE} = 0.6$ eV; with $E_{\text{photon}} = 4$ eV in Eq. 3.1, one obtains a value for the ionization potential $\chi = 3.7$ eV, consistent with previously reported values for this surface [27, 45, 47]. This value is also consistent with the high energy cut-off of the spectrum at $E_{KE} = 3.5$ eV, because this energy maximum must arise from two-photon emission from the valence band maximum, and $2 \times E_{\text{photon}} - (\chi + E_{\text{gap}}) = 3.5$ eV.

The assignment of the conduction band minimum feature in Fig. 3.7 also is the proper assignment for the low probe intensity data presented in the next section. This is true because one-photon 4-eV probe photoemission from the conduction band minimum has the same final energy as two-photon 4-eV photoemission transition from the valence band with an intermediate state at the conduction band minimum.

### 3.4.3 Low-probe-intensity regime

Figure 3.8 shows electron energy distributions obtained at pump-probe delays of 120-fs and 180-fs. These spectra are obtained in the low probe intensity regime. They are plotted against both the experimental electron kinetic energy $E_{KE}$ axis at the top, and against $E_{cb}$, where $E_{cb} = 0$ at $E_{KE} = 0.6$ eV.

Based on the arguments presented in Sect. 3.2.2, and given the spectral assignment discussed in Sect. 3.4.2, we interpret the photoemission signal at energies $E_{cb} > 0$ in Fig. 3.8
as one-photon 4-eV probe photoemission from bulk and near-surface conduction band states. Photoelectrons with energies $E_{cb} \leq 0$ arise from gap state emission.

To obtain the low probe intensity spectra of Fig. 3.8, a 4-eV probe beam intensity of 10 MW/cm² is used, an intensity which does not generate any photoelectrons by itself; i.e. when the probe is the only incident beam, no probe two-photon emission is observed. The incident 2-eV pump fluence was 0.25 mJ/cm², which corresponds to $5 \times 10^{18}$ electrons/cm³ excited into the conduction band. No photoemission is observed from the pump beam alone. We note that at approximately an order of magnitude higher 2-eV beam intensity, photoemission can in fact be observed; these photoelectrons arise from three-photon 2-eV photoemission.

![Graph](image)

**Fig. 3.8** Low probe intensity photoemission data for pump-probe delays of 120 fs and 180 fs. The top axis shows the experimental energy axis; the bottom axis shows the electron conduction band energy based on the assignment discussed in Sect. 3.4.2. Solid lines are data. Dashed lines are thermal distribution fits to the conduction band portion of the data ($E_{cb} > 0$).
As discussed in Sect. 3.3.3, a sharply temporally peaked photoemission signal is observed when the pump and probe beams overlap at zero pump-probe delay. The FWHM of this photoemission is 150-fs pump-probe delay. The sharp feature arises from two-photon ‘probe-pump’ (4-eV/2-eV) photoemission. This two-photon photoemission is an undesired background which one could in principle reduce by using lower probe beam intensities; however lowering the probe intensity reduces the amount of signal as well. In order to eliminate the undesired background, we collected a complete set of photoemission spectra at symmetric positive and negative pump-probe delays. The distributions in Fig. 3.8 are then obtained by plotting the difference signal between positive and negative pump-probe delays. This approach subtracts out the 4-eV/2-eV background. The difference signal therefore represents excited conduction band electrons produced by the 2-eV pump pulse.

We note that the difference signal cannot be interpreted as a measure of the lifetime of some real state in the bulk Si band structure which serves as the intermediate state of a two-photon (pump-probe) transition. This is an important possibility to consider, because it would imply that the measured difference signal between positive and negative pump-probe delays is just the asymmetry of the pump-probe cross-correlation in the sample. We can definitively rule out this possibility. An examination of the Si band structure (cf. Fig. 3.1 and more extensive data in Ref. [48]) show that no states exist which can serve as the intermediate state of a two-photon transition from the valence band for a 2-eV pump photon (i.e. the minimum direct gap is 3.5 eV). While there are direct 4-eV transitions available, these occur only along the X direction (cf. Fig. 3.1), from the valence band to the conduction band minimum. This intermediate state energy is too far below the vacuum level (\(\chi = 3.7 \text{ eV}\)) for 2-eV light to serve as the second photon in a photoemitting transition. Hence the photoemission signal of Fig. 3.8 for \(E_{\text{cb}} > 0\) can only be interpreted as arising from one-photon 4-eV photoemission of conduction band electrons produced by indirect 2-eV excitation.
The dashed curves in Fig. 3.8 are Boltzmann fits to the conduction band portion \((E_{cb} > 0)\) of the distributions. These curves were produced by assuming a density of states proportional to \(E_{cb}^{1/2}\). The assumption of an \(E^{1/2}\) dependence in the conduction band density of states is an excellent approximation to the calculated density of states for \(E_{cb} \leq 1\) eV (see Fig. 3.9). The fitting procedure was to adjust the temperature \(T\) and normalization constant \(N_0\) until a good fit was obtained, i.e.:

\[
N(E_{cb}) = N_0 E_{cb}^{1/2} e^{-E_{cb}/k_B T}. \tag{3.4}
\]

The data at 120-fs delay is fit well by a \(T = 1600 \pm 100\) K thermal distribution, and the 180-fs delay data is fit well by a \(T = 800 \pm 100\) K distribution as shown in Fig. 3.8. We do not attempt to fit portions of the distribution near and below \(E_{cb} = 0\), since details of the surface state density of states and relative contribution of these states to the photoemission are unavailable.

![Si electronic density of states](image)

**Fig. 3.9** Si electronic density of states \(\rho_{DOS}\) from Ref. [48]. The dark line shows an \(E^{1/2}\) fit to the conduction band density of states at low energies.

The fact that Boltzmann distributions, rather than Fermi distributions, fit the distributions well is simply due to the high temperature of these distributions compared to the effective Fermi level \(E_f\). An estimate of \(E_f\) can be obtained by calculating the energy up to which the conduction band would be entirely filled if one fills all states starting from \(E_{cb}\)
$= 0$ with the available $5 \times 10^{18}$ electrons/cm$^3$. Taking the density of states $\rho(E_{cb})$ to be ($g.$ Fig. 3.9, and Ref. [48]):

$$\rho(E_{cb}) = (3.5 \times 10^{22} \text{ states eV}^{-1} \text{ cm}^{-3}) \times E_{cb}^{1/2},$$  \hspace{1cm} (3.5)

we find an effective Fermi level of 4 meV for a conduction band electron density of $5 \times 10^{18}$ cm$^{-3}$. Since even at 800 K the average electron energy is 100 meV, $T >> T_{\text{Fermi}}$ and a Fermi distribution looks like a Boltzmann distribution in this limit. As a check, we verified that Fermi distribution fits using a Fermi level of 4 meV give temperatures consistent to within $\pm$ 100 K of the Boltzmann fits.

The fact that thermal distributions are good fits to the conduction band data imply that carrier-carrier interactions produce electron thermalization within 120 fs. As discussed above, the actual timescale for this process is likely to be much faster, on the order of 10 fs or less, depending on carrier density.

The fast cooling from 1600 K to 800 K in the interval $\Delta t = 60$ fs is compatible with electron-phonon scattering rates calculated for Si using the pseudopotentials approach discussed earlier [2, 11]. This temperature drop $\Delta T$ corresponds to an average energy loss $\Delta E$ of 100 meV per electron ($i.e.$ $\Delta E = 3/2 k_B \Delta T$). Zone center LO or TO phonons, with energy $E_{\text{phonon}} = 60$ meV, are the highest energy phonons available for emission. Assuming that these phonons are the dominant contribution to electron cooling, we can compute an approximate electron-phonon scattering rate from the data. An average scattering rate $R_{e-p}$ is obtained by dividing the cooling rate ($i.e.$ the energy drop $\Delta E$ in the time interval $\Delta t$) by the energy per phonon:

$$R_{e-p} \approx \frac{(\Delta E/\Delta t)}{E_{\text{phonon}}},$$  \hspace{1cm} (3.6)

which gives a value $R_{e-p} = 3 \times 10^{13}$ s$^{-1}$. This value is consistent with calculations for electrons in the energy range $0 \text{ eV} < E_{cb} < 0.5 \text{ eV}$. We plot this value for the scattering rate in Fig. 3.2 (c) to show how it compares to the computed rate. Note that the error bars on
this point are given as the range $\Delta E$ since our value for $R_{e-p}$ is an average rate over this interval.

For further comparison to the computed rate, we can estimate the scattering rate between zero and 120-fs pump-probe delay using Eq. 3.6. If one assumes a peak average electron energy of 0.5 eV at zero delay, as suggested in Section 3.2.3, this implies an initial cooling rate from 4000 K to 1600 K in 120 fs. From Eq. 3.6, this corresponds to a scattering rate of $R_{e-p} = 4 \times 10^{13} \text{ s}^{-1}$. This value is also plotted in Fig. 3.2 (c), showing that it is consistent with the calculation.

Based on the compatibility of the observed and computed scattering rates, we conclude that the data supports the general picture of electron relaxation described above. An energy-dependent electron-phonon scattering rate leads to electron cooling on a timescale longer than the carrier equilibration rate. According to the simple model of Fig. 3.3, electron-phonon scattering should lead to electron-lattice equilibration on a ps timescale. As discussed in the next section, we were unable to obtain electron distributions on this timescale in the low probe intensity regime. Instead, in order to examine the ps timescale relaxation, we obtained additional data in a high-probe intensity regime (Sect 3.4.4) which revealed the ps timescale dynamics.

Before we move on to a discussion of the ps timescale dynamics, we first discuss in more detail why moving to a high probe intensity regime was necessary. The basic problem is illustrated in Fig. 3.8. The overall amplitude of the distribution at 180-fs delay is down by roughly a factor of two from the 120-fs distribution. For delays $> 200$ fs we were unable to generate distributions above the noise level in the low-probe regime by averaging $\leq 30,000$ laser shots. We attempted very long term averaging, but found that with the current laser apparatus, averaging for longer times is not feasible due to long-term drift in the laser energy.
The fact that our signal is small and requires averaging many laser shots is not surprising based on the signal levels of previously reported work. Previous laser-photoemission experiments on Si used orders-of-magnitude longer pulses than reported here. This has important consequences for detecting conduction band electrons in the low-probe-intensity regime. At a fixed intensity, a 150-fs pulse has 400,000 times fewer photons than Long’s [29] 60-ns pulses, and 400 times fewer photons than Bokor’s [22] 60-ps pulses. For a given conduction band electron population, the conduction band electron photoemission signal is linearly proportional to the number of probe photons in this intensity regime. As a result, we expect a significantly smaller signal than that detected in previous experiments. In order to increase the signal, one needs to increase the probe intensity, but well before one regains the 400-fold decrease compared to 60-ps pulses, two-photon probe photoemission becomes significant and even dominant. In spite of the lower signal obtained in the low probe intensity regime, by averaging 12,000 laser shots we are able to reproducibly observe the spectra of Fig. 3.8 at shorter time delays.

Why then is there a small signal at longer delays? One possibility is that the excited electrons diffuse away from the probe surface region. This possibility was discussed at length by Rowe, et al. [20] They show that diffusion out of the 1-µm region pumped by a 2-eV pump pulse can significantly reduce the excited carrier density in 0.5 ns. The thin 10-nm region at the surface which we probe represents the first 1% by volume of the excited carrier distribution generated by the 2-eV pump. If diffusion causes a rapid ‘flattening’ of the excited carrier density distribution, the drop in the near-surface carrier density would explain the smaller signal at longer delays.
3.4.4 High probe-intensity regime

3.4.4.1 Introduction

During the course of the previous experiments in the low probe intensity regime, we tried to increase the conduction band photoemission signal by increasing the 4-eV probe intensity. As already noted, this resulted in an overwhelming two-photon photoemission from the valence band.

![Graph showing two-photon photoemission](image)

**Fig. 3.10** Two-photon photoemission before and after pumping in the high probe intensity regime. Solid line shows the photoemission with no pumping. Dashed line shows the photoemission for a probe beam incident 700 fs after 0.25-mJ/cm² 2-eV pumping. Note the reduction in photoemission in the 0.5–1.0 eV region.

It may seem surprising at first that the higher-order two-photon process can dominate the linear conduction band photoemission. This can be understood due to the fact that the valence band electron density ($10^{23}$ cm$^{-3}$) is four orders of magnitude greater than the conduction band electron density. Even though the two-photon transition cross-section must be significantly smaller than the one-photon cross-section, the orders-of-magnitude difference in initial state population allows the net nonlinear transition probability to exceed
the linear one. Once the probe intensity $I_{\text{probe}}$ is sufficient to observe this effect (>100 MW/cm²), further increases only enhance the difference, since the two-photon process scales as $(I_{\text{probe}})^2$ while the one-photon probe scales linearly with $I_{\text{probe}}$.

![Diagram of Si band structure](image)

**Fig. 3.11** Schematic illustration of intermediate state blocking. The 2-eV pump beam excites electrons to the hatched region of the conduction band. These electrons block the intermediate states of two-photon probe photoemission from the valence band.

In the high probe intensity regime, we find that the two-photon probe photoemission is reduced in amplitude when the 2-eV pump precedes the probe. This effect is observable only when the pump precedes the probe by 0.5 ps or more. Figure 3.10 shows a typical two-photon probe photoemission spectrum, and the same spectrum when the 2-eV pump precedes the probe by 700 fs. An obvious drop in the photoemission signal is apparent between 0.5 and 1 eV. We find that a decrease is still observed even at a 1-ns pump-probe delay.
Chapter 3 Ultrafast time- and energy resolved electron distributions

This pump-induced drop in photoemission can be understood in terms of intermediate state blocking of the two-photon probe transition by excited conduction band electrons. Figure 3.11 schematically shows how conduction band population can occupy intermediate states of a two-photon probe transition from the valence band. Any occupation of the available intermediate states will reduce the two-photon transition probability. To quantitatively estimate the size of this effect, we developed a simple model.

3.4.4.2 Simple model of intermediate state blocking

To begin, we consider a three-level system as shown in Figure 3.12 below. The symbols \( |v\rangle, |c\rangle, \) and \( |f\rangle \) denote valence band, conduction band, and photoemitting final states, respectively.

![Fig. 3.12 Schematic three-level system of our experiment, showing valence band \( |v\rangle \), conduction band \( |c\rangle \), and photoemitting states \( |f\rangle \). The open arrow represents one-photon probe photoemission from the conduction band. The double filled arrow represents two-photon probe photoemission from the valence band.](image)

Let \( n_c \) be the number of conduction band states in an energy interval \( \Delta E \), and \( N_{|c\rangle} \) be the occupation number (0 < \( N_{|c\rangle} < 1 \)) of each level. If some electron population is present in the conduction band due to the 2-eV pump, linear probe photoemission of these conduction

\[12\] We acknowledge many helpful discussions with J. Denker of AT&T Bell Labs, who helped us arrive at this conclusion, and helped develop the simple model of Sect. 3.4.4.2.
band electrons is represented by the open arrow in the figure. The linear photoemission yield $Y^{\text{linear}}$ is proportional to:

$$Y^{\text{linear}} \propto \sum_{v \rightarrow f} N_{v,c} |\langle f | H' | c \rangle|^2$$  \hspace{1cm} (3.7)

where the sum is over the conduction band states, and $H'$ is the electric dipole interaction. It is reasonable to assume that the dipole matrix elements can be taken as a constant if the energy interval over which the sum is performed is small, and furthermore, if the effect of the final state $|f\rangle$ is also constant in this range. We proceed on this assumption for now and discuss the limitations of this approach afterwards. Assuming constant dipole matrix elements, Eq. 3.7 becomes simply:

$$Y^{\text{linear}} \propto n_c \langle \rho \rangle_c ,$$  \hspace{1cm} (3.8)

where $\langle \rho \rangle_c$ is the average fractional occupation of the conduction band in the interval $\Delta E$ produced by the 2-eV pump.

Two-photon photoemission transitions from $|v\rangle$ to $|f\rangle$ through the intermediate state $|c\rangle$ are represented by the filled arrows in Fig. 3.12. Because this photoemission has an observed quadratic dependence on 4-eV probe intensity, we refer to the two-photon probe photoemission as $Y^{\text{nonlinear}}$. The probability of making a two-step transition through the intermediate state is proportional to the probability of the first $|v\rangle$ to $|c\rangle$ transition. This transition probability is linearly proportional to the number of valence band electrons, $n_v$, in the initial state, and linearly proportional to the number of available (unoccupied) conduction band states, $n_c \times (1 - \langle \rho \rangle_c)$, so that:

$$Y^{\text{nonlinear}} \propto n_v \ n_c \ (1 - \langle \rho \rangle_c) .$$  \hspace{1cm} (3.9)
Note that in this notation, the ‘probe-only’ photoemission signal \(Y_{o}^{\text{nonlinear}}\) \((i.e.\text{ the two-photon probe photoemission with no 2-eV pump})\) is obtained by setting \(\langle \rho \rangle_c\) equal to zero, giving \(Y_{o}^{\text{nonlinear}} \propto n_c n_e\).

Equation 3.8 represents the linear contribution to the photoemission, which is the same as the signal in the low-probe-intensity regime. Eq. 3.9 represents the photoemission in the high probe-intensity regime, when the probe follows the 2-eV pump. Given that \(n_p\) is orders of magnitude greater than \(n_c\) as discussed previously, the contribution of Eq. 3.8 to the total photoemission in the high probe intensity regime is negligible.

To characterize the reduction in probe photoemission following pump excitation, we define the ‘depletion’ signal \(D\):

\[
D \equiv \frac{Y_{o}^{\text{nonlinear}} - Y_{nonlinear}}{Y_{o}^{\text{nonlinear}}}. \tag{3.10}
\]

Given Eq. 3.9 the depletion signal \(D\) is proportional to:

\[
D \propto \langle \rho \rangle_c. \tag{3.11}
\]

In other words, the depletion \(D\) for a transition through a particular intermediate state in the conduction band is proportional to \(\langle \rho \rangle_c\), the fraction of occupied conduction band states in the energy interval. Furthermore, if the assumption of constant matrix elements is good throughout the entire region of the conduction band that is potentially involved in intermediate state blocking, \(i.e.\) the region \(0.0\text{ eV} < E_{cb} < 1.0\text{ eV}\), then \(D\) should be proportional to the fraction of occupied states at each energy \(E_{cb}\).

An experimental test of the validity of Eq. 3.11 is to measure the depletion \(D\) as a function of pump beam fluence at a fixed pump-probe delay. The fraction of occupied states \(\langle \rho \rangle_c\) is linear in pump beam fluence if each pump photon excites one electron to the conduction band. Therefore \(D\) should be linearly proportional to the pump beam fluence. We find that the amplitude of the depletion signal \(D\) for \(0.0 < E_{cb} < 0.5\text{ eV}\) is indeed linear in 2-eV pump fluence in the range of this experiment, \(0.1–0.3\text{ mJ/cm}^2\).
The fact that we experimentally verified the prediction of linear fluence dependence for the depletion in Eq. 3.11 suggests that the assumptions of the simple model are valid in the small energy range which corresponds to two-photon probe transitions through the bottom (0.0–0.5 eV) of the conduction band. Equation 3.11 implies that measuring the depletion gives a signal proportional to the fraction of occupied states at each energy in the conduction band. Therefore, characterizing the reduction in probe photoemission following the 2-eV pump using Eq. 3.11 gives a direct measure of the conduction band electron population distribution.

### 3.4.4.3 Results and discussion

A complete set of high-probe-intensity regime data is shown in Figure 3.13. In this figure, the depletion signal $D$, defined by Eq. 3.10, is plotted vs. $E_{cb}$ for pump-probe delays from 700 fs to 1 ns, for a 0.25-mJ/cm$^2$ pump beam fluence.

Before analyzing the data of Fig. 3.13, we note that we collected data in the high probe intensity regime only for pump-probe delays $> 700$ fs. The reason for this is that data collected in the high probe intensity regime at shorter delays has a large background signal centered at zero pump-probe delay with a cross-correlation width of 150 fs. This background arises from coherent three-photon (2-eV/4-eV/4-eV) photoemission when the pump and probe overlap in time. This three-photon process represents an undesired background contribution similar to that which is observed in the low probe intensity regime. We completely avoid this background by obtaining data only at pump-probe delays for which the background is negligible. We find that data collected at delays $> 700$-fs gives reproducible depletion curves.
Fig. 3.13 High probe intensity regime data at various pump-probe delays, for a 0.25-mJ/cm² 2-eV pump and 100 MW/cm² 4-eV probe. Horizontal axis is the electron conduction band energy $E_{cb}$. Vertical axis is the depletion $D$ defined in Eq. 3.10. Vertical dashed line is at the conduction band minimum energy.

To interpret the data of Fig. 3.13, we begin by considering only the signal with $E_{cb} > 0$, since we expect signal near and below the conduction band minimum to arise from surface state occupation. From 700-fs to 1-ps delay, the conduction band portion of the data changes considerably, with a flat shoulder forming near the conduction band minimum which extends out to about $E_{cb} = 0.2$ eV at 1 ps. This feature persists out to 1-ns delay. The low-energy part of the distribution ($0 < E_{cb} < 0.1$ eV) lowers in amplitude near the conduction band minimum at 1-ns delay.

Given the ps timescale for electron-phonon scattering, we interpret the changes from 700-ps to 1-ps delay as corresponding to electron cooling due to electron-phonon scattering. The fact that the shoulder feature which forms by 1 ps remains nearly constant out to 1-ns delay suggests that electron-lattice equilibration occurs in 1 ps, after which the electron-lattice system changes very little in temperature in 1 ns.
To obtain a more quantitative interpretation, we appeal to Eq. 3.11. The simple intermediate state blocking model suggests that the depletion $D$ is proportional to the fractional conduction band occupation. The fractional conduction band occupation is proportional to the Fermi distribution, which gives the fraction of occupied states at each energy. We therefore fit the conduction band data ($E_{cb} > 0$) in Fig. 3.13 with a Fermi function $F(E_{cb})$:

$$F(E_{cb}) = \frac{N_0}{e^{(E_{cb} - E_f)/k_B T} + 1}$$  \hspace{1cm} (3.12)

where $E_f$ is the effective Fermi level in the conduction band, and $N_0$ is an adjustable normalization. Note that because the shape of the curves in Fig. 3.13 changes considerably from a continuously decreasing function at 700–800-fs delay, to a shoulder-shaped function after 1 ps, fitting these curves with Eq. 3.12 requires a significant change in the Fermi function fitting parameters from 700-fs delay to 1-ps delay. The shorter-delay data have shapes characteristic of a high-temperature distribution ($T >> T_{Fermi}$) while the longer delay data have the shape of lower temperature distributions.

Figure 3.14 shows Fermi function ‘fits’ using Eq. 3.12 to the conduction band data for 700-fs, 800-fs, 1-ps and 1-ns pump-probe delays. The fits were achieved by varying the temperature $T$, effective Fermi level $E_f$, and $N_0$ in Eq. 3.12. The resulting values for $E_f$ and $T$ are shown in each panel. The fits were performed by eye; to achieve these good fits the values for Fermi level and temperature can be varied only within ± 10% of the values shown. The effective Fermi level of 40 meV at 700-fs pump-probe delay is already larger than the computed $E_f$ (4 meV) for the 0.25-mJ/cm$^2$ 2-eV pump discussed in Sect. 3.4.3. In order to fit the shoulder-shaped feature at 1 ps and 1 ns, $E_f$ needs to be increased even more to 0.25 meV. Note also that the temperature falls by about 300 K from 700-fs to 1-ps pump-probe delay, and then falls only another 100 K from 1-ps to 1-ns delay.
The changes in temperature and $E_f$ obtained from these fits can be explained in a manner consistent with the low probe-intensity results. The slow cooling from 700-fs to 1-ps delay is indicative of the electrons accumulating near the bottom of the conduction band. As the temperature of the distribution approaches $T_{\text{Fermi}}$, fewer lower energy unoccupied states are available for electrons to scatter into; the electron-phonon scattering rate is thus reduced, leading to slower cooling. The fact that the electron temperature stabilizes in the 400–500 K range from 1 ps to 1 ns implies that the electrons have equilibrated with the lattice at about 100 K above room temperature within 1 ps. This result is broadly consistent with the predictions of the simple electron cooling model (cf. Fig. 3.3), except for the apparent 100 K rise in lattice temperature. Recall (Sect. 3.2.3) that the absorbed fluence gives a predicted temperature rise of the lattice of only 2 K.

In order to understand the apparent 100 K rise in lattice temperature and the changes in $E_f$, we first note that the observed temperature rise occurs in a region which is actually only about 5-nm thick at the surface. This is because the two-photon photoemission $Y_{\text{nonlinear}}$ is quadratically dependent on the probe intensity $I_{\text{probe}}(z) = e^{-z^d}$, where $z$ is the depth into
the sample and \( d \) is the penetration depth. Therefore the penetration depth \( d = 10 \text{ nm} \) of 4-eV light implies that most of the signal is derived from a region < 5-nm thick (i.e. \( \gamma_{\text{nonlinear}} \propto (\exp(-\frac{z}{d})) \)). Therefore the high-probe-intensity data samples only a thin slab of the conduction band electron population in the near-surface region. A relatively small lattice temperature rise of 100 K in the near-surface region is not surprising; the rate of energy deposited by laser shots at a 100-Hz repetition rate may exceed the rate at which heat diffuses into the sample bulk. An increase of the effective Fermi level from 10 meV to 0.25 meV is surprising however. The most likely explanation for this effect is that the electron density in the near-surface region is increasing with increasing pump-probe delay.

Given the density of states from Eq. 3.5, an effective Fermi level of 0.25-meV corresponds to an electron density of \( 3 \times 10^{21} \text{ cm}^{-3} \); in other words, the fits of the depletion curves in Fig. 3.14 do not conserve electron number. This is a dramatic increase in electron density from the initial \( 5 \times 10^{18} \text{ cm}^{-3} \). Even though the electrons are presumably equilibrated with the lattice at the 1-ps pump-probe delay, one needs to consider many-body effects at such a high carrier density [6]. These effects, such as Auger recombination [6] could significantly affect recombination.

The increase in electron density in the near-surface region may be understood as the formation of a surface space charge layer. The formation of a surface space charge layer on a Si surface has been predicted and modeled in two previous experiments, one with ns-pulses [49] and one with 60-ps pulses [22], both on a Si(111)2×1 surface. In both cases, space-charge layer formation arises due to surface states which capture carriers at the surface. In the case of Bokor et al. [22], modeling showed a rise in electron density from \( 4 \times 10^{18} \text{ cm}^{-3} \) to \( 7 \times 10^{19} \text{ cm}^{-3} \) in a region 2-nm thick at the surface. In this model, the initial excited electron density profile is calculated given the penetration depth and intensity of the pump beam. The calculation evolves the initial distribution as electrons diffuse due to the electron density gradient, subject to the force of the electric field of all the other electrons and holes (these fields are obtained via Poisson’s equation). This is identical to the treatment of
electron diffusion and drift at a $p$-$n$ junction discussed in Ashcroft & Mermin Eq. (29.27) [7]. In order to match experimental results, the model must include adjustable parameters for surface-state electron and hole capture, and electron-hole recombination rates through these surface states. The model results indicate that electrons accumulate in the near-surface region because the surface becomes positively charged due to higher surface-state capture rates for holes compared to electrons. This positive charging drives electrons to the surface [22]. This model, and another model by Long et al. [49] both show that when a surface layer forms, electrons which accumulate near the surface leave behind an electron depletion region which in Long’s calculation extends from about 10 nm to beyond 0.2 $\mu$m into the bulk. This result is shown in Fig. 3.15. The solid line is the electron distribution accumulated at the surface, and the dashed line shows the depletion region where there is a higher density of holes left behind.

**Fig. 3.15** Space charge layer formation from the calculation of Ref. [49]. Horizontal axis is the depth $z$ into the sample. Vertical axis is the carrier density $\rho$. The solid line is the electron density; the dashed line is the hole density. Note change of scale for the hole distribution.

Based on the data and interpretation of Fig. 3.14, collecting data in the high probe intensity regime appears to provide a new, highly sensitive, method of directly observing space charge layer formation. Because surface state densities and surface state capture rates
for electrons and holes are not available for the Si(100)2×1 surface, we have not yet attempted numerical modeling of our system to compare to the present experimental results. To account for the very high observed electron densities given by the fits to the data in Fig. 3.14, we believe the surface would need to possess an even higher hole capture rate than what was determined by Bokor, et al. for the Si(111) surface.

Summarizing the discussion of the high probe intensity regime results so far: (1) we have fit the depletion data for $E_{cb} > 0$ in Fig. 3.13 with a Fermi function, (2) changes in the data on ps and ns timescales, combined with the results of the Fermi distribution fit imply electron-lattice equilibration in 1-ps and the formation of a space charge layer of high electron density in 1-ns.

Next we proceed to discuss some additional details of the data of Fig. 3.13. We note that the occupied fraction of states near the conduction band minimum has slightly increased at 1-ps pump-probe delay and then decreased by 1-ns delay. We attribute the increase to electron relaxation to surface states near the conduction band minimum; we attribute the subsequent decrease to surface recombination beginning to empty these surface states on a 1-ns timescale. The change in amplitude of features in the gap ($E_{cb} < 0$) is also attributed to electron relaxation into, and recombination from, surface states.

A question that arises from the interpretation of the data in this section is: Given that the high probe intensity data suggests an electron accumulation near the surface at longer delays, why are we unable to detect any signal at longer pump-probe delays in the low probe intensity regime? This question is resolved by noting that the two-photon probe measurement is sensitive to the fraction of occupied states, rather than directly photoemitting the electrons that occupy those states. Our results suggest that the effect of one conduction band electron blocking the intermediate state of a two-photon transition is easier to detect than the direct photoemission of that one electron. This difference arises in the two-photon probe regime because occupation of a single intermediate state of the two-photon probe blocks all possible two-photon transitions through that state (i.e. all the electrons that start in
the same initial valence band state that could be driven through this particular intermediate state are blocked). Further enhancing the sensitivity of the two-photon probe at long pump-probe delays is the fact that in the high probe intensity regime, the probe effectively samples a region only half as thick as in the low probe intensity regime. In the low probe intensity regime, one samples a larger region in which some electrons are accumulating in the very thin near-surface region, but many electrons are also diffusing away deeper into the bulk (cf. Fig. 3.15). As a result, collecting data in the high probe intensity regime offers a distinct advantage at longer pump-probe delays.

Interpreting the drop in the low probe intensity photoemission as due to diffusion out of the probe region is consistent with the fact that Rowe, et al. [20] did not observe excited conduction band population with time-delayed 4.66-eV 100-MW/cm², 1-ps pulses. The greater penetration depth of our 2-eV light, coupled with our shorter probe pulses allows us to observe hot electrons in the low probe intensity regime, albeit at short pump-probe delays.

Finally we note that because Eq. 3.11 obviously arises from a number of simplifying assumptions, a more detailed analysis of the data of Fig. 3.13 is desirable which takes into account the Si band structure and attempts to exactly compute the two-photon transition matrix elements. We have not attempted this here. Future efforts are planned at AT&T Bell labs to perform such a computation and compare the results to the experimental data.

3.5 Conclusion: Improvements and Future Work

3.5.1 Summary of results

In conclusion, time-resolved photoelectron spectroscopy is used to determine for the first time the subpicosecond (100-fs) evolution of an optically excited hot electron distribution in silicon. We observe an electron-electron thermalization time of less than 120 fs, and an electron energy-dependent cooling rate consistent with a simple picture of
electron cooling through electron-photon scattering. The observed cooling rates are also consistent with published calculations of the electron-phonon scattering rate. The electrons equilibrate with the lattice in 1 ps. We also observe evidence for the formation of a surface space-charge layer of electrons which increases the near-surface electron density by approximately two orders of magnitude in 1 ps. This space charge layer persists on a 1-ns timescale.

We obtain long pump-probe delay data using a new approach to two-photon photoemission. In a high probe intensity regime, we observe reduction of the two-photon photoemission signal which corresponds to occupation of conduction band states by excited electrons. We present a simple model which shows this approach to be a method for directly measuring the fractional occupation of electronic states in the near surface region, and our experiments suggest that it does so with higher sensitivity than a conventional low-probe-intensity approach.

3.5.2 Improvements and Future Work

There are numerous technical improvements to the methods used here which would improve the quality and quantity of data that can be obtained in this experiment. To begin with, a more stable, higher repetition rate laser system such as the one built and designed here at Harvard (see Ch. 5), would be especially useful. If photoemission spectra are to be averaged at a higher repetition rate and for longer averaging times using a new laser system, the data acquisition rate and data storage capacity of the present apparatus have to be increased. The use of a LeCroy digitizing oscilloscope or other fast time-of-flight electronics which can perform true histogramming for time-of-flight data at kHz acquisition rates would greatly improve the signal-to-noise ratio over that obtained here; such instruments were not available to us at the time of this study. Another important improvement would be to use orthogonal pump and probe polarizations. This will reduce or eliminate the coherent interaction between pump and probe beams, eliminating unwanted background from both
the high and low probe intensity experiments. All these improvements taken together might
make it possible to obtain longer pump-probe delay data in the low probe intensity regime,
and likewise make shorter delay data obtainable in the high probe intensity regime.

Another technical improvement would be to use shorter laser pulses. The kHz repetition
rate system now available at Harvard can produce amplified 50-fs pulses; using these pulses
will improve the time resolution of this work by a factor of two. Better time resolution
would provide more data points to test the energy dependence of the scattering rate,
especially for high energy electrons at short pump-probe delays.

Beyond the above technical improvements, the experiment should be performed with
some variations in order to examine the physics of electron relaxation over a wider range of
conditions. At the current time, work is underway at AT&T Bell labs to examine some of
these possibilities:

Repeating the experiment with a 6-eV or higher probe photon energies may provide a
way to study the dynamics of electrons in surface states deeper in the gap. The problem of
valence band photoemission needs to be addressed, but this study is worthwhile given the
lack of detailed data regarding Si surface states, especially on the Si(100) surface.

Using a higher photon energy pump, such as 4 eV or 6 eV, would allow the study of
higher energy conduction band electrons, testing the results of calculations at higher
energies. Two possible limitations that one may encounter in such a study are the short
penetration depth of higher energy photons, and the possibility of producing more pump-
probe nonlinear photoemission background. The latter might be avoided using orthogonally
polarized pump and probe beams.

Repeating the entire experiment with an angle-resolved technique will yield more detailed
information about where in the band structure the observed dynamics occur, and would
furthermore help identify which specific surface states are participating in the electron
dynamics.
The experiment should also be performed as a function of bulk sample temperature down to LN$_2$ temperature (77 K). Fig. 3.2 (a) shows that a dramatic change in the energy dependence of the electron-phonon scattering rate occurs at 77 K, with the slope of the rate lowering from about $0.7 \times 10^{14}$ s$^{-1}$ eV$^{-1}$ to about $0.3 \times 10^{14}$ s$^{-1}$ eV$^{-1}$ in the region $0 \text{ eV} < E_{\text{cb}} < 1 \text{ eV}$.

Additionally, though some work was done here to test the effects of dosing the surface with oxygen, a more complete study of the effect of adsorbates on the surface dynamics should be performed. The effects of oxygen and hydrogen adsorption on the photoemission yield should be tested, and compared to electronic surface-state calculations. If one could obtain a passivated surface, in which no unoccupied surface states are available to interact with conduction band electrons, the dynamical picture observed in this work will change dramatically from that described here. All recombination would have to occur via bulk recombination, and no space charge layer should form since no surface states are available to trap electrons or holes.

Finally, it is important to emphasize the need for computational modeling of the ps and ns timescale electron dynamics observed in this experiment. Future models may be able to predict the electron and hole capture rates of the Si(100) surface from first principles, allowing a model of space charge formation to be performed.

Additional future work may involve application of the techniques discussed here to other more complex systems. For example, a major motivation of this work was to demonstrate a method for observing electron dynamics in a system important to industry. The possibility that real devices could be probed using the techniques presented here should be investigated. One might be able to observe electron dynamics in buried interfaces or layers of actual semiconductor devices, as long as the electron mean free path is sufficient to allow emission through any overlayers. In principle, these studies could be done while voltages and magnetic fields are applied to the device. Ultrashort pulse photoemission of such a system
might offer a new approach to device characterization, or even perhaps to the study of quantum electronic effects in quantum well multi-layered samples, for example.

Another future possibility is to apply this technology to the study of adsorbate systems, and to the study of laser-induced surface reactions, the subject of Chapter 4. This idea has been proposed previously but has not been attempted. The idea is that the presence of an adsorbate can be detected by photoemission, and that photoemission may be able to distinguish between different adsorbed species. Time-resolved photoemission could offer a new approach to time-resolving the formation of new molecular species on a surface. A potential disadvantage of this technique for this application is the small signal obtained with each laser shot. Photoemission from thousands of laser shots needs to be averaged to obtain a spectrum for a single pump-probe delay. If a reaction is proceeding on the surface at each laser shot, the initial condition is changing. If this reaction is not reversible, the only ideal way to perform the measurement would be to hit a fresh spot on the sample with each laser shot. This is impractical, at least given the present-day limits of UHV sample preparation technology. Model systems that offer reversible reactions may allow at least a demonstration of the potential versatility of this technique.

Finally, ultrashort-pulse time-resolved photoemission with ≤ 50-fs time resolution should be applied to characterize electron distributions in metal substrates. Studies with 700-fs resolution show that non-thermalized electron distributions can be observed in gold films [35]. Extending the work to shorter timescales is important because current theories of substrate-mediated laser-induced surface reaction mechanisms (see Ch. 4) suggest that transient non-thermalized electrons interact with adsorbates to drive surface reactions. This issue is discussed at length in the next chapter.

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1W. Mieher, W.S. Fann, personal communications.
References:

Chapter 4

Ultrafast initiation of surface reactions

4.1 Motivation

4.1.1 Reaction dynamics induced by a 100-fs pulse on a crystal surface

An extension of the work reported in the previous two chapters is the investigation of ultrashort pulse interaction with a metal surface upon which a molecule is attached. A 100-fs pulse with 1-mJ/cm² fluence creates a highly non-equilibrium electron distribution in the substrate, because the electrons absorb this energy on a timescale an order of magnitude shorter than the 1-μs electron-lattice equilibration timescale [1, 2]. One must ask what effect these hot electrons have on surface chemical processes, including molecular bonding to the surface (adsorption and desorption) and molecular reactions that occur on the surface (dissociation, and bimolecular reaction). As we discuss shortly, the interaction of excited substrate electrons with molecular adsorbates leads to new ultrafast mechanisms for these surface processes. These new mechanisms, which are still not completely understood,
provide fertile ground for new experimental and theoretical work in the fields of catalytic surface chemistry, fundamental surface science, and molecular physics.

The goals of the experiments here are (1) to use a 100-fs laser pulse to initiate molecular desorption and reaction on an atomically clean metal surface, and (2) to vary the energy, wavelength and pulsewidth of the laser pulses to investigate the light-induced excitation mechanism. These experiments utilize surface science techniques for preparation of substrate/adsorbate systems that have a well-characterized, high-purity, ordered arrangement useful for desorption and reaction experiments.

Molecular energy and charge transfer dynamics on a crystal surface are considerably different than in the gas phase. Bonding to the surface alters the electronic structure of both adsorbate and substrate in the near-surface region, providing a channel for electronic and vibrational relaxation between adsorbate and substrate. Via the adsorbate-substrate interaction, excited substrate electrons couple their energy to the adsorbate, and drive reactions. In the gas phase, isolated excited molecules relax via radiative transitions on a µs timescale, and interacting ensembles relax on the collisional timescale (cf. Ch. 2). On a surface, adsorbate-substrate bonding quenches radiative transitions [3]. As a result, electronic and vibrational excitation of the adsorbate relaxes via energy transfer to the lattice on a ps timescale. Relaxation occurs via excitation of carriers (i.e. electron-hole pairs) in the substrate, or via thermal excitation of the lattice (i.e. phonon generation) on a 1–10 ps timescale [4].

Due to the presence of the substrate, electronic and vibrational modes appear that are absent in the gas phase. Frustrated rotational and translational modes arise in adsorbate vibrational spectra (EELS [5] and IR absorption [6, 7]). Dynamic charge transfer [8, 9], and image potential interactions [10] provide new electronic and coulombic couplings. All these adsorbate-surface interactions can participate in energy transfer during a reaction.

To facilitate study of surface reaction dynamics, one needs to find model systems which are easily prepared, readily characterizable, and exhibit reactions that can be initiated and
probed at available wavelengths. A further goal is to develop spectroscopic techniques suitable for a given system that will help in distinguishing among the many channels for energy and charge transfer. With suitable systems and techniques, a detailed understanding of the dynamics of adsorbate/substrate interaction during a laser-initiated reaction process is obtained.

There are in general four basic types of excitation mechanisms for adsorbate-substrate systems that may lead to desorption or reaction following absorption of a 100-fs laser pulse [11]:

1. **Direct adsorbate-localized excitation**, for example, an optical transition within the electronic levels of the adsorbate;

2. **Excitation of surface-localized states of the substrate**, with subsequent energy transfer to adsorbate electronic or vibrational states; this involves either an optical transition within the surface band structure, or bulk electronic relaxation to surface states. An example of this would be indirect optical transitions to gap surface states on a Si(100) surface (described in Ch. 3) followed by charge transfer from a surface state to an adsorbate electronic level;

3. **Excitation of bulk carriers in the substrate**, which subsequently couple their energy to excited states of the adsorbate. This coupling can occur via surface states (demonstrated in Ref. [12]) or via direct substrate-adsorbate coupling [13];

4. **Excitation of bulk substrate carriers as in #3, but with subsequent release of energy to the substrate lattice**, which drives a thermal excitation of an adsorbate.

Mechanisms (1)–(3) can occur on a fs–ps timescale, while the thermal mechanism (4) requires at least several hundred picoseconds to produce reaction probability comparable to that measured in the experiments discussed here (see Sect. 4.4.2). Previous studies of desorption from metal surfaces driven by subpicosecond pulses (see Sect 4.2.4) provide strong evidence that excited substrate carrier mechanisms (type 3) dominate ultrafast desorption and reaction on metal surfaces.
In the experiments described here, a 100-fs laser pulse excites a single crystal platinum (Pt(111)) surface which has an adsorbed monolayer of molecular oxygen (O\textsubscript{2}) or coadsorbed oxygen and carbon monoxide (CO/O\textsubscript{2}). We observe desorption of O\textsubscript{2} and CO\textsubscript{2} following irradiation. Our results indicate that a hot electron mechanism (type 3 above) produces laser-induced desorption of O\textsubscript{2} from the Pt substrate.

### 4.1.2 Desorption, dissociation, and reaction of O\textsubscript{2}/Pt(111) and CO/O\textsubscript{2}/Pt(111)

The choice of the oxygen/platinum system is based on practical as well as scientific reasons. The CO/O\textsubscript{2}/Pt(111) is the most studied bimolecular reaction system [14]; it has been previously well-characterized, and is readily prepared by standard methods discussed in Sect. 4.2.2. At liquid nitrogen (LN\textsubscript{2}) temperatures, oxygen adsorbs as a molecule (i.e. it does not dissociate) on the Pt(111) surface, with its bond axis parallel to the surface. Previous photochemistry work [15] shows that molecular carbon monoxide (CO) can be co-adsorbed with O\textsubscript{2}, and that UV light can be used to initiate a reaction between the two species to form CO\textsubscript{2}. Recent results [16, 17] reported after the initiation of this work also show that O\textsubscript{2} desorption, as well as the CO\textsubscript{2} formation reaction can be initiated with a 100-fs laser pulse. These results were the first demonstration of ultrafast initiation of a surface bimolecular reaction; the results show a highly nonlinear dependence of the desorption and reaction yield on the laser fluence, as well as a picosecond timescale for desorption, suggesting that a hot carrier mechanism is important. Hence the O\textsubscript{2}/Pt(111) and CO/O\textsubscript{2}/Pt(111)\textsuperscript{1} systems offer an attractive starting point for detailed study.

The work presented here extends the work of Refs. [16, 17] to new wavelengths and a higher laser fluence regime. We observe nonlinear desorption and reaction fluence dependences in the high fluence regime (1–20 mJ/cm\textsuperscript{2} absorbed); we also observe a change

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\textsuperscript{1}Point of notation: the sequence CO/O\textsubscript{2}/Pt indicates that the system was prepared by first adsorbing O\textsubscript{2} on the surface, then dosing with CO. This is critical since O\textsubscript{2} will not adsorb if CO is first dosed on the clean sample.
in the ratio of desorption to reaction as a function of wavelength, and for the first time obtain experimental conditions in which the reaction channel is favored over desorption.

4.2 Description of Experiment, and Previous Work

4.2.1 Overview

In the experiments described here, we initiate desorption and bimolecular reaction in the O₂/Pt(111) and CO/O₂/Pt(111) systems, using laser pulses in the range of 70-fs to 3.6-ps, at wavelengths of 800-nm, 400-nm, and 266-nm, with absorbed fluences between 1–20-mJ/cm². The experiments are carried out in ultrahigh vacuum (5 × 10⁻¹¹ torr) at a sample temperature of 90 K. Desorption and reaction products produced by the laser pulses are measured using a mass spectrometer. Analysis of the results confirms a highly nonlinear dependence in desorption and reaction yield on laser fluence. The results also show a strong wavelength dependence, with higher nonlinearity at longer wavelengths, and a greater cross-section for reaction with increasing photon energy.

The results obtained here also show that previous simple models used to describe desorption introduced by 100-fs pulses do not adequately describe the experimental results. The DIMET model (desorption induced by multiple electronic transitions), which is discussed in detail in Sect. 4.2.5, has been applied to the results of 100-fs laser desorption of NO from Pd(111) [18] and O₂ from Pt(111) [17]. In the DIMET model, no wavelength dependence is incorporated; the model suggests that ultrafast desorption can be characterized by the substrate electron temperature in the laser-excited region. However, in the work reported here, we observe a wavelength dependence to the desorption at 400 nm and 800 nm even though the absorbed laser fluence was controlled so that the same peak electron temperatures were generated at both wavelengths (Sect. 4.4.3 explains the method.

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²This work was done at Harvard in collaboration with S. Deliwala, R. Finlay, T. H. Her, Dr. W. D. Mieher, and Prof. E. Mazur.
for electron temperature computation). This observation indicates that the observed surface reactions cannot be simply accounted for by a model which characterizes the substrate-adsorbate interaction as dependent on the substrate electron temperature.

### 4.2.2 Review of O₂/Pt(111) and CO/O₂/Pt(111) surface science

Detailed characterization of the O₂/Pt(111) and CO/O₂/Pt(111) systems has been carried out and reported in the literature ([15, 19, 20] and references therein). Molecular oxygen is known to physisorb to the Pt(111) surface below 30 K; it is molecularly chemisorbed (π bonded) above 30 K, and desorbs at 150 K. Figure 4.1 shows a typical temperature programmed desorption (TPD) measurement in which the dosed sample is uniformly heated at 2 K/s. The vertical axis shows the molecular oxygen mass spectrometer signal (32 a.m.u.), plotted against temperature as the temperature is increased. Two peaks are evident, a sharp peak at 150 K and a broad peak between 600–800 K. The 150 K peak corresponds to O₂ desorption and dissociation; the high temperature peak occurs due to thermally activated O₂ formation from atomic oxygen on the surface, which desorbs once the O+O reaction is completed. The 600–800 K peak is referred to as the recombination peak. The atomic oxygen which recombines to form this peak in the TPD measurement is present due to O₂ dissociation at 150 K [14, 15, 19, 20].

Electron energy loss spectroscopy (EELS), which is sensitive to surface vibrational modes, and low-energy electron diffraction (LEED), which reveals the arrangement of adsorbates on the surface, have been used to determine that the molecule lies flat on the surface in majority ‘atop’ and minority ‘bridge’ sites on the Pt(111) face [15, 19, 20]. By comparing the desorption signal in TPD experiments to the integrated thermal desorption probability, one obtains a chemisorbed O₂/Pt(111) bonding energy of 400 meV.³

³More specifically, one uses Eq. 4.2, with a value for the attempt frequency obtained from the atop mode vibrational frequency in EELS spectra. The TPD measurement is performed by heating the O₂/Pt(111) surface from 90 K to 1000 K at 2 K/s. Since all the products desorb at about 150 K, assuming unity desorption probability in Eq. 4.2 at 150 K gives the 400 meV bond energy.
Fig. 4.1 O₂ TPD spectra of O₂/Pt(111). We show three spectra obtained for three separate dosings with the sample flash annealed between each dose; note the excellent reproducibility. The arrow indicates a change of vertical scale by ×10.

Co-adsorption of CO with O₂ is accomplished by first saturating the surface with O₂, then dosing with 1 Langmuir (1 L) of CO afterwards. As determined by EELS spectroscopy, this dosing procedure results in CO occupation of atop sites with CO bound to Pt through a C–Pt chemisorption [15]. Heating the surface with both species adsorbed results in the production of CO₂ in two peaks, at 150 K and at 320 K. A peak also occurs at 320 K when CO is coadsorbed with atomic O. These facts indicate that the first 150 K CO₂ desorption peak occurs due to CO combining with excited (‘hot’) O atoms produced by O₂ dissociation at 150 K, while the 320 K peak in the CO/O₂/Pt(111) system arises from ‘left over’ O atoms bound to the Pt surface which combine with CO in a thermally activated

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4The unit 1 L indicates a timed exposure of a surface to a foreign gas at fixed ambient pressure in units of 10⁻⁶ torr × s. From Eq. 6.1 (Chapter 6), one can estimate the number of molecules that strike the surface during this exposure [21]. Then using measured estimates of the number of molecules that stick to the surface and TPD characterization, one can estimate the surface coverage that results from a given dosing procedure [14, 15].
reaction. The CO$_2$ that forms on the surface desorbs, since the CO$_2$ that forms has excess energy after reaction, and is weakly bound to the Pt(111) surface, desorbing at $\geq 93$ K \cite{14}.

The ratio of O$_2$ desorption to CO$_2$ production in the thermal desorption experiments is about 10:1. One might expect that this ratio could be predicted given information about the surface reaction geometry. For example, it has been determined that the CO surface coverage is about 0.3 monolayers, the initial O$_2$ coverage is 0.4 monolayers, and the presence of CO reduces the O$_2$ atop site EELS signal by a factor of two \cite{15}. So far, efforts to compute the O$_2$/CO ratio using these data have not succeeded\textsuperscript{5}, which indicates that the understanding of the surface geometry and knowledge of other parameters such as reaction cross-sections are incomplete. Even so, the experimentally measured O$_2$/CO ratios are repeatable, and one can still use observed changes in this ratio measured as a function of laser pulsewidth and wavelength to observe changes in the reaction mechanisms.

The photochemistry of O$_2$/Pt(111) and CO/O$_2$/Pt(111) is also reported in the literature for continuous-wave (cw) irradiation at wavelengths from 546 nm (2.3 eV) to 240 nm (5.2 eV) \cite{15}. O$_2$ is observed to desorb in this wavelength range with a linear dependence on incident light intensity. As a function of wavelength, the desorption cross section drops sharply with increasing wavelength, with a maximum yield at UV wavelengths which drops by two orders of magnitude from 240 nm to 546 nm. No photochemical activity is observed for CO adsorbed alone on the Pt surface. The ratio of O$_2$ to CO$_2$ desorption yield for the cw photoprocess is 2.5:1 in the range 240 nm to 400 nm, independent of wavelength. CO$_2$ formation for the CO/O$_2$/Pt(111) system is found to have the same photon energy and polarization dependence as O$_2$ desorption, indicating that the desorption and reaction products result from the same initial excitation \cite{15}.

The wavelength and polarization dependences of photoinduced desorption and reaction are shown to be compatible with a direct optical process in Refs. \cite{14, 15}. The mechanism

\textsuperscript{5}W. Mieher, personal communication.
for CO₂ formation is attributed to photodissociation of O₂, followed by a reaction between the excited (‘hot’) O atoms and coadsorbed CO. This conclusion is supported by the fact that no CO₂ formation is detected following irradiation of a surface with CO and atomic oxygen coadsorbed. This suggests that immediately following a single photoexcitation event, excited transient O atoms (‘hot’ atoms) combine with CO driving the O+CO reaction. This ‘hot O’ mechanism, which proceeds through a transient intermediate state, is exactly the sort of ultrafast process that one would like to time-resolve using ultrafast spectroscopy, as discussed in Chapter 1.

If the cw photoreaction proceeds via direct laser-induced dissociation of O₂ followed by hot atomic O reaction with CO, then CO₂ formation is a direct probe of laser-induced dissociation on the surface. The mechanism for cw photoinduced reactions is however a topic of debate in the literature. First of all, at least two groups, one studying the CO/O₂/Pt(111) system [22] and the other studying the O₂/Pd(111) system [23], have proposed that the initial excitation in their (ns pulse) experiments is not a direct optical excitation, but rather a substrate-mediated mechanism involving optical excitation of substrate carriers which subsequently interact with the adsorbates. Secondly, Ukraintsev, et al. propose that the observed CO₂ formation does not result from O₂ dissociation, but rather from the direct interaction of vibrationally or electronically excited O₂ with adsorbed CO.

Because these experiments employed ns pulses, they are in the linear fluence-dependence regime. It is therefore beyond the scope of this chapter to discuss these experiments in detail. The important point is that a number of possible interpretations exist, and that the reported results do not conclusively identify the mechanisms. This has important implications for the work reported here. For example, a direct optical process that occurs in cw photochemistry is expected to occur in the fs photochemistry as well. However, as discussed in the next section, a 100-fs pulse creates a very different substrate electron distribution than a cw excitation. Hence a substrate-mediated process might produce
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significantly different results depending on whether cw or 100-fs pulse excitation is used. In the discussion of our data that follows, we consider all of the above-mentioned mechanisms.

4.2.3 Peak electron temperatures

In 100-fs laser-pulse surface reaction experiments, the role of substrate electrons in substrate-mediated mechanisms is crucial. A 100-fs pulse creates a highly excited non-equilibrium electron energy distribution in the laser-excited region (this is discussed for the case of semiconductors in Ch. 3), and these highly excited electrons can interact with adsorbates producing new effects. We discuss the reaction mechanisms in Sect. 4.2.5; in this section we explain a method [1] for characterizing the non-equilibrium electron and lattice energy distributions generated by 100-fs laser pulses incident on a metal. Characterizing these distributions is important for both the discussion of reaction mechanisms in Sect 4.2.5, and for interpretation of the data in Sect. 4.5.

For the discussion that follows, we need to define two types of non-equilibrium electron distributions: ‘thermalized’, and ‘nascent’. Both types of distributions are created by absorption of a 100-fs laser pulse; they are non-equilibrium distributions because the electrons are excited in 100-fs, a timescale faster than the 1-ps electron-lattice equilibration timescale. A thermalized non-equilibrium electron energy distribution results when electron-electron interactions equilibrate the electrons so that the distribution is characterizable by a single parameter, \textit{i.e.} the electron temperature. A nascent non-equilibrium electron distribution is one that has not yet thermalized; such a distribution evolves into a thermalized distribution on approximately a 1–100-fs timescale. A nascent distribution cannot be characterized by a single temperature, but might be characterized by the photon energy, depending on the electron relaxation dynamics. For example, one possible nascent electron distribution is a sharply peaked distribution in the substrate band structure centered around the final energy and momentum of the photo-induced optical transition. Nascent electron distributions have been modeled [24] and observed experimentally [25]. To
compute nascent distributions requires a microscopic approach, computing cross sections for all possible optical transitions in the Pt band structure to determine the initial electron distribution; to predict the subsequent evolution of the nascent distribution requires modeling of the electron-electron and electron-phonon interactions.

A distinction between nascent and thermalized distributions is made here simply to point out that the thermalized electron description used in published DIMET-model interpretations [16, 18] of 100-fs pulse desorption experiments is not necessarily complete. The results of some laser-induced desorption experiments [24, 26] show that the desorption yield depends upon the substrate nascent electron distribution. The results discussed in Sect. 4.5 show that the observed desorption and reaction yield cannot be directly related to the peak substrate electron temperature. It may be that future theoretical models of 100-fs pulse laser desorption and reaction will need to incorporate nascent electrons.

We have calculated the thermalized non-equilibrium electron and lattice temperatures following the treatment of Anisimov, et al. [1] in which separate electron and lattice temperatures evolve as follows:

\[
C_e \frac{\partial}{\partial t} T_e = \frac{\partial}{\partial z} \kappa (T_e) \frac{\partial}{\partial z} T_e - g (T_e - T_{lat}) + U_{\text{laser}} (z, t)
\]

\[
C_{lat} \frac{\partial}{\partial t} T_{lat} = g (T_e - T_{lat}), \tag{4.1}
\]

where \(C_e\) and \(C_{lat}\) are the electronic and lattice specific heats, \(g\) is the electron-lattice coupling constant, \(\kappa\) is the electron thermal diffusivity, taken to be linearly dependent on \(T_e\), \(U_{\text{laser}}\) is the rate of laser energy deposition per unit volume and time, and \(T_e\) and \(T_{lat}\) are the electron and lattice temperatures (both also functions of depth \(z\) into the substrate and time \(t\)). The calculation evolves both temperatures in space \(z\) and time \(t\). Diffusion of heat in the lattice can be ignored since it occurs on a ns timescale; adding a lattice diffusion term to Eq. 4.1 had no effect on the resulting temperature evolution for a full 250-ps elapsed time following the laser pulse.
Fig. 4.2 Electron and lattice temperature calculation using Eq. 4.1 for a 20-mJ/cm² absorbed fluence at 800 nm in platinum. \( T_e \) is the electron temperature, \( T_{\text{lat}} \) is the lattice temperature. Inset (a) shows electron temperature depth profiles \( T_e(z) \) for three times. Inset (b) shows the 250-ps evolution of the electron and lattice temperatures.

For clarity, we point out the distinction between this calculation of an electron temperature and the one described in Ch. 3. The electron temperature \( T_e(z,t) \) in Eq. 4.1 is the temperature of all the electrons in the laser-excited region of the metal substrate, because all these electrons can freely interact with each other following the absorption of the laser pulse. This contrasts with the definition of the temperature of Si conduction band electrons in Ch. 3, in which the conduction band electrons only interact with other conduction band electrons.

Figure 4.2 shows the evolution of \( T_e \) and \( T_{\text{lat}} \) at a Pt surface for a 20-mJ/cm² absorbed fluence (absorbed fluence is defined in Sect. 4.3.2, Eq. 4.3). From the 100 K initial
temperature, the surface electron temperature rises to a peak at 8800 K within 1 ps, and falls to meet the lattice temperature at 250 K after 7 ps. The inset (b) shows the long time behavior of the both temperatures. Inset (a) shows a depth profile of the electron temperature at three times, illustrating the cooling due to electron diffusion away from the surface. Note that since the absorption depths of all our experimental wavelengths in Pt varies only between 11–13 nm, this calculation yields essentially the same results for all wavelengths between 800 nm and 266 nm. Thus, in this model the surface electron temperature is only a function of absorbed fluence.

Figure 4.3 shows the peak electron and lattice surface temperatures as a function of fluence and pulsewidth. The peak surface temperature is typically reached shortly after the peak of the laser pulse intensity. Note that while peak lattice temperatures vary only a small amount for the three pulsewidths, a 100-fs pulse reaches about a four times higher electron temperature than a 3.6-ps pulse at the same fluence. Note also that at a given pulsewidth, the electron temperature varies by a factor of 5–10 over the range 1–20 mJ/cm².

### 4.2.4 Previous ultrafast work

Experimental and theoretical work on 100-fs laser-initiated surface reactions has been reported with a variety of systems, on metals and semiconductors. An excellent recent review of these developments has been published by Cavanagh et al. [11]. To provide a context for the results presented here, a few recently published results need to be discussed.
With 200-fs, 2-eV pulses, NO was observed to desorb from Pd(111) with a nonlinear dependence on laser fluence, a large cross section at least one order of magnitude larger than the highest reported cross section for low-intensity cw or ns-pulse experiments, and an internal vibrational energy after desorption with $T_{\text{vib}} = 2000 \text{ K}$, significantly hotter than the predicted peak lattice temperature\footnote{More recent results with the same system have found vibrational temperatures as high as 2900 K using laser pulses with a fluence capable of producing a peak electron temperature of 4500 K [27].} [28]. Compared to excitation with cw or nanosecond excitation, the desorption mechanism was clearly different. Subsequently, another experiment with this system revealed that the desorption occurred on a subpicosecond
timescale [29]. This was achieved by measuring the desorption yield in a two-pulse correlation scheme, in which two identical ultrashort pulses were scanned past each other in time while overlapped spatially on the sample. This result demonstrates that the desorption event occurs too fast to be driven by a thermal lattice heating mechanism, but occurs too slowly (600-fs correlation width for 400-fs pulses) to be a direct optical mechanism. Then, in another experiment with 100-fs, 2-eV pulses, CO was observed to desorb from the Cu(111) surface within 300-fs [30]. This observation was made in the time-domain by measuring the change in second harmonic generation of a probe beam reflecting from the surface following the desorbing pump pulse. The authors suggest that the 300-fs response of the desorption occurs via a mechanism in which multiple excited substrate electrons interact with the adsorbate on a fs timescale. This idea is the basis of the so-called DIMET model (desorption induced by multiple electronic transitions) [18] discussed in Sect. 4.2.5.

Most recently, a series of experiments with the CO/O2/Pt(111) system by Ho and coworkers has further characterized 100-fs laser-induced O2 desorption [17], and observed the ultrashort pulse initiation of the reaction O2+CO→CO2 [16]. Desorption of O2 from Pd(111) surface using 100-fs pulses has also been observed [31]. In Refs. [16, 17], 150-fs and 600-fs pulses at 620 nm and 310 nm with 1–5-mJ/cm² fluences were used to initiate desorption of O2 and reaction of CO with O2 to form CO2. The reaction products were detected using mass spectroscopy. The results were compared to those obtained with 3-ns, 355-nm pulses7. In contrast to the linear fluence dependence obtained for ns pulses, highly nonlinear fluence dependences were observed for the ultrashort pulses. Fitting the observed yields to a power-law fluence dependence resulted in exponents of 5.5 ± 0.7 and 3 ± 0.5 for 150-fs pulses at 620 nm and 310 nm respectively. Note that roughly the same exponential behavior (yield ∝ F6) is observed for 100-fs, 620-nm pulses on NO/Pd(111) [31]. Slightly different exponents were observed for 600-fs pulses (see Table 4.1). The ratio of O2 to CO2

7Similar results for 15-ns pulses were also obtained by Ukrainsiev, et al. [22]
yield was also found to vary with wavelength and pulsewidth, see Table 4.1. Two-pulse desorption correlation measurements performed with 620-nm, 150-fs pulses had a full-width at half-maximum of 1.2 ps. As with the NO/Pd(111) experiments, this long width is too fast for a lattice-heating, thermally activated mechanism, but much wider than expected for a direct optical mechanism. The authors suggest that 1.2 ps is the electron-lattice energy relaxation timescale [32].

4.2.5 Theoretical issues

The primary features of the above experiments which need to be explained are: (1) the highly nonlinear dependence of desorption (and reaction) yield on absorbed laser fluence, characteristic of ultrashort pulse measurements; note that this behavior appears to be universal for the molecular adsorbate on metal substrate systems studied so far; (2) the less than 1-ps timescale for the desorption event, determined by surface second-harmonic generation measurements; (3) the long, greater than 1-ps width of two-pulse correlation measurements which indicate that the excitation process occurs on that timescale; (4) the observed desorption wavelength dependence, which gives lower power laws at shorter wavelengths; and (5) the observed O\textsubscript{2} desorption/CO\textsubscript{2} reaction ratio dependence on wavelength. Note that the mechanism for CO\textsubscript{2} formation could involve either O\textsubscript{2} dissociation or an activated molecular O\textsubscript{2} reaction with CO. Since these two possibilities are quite distinct, it will be difficult to address point (5) until this question is resolved.

While no theoretical treatment is attempted here, it is worth discussing some previously proposed models for ultrafast desorption experiments. The experimental results presented below can then be considered in light of these ideas as a test of their validity.

Before considering the 100-fs pulse case, we first discuss models of desorption by continuous or ns-pulse irradiation. Experimentally, the observed desorption yields for cw and ns irradiation have the same dependence on absorbed energy. As mentioned before, one finds a strong wavelength dependence on yield, and a linear dependence on fluence. State-
resolved measurements with NO/Pt(111) show a strong wavelength dependence in the rotational, vibrational and translational distributions of desorbed products, uncorrelated with the predicted surface temperature change induced by the laser [26]. To account for all of these characteristics, one generally invokes a combination of a thermal model and a so-called DIET model (desorption induced by electronic transitions, see [8, 9] and references therein).

The thermal model [21] assumes that desorption occurs from simple heating of the lattice by the laser pulse. Since the incident irradiation is either continuous or on a ns timescale, the electrons and lattice are always in equilibrium with each other; non-equilibrium electron effects do not play a role. The thermal desorption probability \( P_{\text{thermal}} \) per unit time is then given by

\[
P_{\text{thermal}} = \nu_o \exp \left( -\frac{E_{\text{bind}}}{k_B T_{\text{vib}}} \right),
\]

where \( \nu_o \) is an ‘attempt’ frequency on the order of \( 10^{13} \) Hz, usually taken as the frequency of the adsorbate-substrate vibration, \( E_{\text{bind}} \) is the surface binding energy, and \( T_{\text{vib}} \) is the temperature of the adsorbate-surface vibrational mode. In this thermal model, the only experimental parameter is the surface mode temperature \( T_{\text{vib}} \). This temperature depends only on the energy deposited in the lattice, and its subsequent transfer to the adsorbate-substrate vibration.

Using the calculated temperature profiles in Fig. 4.2 and Eq. 4.2, we can estimate the desorption yield in our experimental data according to the thermal model. For our maximum fluence of 20 mJ/cm², a 250-K peak lattice temperature is reached, which is well above the 150 K desorption peak in the TPD spectra. The lattice temperature drops to about 200 K within 250 ps (cf. Fig 4.2). Assuming ideal coupling between the lattice and the adsorbate-substrate mode, we have \( T_{\text{vib}} = T_{\text{lattice}} \), which gives an upper bound on the desorption probability. Integrating the resulting thermal desorption probability given by Eq. 4.2 (\( \nu_o = 2.4 \times 10^{13} \) Hz, \( E_{\text{bind}} = 400 \) meV) over 250-ps gives a net thermal desorption probability of
less than $10^{-4}$. This computed yield is far less than the observed yield of $10^{-1}$ at 20 mJ/cm² for 100-fs, 800-nm pulses (see Sect. 4.4.2).

If the absorbed energy in a cw or ns-pulse photoreaction experiment is too small to create significant desorption via a thermal process, or if a wavelength dependence is observed even when the amount of heating is held constant for different wavelengths, then the thermal model must be rejected. In this case, an electronic mechanism must be involved. Desorption induced by electronic transitions (DIET) has been studied in detail (see for example Refs. [26, 27]). In the DIET model, the adsorbate-substrate complex undergoes an electronic transition to an excited potential energy surface (PES). This transition is schematically illustrated in Figure 4.4 (a–b). Subsequent relaxation of the excited state on a ps timescale can leave the adsorbate with excess vibrational energy above the desorption threshold, in which case the adsorbate desorbs (Fig. 4.4 (b)). Two types of DIET processes are possible. The initial excitation can occur due to an optical transition within the adsorbate-substrate complex, or via charge transfer of an excited electron (or hole) from the bulk substrate to the adsorbate after optical absorption by the substrate. This second type of DIET process is referred to as substrate mediated.

Both of these types of processes have been observed experimentally. In the NO/Si(111) system [13], the cw NO photodesorption was shown to have the same wavelength dependence as the substrate absorption spectrum, demonstrating a substrate-mediated mechanism. In the Mo(CO)₆/Si(111) system [33], the cw photodissociation wavelength dependence matched the molecular Mo(CO)₆ absorption spectrum, demonstrating a direct molecular optical absorption process. The difference between these two systems was attributed to the fact that adsorbed NO has electronic levels close to the substrate Fermi level that can interact with excited substrate electrons, while Mo(CO)₆ does not. However, co-adsorption of K with Mo(CO)₆ on Si(111) shifts the substrate Fermi level to higher energy where the adsorbate levels overlap with the Fermi level [33]. In this case, a substrate-mediated mechanism is in fact observed.
Fig. 4.4 Trajectories for motion on the ground and excited potential energy surfaces (PES) for NO/Pd(111) from Ref. [18]. Vertical dashed lines indicate Franck-Condon transitions, horizontal dashed lines indicate motion on the PES. (a)–(b) show trajectories for a single excitation DIET process; (a) is an excitation that does not lead to desorption, while (b) is an excitation that does produce desorption. Panels (c)–(d) are trajectories for the DIMET process. (c) is a simplified example of DIMET with two excitation/de-excitation cycles, while (d) shows a more complex series of multiple transitions leading to desorption.

A detailed microscopic implementation of a DIET model that can predict DIET rates, yields, and desorption product internal states requires accurate potential energy surfaces for the adsorbate/substrate complex, as well as complete knowledge of the substrate band structure and optical transition matrices. Furthermore, for substrate-mediated processes, one needs to know details of electron transport, and charge transfer to the adsorbate-substrate complex. A practical limitation is that in many cases such data is not available either from theory or experiment.
An example of a detailed substrate-mediated DIET calculation can be found in Buntin, et al. [24, 26]. In this analysis of ns-timescale desorption experiments on NO/Pt(111), the authors relate the substrate *nascent* hot electron distribution to a non-thermal component of the NO desorption yield. These authors computed the nascent electron distribution and demonstrated that for wavelengths \( \leq 532\text{-nm} \), this distribution has electrons with energy sufficient to excite an electronic resonance; this excitation leads to desorption via a DIET mechanism. Products that desorbed through this mechanism can be identified since they have different internal state distributions than thermally-desorbed products. Excitation with 1064-nm ns-pulses produces nascent electron distributions with insufficient energy for the DIET process; as a result 1064-nm excitation produces only thermal desorption products. This work provides compelling evidence that nascent electrons can induce a substrate-mediated DIET desorption event, and that such a process can exhibit a wavelength dependence which can be related analytically to the substrate nascent electron distribution.\(^8\)

Now we consider the mechanisms in 100-fs pulse desorption and reaction experiments. Two main differences with the ns case are immediately evident: (1) the 100-fs pulse is capable of producing a highly-excited non-equilibrium electron distribution without significant heating of the lattice (cf. Sect. 4.2.3), and (2) all of this energy can be deposited on a timescale comparable to the electronic relaxation time of substrate and adsorbate, and shorter than the characteristic vibrational relaxation timescale for the adsorbate.\(^9\) Given that all the optical energy is deposited within the 10 nm penetration depth\(^10\) of the laser pulse, and that electron mean free paths are also about 10-nm in metals for our 266-nm to 800-nm

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\(^8\)For a more detailed discussion, see Gadzuk, et al. [34]. This work attempts to develop a detailed treatment of the NO desorption, using simplified Morse potentials and assumptions about electron transfer to excited states and the wave-packet evolution dynamics of these excited states. In this treatment, the authors are able to use the experimental data to estimate the lifetime of the intermediate state during desorption.

\(^9\)Time-resolved reflectivity/absorption measurements indicate that the timescale for vibrational relaxation of molecular adsorbates on metal surfaces is on the order of 1-ps [35].

\(^10\)The penetration depth in Pt varies only from 11 nm to 13 nm from 800 nm to 266 nm, respectively [36].
excitation [21], it is reasonable to assume that a significant fraction of the excited electrons will arrive at the surface.

In light of these facts and the observed nonlinear fluence dependence of the desorption yield, a variation of the substrate-mediated DIET model has been proposed that involves multiple substrate-mediated electronic excitations. In this model, called the DIMET model, once excitation has occurred and the system returns from the excited potential energy surface (PES) to the ground state, the system is allowed to be re-excited again. Out of many random excitation/relaxation events that occur, those which are appropriately phased with the motion of the adsorbate-substrate bond on the excited PES increase the amount of time the system stays on the excited PES, increasing the probability for desorption (see Fig. 4.4 (c–d)).

As already noted, the DIMET model [18] has been used previously to predict the results of a 100-fs pulse desorption experiment. The computational scheme for this work [18] assumes a simple Morse potential for the excited state, an electron-temperature dependent excitation rate, and tunable parameters for the excited state life-time and Morse potential parameters. Using electronic life-times tuned between 1–5 fs and a peak electron temperature of 5500 K, it was found that as many as 30 excitation-de-excitation cycles can occur in a single desorption event, as schematically illustrated in Fig. 4.4 (d) The computed desorption probability is nonlinear in fluence and is five orders of magnitude greater than the corresponding single-excitation DIET yield. Of course, the exact results are model-dependent and can thus only be considered illustrative of the basic concept. Nevertheless, the model is a compelling example of a calculation which considers how the details of electron transfer affect the desorption dynamics.

As originally proposed by [18], the DIMET model does not produce any wavelength dependence of the desorption yield. A wavelength dependence could be introduced by computing a wavelength-dependent initial substrate electron distribution. A complete model would furthermore model the dynamics of the electron distribution as well as the interaction
between substrate electrons and the adsorbate-substrate complex. Future theoretical models of 100-fs pulse desorption experiments will need to incorporate a wavelength dependence in order to account for the experimental results presented here.

In addition to substrate-mediated mechanisms, one needs to consider the role of direct adsorbate-substrate optical excitation (type 1 in Sect. 4.1.1) in 100-fs pulse desorption and reaction experiments. Such a mechanism has been ruled out at visible wavelengths by two-pulse correlation desorption experiments which show a timescale for the desorption excitation greater than the optical cross-correlation [17, 29]. However, this type of experiment has not yet been reported at UV wavelengths. Based on the observed cw wavelength dependence of desorption which shows that the linear process is most effective at UV photon energies, it is reasonable to assume that in 100-fs desorption experiments with UV pulses a contribution from a direct optical process may be important. We discuss this possibility in more detail in Sect. 4.5.2.

4.3 Experimental Technique

The primary goal of this experiment is to measure the fluence, wavelength, and pulsewidth dependence of the ultrafast desorption and reaction yield in the CO/O₂/Pt(111) system. Figure 4.5 schematically illustrates the design of the experiment. The samples were prepared in UHV. Desorption and reaction were induced by 800-nm, 400-nm and 266-nm pulses produced by a 1-kHz amplified Ti:sapphire laser system. Desorption and reaction yields were measured in UHV using a quadrupole mass spectrometer in pulse-counting mode.

4.3.1 UHV chamber and sample preparation

The measurements described here were carried out on a 1-cm diameter × 1.5-mm thick single crystal Pt(111) sample (Princeton Scientific) at 90 K in ultrahigh vacuum at a base...
pressure of $5 \times 10^{-11}$ torr. The UHV chamber was custom designed and built in our research group. Chapter 6 provides a detailed description of the chamber design and operational methodology.

For all the measurements here, the sample was positioned with the crystal normal facing directly into the mass spectrometer (UTI), at the minimum distance of 5 cm from the spectrometer. Given the 2-cm diameter of the spectrometer entrance, we estimate that we collect between 2% and 10% of the desorbing molecules, depending on their angular distribution\(^\text{11}\). Laser pulses were incident on the sample at 45° from the normal, through a fused-silica window on the same level as the mass spectrometer.

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\(^{11}\)The upper bound of 10% is estimated from the sharply peaked ns-laser-induced desorption distribution observed by [22] which had a half-width at half maximum of 18 degrees.
Chapter 4

Ultrafast initiation of surface reactions

The mass spectrometer is equipped with a channeltron electron multiplier operated at high gain. At the entrance to the mass spectrometer an electrically isolated 25-mm diameter stainless-steel mesh screen is suspended via a floating electrical feedthrough mounted on a port above the mass spectrometer. The screen is necessary to capture the 70-eV electrons which escape from the spectrometer ionizer and impact the sample causing desorption of O₂. With the screen absent or grounded, a strong desorption signal of about four times the background is detected from the O₂-dosed sample when it faces the mass spectrometer. With the screen electrically floating, no increase in background counts could be detected.

The sample is cleaned and dosed with O₂ and CO as follows. The Pt crystal is first cleaned in about 100 sputter-anneal cycles after initial chamber pump-down. The cleaning process is automated to facilitate completing this repetitive process. Sputtering was performed in 99.999% pure Ne, with the chamber backfilled to \(5 \times 10^{-5}\) torr; the ion gun was set to provide 0.5-kV ions at 25-mA gun emission current, which gave a 6-μA current to the sample. Annealing was performed at 1100 K in UHV and in O₂ at a pressure of \(5 \times 10^{-8}\) torr. Surface cleanliness was verified by LEED and TPD of O₂ (see Ch. 6 for a more detailed discussion of the sample cleaning technique). Daily, before collecting data, several sputter-anneal cycles were performed; between data runs on the same day, oxygen anneals were done to preserve sample cleanliness. Sample dosing for measurement was performed using a capillary array doser to minimize any rise in chamber pressure [14]. The sample was dosed to saturation coverage by exposure first to 10 L of \(^{18}\)O₂ or \(^{16}\)O₂, then to between 0.3–1.0 L of \(^{12}\)C\(^{18}\)O for the reaction measurements. Isotopic oxygen was used in the reaction measurements to avoid the large \(^{12}\)C\(^{16}\)O₂ background at mass 44. This dosing procedure produces highly reproducible TPD spectra (cf. Fig. 4.1).

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12This electron-induced increase in the background is attributed to electron-stimulated desorption. The signal has a bi-exponential decay, with fast (1-minute time constant) and slow (several hour time constant) components. Similar effects have been observed in other laboratories, and this effect is even being used to induce surface reactions (C. Arumainayagam, personal communication).

13Software and hardware for this automated cleaning system were designed, assembled and coded by S. Deliwala, R. Finlay and T.H. Her.
4.3.2 Laser system and optics

The 800-nm, 400-nm, and 266-nm ultrashort laser pulses used here were derived from the output of an amplified 1-kHz femtosecond Ti:sapphire laser system. This state-of-the-art system was designed and constructed in our research group over a several-year period. Chapter 5 provides the details and design of this system. In this section, we describe the performance of the system as it was for the measurements presented here.

An 80-MHz train of ≤ 70-fs pulses at 800-nm center wavelength is generated in a home-built self-mode-locked Ti:sapphire laser oscillator. The oscillator pulses have 5-nJ per pulse (0.4-W average power) and a 40-nm bandwidth. An all-reflective optics, single-grating stretcher is used to stretch the pulses to 400 ps. These long pulses are then injected at 1 kHz into a Ti:sapphire regenerative amplifier pumped by a 1-kHz intracavity-doubled Nd:YLF laser. An all-reflective single grating compressor restores the pulses to typically 100-fs duration. Longer pulsewidths for pulsewidth-dependent measurements are obtained by mistuning the compressor length to obtain frequency-chirped pulses of up to several picoseconds duration. All pulsewidths are measured by background-free, non-collinear, autocorrelation using a 100-μm thick BBO crystal. The amplified output energy, spectrum and autocorrelation (pulsewidth) are continuously monitored during the course of the measurements. The system produces 300-μJ, 100-fs pulses at 800 nm, with a smooth nearly-Gaussian, albeit slightly elliptical, spatial profile. Second-harmonic generation in a 1.5-mm thick LBO crystal (Type I phasematching) is used to generate 400-nm pulses, and third harmonic generation in 0.3-mm thick BBO (Type II phasematching) is used to create 266-nm pulses. Calculations\(^{14}\) of pulse propagation through the nonlinear crystals show that the pulsewidths were 150 fs and 200 fs at 400 nm and 266 nm respectively.

\(^{14}\)Calculations by R. Finlay. Our SHG and THG setup is based on the work of Ringling et al. \[37\].
A fast mechanical shutter (nm Laser) is used to select pulses at 1–3 Hz for the desorption measurements (cf. Figs. 4.5 and 4.6). The pulse energy is attenuated and adjusted either with a half-wave plate/cube beamsplitter combination, or with UV-grade neutral-density filters. The pulse polarization is arranged using half-wave plates to produce $p$-polarized light on the sample at every wavelength. The wavelengths are separated after generation by the use of a filter (Schott BG-39) to absorb 800-nm light and transmit 400-nm light, and by the use of three reflections from 266-nm dichroic mirrors to separate the third harmonic from the fundamental and second-harmonic wavelengths. In this way, less than 1% residual fundamental or second-harmonic was incident on the surface for the 400-nm and 266-nm measurements, respectively.

Given the expected highly nonlinear desorption yield fluence dependence, it is critical to quantitatively characterize the laser spatial profile on the sample. This characterization is achieved by direct imaging of the spatial profile using a CCD array. The laser beam is brought to a gentle focus in a plane about 10 cm beyond the crystal, leading to a spot of approximately $10^{-3}$-cm$^2$ area on the sample. A mirror is inserted to reflect the beam outside the chamber to measure the spot size at the equivalent path distance to the sample. Spot size measurements are performed by attenuating the beam and impinging the light directly on the CCD array, capturing the resulting image with a frame-grabbing board and a Macintosh PC. Two intensity profiles along two orthogonal axes, $x$ and $y$, are derived from the resulting image. A Gaussian is fit to each profile in order to characterize the spot size. The absolute energy of the light incident on the sample is measured for every laser shot using a calibrated photodiode monitoring a 4% reflection off a beam splitter. The absorbed fluence $F_i$ for each laser shot $i$ is then calculated given the measured pulse energy $E_{\text{measured}}$, the measured spot size corrected for 45° incidence, and literature values for the $p$-polarized 45° reflectivity at each wavelength, using the convention:

$$E_{\text{measured}} = \int F_i \exp \left( -\left( \frac{x}{a} \right)^2 - \left( \frac{y}{b} \right)^2 \right) \, dx \, dy , \quad (4.3)$$
where $a$ and $b$ are parameters derived from the Gaussian fits to the image spot.

Characterizing the laser spatial profile at the sample as a Gaussian is only a good approximation for a beam of good quality, i.e. a smooth spatial profile with no ‘hot spots’ or shot-to-shot spatial intensity variations. Our laser system produces a beam meeting these requirements at 800 nm. However, in generating the harmonic wavelengths (400 nm and 266 nm), a poor-quality spatial mode can result unless precautions are taken to ensure that the fundamental beam intensity incident on the nonlinear LBO or BBO crystal is below the critical self-focusing intensity. We verified by visual observation of the expanded 400-nm spot that significant spatial intensity fluctuations characteristic of self-focusing were present when the fundamental 800-nm light was focused too tightly in the LBO crystal. These fluctuations were eliminated by expanding the 800-nm beam on the crystal. This produced a good quality 400-nm beam but reduced our second harmonic efficiency from about 20% to less than 10%. The resulting 400-nm intensity was too weak to subsequently generate 266-nm light in BBO with sufficient energy for the experiment. Therefore for the 266-nm data presented here we were compelled to generate 266-nm light in the self-focusing regime, resulting in a 266-nm spatial profile on the sample of poor quality. Improvements in the laser system are now underway to eliminate this problem by increasing the amount of energy available at 800 nm so that 266-nm light can be generated below the self-focusing intensity. Despite the limitation faced here, we present desorption data obtained at 266 nm. Given the poor spatial mode quality we did not attempt to characterize the fluence dependence at 266 nm for these data.

4.3.3 Data acquisition

To collect data, about 20–30 individual spots on the sample were irradiated separately per sample preparation. Each spot is irradiated by 100–1000 successive laser shots at 1–3 shots per second, depending on the measurement. The desorption yield for every laser shot
is measured by the mass spectrometer tuned to either mass 32 or 36 (^{16}\text{O}_2 or ^{18}\text{O}_2), or for the reaction measurements, to mass 48 (^{12}\text{C}^{18}\text{O}_2).

The data acquisition system is schematically illustrated in Fig. 4.6. The mass spectrometer is operated in pulse counting mode. This means that the voltage on the channeltron electron multiplier is set in the saturation limit, so that every electron incident on the channeltron will produce an equal height amplified pulse (at a gain of about $10^5$ gain). The ionizer efficiency is approximately $10^{-3}$ A/torr according to UTI specifications, which corresponds to about $10^{-6}$ electrons/incident molecule for \text{O}_2. Combining the ionizer efficiency with the 2–10% collection efficiency gives a net detection efficiency per molecule of $0.2–1 \times 10^{-7}$. The channeltron multiplier output is fed directly into a 100-MHz amplifier/discriminator (ARI). The discriminated output is fed to a gate and delay generator (Ortec) which converts the input pulses to 20-ns pulses\textsuperscript{15}, which are then fed into two 100-MHz digital counters (Ortec). The counters obtain desorption counts during two sequential 20-ms windows, and are controlled remotely by a computer GPIB-interface. The first 20-ms window is synchronized to occur before the laser shutter opens, in order to obtain a background count. The second window is synchronized to open with the laser pulse. Our signal is derived as the difference between the second and first counters for each laser shot. All timing control (laser shutter triggering, counters) and data acquisition (counts, laser fluences) is done by a Macintosh Quadra equipped with a data acquisition board and LabView\textsuperscript{TM} software (National Instruments)\textsuperscript{16}.

\textsuperscript{15}It was necessary to stretch the signal pulses to 20 ns to ensure reliable triggering of the counting electronics.

\textsuperscript{16}Data acquisition software was developed by S. Deliwala.
The 20-ms window is selected to collect > 90% of the total counts generated by each laser shot, determined by examining the total time-of-flight of the mass spectrometer signal. This time-of-flight is measured using a digital oscilloscope in single-shot mode triggered by the laser pulse. We find that while a 5-ms window is sufficient to collect more than 90% of the total counts at low laser fluences, a 20-ms window is required at the maximum fluence (20 mJ/cm²). The long 20-ms decay time of the peak signal is attributed to a long pump-out time for the enclosed mass spectrometer ionizer volume.

Given our collection efficiency (2–10%) and ionizer efficiency (10⁻⁶), one can estimate the expected number of counts and compare this to our maximum count rate to check for saturation. As an upper limit, consider a single pulse entirely desorbing all the molecules
from a single spot (10^{-3} \text{ cm}^2). For total desorption of a one monolayer coverage (10^{15} \text{ molecules/cm}^2), one would expect between 10^4 and 10^5 counts. If all these counts occur within 20 ms, this corresponds to a peak count rate of 5 MHz, an order of magnitude below our maximum counting rate of 50 MHz (limited by the use of 20-ns pulses), and higher than the maximum observed counting rate of \leq 1 MHz.

4.4 Results

4.4.1 Overview

We present data for O_2 and CO_2 desorption from Pt for absorbed fluences in the range 1–20-mJ/cm^2, at 800, 400 and 266 nm. The pulsewidth-dependence for pulses between 100 fs and 3.6 ps at 800 nm is also presented. Using a model fit, we are able to quantitatively characterize the 800-nm and 400-nm data. We show that as much as 10% of the adsorbate coverage is desorbed at our highest fluence of 20 mJ/cm^2. We report the nonlinear desorption fluence dependence at 800 nm and 400 nm, and the ratio of O_2 to CO_2 desorption at all three wavelengths (results summarized in Table 4.1). While this ratio always favors O_2 desorption for the first laser shot on a fresh sample spot, we find that for 266-nm pulses, CO_2 desorption is actually greater after 200 shots on a single spot.

4.4.2 O_2 and CO_2 desorption: fluence dependence at 800 nm and 400 nm

Figure 4.7 shows desorption data obtained at three different fluences for 800-nm (100-fs) and 400-nm (150-fs) pulses. Each trace is obtained by recording the O_2 or CO_2 mass spectrometer signal for a series of laser shots on a single spot on the dosed Pt sample. The figure shows only the first 15 laser shots out of 200 shots recorded for each spot. After 200 shots, the signal typically is indistinguishable from the background. The rapid decay in signal is due to a decrease in surface coverage for each subsequent laser pulse. The absolute yield, on the left hand axis, is normalized to show counts per unit area. The absorbed fluence, on
the bottom axis, is computed from the measured incident laser energy and spot size using Eq. 4.3 (cf. Sect. 4.3.2). Typical shot-to-shot fluctuations in the fluence were less than 5%. The data shown were obtained for O₂ and CO coadsorbed on Pt. Desorption data obtained for samples with only O₂ coverage had identical desorption yield and fluence dependence. For each wavelength, we take the precaution of obtaining a complete set of data in the 1–20-mJ/cm² fluence range using a single sample dose to ensure that we compare data obtained with identical initial conditions. However, we obtain excellent reproducibility even for data collected from separate sample dosings. For the purposes of quantitative analysis, data are

![Fig. 4.7](image_url)  
**Fig. 4.7** O₂ and CO₂ desorption/reaction from the Pt(111) surface induced by 800 nm and 400 nm pulses for three absorbed fluences. Plots show desorption yield Yₐ following each laser shot i. Note the change in scale between the O₂ and CO₂ data; note also the change in scale (× 0.5) between the 800-nm and 400-nm data.
collected at each wavelength over the complete 1–20 mJ/cm² absorbed fluence range for each sample preparation, with several traces like those in Fig. 4.7 obtained at each fluence.

Some features of the data in Fig. 4.7 are immediately apparent. First, the absolute desorption yield at 400 nm is larger than at 800 nm (note the difference in scale). Secondly, even though the 400 nm desorption yield is always larger than at 800 nm for the first laser shot, the yield decays more slowly vs. shot number at 400 nm compared to 800 nm. This indicates a lower-order nonlinearity in the fluence dependence at 400 nm. Finally, the O₂ desorption signal is about an order of magnitude larger than the CO₂ signal, and this ratio is independent of incident fluence and nearly the same for both wavelengths.

We characterized the desorption traces using a model which assumes a yield with nonlinear fluence dependence. To do this, one needs to compute changes in the coverage, \( \Theta_i(r) \) (\( \Theta(r) \leq 1; \Theta_1(r) \equiv 1 \)), for each laser shot \( i \), taking into account the laser pulse shape on the sample.¹⁷ Using the assumption of a Gaussian laser spot, as in Eq. 4.3, we fit the measured desorption yield \( Y_i \) at each laser shot \( i \) to:

\[
Y_i = 2\pi N \int r \; dr \; Y_i(r)
\]

\[
Y_i(r) = \sigma F_i(r)^p \Theta_i(r); \quad Y_i(r) \leq 1,
\]

where \( F_i(r) \) is the measured absorbed fluence profile for each laser shot (i.e. the integrand of Eq. 4.3), \( p \) is an exponent which characterizes the nonlinear fluence dependence, and \( \sigma \) and \( N \) are normalization factors (independent of the coverage). The coverage \( \Theta_i(r) \) at each laser shot is computed using Eqns. 4.3 and 4.4 with the assumption of a single value for \( p \). The coverage for subsequent laser shots is computed taking into account the desorption by previous laser shots:

\[
\Theta_i(r) = 1 - \sum_{j=1}^{i-1} Y_j(r).
\]

The desorption yield \( Y_i(r) \) at position \( r \) is always less than or equal to one. The calculated fit includes the possibility of totally depleting part (or all) of the adsorbate on a given spot. The

¹⁷Note the change to radial coordinates, \( (x,y) \rightarrow r \), for convenience.
normalization factor $N$ is included in Eq. 4.4 to scale the integral to match the measured yield. The model of Eq. 4.4 thus includes three fitting parameters ($N, \rho$, and $\sigma$). To determine the normalization factors and the exponent $\rho$, we simultaneously fit the yields given by Eq. 4.4, through all 200 points of each desorption trace, for all the traces obtained over the entire range of fluences obtained with a given sample preparation.

Figure 4.8 shows a typical fit for 800-nm desorption at 15-mJ/cm² absorbed fluence, with the calculated spatial coverage indicated for three particular laser shots. Because we ensured that (1) the model fits match each trace using the measured fluence for each laser shot and (2) the same parameters must similarly fit all the data at a given wavelength, we estimate that the resulting value for $\rho$ has an uncertainty of about 5%.

The results of the analysis of the 800-nm and 400-nm data are summarized in Table 4.1. The $O_2$ desorption yield has a fluence dependence of $\rho = 5.9$ and 3.8 at 800 nm and 400 nm.
respectively. Figure 4.9 shows a plot of all the first-shot yields per unit area vs. absorbed fluence for 800 nm and 400 nm. By examining the first shot yields one can compare data with a single initial condition across a range of fluences. As Fig. 4.9 shows, the model of Eqns. 4.4 and 4.5 produces a good fit to the first-shot data over the entire fluence range.

<table>
<thead>
<tr>
<th>parameter</th>
<th>pulsewidth</th>
<th>This Work</th>
<th>Refs. [16, 17]</th>
<th>Ref. [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponent $p$ at:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 nm</td>
<td>100 fs</td>
<td>5.9 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>600 fs</td>
<td>5.9 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.6 ps</td>
<td>5.9 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>620 nm</td>
<td>150 fs</td>
<td></td>
<td>5.5 ± 0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600 fs</td>
<td></td>
<td>4.5 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>400 nm</td>
<td>150 fs</td>
<td>3.8 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>310 nm</td>
<td>150 fs</td>
<td></td>
<td>3.0 ± 0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600 fs</td>
<td></td>
<td>3.0 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>$O_2/CO$ ratio for:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 nm</td>
<td>100 fs</td>
<td>14 ± 1</td>
<td></td>
<td>30 ± 10</td>
</tr>
<tr>
<td>620 nm</td>
<td>100 fs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 nm</td>
<td>150 fs</td>
<td>12 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>310 nm</td>
<td>150 fs</td>
<td></td>
<td>15 ± 5</td>
<td></td>
</tr>
<tr>
<td>266 nm</td>
<td>200 fs</td>
<td>3 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>266 nm; after 200 shots</td>
<td>200 fs</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>355-nm</td>
<td>3 ns</td>
<td></td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>cw arc lamp (400–250 nm)</td>
<td>cw</td>
<td></td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>thermal</td>
<td>n/a</td>
<td></td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.1** Measured parameters for desorption and reaction data in this work and in the literature. The parameter $p$ for this work is obtained using Eq. 4.4; see Refs. [16, 17] for explanation of method for determining the power law exponent $p$.  


Fig. 4.9 First-shot O$_2$ desorption yields for 100-fs, 800-nm and 150-fs, 400-nm pulses vs. absorbed fluence. The solid lines are model curve fits to the data from Eq. 4.4 with $p = 5.9$ and $p = 3.8$ for the 800-nm and 400-nm data, respectively. The dashed lines are simple power law curves. Note the deviation at high fluences between the model curves and power law curves.

The dashed lines in Fig. 4.9 show simple power law fits to the data (i.e. $Y = \text{constant} \times F^{5.9}$). Note the deviation between the model and power law curves at high fluences. The model curves are a better fit to the data above 15 mJ/cm$^2$; since coverage depletion is incorporated in the model, the better fit of the model curves in Fig. 4.9 indicates that above 15 mJ/cm$^2$, we are desorbing all of the molecules from a portion of the irradiated spot on the sample. Figure 4.10 shows an expanded view of the fit for the 800-nm data in Fig. 4.9 (dashed line).
compared to a single power law, \( Y = \sigma F^{5.9} \) (solid line). The two curves are nearly identical below about 15 mJ/cm\(^2\), where the model curve begins to grow more slowly,

\[
\begin{align*}
\text{counts/cm}^2 & \\
10^7 & \quad 10^6 & \quad 10^5 \\
\text{Y} & \\
10 & 12 & 14 & 16 & 18 & 20 \\
F & \quad \text{mJ/cm}^2 \\
\end{align*}
\]

\( \text{O}_2/\text{Pt}(111) \)

\textbf{Fig. 4.10} Comparison of a simple power law desorption dependence, \( \sigma F^{5.9} \), to the model curve from Eq. 4.4 for the 800-nm data of Fig. 4.9.

indicating that already on the first laser shot, part of the irradiated spot is entirely depleted. An example of partial depletion of a spot is seen in Fig. 4.8; for laser shot #15 in Fig. 4.8 the coverage profile shows a depletion at the center of the laser-irradiated spot.

Note that the absolute first-shot yield as a function of fluence in Fig. 4.9 is roughly an order of magnitude greater at 400 nm than at 800 nm (6 \( \times \) 10\(^6\) counts/unit area vs. 1 \( \times \) 10\(^6\) counts/unit area at 15 mJ/cm\(^2\)).

We also measured the first-shot \( \text{O}_2 \) desorption yield at 266 nm at one fluence. For a 5-\( \mu \)J pulse energy we had an estimated spot size of 3 \( \times \) 10\(^{-3}\) cm\(^2\), giving an absorbed fluence of 1 mJ/cm\(^2\) (assuming 30% \( p \)-polarized reflectivity). The error in this fluence may be as high as 50% since we did not have a good quality spatial mode at this wavelength (see Sect. 4.3.2).
An average of 70 counts/3 × 10⁻³ cm² were obtained at this fluence, corresponding to 2 × 10⁴ counts/cm². This value is comparable to the yield for the 400-nm, 1-mJ/cm² data in Fig. 4.9.

In desorption experiments in the linear intensity or fluence regime, it is common to define a cross section for the desorption process such that the cross section × (absorbed photons/cm²) equals the change in coverage due to desorption. To facilitate a comparison with linear cross sections, we define an ‘equivalent one-photon cross section’, \( \sigma_{1\text{-photon}} \), as follows:

\[
\sigma_{1\text{-photon}} = \frac{Y_1 \text{(counts / unit area)}}{(\text{Total Coverage / unit area}) \times F_1 \text{(photons / unit area)}},
\]

where \( Y_1 \) is the first shot desorption yield corrected for the collection efficiency \((0.2 \times 10^{-7})\), \( F_1 \) is the first shot fluence, and the total coverage is the initial surface coverage, which we take as one monolayer \((10^{15}/\text{cm}²)\). Because the exact collection efficiency and initial coverage are not known, the values we obtain for \( \sigma_{1\text{-photon}} \) are approximate. Note also that \( \sigma_{1\text{-photon}} \) is a function of fluence, and is useful only as a point of comparison to the cross-sections for linear processes. Table 4.2 shows values for \( \sigma_{1\text{-photon}} \) for the three wavelengths. The values we obtain using Eq. 4.6 and the assumptions for collection efficiency and coverage are at least several times larger than the largest cross sections reported for linear cw photoinduced desorption or reaction \((\sigma = 3 \times 10^{-19} \text{ cm}²) [11]\).

### 4.4.3 O₂ desorption: 800-nm pulsewidth dependence

Figure 4.11 shows a plot of the 800-nm desorption yield for three different pulsewidths, 100 fs, 600 fs, and 3.6 ps, as a function of absorbed fluence. The measured yields for 600 fs and 3.6 ps pulses are within ± 15% of the 100-fs data; these data are normalized to the 100-fs data in Fig. 4.11 in order to overlap the three data sets. As the data show, the desorption yield is described by the same power law dependence \((p = 5.9)\) independent of pulsewidth.
Table 4.2 Equivalent one-photon desorption cross sections $\sigma_{1\text{-photon}}$ obtained in this work from Eq. 4.6 for particular absorbed fluences.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>Abs. Fluence (mJ/cm²)</th>
<th>$\sigma_{1\text{-photon}}$ ($\times 10^{-19}$ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>15</td>
<td>8.0</td>
</tr>
<tr>
<td>400</td>
<td>15</td>
<td>1.0</td>
</tr>
<tr>
<td>266</td>
<td>1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

over this range. Note, however, that the peak electron temperature achieved with these three pulsewidths differs significantly (cf. Fig. 4.3). This result is quite different from the results reported by Ref. [16], in which, for example, the power law dependence at 620 nm changes from $p = 5.5$ to $p = 4.5$ for 150-fs to 600-fs pulses (see Table 4.1).

### 4.4.4 O₂/CO reaction: Wavelength and fluence dependence

We fit model curves from Eq. 4.4 to the CO₂ desorption data (cf. Fig. 4.7 (b)) in an identical fashion to the O₂ desorption data. We find that the CO₂ desorption traces are characterized by model curves with the same value of $p$ as for the O₂ data at both 800 nm and 400 nm. The ratio of the normalization factors $N$ (see Eq. 4.4) for the O₂ and CO₂ model curves gives an observed ratio¹⁸ for O₂ to CO₂ desorption of 14:1 and 12:1 at 800 nm and 400 nm respectively. To within an estimated error of 10% these ratios show no fluence dependence.

¹⁸Ratio computed taking into account the relative ionization efficiency for O₂ and CO₂ given by the UTI manual: efficiency(CO₂) = 1.2 × efficiency(O₂).
Fig. 4.11 First shot O₂ desorption yields vs. absorbed fluence for three pulsewidths at 800 nm. The data for 600-fs and 3.6-ps pulses are normalized to the 100-fs data to allow comparison of the desorption fluence dependence. The solid line is a power law curve proportional to $F^{5.9}$ as in Fig. 4.9.

Desorption and reaction decay curves were also obtained using 266-nm pulses. Figure 4.12 shows the O₂ and CO₂ desorption yield for 1200 laser shots at 266 nm at an absorbed fluence of approximately 1 mJ/cm². The data were averaged over ten points since the signal-to-noise ratio at this wavelength was not as good as at the other wavelengths.

The 266-nm data shown in Fig. 4.12, albeit preliminary, give a very different O₂ to CO₂ desorption yield ratio than at 800 nm and 400 nm. At the first shot the ratio of O₂ to CO₂ desorption yield is $(3 \pm 1)$:1. Note also that at 266-nm, after about 200 laser shots on the same spot, we see, for the first time, a higher yield of CO₂ than O₂. For the 800-nm and 400-nm data, the O₂ yield is always observed to exceed the CO₂ yield. This change in O₂/CO₂ ratio is caused by a change in O₂ coverage as a function of shot number (see discussion in Sect. 4.5.2).
Chapter 4 Ultrafast initiation of surface reactions

4.5 Discussion and conclusions

4.5.1 O₂ desorption: wavelength and fluence dependence

The data presented here further corroborate the conclusion from previously reported results (see Section 4.2.3) that desorption at 800 nm and 400 nm is dominated by an excited substrate electron mechanism. The two-pulse correlation width for this system reported by Ref. [16] is 1.2 ps at 620 nm, which rules out a direct optical mechanism at 620 nm. The extremely high yields at 800 nm and 400 nm reported here exceed by about an order of magnitude the highest reported cross-sections observed with cw irradiation or ns-pulses. The first-shot desorption yield per unit area at 800 nm (10⁶ cm⁻² for 20-mJ/cm² absorbed...
fluence) corresponds to desorbing between $10^{13}$ to $10^{14}$ molecules/cm² in a single shot (see Sect. 4.3.3), which is between 1–10% of the total coverage per spot. The desorption yield at 400 nm is nearly an order of magnitude higher. In contrast, as discussed in Sect. 4.2.5, a thermal mechanism can only account for at most $10^{-4}$ of the coverage per shot. We know that assuming a linear absorption, a 20-mJ/cm² absorbed fluence at 800 nm directly excites $6 \times 10^{16}$ electrons/cm². This means that on the order of 10 excited electrons can interact with each adsorbate molecule. Hence a substrate-mediated electronic mechanism is not incompatible with the observed results.

As discussed in Sect. 4.2.5, DIMET-type models have been applied to model 100-fs pulse-induced substrate electron mechanisms. Yet the treatments reported previously do not incorporate a wavelength dependence, and instead rely upon a single temperature characterization of the electrons to capture all the physics. We observe a strong wavelength dependence, with different desorption cross-section and fluence dependence at 800 nm and 400 nm (results summarized in Tables 4.1 and 4.2). Furthermore, our experiments with variable pulsewidth, in which the electron temperature changes at a fixed fluence, show that the fluence dependence is independent of pulsewidth. These two results clearly indicate that any theoretical treatment of the data will require a wavelength dependent mechanism. More specifically, it seems most likely that the results presented here can only be accounted for by considering the details of the electron distribution in energy and momentum space created by the 100-fs pulses, as discussed in Sect. 4.2.5.

Assuming a substrate-electron-mediated mechanism, the fact that we do not observe a pulsewidth-dependence in the 800-nm desorption suggests that the different peak temperatures of the thermalized electron distributions for the three pulsewidths at a fixed wavelength does not affect the desorption mechanism. Since the peak temperature alone is not adequate to explain the results, perhaps including the time-dependence of the temperature is necessary. As a more stringent test of pulsewidth-dependence, it would be
interesting to repeat this experiment making an accurate absolute yield comparison, to see if \( \sigma_{\text{1-photon}} \) shows any variation with pulsewidth.

Note that the results presented here differ from the previously reported work of Ref. [16] where a change was observed in the nonlinear yield exponent with pulsewidth in the 150-fs to 600-fs range. A possible explanation is that a fluence dependence is evident only in the low fluence regime where the data of Ref. [16] were obtained. Experiments to investigate this possibility are in progress. Another possibility may be related to the recent observation of a long-timescale (10-ps) desorption component in a two-pulse desorption correlation experiment with \( \text{O}_2/\text{Pd}(111) \) [31]. The long timescale contribution is attributed to a second channel for desorption through vibrational excitation of the adsorbate which occurs on a 10-ps timescale. It may be that such a process also occurs on the Pt(111) surface, and that the longer pulse durations in our experiment (600 fs and 3.6 ps) may be less efficient at driving the fast 1-ps channel but more efficient at driving the 10-ps channel; the net effect of such a phenomenon would be that longer pulses had a fluence dependence the same as 100-fs pulses. Misewich et al. suggest that an experiment in which the surface is pre-heated with a ns-laser pulse could distinguish between the two desorption channels [31]. Another option is to study the effect of co-adsorbates on the long-timescale component, since a suitable co-adsorbate could increase or decrease the \( \text{O}_2/\text{Pt} \) vibrational coupling and hence alter the timescale of the 10-ps excitation channel.

The fitting of desorption data using Eq. 4.4 takes into account depletion of the adsorbate coverage for each laser shot. This new approach represents an improvement over previously reported analyses (i.e. those used in Refs. [16, 17]), and is necessary for application in the high-fluence regime reported here. The fitting procedure works very well for characterizing both the data at 800 nm and 400 nm. Except for the lack of an observed pulsewidth dependence, our characterization results agree with the previously reported decrease in nonlinearity with decreasing wavelength from 800 nm to 300 nm [16, 17]. It is not clear what, if any, physical interpretation can be attributed to the exponent obtained from the
model fits of Eq. 4.4 to the depletion data; however this characterization is useful for making quantitative comparisons between desorption yields as a function of wavelength.

### 4.5.2 CO₂ desorption: reaction mechanisms

For the O₂ and CO₂ desorption data, the observed exponent \( p \) from the model fits of Eq. 4.4 are the same; this is true at 800 nm \( (p = 5.9) \) and 400 nm \( (p = 3.8) \). This observation is consistent with the results of Ref. [16], but our observed O₂/CO₂ desorption ratios are lower than those reported by these authors. At 266 nm, we observe a first-shot O₂/CO₂ desorption ratio of \((3 ± 1):1\); after 200 shots on the same spot, this ratio drops below 1:1.

The identical O₂ and CO₂ desorption yield fluence dependence at 800 nm and 400 nm suggests that the same initial excitation is responsible for both O₂ desorption and CO₂ formation. At least two types of reaction mechanisms are possible. The initial excitation may dissociate molecular oxygen, leading to a reaction between an excited O atom and CO. In this case, the observed O₂/CO₂ desorption ratio is interpreted as a branching ratio between O₂ desorption and dissociation for the same initial excitation. On the other hand, the reaction may occur between excited O₂ molecules that react with CO before they can desorb. In this second case, the observed ratio is a measure of the molecular fraction that reacts with CO instead of desorbing, and is thus related to the O₂+CO cross section.

We note that the O₂/CO desorption ratio is independent of absorbed fluence for the 800-nm and 400-nm data. This suggests that whatever the initial excitation mechanism is that leads to O₂ desorption and/or dissociation, a fixed fraction of the desorption/dissociation products combine with CO to form CO₂. If the mechanism involves dissociation, this result would imply that the fraction of O₂ that dissociates is independent of absorbed fluence at a given wavelength. If the mechanism involves activated O₂ interaction with CO, this result suggests that the cross section of the O₂/CO reaction doesn’t depend on fluence. This could imply that there is no variation of internal excitation of the desorbing O₂ molecules with
fluence. This can be verified using laser spectroscopy, and might rule in favor of one mechanism or the other.

The $O_2/CO$ desorption ratio appears to follow a trend from a maximum at 800 nm (14:1) to a minimum at 266 nm (about 3:1). The strong difference at the UV end of the spectrum suggests either an increase in the relative amount of dissociation, or a change in the excited state of desorbing molecular $O_2$ that favors reaction with CO. Again, this second possibility could be examined by measuring the kinetic and internal energy spectra of the desorbing $O_2$ molecules.

The observation that the CO$_2$ desorption yield from a single spot exceeds the $O_2$ desorption yield after 200 shots at 266 nm is surprising if one assumes (1) that the first shot $O_2/CO_2$ ratio (3:1) is either the ratio of desorption to dissociation or is proportional to the fraction of excited $O_2$ that reacts, and (2) that in both cases this ratio does not change as a function of surface coverage. If (1) and (2) are true, the $O_2/CO_2$ desorption ratio should be fixed. It is possible that assumption (2) above is incorrect, and that changes in surface coverage do change, for example, the reaction probability of either nascent O or excited $O_2$ with CO. However, this interpretation is difficult to reconcile with the lack of a similar observed effect at 800 nm and 400 nm, unless the excitation mechanism is different at these wavelengths from the mechanism at 266 nm.

At least two possible explanations exist for the observed change. If we assume that the initial excitation mechanism at 266 nm for the first several laser shots is the same nonlinear fluence dependent, substrate-mediated mechanism observed at 800 nm and 400 nm, the observed change in $O_2/CO_2$ ratio may be due to the presence of a second, competing mechanism which becomes dominant as the surface coverage changes. For example, a direct optical dissociation process which has a linear fluence dependence could compete with the nonlinear substrate-mediated desorption mechanism. Initially, at maximum surface coverage, the higher-yield nonlinear desorption process would dominate $O_2$ desorption, leading to depletion of the $O_2$ coverage near the center of the spot on the sample where the laser
intensity is highest. At this point, only O$_2$ molecules in the wings of the laser spatial intensity distribution are left on the surface. Because of the lower intensity in the wings, a linear process could produce a CO$_2$ yield which exceeds that of a nonlinear process, so if the linear process favored reaction, CO$_2$ production could then become dominant. An example of a linear process favoring reaction would be O$_2$ photodissociation leading to a O$+$CO$\rightarrow$CO$_2$ reaction. If this explanation is correct, then the observed O$_2$/CO$_2$ ratio of about 0.5:1 after 200 shots would reflect the ratio of O$_2$ dissociation to O$_2$ desorption in the linear mechanism.

A second, quite different, interpretation of the observed change in O$_2$/CO$_2$ ratio in Fig. 4.12 is required if we assume that at 266 nm, no nonlinear fluence dependent mechanism contributes to the desorption or reaction, and that instead, desorption and reaction are initiated by a process with only linear fluence dependence at 266 nm. Such an assumption must be considered, since cw desorption measurements show that linear desorption mechanisms have a $100 \times$ higher cross section at 240 nm compared to 546 nm [15]. This same work also indicates that two types of O$_2$ surface species exist, and that one has an order of magnitude greater desorption rate than the other in the linear regime. Therefore the observed change in O$_2$/CO$_2$ ratio could be interpreted as due to depleting one type of surface species after 200 laser shots in a linear fluence regime, leaving a second species which favors reaction over desorption to dominate the observed desorption and reaction. Until the fluence dependence of desorption and reaction is measured at 266 nm, we cannot determine which of the two above interpretations of the result of Fig. 4.12 is most likely.

Thus, one needs to consider the possibility that at least two mechanisms (nonlinear substrate electron mediated, and possibly direct linear photoexcitation, or vibrationally assisted electronic excitation [31]) may be responsible for the O$_2$/CO reaction, and that these mechanisms may compete depending on the excitation wavelength. Further study, particularly the determination of the fluence dependence at 266 nm and deeper into the UV, will shed additional light on this matter.
The work here demonstrates the potential of the CO/O₂/Pt(111) as a model system for the study of desorption and surface reaction. Varying the wavelength enhances the ratio of reaction to desorption, making this system an attractive candidate for future study of time-resolved surface reactions. Furthermore, the results suggest that time-resolved spectroscopy will contribute to a better understanding of the mechanisms for 100-fs laser-induced desorption.

4.5.3 Future Work

The data presented here represent the first results of a new study of ultrafast laser-induced surface reactions. These results extend previous studies to new wavelengths and fluences. While a nonlinear fluence dependence for desorption and reaction is verified in the 800-nm to 400-nm region, the detailed mechanism responsible for this behavior and for the values of the absolute yield and O₂/CO desorption ratio needs to be addressed experimentally and theoretically.

Future work in this area needs to provide a strict test for theoretical models. Obtaining additional 100-fs laser-induced desorption data at new wavelengths is therefore desirable. The fluence-dependence and absolute yield should be measured at 266 nm and at 200 nm, the fourth harmonic of the fundamental wavelength. An even wider range of wavelengths could be obtained by adding a 100-fs pulse optical parametric amplifier (OPA) to our laser system. Two-pulse correlation desorption experiments [17, 29] should be performed for all available wavelengths and pulsewidths, as this is a critical test of the contribution of any direct optical mechanisms. The polarization dependence at each wavelength may also yield information about the desorption and reaction mechanism at each wavelength [15].

Some technical aspects of this work can be improved or enhanced. Better spatial profile measurement of the laser spot incident on the sample would reduce errors in absolute fluence and absolute desorption yield. The use of larger spatial profiles, or even selectively shaped profiles, such as a top hat distribution, would make the interpretation of the data
easier because there is less variation in desorption yield across the irradiated spot. An improvement in measured desorption yield, and hence signal level, can be achieved by reducing the sample distance to the mass spectrometer. In addition, by performing angle-resolved or time-of-flight mass spectroscopy, the desorption products energy distribution could be characterized (although this would require significant modification of the existing mass spectrometer apparatus).

Two additional experiments could shed new light on the desorption and reaction mechanisms. A time-resolved photoemission study of hot electrons in the Pt sample, like that reported in the previous chapter, could characterize the nascent and thermalized electron distributions created in the substrate for various pump wavelengths and pulsewidths. This data is important input for any theoretical treatment which involves exited substrate electrons, such as the DIMET model. A second experiment would be time-resolved electronic or vibrational spectroscopy of the adsorbates and desorption products (or even simply non-time-resolved final product internal-state measurement). A nonlinear optical technique such as multiplex CARS (cf. Ch. 2) could yield the surface vibrational spectrum for O$_2$ and CO$_2$, or spectrally identify the excited O–CO intermediate of the reaction. As described in Chapter 7, efforts are already underway in our laboratory to demonstrate the use of ultrafast surface CARS to characterize an adsorbate monolayer. In addition to the CO/O$_2$/Pt(111) system, we are investigating the use of other model systems including OH/Pt(111).
References:

Chapter 5

High repetition rate ultrashort pulse Ti:sapphire laser system

5.1 Overview

5.1.1 The Ti:sapphire revolution

The advent of ultrashort laser pulse technology created the exciting possibility of direct time-domain study of subpicosecond phenomena. In the mid-1970’s, the colliding-pulse mode-locked (CPM) dye laser oscillator proved to be a reliable source of \( \leq 100 \text{-fs} \) pulses.

Today we are witnessing a revolution in ultrashort pulse laser technology that will make \(< 100 \text{-fs} \) pulses routinely available. Ultrashort pulse lasers will soon be commercially available from the near-infrared to the vacuum ultraviolet, at pulse energies from several microjoules up to tens of joules and at kHz repetition rates. These systems will offer peak intensities in excess of \( 10^{18} \text{W/cm}^2 \) from a tabletop apparatus. The systems will incorporate...
entirely solid-state technology (no gas pump lasers, no dyes), and have relatively high ‘wall-plug efficiency’ (perhaps as high as 0.1%, compared to today’s 0.003%).

This revolution is driven by at least two factors. On the demand side is the expanding scope of ultrashort pulse applications. Ultrashort pulses have been used for generating x-rays from solid targets [1], for ballistic photon transport/imaging through non-transparent materials [2], and for holographic information processing in nonlinear media [3, 4]. Advances in ultrashort pulse shaping [5] may make coherent control of reactions a reality, creating large demand for ultrashort pulses within industry and the chemistry community. The other factor in this revolution is the Ti:sapphire material itself, which has ideal characteristics for ultrashort pulse generation and amplification. New applications of Ti:sapphire and similar materials have developed with unprecedented speed by taking advantage of these characteristics.

In the early 1980’s, lasing action was discovered in titanium doped sapphire (Ti:Al₂O₃, or Ti:sapphire) [6]. Within a few years, efficient continuous (cw) room-temperature operation was demonstrated [7, 8]. In 1989, the potential for ultrashort pulse amplification in Ti:sapphire was demonstrated [9]. Shortly thereafter, ultrashort pulse generation in actively and passively mode-locked Ti:sapphire oscillators was demonstrated [10-12]. In the summer of 1990, self-mode-locking, originally called ‘magic mode-locking’, was reported [13]. Within a year of this report, the first commercial ultrashort pulse Ti:sapphire oscillators became available. By the end of 1991, multi-kilohertz repetition-rate amplification of ultrashort pulses in Ti:sapphire was described [14], and with subsequent advances in high-repetition rate pump laser technology, complete oscillator/amplifier systems became commercially available in early-1993. Today, the Ti:sapphire laser is the ultrashort pulse laser standard, with performance that significantly exceeds that of all previous ultrashort pulse technology.
5.1.2 Comparison to CPM and dye technology

To illustrate the new characteristics of the Ti:sapphire laser, we make a comparison with the CPM dye technology it is replacing. For more complete references, previous theses from our group provide an excellent review of CPM technology [15, 16] and ultrashort pulse dye amplifiers [17].

One advantage of the Ti:sapphire mode-locked oscillator over the older mode-locked dye lasers is the all-solid-state design. No flowing carcinogenic dyes dissolved in flammable or potentially harmful solvents are required. The Ti:sapphire crystal acts both as gain medium and passive mode-locking agent (see below), so no flowing jets are needed, and only one intracavity focus is required. Except for crystal cooling, the cavity is entirely passive, and in comparison to a typical CPM laser, requires no maintenance.

A second difference is that the Ti:sapphire oscillator is tunable over a wide range from 700 nm to 900 nm, depending on the bandwidth of the intracavity optics. A CPM dye laser operating with Rh6G dye is less broadly tunable (typically only 20 nm). Changing wavelengths is achievable only by changing dyes.

The use of self-mode-locking in Ti:sapphire compared to passive colliding-pulse modelocking is another significant difference. Both techniques are effective for producing stable mode-locked pulse trains of ultrashort pulses. The methods for optimizing each technique are very different however (see Sect. 5.4.1). Self-mode-locking works across the entire tuning range of the oscillator, while in a CPM, the saturable absorber dye needs to be changed to achieve modelocking when the CPM wavelength is changed. The self-mode-locking technique does not require the use of a ring oscillator cavity like the CPM; this simplifies cavity design and alignment.

Finally, for ultrashort pulse amplification, Ti:sapphire has the advantages over dye-based amplifiers of higher damage threshold, three-orders of magnitude greater gain lifetime (3 µs compared to 1–2 ns for dye), broad gain bandwidth, several orders of magnitude higher saturation fluence (5 J/cm² compared to 1 mJ/cm² [18]) and the convenience of
solid state design. These advantages allow construction of efficient regenerative amplifiers compared to multi-stage linear dye amplifiers (20% vs. 0.002% efficiency, respectively).

5.1.3 Organization of chapter

The purpose of this chapter is to describe the design, construction, and performance of our state-of-the-art ultrashort pulse Ti:sapphire laser system. The work in developing this system represents new and original contributions to the development of this technology. At the time of writing, our system exceeds the performance of available commercial systems, and our regenerative amplifier design is unique in several respects from any previously reported work.

Section 5.2 gives a review of previous work in this field, placing our contributions in a larger perspective. Section 5.3 outlines the design goals and constraints we considered when constructing the system. Section 5.4 gives detailed descriptions of the system we built, and details its operation and performance. Section 5.5 offers suggestions for future improvements that may further extend system performance and capabilities.

5.2 Previous work

While a number of developments in laser technology made the development of our system possible, two major techniques, self-mode-locking and chirped-pulse regenerative

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1History of laser system: We began developing a Ti:sapphire laser oscillator in the fall of 1990, a few months before the appearance of the first self-mode-locking paper. The laser system was designed in collaboration with S. Deliwala and R. Thompson. The self-mode-locked oscillator and stretcher/compressor designs were primarily worked out by S. Deliwala while the author was at AT&T Bell Labs. Technical challenges delayed achieving an experiment-ready oscillator until the end of 1991. Design and development of the regenerative amplifier system took place simultaneously with the UHV chamber work described in Chapter 6. The amplified system was operational in early fall 1993. We completely redesigned the amplifier during the next winter and spring of 1994. Additional improvements were incorporated in the summer of 1994 which were still being tested at the time of this writing.
amplification (CPA), were most important. A good general reference that explains the basics behind mode-locked pulse generation and laser amplification is *Lasers*, by Siegman [19].

**Definition of terms.** In this chapter, we use several terms that may be unfamiliar. We refer to the laser which is the source of unamplified ultrashort pulses as the Ti:sapphire ‘oscillator’ (in analogy to an electronic crystal oscillator). The general process by which short pulses are formed is called mode-locking [19]; this process is specifically called self-mode-locking in a Ti:sapphire oscillator since no intracavity mode-locking element is (apparently) present. In reality, the Ti:sapphire crystal itself is a passive mode-locking element. The laser cavity which is used to amplify the pulses from the oscillator is called a regenerative amplifier. This is a term also borrowed from electronics. Such a device is a gain cavity excited to the threshold of oscillation which bursts into oscillation, producing an amplified output, when ‘seeded’ with a tiny pulse.

### 5.2.1 Self-mode-locking of Ti:sapphire laser oscillators

Shortly after cw operation of an Argon-laser-pumped Ti:sapphire laser was observed [7, 8], it was realized that this new material had many desirable properties for laser oscillators and amplifiers, including wide gain bandwidth, high quantum efficiency, high thermal conductivity, and high damage threshold [20]. The first demonstration of single-frequency, broadly tunable, efficient cw operation also described the use of active mode-locking with an acousto-optic mode-locker to obtain 200-ps pulses at a 250-MHz repetition rate [21]. This work also demonstrated the proper technique for Ar-laser pumping in a cavity compensated for the astigmatism introduced by the Brewster cut faces of the Ti:sapphire crystal using the technique of Kogelnik, *et al.* [22]. The ring cavity was wavelength tuned using a birefringent filter, a method which utilizes the birefringence of the Ti:sapphire crystal. Pulsed Nd:YAG-laser pumping of a Ti:sapphire oscillator was also demonstrated in the same year [23].
Mode-locking of lasers can be achieved using an external coupled cavity with nonlinear intensity-dependent reflection [10, 24]. This idea arises from earlier work with soliton lasers [25]. External coupled-cavity mode-locking of a Ti:sapphire laser was demonstrated by French, et al. [11]; pulses as short as 200-fs were achieved with this technique [12]. This approach is also called additive pulse mode-locking in the literature. It was ultimately superseded by the discovery of self-mode-locking, since the latter method does not require an external cavity.

Given the large bandwidth of Ti:sapphire, it is clear that it has great potential for ultrashort pulse generation. One of the more surprising developments in the laser science community was the report that even without intracavity elements designed to produce and sustain mode-locking, a Ti:sapphire oscillator may spontaneously begin mode-locking and producing ps pulses.

During the summer of 1990, the ultrafast community was abuzz with talk about the discovery of ‘magic mode-locking’ in Ti:sapphire [13]. In a dispersion-compensated cavity, using intracavity prisms (see Sect. 5.4), 60-fs pulses were achieved directly from an oscillator with no active or passive mode-locking elements such as an acousto-optic modulator or saturable absorber jet. The output pulses were frequency chirped and were further compressed outside the cavity to 45-fs duration. The description from this paper of how mode-locking was achieved is perplexing:

“With an appropriate cavity alignment, self-mode-locked operation could be induced by applying some external perturbation, for instance, tapping one of the resonator mirrors. Occasionally the mode-locking process was observed to start spontaneously, although any sudden physical shock could also start or stop mode-locked operation” [13].

Due to the absence of any intracavity mode-locking elements, and the absence of any previously known type of active or passive mode-locking at that time, the self-mode-locking mechanism was widely referred to as ‘magic mode-locking’. 
A flurry of research activity followed this discovery. The physical principles behind the self mode-locking mechanism were first reported by Salin, et al. [26]. From a practical point of view, questions about the stability and reliability of self-mode-locking were raised, and a number of groups proposed inserting active or passive intracavity elements to provide a ‘starting’ mechanism to help ensure stable self-mode-locking. For example, introducing a saturable absorber jet using HITCI dye was shown to produce stable mode-locking [27-29]. Other approaches use microdot mirrors [30] or acousto-optic mode-lockers [31].

The self-focusing, or Kerr-lens mode-locking model of self-mode-locking proposed in late 1991 [26], shows that reliable, stable, and reproducible self-mode-locked operation can be achieved with proper cavity design. Intracavity prisms are required to compensate for group velocity dispersion of the Ti:sapphire crystal and cavity optics, but otherwise no active or passive mode-locking elements are needed.

**Model of self mode locked operation.** The basic model of self-mode-locked operation [26, 32] is as follows. The Ti:sapphire crystal has an intensity-dependent index of refraction, a material nonlinearity which leads to self-focusing of the 800-nm cavity mode by the crystal. Self-focusing is a third-order nonlinear optical phenomenon, well known in the literature [33]. Since the transverse spatial mode of the laser cavity has a Gaussian intensity profile, the cavity mode-intensity varies spatially in the Ti:sapphire crystal. This leads to a spatially-varying index of refraction in the crystal due to the intensity-dependent index of refraction of the Ti:sapphire crystal [33]. In much the same way that an ordinary lens focuses light using a spatially-varying thickness of glass across an incident light beam, the spatially-varying index of the Ti:sapphire crystal acts like a lens and focuses the cavity mode.

The lensing effect is what leads to self-mode-locking. In the ordinary, continuous (cw) mode of operation, the lensing effect is nonexistent or very small, since the intracavity intensity is low. However if the laser spontaneously began to pulse, the intensity of the cavity mode can increase by orders of magnitude, assuming that the average output power
of the laser stays the same in pulsed vs. cw operation. In the pulsed mode, the higher intensity produces a significant self-focusing effect. One aligns the cavity so that when self-focusing occurs, the cavity mode is focused to more closely overlap with the Argon-laser-pumped gain region in the Ti:sapphire crystal. In this case, the pulsed mode more efficiently extracts gain compared to the cw mode. In effect, the two modes (pulsed vs. cw) compete for gain in the cavity in a transient period following the external perturbation which induced the first pulsing. The pulsed mode ‘wins’, since it saturates the gain faster. The laser then switches from cw operation to a stable pulsed mode. In practice, the self-mode-locked oscillator is an excellent example of a bi-stable system; it can be switched back and forth between both stable states by applying a perturbation, in this case, tapping on the laser table.

The Ti:sapphire crystal and intracavity optics have positive group velocity dispersion, i.e. blue frequency components experience a greater effective path length delay than red components, so that after traversing the crystal, red components lead the blue components in time. This spreading out of frequency components in time is referred to as ‘frequency chirping’.

If this effect is not compensated for in the cavity, the output pulses are 1–5 ps in duration, and self-mode-locked operation is not as stable. Group velocity dispersion is compensated for by inserting a prism pair with negative group velocity dispersion into the cavity [19, 34]. Doing so leads to the production of nearly transform limited output [13]; i.e. the time-bandwidth product of the output pulses is minimized given the pulse shape [35].

In summary, previous work shows that the production of ultrashort pulses via self-mode-locking in Ti:sapphire relies upon: (1) the very broad gain bandwidth of the Ti:sapphire crystal, (2) the bi-stable cavity which utilizes self-focusing in the Ti:sapphire crystal to provide a mechanism for passive mode-locking, and (3) the use of intracavity prisms to provide group velocity dispersion compensation.
Optimizing self-mode-locking. Self-mode-locked Ti:sapphire cavities are currently producing record performance with optimized dispersion-compensation designs. Transform limited pulses produced directly from the oscillator in the 17-fs to 50-fs range were reported by a number of groups [36-39]. Recently, one group developed a set of specially coated optics which compensate for dispersion in the cavity, leading to the production of 11-fs output pulses without using intracavity prisms, radically simplifying the cavity design [40].

5.2.2 Chirped pulse regenerative amplification

The advent of solid-state chirped pulse amplification technology has lead to significant advances in ultrashort pulse amplification. Previously, amplification of ultrashort pulses was typically performed in laser- or flashlamp-pumped dyes, or in gas laser amplifiers (excimer or CO2).

The essential idea behind chirped pulse amplification actually was developed for high-frequency electronics. If a gain medium’s damage threshold is the limiting factor to amplification, one needs to lower the intensity of the pulse to be amplified. This is achieved by stretching the pulse out in time. The stretched pulse is then amplified to an intensity near the damage threshold; it now contains extra energy proportional to the amount the pulse is stretched. After amplification, a ‘compressor’ is used to restore the original pulsewidth.

To stretch optical pulses, a positive dispersive element, such as a pair of diffraction gratings is used to stretch the pulse by several orders of magnitude in time [41]. The resulting stretched, or chirped, pulse has red frequency components traveling ahead of blue components in time. Given the large bandwidth of ultrashort pulses, stretching of a pulse to $10^4$ times its original width is possible, meaning that 100-fs pulses can be stretched to the ns regime. Compression of stretched pulses is achieved using a diffraction grating pair with negative dispersion exactly opposite to the stretcher [42].
Note that amplifying a ns pulse in a multipass amplifier requires a gain lifetime on the order of tens of ns or greater. This fact limits the practical application of chirped pulse amplification to solid-state gain media like Ti:sapphire (3-µs gain lifetime).

The combination of chirped pulse amplification with regenerative amplification leads to efficient amplification of ultrashort pulses. A laser regenerative amplifier is a laser cavity pumped to threshold, but not allowed to spontaneously lase before a seed pulse in injected into the cavity. The seed pulse in this case is the stretched pulse which is to be amplified. Seeding the cavity pre-empts free lasing of the amplifier. The cavity energy is extracted by the seed pulse. With proper design, the seed pulse extracts the entire free-lasing energy; this produces up to $10^6 \times$ amplification. Furthermore, the amplified output pulse acquires the spatial mode characteristics of the amplifier cavity, a high-quality TEM$_{00}$ output, independent of the spatial mode quality of the seed beam. This is advantageous given that self-mode-locked cavities typically produce a slightly elliptical, astigmatic output.

Amplification of ns and ps pulses to high energies in Ti:sapphire was first demonstrated at Lincoln Labs [43, 44] and IBM [45]. Chirped pulse amplification of fs pulses in a solid state regenerative amplifier was demonstrated by Mourou’s group when 300-fs pulses were amplified in flashlamp-pumped alexandrite [46]; this work was later extended to 100-fs pulse amplification [18]. Amplification in an injection seeded Ti:sapphire laser was first demonstrated at MIT [9]. Regenerative chirped pulse amplification of 100-fs pulses in Ti:sapphire to mJ energies was first reported in 1991 [47]; this system was the first to incorporate both a Ti:sapphire self-mode-locked oscillator and regenerative amplifier, and served as the model upon which our system was based. We describe our modifications to this design in Sect. 5.4. High repetition rate (kHz) amplifier designs for 150-fs [14] and 55-fs [48] pulses were subsequently reported using new kHz pump laser technology; this work achieved amplification of 55-fs pulses to 0.35-mJ energies, a peak power of 6 GW, at a 1-kHz rate.
5.3 Design goals and constraints

Before describing the laser system, we first outline our goals and constraints in order to show the logic behind the system’s design.

For the planned ultrafast surface reaction studies, we required, in roughly this order of importance: (1) as short an amplified pulse as could be achieved practically, preferably $\leq 100$-fs, (2) a range of wavelengths, extending from the visible to about 200 nm, which is the short-wavelength transmission edge of our fused-silica UHV chamber windows, (3) sufficient energy at each wavelength to initiate desorption and determine a desorption fluence dependence, as well as enough energy for future experiments with pump and probe beams at different wavelengths, (4) a high-quality spatial mode output, (5) excellent pulse-to-pulse and long-term amplitude stability, (5) high amplitude-contrast between the output pulse and noise in the output such as extra pulses or spontaneous emission background, (6) $\geq 20\%$ efficiency of conversion of pump laser energy to amplified output, (7) a compact, simple design which fits the physical space allotted (an 8-foot optical table) and is easy to operate, and (8) a design which minimizes the expense of the final system. As with any complex system, most of these design goals are interrelated; this means that optimization requires some compromises.

**Short Pulses.** For the planned desorption studies, 100-fs pulses are adequate to drive the ultrafast reaction mechanism. For our planned spectroscopy work, pulses in the 50-fs to 70-fs range are required to provide time resolution much faster than the surface vibrational relaxation timescale ($\leq 1$ ps). Ultimately, we have the option of amplifying the $\leq 40$-fs pulses which our oscillator produces. Such short pulses may be required for resolving the dynamics of nascent electron distributions (see Ch. 4).

**Wavelengths.** By second, third, and fourth harmonic generation in nonlinear crystals, we planned to use our fundamental 800-nm beam to generate 400 nm (with 25% efficiency), 266 nm (5–10% efficiency) and 200 nm (1–5% efficiency). This wavelength
range could be enhanced by later construction of an optical parametric amplifier (20% efficiency at the design wavelength, across the visible and near-infrared range).

We note that the fourth harmonic of Ti:sapphire is very close to the 200-nm absorption edge of BBO, the only crystal good for fourth harmonic generation of Ti:sapphire lasers. Therefore it is desirable to tune our oscillator and amplifier to operate above 800 nm.

**Energy.** For a given fundamental beam mode quality, in order to produce more output with the wavelength generation methods above, one needs more energetic pulses. Even 300-μJ amplified output at 800 nm is insufficient energy to produce a good quality beam needed for desorption studies (see Ch. 4, Sect. 4.3.2). Therefore in general, we need as much energy as possible; we set a practical design goal of 1-mJ compressed, amplified, output at 800 nm per pulse. A practical upper limit is set by the energy damage threshold of the diffraction gratings used for compression, which is roughly 1 J/cm².

**Spatial mode.** The efficiencies of the wavelength conversion processes are strongly dependent on the spatial mode quality. As noted above, the spatial mode of the amplified output is determined by the regenerative amplifier cavity design. To a lesser extent, the compressor design also affects the mode. Some amplifier cavities were found to be more efficient, but produced poor quality modes. Ideally, the output should be characterizable as TEM₀₀.

**Stability.** This is an important issue which is often avoided in published reports of new laser designs. Laser development groups often only aim to demonstrate feasibility of a new concept; we have the additional constraint of needing to perform physics experiments with the laser. This means that the design goals have to be met continuously, all day, every day during the course of measurements. We require minimal pulse-to-pulse variation in energy, wavelength, pulsewidth, and spatial mode. These parameters should not slowly drift, nor should the laser unpredictably un-mode-lock or otherwise shut down. In practice, these criteria were the most difficult to achieve once the system was operational.
**Contrast.** The temporal output of a regenerative amplifier contains undesired background due to free-lasing of the amplifier cavity, and from additional pulses that leak out of the cavity before or after the main amplified pulse. We desire a high contrast ratio between these background signals and the main pulse. As discussed in Sect. 5.4.2, the contrast ratio is primarily determined by the choice of Pockels cell and thin-film polarizers (TFP) used in the amplifier cavity.

**Efficiency.** The output energy of the system depends principally on the efficiency of the amplifier and the available pump energy (maximum of 15 mJ per pulse at 1 kHz). Therefore we desire a high efficiency. A higher efficiency also allows one to reach the energy design goal while operating the pump laser at lower power, extending the pump-laser lamp life. Amplifier efficiency is determined by the amplifier cavity design.

**Simple, compact design.** The current laser system occupies half the space of the CPM/dye amplifier system in the adjacent lab, yet produces comparable output energy at a higher repetition rate. The simplicity of the design enhances the reliability and ease of use.

**Expense.** At several design junctures, we had the option of simplifying the design task by adding on new components. We chose instead to keep the system cost low by using fewer components when possible. For example, our stretcher and compressor designs use only one grating each, while many other groups use multiple grating setups at a significantly higher cost; the single-grating designs are not only cheaper, they are also simpler to align.

### 5.4 System description: component design, function, operation

The femtosecond Ti:sapphire laser system built in our group has two main components: the self-mode-locked oscillator, which produces an 80-MHz train of 50-fs pulses, and the regenerative amplifier, which amplifies a subset of those pulses, producing a 1-kHz train of < 100-fs pulses. The system is schematically illustrated in Fig. 5.1. The
system was designed and assembled in our laboratory from selected commercial components.

Fig. 5.1 Schematic of Ti:sapphire laser system. A continuous wave (cw) Ar laser producing 8-W multiline visible output (MLVS) pumps the Ti:sapphire oscillator. The oscillator pulses are stretched to 400 ps, amplified, and compressed to 70–100 fs. The amplifier system runs at 1 kHz, pumped by an intracavity doubled Nd:YLF laser.

5.4.1 Ti:sapphire self-mode-locked oscillator

The layout of the Ti:sapphire mode-locked oscillator is shown in Fig. 5.2. The oscillator is a folded X-shaped cavity similar to that reported in [26]. The entire oscillator is housed in a Class 100 filtered air (Laminaire) enclosure. A Ti:sapphire crystal (Crystal Systems; 0.5 diameter × 2.2-cm length, Brewster cut; doped for 99% absorption; figure of merit ≈ 200) is located at the cavity beam waist between two 10-cm radius of curvature mirrors (Lightning Optical) coated for 19° incidence (labeled $M$ in Fig. 5.2). This angle is
selected to compensate for the astigmatism introduced by the Brewster cut crystal faces [22]. The crystal is mounted on a thermoelectrically cooled (Melcor) base, and is pumped by 8-W from a cw multi-line visible Argon laser (Coherent Innova-20), with the pump beam tightly focused into the crystal by a 10-cm lens through one of the 10-cm radius of curvature cavity mirrors. A 22% output coupler (Lightning Optical), OC in Fig. 5.2, is used in one arm of the X-shaped cavity. Two LaKL31 prisms (Lightning Optical) are mounted on translation stages in the other arm of the cavity, spaced apart by 55 cm to provide opposite, negative, group velocity dispersion to the Ti:sapphire crystal and intracavity optics dielectric coatings. The prisms are cut at 60° so that the angle of incidence equals the Brewster angle at minimum deviation. Translation of one or both of the prisms allows fine tuning the dispersion compensation. Inserting a 2-mm wide slit 5 mm from the back mirror \(B\) (cf. Fig 5.2) improves mode-locking stability. Also, this slit ensures that the oscillator center-wavelength does not vary. When aligned for good self-mode-locked operation, this cavity produces 400-mW output at 80-MHz for an 8-W pump (5 nJ per pulse) at 800 nm.

Procedure to obtain self-mode-locking. Achieving the bi-stable self-mode-locking alignment is a peculiar task, as the quote of Sect. 5.2.1 indicates. This section explains how the theoretical model of self-mode-locking (Sect. 5.2.1) is put into practice. A more complete recipe has been recorded in the Mazur group lab notebook\(^2\).

In general, the procedure to obtain self-mode-locking is empirical. Experience dictates that the self-focusing effect works most effectively for an intracavity peak power in the 1–5-MW regime. Given 22% output coupling and 50-fs pulsewidth, this implies that the cavity should produce a continuous-wave output power of 0.20–1.0 W for an 80-MHz pulse rate.

With both cavity arms approximately equal length, and the prism separation about 55 cm (determined from the crystal dispersion [34, 49]), one peaks the continuous-wave

\(^2\)Ti: Sap laser notebook #2, pp. 13–19.
output power for an 8-W Ar laser pump to achieve an output power in the range 400–600 mW. Next, one looks for pulsing by monitoring the temporal output with a fast photodiode (Thorlabs) and by observing the output spectrum. When the laser mode-locks, the output spectrum changes dramatically from a series of sharp lines to a broad 40-nm, smooth, spectrum.

We find that one should align the cavity for an irregularly-shaped spatial mode which looks like a horizontal triangle. When the cavity begins to pulse, temporal variations in the mode are apparent, and when it stably mode-locks, the mode becomes nearly round.

The rest of the process involves many hours of patient experimentation. At peak cavity power, one adjusts the cavity elements, primarily the prisms, back mirror $B$, and Ar laser beam pointing, while simultaneously providing an external perturbation by knocking
on the laser table with a solid object such as a ball driver. Pulsing eventually appears in the
temporal output seen on a photodiode, and evidenced by spectral broadening coinciding
with knocking on the table. Systematically ‘tweaking’ all the cavity optics and prisms, one
enhances the tendency towards pulsing with each series of adjustments. Ultimately, diligent
efforts are spontaneously rewarded when the laser mode-locks, and stays mode-locked for a
few seconds. With further minor adjustments, one finds a very stable arrangement. In this
alignment, the laser will stay mode-locked all day following just a single tap on the laser
table; the laser is then operated each day by warming up the Argon laser for about one hour,
and then knocking the laser table to start mode-locking.

**Stability of self-mode-locking.** A dust-free environment is crucial to the stability
of self-mode-locking. When we added a dust-free enclosure around our laser\(^3\), our mode-
locking stability improved dramatically, presumably because dust in the cavity can un-mode-
lock the laser. The beam-pointing stability of the Ar pump laser is also critical. Since the Ar
laser overlap with the mode-locked cavity mode is what leads to self-mode-locking, the Ar
laser beam direction must not drift over the course of the day. Warming up the laser for at
least one hour before mode-locking the oscillator helps considerably.

We spent considerable effort trying to use a HITCI-dye/ethylene glycol saturable-
absorber jet to improve mode-locking stability. This jet was located in a second cavity focus
in the currently empty cavity arm *(cf. Fig. 5.2)*. We found that using a saturable absorber jet
gave no improvement over the empty-cavity self-mode-locking. Furthermore, the jet
introduced other problems such as more difficult cavity alignment, and the accumulation of
ethylene glycol vapor on the cavity optics.

**Oscillator Performance details.** As noted above, the oscillator output is not
transform limited. The 40-nm wide output spectrum is centered between 770–805 nm and
can theoretically yield a 25-fs transform-limited pulse \([35]\). We obtain 50-fs

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\(^3\)Suggested by B. Clark, of Clark Laser Inc.
autocorrelations. The reason for this is that our prism pair compensates for the group velocity dispersion of the crystal and optics, but does not completely compensate the higher-order dispersion terms [49]. Shorter pulses can be achieved directly out of the oscillator by introducing less third-order dispersion via the use of a thinner Ti:sapphire crystal and output coupler, and flint-glass prisms [37]. Since we stretch the pulses before amplification, the pulsewidth out of the oscillator is not important as long as the large bandwidth is present.

The oscillator is easily tunable over the range 770–805 nm. Given this broad bandwidth, we find that one often achieves stable mode-locking at a different wavelength than was intended. Also, we find that after several days of the minor tweaking required to stabilize mode-locking, the laser center wavelength can drift; this happens by accident because 775-nm light is much more readily visible to the eye than 800-nm light, so one is naturally inclined to tune the oscillator towards more visible wavelengths. Addition of a slit in the cavity (cf. Fig. 5.2) solves this problem by selecting out a portion of the intracavity spectrum dispersed by the prism pair, ‘locking’ the laser at a particular center wavelength as long as the intracavity prisms are not adjusted.

### 5.4.2 Ti:sapphire 1-kHz regenerative amplifier

The amplifier system (see Fig. 5.1, and Figs. 5.3–5.5) is composed of a pulse stretcher, optical diode, regenerative amplifier, and pulse compressor. The stretcher takes the fs pulses from the oscillator, and frequency chirps them to 400-ps duration. The stretched pulses pass through the optical diode which prevents feedback to the oscillator from the amplifier. The amplifier selects out pulses from the 80-MHz train at 1 kHz, and amplifies them in energy by a factor of $10^5$. The amplified pulses are compressed back to 100-fs pulsewidth in the compressor.
5.4.2.1 Stretcher and compressor

The use of diffraction grating pairs to stretch or compress ultrashort pulses has been described previously [42, 50]. The application of stretching and compressing technology for chirped pulse amplification has been described by several authors [41, 51, 52]. Stretching and compressing using diffraction gratings is achieved by using a geometry in which the path length through the arrangement depends on wavelength. Positive and negative group velocity dispersion are obtained in the stretcher and compressor, respectively.

We use compact, multiple-pass, single-grating designs for both stretcher and compressor. These designs use only reflective optics in order to avoid additional dispersion from glass lenses.

Figure 5.3 shows schematically how the conventional stretcher and compressor designs were folded to our current design. The conventional two-grating, double-pass stretcher geometry is shown in Fig. 5.3 (a). The lenses are spaced apart by twice their focal length $f$. Since the vertical dashed line is a plane of symmetry, placing a mirror M (cf. Fig. 5.2 (b)) at that position allows folding the geometry. In this case, the return beam after the second grating reflection passes the grating to reflect off M'. To allow the beam to reach M', the beam is reflected in the vertical plane. The final step, shown in Fig. 5.2 (e), is to replace the lens with a focusing mirror. Note that this again reverses the symmetry of the geometry so that M' moves behind the focusing mirror. In all the geometries, the input beam diffracts from the grating four times, and exits along the input path. We align the stretcher so that all the beam paths lie in a single vertical plane (orthogonal to the plane of the figure).

The compressor folding is illustrated in Fig. 5.3 (d)–(e). In this geometry, the back mirror M' is replaced by a retro-reflector RR, so that the return spectrum hits the grating on the second pass with the correct orientation. Note that the retro-reflector is only illustrated schematically here; it actually lies in the plane orthogonal to the page. As in the stretcher design, all the beam paths are aligned in the vertical plane orthogonal to the page, and the
input beam diffracts four times from the grating and exits along the input path. The compressor length is adjusted by translating the retro-reflector to adjust \( x' \) (see Fig. 5.3 (c)).

The stretcher and compressor use a matched pair of 1200 lines/mm gold-coated reflection gratings (Milton Roy), blazed for 750 nm (26\(^\circ\)). The 750-nm blaze is not optimum for our 800-nm pulses, but is the nearest standard blaze available. The gratings are 90% reflective between 750–850 nm. They are used in Littrow configuration, meaning that the reflected beam, which is the first order diffraction beam, is reflected back parallel to the incident beam. This arrangement reduces the higher order dispersion according to beam-propagation calculations.\(^4\)

The stretcher (cf. Fig. 5.3 (c)) employs a 50-cm focal length spherical gold coated mirror at \( x = 20 \) cm from the grating to produce 8000 \( \times \) stretching, verified using a streak camera (Hamamatsu). The compressor uses dielectrically coated high-reflector optics (Lightning Optical) to obtain 70% energy efficiency in compression, with essentially all loss accounted by four 90% reflections from the compressor grating. This efficiency could be improved if a higher density of lines/mm grating was used, but our calculations show that using a 1200 lines/mm grating for stretching and compressing improves compensation for higher-order group velocity dispersion. Also, the spatial extent over which the pulse spectrum is spread in the grating is smaller for a 1200 lines/mm grating, allowing the use of 3"-wide optics to reflect the entire spectrum. Even wider, more expensive optics are required if an 1800 lines/mm grating is used. The size of the expanded spectrum in the stretcher and compressor is a significant practical issue in stretcher and compressor designs [52].

The stretcher and compressor are aligned in Littrow so that the input beam returns on itself after four reflections off the grating. The mirrors of each setup are slightly misaligned in the horizontal plane so that the output beam is separated by two beam

\(^4\)Calculations performed by S. Deliwala.
Fig. 5.3 Stretcher and compressor folding schemes. G: diffraction grating. L: lens. M and M': flat mirror. FM: focusing mirror. RR: retro-reflector. (a) shows the conventional stretcher arrangement for positive dispersion (Ref. [41]). The vertical dashed line is a plane of symmetry. The sequence (a)→(c) shows how we fold the design to use a single grating and only reflective optics. (d) shows the conventional compressor arrangement [42], and (e) is the folded arrangement. See text for details. Note that in the actual design, the injection/ejection beams illustrated schematically in the figure are aligned in Littrow (not shown).
diameters from the input in the horizontal plane after a distance of about 30 cm. This separation allows the output to be reflected downstream by a separate mirror. In order to produce the shortest amplified pulses, the stretcher and compressor grating angles (in the horizontal plane) are adjusted along with the compressor length $x'$ (cf. Fig. 5.3) while monitoring the compressed pulsewidth. Calculations and experimental results show that by slightly tuning the gratings away from the Littrow angle, compensation for third-order dispersion introduced by the intracavity elements of the amplifier (Ti:sapphire crystal and Pockels cell) is achieved, resulting in compressed pulses of $\leq 70$-fs duration. For the experiments of Ch. 4, we did not find it convenient to make the finer adjustments necessary to achieve such a short pulsewidth. In this case, we aligned the stretcher in Littrow and adjusted only the compressor to routinely produce 100-fs pulses.

### 5.4.2.2 Optical diode

Once the seed pulse is stretched, it is injected into the amplifier. Feedback from the amplifier can occur if light returns from the amplifier along its original input path. An optical diode must be employed to prevent this feedback; otherwise, the return light will unmode-lock the oscillator.

The optical diode has four parts, illustrated in Fig. 5.4: a half wave plate (Special Optics), two polarizers (Special Optics cube beamsplitters), and a Faraday rotator (ConOptics). The rotator is a nonlinear optical crystal in a permanent magnetic field which rotates the input polarization of the light by 45° with a fixed ‘sense’, or handedness (see Fig. 5.4). Therefore, the light polarization is always rotated in one direction with respect to the rotator’s axis, independent of the direction of travel of the light. This is unlike a standard polarization-rotating element such as a half-wave plate, which always rotates with the same sense with respect to the light’s $k$-vector. The half-wave plate/rotator combination is arranged so that the input $p$-polarized light is rotated by 90° into $s$-polarized light. Feedback from the amplifier, traveling in the reverse direction, experiences no
rotation. A cube polarizer on the input side of the diode transmits the input beam but reflects the feedback beam, achieving optical isolation of the oscillator from the amplifier.

![Diagram](image)

**Fig. 5.4** Optical diode. BS: cube beamsplitter. $\lambda/2$: half wave plate. The arrowed loop around the Faraday rotator indicates its fixed polarization rotation direction. Pulses heading towards the amplifier travel from left to right, starting out $p$-polarized and ending up $s$-polarized. Feedback pulses returning from the amplifier travel the opposite direction and are dumped into the two beam blocks as shown.

The problem of feedback from the amplifier was a major technical challenge during laser development. We find that for non-optimum arrangement of the optical diode, un-mode-locking occurs exactly correlated with unblocking the return beam path from the amplifier.

In other group’s designs, feedback was less of a problem than in our case because of their use of high $s$-polarized-reflectivity thin-film polarizers (TFP’s, see next section). In these designs, the input and output path to the amplifier are overlapped, so that the optical diode serves the additional role of separating the input and output beams after amplification. Both the input and output must pass through the Faraday rotator in such a design. Passing the amplified pulse back through the rotator is not ideal because the rotator can be damaged by the intense beam, and also because the rotator introduces extra
dispersion. Also, in the case where the diode is used to separate input and output beams from the amplifier, the thin-film polarizers must have nearly 100% reflectivity for $s$-polarization and 0% reflectivity for $p$-polarization. Otherwise, the optical isolator will not effectively prevent feedback to the oscillator. However, thin-film polarizer designs which have the lowest insertion loss in the amplifier cavity (Alpine Optics) unfortunately have poorer polarization contrast than polarizers optimized for maximum $s$-polarized reflectivity. The polarizers that we decided to use have 84% $s$-polarized reflectivity and 2% $p$-polarized reflectivity. This choice is discussed in more detail in the next section.

In order to avoid feedback while using the Alpine Optics polarizers, we adopted a design in which the input and output paths to and from the amplifier are different. Only the input beam passes through the optical diode. In addition, we use two cube beamsplitters (cf. Fig. 5.4) instead of one; this enhances the optical diode performance. With a polarizer on the output side of the waveplate/Faraday rotator combination, we ensure that only $s$-polarized light returns to the diode from the amplifier; this significantly improves rejection of the return beam (i.e. without the extra polarizer, the return beam has a $p$-polarized component from the 2% $p$-polarized reflectivity of the thin-film polarizer).

We are able to directly observe the performance of the optical diode by monitoring the long-time ($\mu$s) behavior of the oscillator pulse train while tuning the half wave plate angle. With proper wave-plate orientation, the oscillator pulse train looks unperturbed following the ejected amplified pulse. However, with a few degrees of wave-plate detuning, one observes a 10-$\mu$s-period damped oscillation in the oscillator output amplitude following each ejected amplified pulse. If the half-wave plate is further mistuned, this amplitude variation grows rapidly and the oscillator un-mode-locks. This is to our knowledge the first reported direct observation of feedback un-mode-locking dynamics in a self-mode-locked Ti:sapphire oscillator.
5.4.2.3 Amplifier

The regenerative amplifier, shown in Fig. 5.5, is a three-mirror V-shaped laser cavity pumped at 1 kHz by an 527-nm intracavity doubled Nd:YLF laser (Quantronix). The pump laser is run at 5 W, producing 5-mJ, 200-ns pump pulses. The amplifier has a 0.5-cm diameter \( \times \) 2-cm long Ti:sapphire crystal (Crystal Systems; 95% pump beam absorption; figure of merit \( \approx 250 \)) with Brewster cut faces, mounted in a water-cooled copper block. The Brewster cut faces ensure that the cavity mode is \( p \)-polarized. The crystal is positioned at a cavity beam waist 19 cm from a 1-m radius of curvature 800-nm high reflector, through which the Nd:YLF pump beam is focused onto the crystal. A second 1-m radius of curvature mirror reflects the beam to the second cavity arm which contains two thin film polarizers (Alpine Research Optics; 98% \( p \)-polarized transmission, 16% \( s \)-polarized transmission at 68° incidence; broadband 700–900-nm coating; anti-reflection coated on second face), and a Pockels cell (ConOptics two-crystal KDP pulse selector). The cavity back mirror is a 4-m radius of curvature high reflector. All high reflectors are Lightning Optical high damage threshold coated optics with a broadband 750–830-nm coating. The cavity round trip time is 9 ns.

The basic operation of the amplifier is as follows. Pulses from the stretcher are \( s \)-polarized by the optical diode and mode-matched [19] into the amplifier cavity by reflection off the ‘injection’ polarizer (cf. Fig. 5.5). Countdown electronics (ConOptics) synchronized to the 80-MHz oscillator pulse train produce one trigger for the Pockels cell after every 80,000 pulses. This trigger pulse fires the Nd:YLF pump laser. To achieve injection, a second synchronized trigger pulse is delayed using a ps delay generator (Stanford Research) and fires the first Pockels cell crystal. This causes the Pockels cell to switch the polarization of one \( s \)-polarized input laser pulse by 90°, trapping this \( p \)-polarized laser pulse in the amplifier cavity. The injected laser pulse makes 30 round trips in the amplifier cavity,
Fig. 5.5 Regenerative amplifier. L: lens. HR: high reflector. X: Ti:sapphire crystal. TFP: thin-film polarizer. PC: Pockels cell. The Nd:YLF pump beam, and injected and ejected pulse trains are indicated by the labeled arrows.

and is then ejected by the second Pockels cell crystal. Ejection is timed by a second delayed trigger pulse generated by the SRS delay generator. The Pockels cell causes ejection by switching the polarization of the $p$-polarized amplified laser pulse in the cavity to $s$-polarization so that it is reflected out of the cavity by the ‘ejection’ thin-film polarizer (cf. Fig. 5.5).

It is important to realize that the amplifier cavity is a laser that free-lases following Nd:YLF pumping; output coupling is provided by the 2% $p$-polarized reflectivity of both thin-film polarizers. When operated as a regenerative amplifier, the seed pulse is injected a few hundred nanoseconds before the cavity spontaneously begins to lase. The injected pulse saturates the gain, pre-empting free-lasing.

Many amplifier design iterations, using a variety of cavity designs, two different sets of thin-film polarizers and two different Pockels cell designs were tested. In the rest of this section, we outline the major design issues and our motivation for arriving at the amplifier design described above.

**Pockels cells.** A Pockels cell is an electro-optical device which uses a nonlinear KDP crystal in an electric field to rotate the polarization state of light transmitted through the cell. There are two varieties of Pockels cells that can be used in a regenerative amplifier.
Prior to our work, the only type used conventionally was a Q-switch type device. In its initial state before injection, the Q-switch Pockels cell, in combination with the thin-film polarizers, blocks lasing of the cavity by preventing any photons from completing a round trip inside the cavity. Such a cavity is called an ‘open’ cavity. Upon injection, the Q-switch Pockels cell closes the cavity, permitting the injected pulse to make a number of round trips. Following ejection, the cavity is again left open. This design has the advantage that no free-lasing can occur before injection, or after ejection.

At the time of construction of our laser, only one manufacturer (Medox) was producing Q-switch type Pockels cells for regenerative amplifiers at 800 nm. The disadvantages of the Medox cell included high cost, inconveniently large size, and a slow switching time which limited the repetition rate to a maximum of 1 kHz and required a minimum 11-ns cavity round-trip time. This single-crystal design is longitudinally excited, i.e. the electric field propagates along the direction of travel of the light. This longitudinal excitation design has electrodes affixed to the entrance and exit faces of the nonlinear crystal. Such an arrangement is susceptible to optical damage and produces a less uniform field in the crystal than a transversely excited design.

We opted to try a new approach using a two-crystal pulse-selector-type Pockels cell (ConOptics). This device is transversely excited in a waveguide geometry; this avoids the above-mentioned problems and offers a fast 7-ns switching time and a 50-kHz repetition rate that can be increased to 40 MHz with additional driver electronics. This design is also compact, and less expensive.

A disadvantage of the two-crystal pulse-selector design is that it does not suppress free-lasing of the cavity. The first Pockels cell crystal selects a single pulse from the 80-MHz oscillator train, trapping it in the cavity. The second Pockels cell crystal ejects out the amplified pulse. Except during the 7-ns injection and ejection switching times, the cavity is left closed and can free-lase.
With the pulse-selector Pockels cell, proper injection timing is critical for avoiding free lasing. We find that the seed pulse must be injected within a 20–30-ns time interval at the peak of the 200-ns Nd:YLF pump pulse. Injecting too late leads to a large free-lasing background.

Beyond its role as a pulse injector/ejector in the cavity, placing a Pockels cell in the cavity has other important effects. The small (3-mm diameter) aperture of the cell means that the cavity must be designed to have a sufficiently small mode at the position of the cell, but not so small that the damage threshold of the cell is exceeded. The mode in the Pockels cell needs to be minimized however because the degree of polarization rotation by the cell varies spatially across the Pockels cell crystals due to electric field non-uniformities at the edges of the KDP crystals. It is critical to make the mode as small as possible to avoid producing non-uniform polarization in the transverse spatial mode.

A related issue is insertion loss. Even a high optical quality Pockels cell such as the one we use has a high insertion loss which reduces the cavity efficiency by 5–10% compared to the empty cavity performance with no Pockels cell. Insertion loss is minimized by precise alignment of the cell with respect to the cavity mode. Good alignment is possible to achieve only if the cavity mode is small at the position of the cell and is precisely aligned in the plane of the cell.

Another concern is proper choice of voltage bias for the Pockels cell. For our pulse-selector design, the bias voltage determines the amount of rotation of the cell in its inactive (i.e. off, or non-switching) state. In combination with the thin-film polarizers, the cell, even when off, provides output coupling for the amplifier cavity; adjusting the bias adjusts the amount of output coupling. To optimize the amplifier cavity, one adjusts the Pockels cell bias so that with the cavity free-lasing, the center portion of the mode forms a dark pattern referred to as a ‘null bar’. This setting minimizes the insertion loss of the Pockels cell; since at this bias setting the output coupling is minimal, the free-lasing energy is reduced to roughly half the maximum free-lasing output. For ejection, the trigger pulse switches the
output coupling to a maximum for the 7-ns ejection interval. This optimization technique ensures that the injected pulse experiences minimum loss until ejection.

**Thin film polarizers.** In tandem with Pockels cell design issues, one must consider the performance of the thin-film polarizers used to reflect the injection and ejection laser pulses. Thin-film polarizers are high quality optical substrates with a multilayer dielectric coating on one face which is highly transmitting for $p$-polarization and highly reflecting for orthogonal $s$-polarization.

A good thin-film polarizer must have very low insertion loss ($\geq 98\%$ $p$-polarized transmission), wide bandwidth, and high $s$-polarized reflectivity. In practice, we have found it very difficult to find an ideal polarizer. Early efforts to use thin-film polarizers from one manufacturer (CVI) caused us months of delays due to defects in their manufacture that were not apparent until after the amplifier was nearly operational. We ultimately settled on thin-film polarizers from Alpine Research Optics which have 700–900-nm bandwidth and 98\% $p$-polarized transmission, but have only 84\% $s$-polarized reflectivity. Other polarizers are available that have higher $s$-polarized reflectivity, but these have lower $p$-polarized transmission, typically about 90\%. The lower transmission of these other designs gives a greater insertion loss for the $p$-polarized amplifier cavity mode.

The tradeoffs between low insertion loss (high $p$-polarized transmission) and high $s$-polarized reflectivity are as follows. Lower insertion loss means higher cavity efficiency. On the other hand, lower $s$-polarized reflectivity (84\% in our case) means that only 84\% of the amplified pulse is ejected. This loss negates part of the gains we achieved by improving the cavity efficiency. Also, 16\% of the light is not ejected, and remains in the cavity. While the crystal Brewster faces reflect about 30\% of this remaining $s$-polarized light out of the cavity, some is amplified and emerges as post-pulses following the main ejected pulse.

In order to optimize the design using Alpine thin-film polarizers, we use two in the amplifier cavity, one for injection and one for ejection. We solved feedback problems as described in the optical diode section; we obtain excellent ($\geq 20\%$) output efficiency.
despite the relatively low $s$-polarized reflectivity. An advantage of the design is that we have a high bandwidth (700–900 nm) cavity, as a result of the high bandwidth of the polarizers and the optical quality of the Pockels cell. The cavity optics (see next section) are what limit the amplifier bandwidth. We note also that the choice of a two polarizer design, while made primarily to eliminate feedback, also has the great advantage of not passing the ejected amplified beam back through the Faraday rotator.

**Cavity design.** Proper cavity design is the most important factor in determining amplifier efficiency. The previous sections indicate that a number of constraints must be satisfied in order to accommodate the Pockels cell and thin-film polarizers into the cavity.

To ensure maximum efficiency, the cavity must maximize gain and minimize loss. Highest gain is achieved by tightly focusing the pump beam to saturation intensity in the crystal, and perfectly overlapping the cavity mode with the pumped volume. Lowest loss is achieved by assembling a stable resonator with the mode size smaller than all apertures in the cavity, especially the aperture of the Pockels cell. However, the mode size must not be so small at the mirrors that the damage threshold is approached, or else mirror performance degrades and the loss is increased, or the mirrors may even burn.

In addition to maximizing efficiency, a good cavity design will have a collimated, near-TEM$_{00}$ output and a sufficiently long round-trip time to allow optimum Pockels cell performance. A good cavity is also stable against minor misalignment; this allows routine realignment without degradation of performance.

We settled on a three mirror cavity (Fig. 5.5) which satisfies all these criteria. We use a simplified cavity modeling scheme to help optimize the cavity designs. Note that detailed calculation of cavity mode propagation in a cavity like that of Fig. 5.5 requires computationally intensive models which are available commercially but are prohibitively expensive. We find that a combination of the simple approach described below with an empirical alignment procedure allows one to arrive at a working design.
A brief overview of the analysis scheme is as follows: (1) We perform a computation in which the three mirror laser cavity of Fig. 5.5 is reduced to an effective two-mirror cavity as shown in Fig. 5.6. This scheme is based on the cavity analysis techniques discussed in Siegman, Sects. 21.2 and 21.6 [19]. (2) The two-mirror cavity in Fig. 5.6 (c) is analyzed for stability by the conventional analysis [19]. (3) The stability analysis yields the TEM$_{00}$ mode size and radius of curvature at mirror 1 (labeled $R_1$ in Fig. 5.6 (c)). Using these parameters the beam is then propagated through the real cavity (i.e. Fig. 5.5 (a)) using Gaussian beam analysis [19].

![Diagram](image-url)
We now explain the analysis in more detail. The three mirror cavity of Fig. 5.6 (a) is equivalent to a linear cavity as shown in Fig. 5.6 (b). The mode parameters at mirror 1 (radius of curvature $R_1$) can be computed if we effectively replace the lens and mirror 3 (radius of curvature $R_3$) by a mirror with radius of curvature $R'_2$ at a distance $L$ from mirror 1, with $L$ given by [19]:

$$L = d_1 + d_2 - \frac{d_1 d_2}{f}.$$  \hfill (5.1)

Two stability parameters $g_1$ and $g_2$ can be computed for this cavity as follows:

$$g_1 = 1 - \frac{d_1}{f} - \frac{L}{R_1}; \quad g_2 = 1 - \frac{d_2}{f} - \frac{L}{R_2},$$  \hfill (5.2)

where $d_1$ and $d_2$ are distances shown in Fig. 5.6. In this case, the cavity is stable when the parameter $G \equiv g_1 \times g_2$ is less than 1.

Having found a stable cavity, one next computes the size of the mode, $w_1$, on mirror 1 from the expression:

$$w_1 = \sqrt{\frac{\lambda L}{\pi} \left( \frac{1}{1 - G} \right) \left( \frac{g_2}{g_1} \right)^{1/2}}.$$  \hfill (5.3)

Finally, the cavity mode can next be computed everywhere in the three-mirror cavity using the standard expressions for TEM$_{00}$ gaussian beam propagation [19] starting from $R_1$. The distance, $\kappa$, between the beam waist near mirror 1 and the mirror, and the diameter, $w_d$, of this beam waist are given by:

$$w_d = \sqrt{\frac{w_1^2}{1 + \left( \frac{\pi w_1^2}{\lambda R_1} \right)}}; \quad \kappa = \frac{R_1}{1 + \left( \frac{\lambda R_1}{\pi w_1^2} \right)^2}.$$  \hfill (5.4)

Following this procedure, we determine the beam diameter at the Ti:sapphire crystal to be 300 $\mu$m at a distance of 19 cm from mirror 1 (for the cavity of Fig. 5.5, using $d_1 = 70$ cm, $d_2 = 66$ cm, $R_1 = 100$ cm, $R_2 = f/2 = 100$ cm, $R_3 = 400$ cm) This beam diameter gives a fluence of 0.4 J/cm$^2$ for the 800-nm cavity mode in the crystal for 5-mJ pumping, which
is near the 0.9-J/cm² saturation fluence [45]. We also compute the beam diameter at the Pockels cell, and find a value of 400 µm, with the beam collimated in the Pockels cell arm. As discussed in the next section, we recently changed the cavity parameters to give a tighter focus in the crystal, achieving saturation fluence and increasing the amplification.

In practice, having computed the parameters of a particular design, the Ti:sapphire crystal position, Nd:YLF focus, and cavity length are adjusted in an iterative empirical procedure. At each step, one notes how the mode quality and cavity efficiency change. Ultimately, a satisfactory compromise is reached, with measured cavity parameters that fall within 10% of the computed values from Eqns. 5.1–5.2.

### 5.4.3 System operation and performance

The system in its final configuration meets all the aforementioned design criteria. During the course of the experiments described in Chapter 4, the amplifier cavity produced 650-µJ uncompressed output for 4.75-mJ YLF pump energy, with ≤ 5% pulse-to-pulse energy variations, an excellent spatial mode and good signal/background contrast. Figure 5.7 (c) shows a time trace of the amplified output. A typical autocorrelation trace of the amplified pulse is shown in Fig. 5.8. The pulse was routinely compressible to ≤ 100-fs. In Section 5.5, we describe how with minor modifications, the amplifier produced 100% more output energy with otherwise comparable performance.

Typical daily operation is as follows. First at least a one-hour warmup of the Nd:YLF pump laser is required, followed by a one-hour warmup of the free-lasing amplifier. Warming up the Nd:YLF laser is required to achieve good energy stability. The oscillator beam is aligned through the stretcher and optical diode. The amplifier adjustment procedure begins with the Pockels cell turned off (no injection or ejection). The amplifier free-lasing energy is optimized by adjusting the Nd:YLF laser beam. The Pockels cell bias is adjusted to produce a good null bar. Figure 5.7 (a) shows the free lasing output as seen from TFP2 (cf. Fig. 5.5) using a fast photodiode (Thorlabs) when there is no injection or ejection.
Fig. 5.7 Time traces of amplifier output, as observed from the reflection off TFP2 in Fig. 5.5. (a) shows the free-lasing output when no injection or ejection takes place. (b) shows the result of injecting a single oscillator pulse, without any ejection. (c) shows the effect of injection. Note the change of scale. (d) shows an expanded view of (c), with the free lasing background evident.

After turning on the first Pockels cell crystal, injection is optimized by aligning the injection optical path and adjusting the synchronization timing. Fig. 5.7 (b) shows the free-lasing output when the injection is optimized. This output corresponds to amplification of a small portion, about 25 pulses, of the 80-MHz pulse train that fits within the free-lasing output pulse envelope. The amplified pulses in Fig. 5.7 (b) ‘sit’ on top of a background free-lasing pulse of diminished amplitude compared to Fig. 5.7 (a). The Pockels cell ejection crystal is next turned on, and optimized by adjusting the ejection timing and voltage. The resulting output pulse is shown in Figs. 5.7 (c) and (d). Note the factor of ten increase in amplitude of the output. The output is higher in amplitude after ejection because the output coupling
from TFP2 is switched from 2% to 84% by the Pockels cell/polarizer combination. Note that in the expanded scale, one still sees some small pre-pulses and a free-lasing background present. The pre-pulses and free-lasing background are smaller in amplitude by a factor of $15 \times$ and $80 \times$, respectively, compared to the ejected pulse.

![Graph](image)

**Fig. 5.8** Autocorrelation of amplified pulse. Circles are data. Solid line is a fit assuming a Gaussian pulse of 100-fs FWHM.

The final step of amplifier operation is to adjust the Nd:YLF laser once more to optimize the ejected mode’s spatial profile. The stretcher and compressor are then adjusted in tandem to produce the shortest amplified pulse. The entire process takes a few hours each day, and results in a stable, experiment-ready operation that requires minor adjustments every few hours to maintain.

Our system performance compares favorably to one commercial design (Clark Laser) recently installed at Harvard. Our system produces 15% lower output energy, but is more easily tunable and produces pulses that are routinely compressible below 100-fs. The Clark system design has a narrower bandwidth which limits their pulsewidths to $\geq 130$-fs.
5.5 Future Improvements

As noted above, we recently made minor changes to the cavity layout which increased the output energy to 1.2 mJ, before compression, for a 5-mJ pump. The major change was the use of tighter pump beam focusing in the Ti:sapphire crystal, and the use of a 50-cm radius of curvature high reflector at 15-cm distance from the crystal to produce a smaller cavity mode closer to the saturation fluence. This cavity was also extended to 11-ns round trip time to allow use of a Q-switching-type Pockels cell (ConOptics 25D). We switched Pockels cells for practical reasons (our other cell needed repair), and do not observe major differences in amplifier performance as a result of using this other type of Pockels cell. As noted above, one advantage of this design is that the amplifier does not free-lase at all.

One future system enhancement we have planned is to use thin-film polarizers with higher s-polarized reflectivity when they become available. This will result in an immediate improvement in output energy proportional to the increase in s-polarized reflectivity.
References:

Chapter 6

UHV chamber

6.1 Overview

This chapter describes the surface-science ultrahigh vacuum chamber (UHV) apparatus constructed for a long-term series of planned laser-induced surface reaction experiments. The purpose of the chapter is to chronicle and detail the design of this facility to provide a general reference for future users of the equipment.

6.1.1 Motivation

Experiments which require an atomically clean crystal surface such as those described in Chapters 3 and 4 must be performed under UHV conditions. Elementary kinetic theory predicts a surface impact rate of gas molecule (mass \( m \), at temperature \( T \) and pressure \( P \)) given by [1]:

\[
\text{surface impact rate} = \frac{P}{(2\pi mk_B T)^{1/2}} \quad (6.1)
\]
which implies that the equivalent of one monolayer ($10^{15}$ cm$^{-2}$) of N$_2$ molecules will strike a surface at an ambient pressure of $10^{-8}$ torr in only three minutes. At a base pressure of $5 \times 10^{-11}$ torr, this time is increased to over ten hours. This is ample time for laser probing of tens of spots on an uncontaminated sample.

### 6.1.2 Organization of chapter

The chapter is divided into two parts. The first describes the design and construction of the UHV chamber; the second gives a brief discussion of the general methodology of chamber operation and Pt sample cleaning.

### 6.2 Design and Construction

#### 6.2.1 Design considerations

Our chamber is designed to allow standard surface science characterization as well as optimal optical access to the sample for spectroscopy experiments. In particular, we want to have the following two capabilities: (1) positioning of the sample close to an optical quality window so that lenses can be located outside the chamber within a few inches of the sample (this allows tight focusing on the sample without significant beam expanding before focusing), and (2) positioning of the sample such that near-grazing incidence spectroscopy could be simultaneously performed with normal incidence optical pumping. This is necessary particularly for infrared spectroscopy or surface plasmon spectroscopy.

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1History of construction: Design of a planned surface science chamber began with the arrival of Dr. W. Mieher, to the Mazur group in January of 1992. A final design, completed primarily by Dr. Mieher, was completed in early spring of that year, and construction began in the summer with the author's return from AT&T Bell Labs, and the arrival of new UHV equipment. The chamber was fully operational, with a cleaned Pt sample in UHV, by February, 1993. Since that time, numerous improvements and modifications have been incorporated, motivated by experimental requirements. Major improvements in the gas handling system, including the addition of an automated sample cleaning system, were completed in the second half of 1993 by two new graduate students in our group, R.J. Finlay and T.H. Her.
Another consideration is that we need to be able to perform optical experiments on a sample positioned in front of the mass spectrometer. This is the configuration for the experiments of Chapter 4. For this case we relaxed the restriction of short-path-length optical access.

Additional design constraints are: (1) numerous surface science instruments need to be located in a convenient way to allow sample cleaning, preparation and characterization, (2) the chamber design and sample mount must be mechanically stable to avoid sample motion (i.e. sway or vibration), and (3) we have limited space in which to locate several bulky, large, heavy pieces of equipment (ion pump and sublimator, turbomolecular pump and gate valve, sample manipulator) and yet we want to be able to physically work very close to the chamber windows for aligning optics.

To satisfy these constraints, we opted for a slim, vertical, two-level design. The upper level is a surface-science level, which incorporates the LEED/Auger and mass spectrometers, sample preparation instruments, sample manipulator, and turbomolecular pump. The lower level is an all-optical level, composed of a six-inch cube with four 4"-diameter windows. The sample is lowered to this level via a sample manipulator translation stage. Below the cube, we located the bulky ion pump which also serves as a ballast weight to stabilize the top-heavy upper level. This design works well, meeting all our design requirements.

### 6.2.2 General description

Figure 6.1 shows a sketch of the chamber and its two-level design. Figure 6.2 shows a top view of the chamber upper level. The upper level is an 11" diameter spherical chamber which accommodates a mass spectrometer (UTI 100 C) on a translation stage, a LEED/Auger spectrometer (Omicron SPECTALEED) also on a translation stage, a ion gun for sputtering, a turbomolecular pump (Balzers TPU 180 H) and gate valve (VAT Series 10), several optical viewports, gas leak valve ports including a capillary array doser,
and an ion gauge. Both spectrometers, the sample doser, the turbo pump and (most of the) optical windows are located in a single horizontal plane on the upper level. The sample is mounted on a 16" vertical travel $x, y, z, \theta$ sample manipulator (VG) which is attached to the top port of the sphere. The sample manipulator is sketched in Fig. 6.3. The 16" travel allows vertical translation of the sample between upper and lower levels. The base of the cube level is located at the height of an optical table (Newport), upon which the chamber legs are also mounted. Through a hole in the center of the optical table, an ion pump (Perkin Elmer), a Ti sublimator with LN$_2$ shroud, sorption pumps, and an ion gauge are attached to the upper chamber via the bottom of the cube. The entire structure is about ten feet tall.
6.2.3 Major components

6.2.3.1 Vacuum Pumps

Ultrahigh vacuum pressures are achieved by pumping the chamber with several types of pumps: a turbomolecular pump (180 l/s), an ion pump (270 l/s) and a Ti sublimator pump with LN2 shroud. LN2-cooled sorption pumps (Perkin-Elmer) are used to initially pump the chamber down to the millitorr range from atmospheric pressure. Depending on the desired mode of operation, one or all of the pumps may be pumping on the chamber. Note that we have chosen to use only oil-free pumps; the turbomolecular pump is backed by an oil-free diaphragm pump. Using oil-free pumps ensures clean chamber conditions, avoiding the possibility of surface contamination by hydrocarbons typically found in pump oils.

The ion pump is useful for maintaining base pressure. It is not backed by any pump, and is sealed to UHV even when the pump is off. In situations where it is desirable to close off the turbo pump, the ion pump can maintain UHV. This is useful especially for overnight periods, during which we often close the gate valve and isolate the turbo pump from the
chamber, in order to avoid the possibility of a chamber vent during a power failure. The ion pump, which is the base of the entire chamber structure, is supported by a spring-loaded frame attached to the optical table stand. The tension in the springs is adjusted to take up some of the weight of the chamber. This attachment minimizes torque placed on the center attachment point of the chamber at the optical table.

![Diagram of sample manipulator, side view.](image)

**Fig. 6.3** Sample manipulator, side view.

The turbomolecular pump is the primary pump for pumping down the chamber from millitorr pressures after initial pumpdown with the sorption pumps. This pump is backed by a diaphragm pump with an unusual design pressure of only about 2 torr. A gate valve is positioned so that the turbo pump can be sealed off from the chamber. This valve has a pneumatic actuator which automatically seals the chamber if the wall power is shut off, which is intended to prevent chamber venting when a power failure occurs (although we often take the additional precaution of closing the gate valve at night as mentioned before). The close proximity of the turbo pump to the sample and mass spectrometer
positions on the upper level is ideal for ensuring rapid removal of desorption products during TPD or laser desorption experiments.

The Ti sublimator pump is effective for pumping reactive gases, especially hydrogen which is not effectively pumped by the turbo or ion pump. It operates by flashing a hot Ti filament, evaporating a layer of reactive Ti onto the surrounding LN2-cooled shroud. This layer reactively absorbs gas in the chamber to the shroud surface. This type of pumping action is referred to as ‘gettering’. The sublimator pump is effective during initial pumpdown, as well as during ion sputtering of the sample, when the ion pump is shut down and the chamber is backfilled with Ne gas. In this case the sublimator pump helps keep the Ne gas free of contaminants as they are sputtered off the sample. A minor disadvantage of our chamber design is that we needed to install a protective shield in front of the lower level ion gauge (located opposite the sublimator) to prevent Ti from the sublimator from evaporating onto the ion gauge filaments.

### 6.2.3.2 Mass Spectrometer

The UTI mass spectrometer has an open ion source and quadrupole design. It is used for three applications: (1) performing background scans for characterizing the chamber vacuum, (2) collecting desorption data during temperature-programmed desorption (TPD) sample characterization, and (3) for direct single-molecule detection in the laser-induced desorption measurements. For (1) and (2), the spectrometer amplifier is usually run in low-gain (1-kV multiplier bias) mode, using the supplied signal amplifier electronics. For (3), we have modified the spectrometer to operate in a pulse-counting mode at high gain (1.4-kV channeltron bias — see Chapter 4).

We replaced the standard spectrometer filament with a thoriated irridium (ThO₂/Ir) filament. This type of filament has the lowest O₂ consumption of the types available (see UTI manual p.III-10). We replaced the supplied electron multiplier with a Channeltron™ multiplier. This amplifier produces shorter pulses, 5-ns, more suitable for
pulse-counting mode operation. As described in Chapter 4, we also added a floating screen in front of the spectrometer to capture the 70-eV electrons emitted from the open ion source.

For background and TPD scans, we wrote a LabView™ software interface that remotely programs the mass setting and reads the mass signal. For pulse counting mode, we directly amplify the signal using the amplifier and discriminator electronics described in Chapter 4 (Sect. 4.3.3).

One point of note for future users of this apparatus is the relatively long pump-out time we observed when using the mass spectrometer for the experiments in Chapter 4. Apparently the ion-source is located such that once molecules enter the ionization region, they bounce around for as long as 20 ms before being either ionized or pumped out. Furthermore, the large size of the ionizer prevents a short time-response. This prevents us from performing time-of-flight measurements to obtain kinetic energy distributions for the desorption products. Recommended modifications for such an experiment include adding differential pumping and using a smaller ion source to reduce the time response to < 1 µs. Note that commercial mass spectrometers which are designed specifically for time-of-flight measurements cost about $40k compared to $13k for our UTI mass spectrometer.

6.2.3.3 LEED/Auger

The Omicron combination reverse-view LEED/Auger spectrometer is installed as supplied (no modifications). We note that the Auger performance of the combo LEED/Auger spectrometer is not as good as that expected from single dedicated devices; however the combined unit costs about half as much as two separate units and takes up only one port on the chamber.

Two points of note to the future users of this device:

1. Use extreme caution when operating the unit due to the fragile nature of the filament. It is very hygroscopic and is easily contaminated if operated at pressures over $10^{-8}$
torr. Furthermore, note that the current must be very slowly ramped through the filament, and that obtaining emission is occasionally a problem which necessitates forming of the filament at high current (see manual).

(2) Due to a manufacturing error, the unit is mounted via threaded rods which hold both the spectrometer unit and the rear view window to the translation stage. A better design would be to use separate bolts to hold the unit to the chamber, and to attach the window to the unit. Use extreme caution when loosening the outer flange nuts because loosening these allows the entire unit to come loose from the chamber.

6.2.3.4 Gas handling and capillary array doser

We constructed a gas handling system for admitting precise amounts of gases into the chamber for sample cleaning and dosing. The system can be pumped by a rough pump or turbo pump depending on base pressure desired. An interesting feature of our setup is the use of automated variable-leak valves (Granville-Phillips VLV Series 216) in a computer-controlled sample cleaning system. The repetitive nature of the sputter/anneal cycles required for sample cleaning are labor intensive and prone to human error. Given the effort required to ready the laser system for a measurement, and the need to have the sample clean and dosed when the laser is ready, we designed and constructed an automated cleaning system. The remotely controlled variable leak valves come equipped with a PID controller which reads the ion gauge signal to determine the chamber pressure and control the pressure in a feedback loop. The computer is interfaced to a variety of relays via National Instruments interface boards which allows pre-programmed opening and closing of the VLV’s and gate valve, as well as control of the sublimator, ion gun, sample heater, and ion gauges.

To facilitate dosing of the sample without a significant increase in chamber pressure, we use a doser of the type developed in W. Ho’s group at Cornell [2]. The device is a gas inlet attached to a manual variable leak valve (Granville Phillips) at one end and to a 1-cm
diameter glass capillary array (Galileo) at the other. The array ensures a laminar directed
flow of gas onto the sample, which is positioned to within a few millimeters of the array.
The doser is mounted on a 4" translation stage which allows precision positioning and
withdrawal of the array to a safe distance (this prevents accidentally crashing the sample
into doser during routine sample positioning).

6.2.3.5 Sample manipulator and sample mount

Mounted atop the upper chamber sphere, the sample manipulator (VG) provides $xy$-
translation in the horizontal plane with precision micrometers, motorized $z$-axis vertical
motion with 16" travel, and motorized rotary motion. The rotary stage is differentially
pumped by a turbo pump. This is necessary for achieving pressures of less than $10^{-10}$ torr.
The rotation stage is always rotated at a controlled speed to keep the pressure rise in the
differential manifold below $1 \times 10^{-6}$ torr; if rotated faster, a pressure rise in the chamber is
observed. We constructed a 36" long LN$_2$ dewar from a 1.5" diameter stainless pipe sealed
at the bottom end by a copper plug. The dewar is mounted inside the manipulator from the
top manipulator flange, and the sample mount (see next section) is attached to the dewar
base via two tapped holes in the copper plug. The top of the dewar is capped to prevent
water condensation inside. The dewar is kept filled with LN$_2$ throughout the course of an
experiment. A feedthrough mounted on a top flange of the manipulator allows electrical
connections to be made to the thermocouples and heater leads on the sample mount. All
wires used are insulated in teflon tubing; the wires are wrapped around the dewar as they
wind down to the sample. Wrapping the wires around the dewar cools them, which
prevents heating of the sample.

The sample mount is constructed of a right-angle shaped copper piece attached to
the bottom half of a two-piece dovetailed block. This design places the sample at an offset
from the chamber center, allowing closer positioning of the sample to the cube windows.
The dovetail is designed to allow interchanging sample mounts by horizontally sliding one
mount out and another in place. The 1.00-cm diameter Pt crystal is clamped in a tantalum clamp which is also attached around a 0.5-cm diameter button-style resistive heater (Spectra-Mat) so that the sample is held in direct thermal contact with the heater but also has excellent thermal contact to the heater through the tantalum clamp. The ground post of the button heater slides through a hole in the right angle copper piece and is held in position by a screw. This grounds the sample to the chamber, although this grounding could be eliminated in principle by electrically isolating the dovetail mounts from the dewar using sapphire washers. All thermal contact from sample to dewar is through the button heater post.

Thermocouple junctions are directly spot welded to the sides of the sample and clamp for measuring sample temperature. The sample mount design allows rapid heating of the sample to a 1100 K annealing temperature in about 1 minute, and subsequent cooling to base temperature of 95 K within 10 minutes. The limited thermal contact between heater and dewar limits the amount of LN2 evaporated when annealing the sample. A one-minute 1100 K anneal results in no measurable change in the temperature of the copper plug at the base of the dewar.

6.2.3.6 Lower level cube

The all-optical cube level affords a wide 50° angular access to the sample through any of the four windows when the sample is positioned at the minimum distance of about 1" from a window. Backing the sample away from a window allows grazing incidence (> 70°) access to the sample from two windows on either side of the sample and simultaneous 30° access around the normal from the window facing the sample.

2The future addition of a load-lock to the chamber may take advantage of this design feature, but currently no system exists for plugging and unplugging the numerous required electrical contacts.
The windows are mounted in differentially-pumped, O-ring sealed mounts backed by a rough pump. These mounts allow changing the windows with whatever materials are appropriate for the wavelength range of an experiment, which is a much cheaper and more flexible arrangement than using large commercially-available glass-to-metal sealed windows. These mounts are less failsafe however. One of the four original mounts was manufactured with incorrect O-ring grooves, which prevented us from pumping on the differential space for that window mount. Although the window still sealed to UHV to about $1 \times 10^{-10}$ torr, a significant mass 32 O$_2$ background was present until the seal was fixed.

### 6.2.4 Future modifications

Depending on planned experiments a number of future modifications have already been considered, including changing the mass spectrometer design and sample mounting. The chamber is designed to accommodate a load lock system on the upper level to allow sample switching in UHV, and room also exists to add a cylindrical mirror analyzer (CMA) or time-of-flight electron measurement apparatus (cf. Chapter 3) to allow photoemission measurements. Another possibility is the addition of a cleaving device to allow study of clean semiconductor surfaces.

### 6.3 Methodology

For the sake of completeness, a few highlights of standard UHV methodology are outlined here.

#### 6.3.1 Obtaining UHV

In assembling the UHV chamber, a careful cleanliness protocol is observed. No ungloved hands are to come in contact with internal chamber surfaces to avoid contamination with dust and oils. All copper gaskets are cleaned in acetone and then
methanol before use. All internal chamber parts are similarly cleaned, often by first soaking in acetone if practical. Effort is made to prevent any dust from settling in the chamber.

To pump down the chamber from atmospheric pressure to the millitorr level, the sorption pumps are used. The chamber is then sealed from the sorption pumps by a torque-wrench tightened gold-seal valve. The turbo pump is run overnight to achieve pressures in the $10^{-8}$ range. Then the chamber is heated up to 150 °C on all surfaces by the use of heating pads and tape, and the built-in heaters on the ion pump and turbo pump. Heating is enhanced by wrapping the entire chamber in Al foil; this procedure is known as a ‘bake’. A typical bake lasts for four days; at the beginning and end of each bake all the instrument filaments (except the LEED filament\(^3\)) are flashed (sublimator, sample heater) or run for several hours (ion gun, mass spectrometer) to degas them. After a successful bake, base pressures in the $10^{-11}$ range are routinely achieved. The reverse process of pumpdown, venting the chamber, is performed with dry nitrogen to reduce water vapor accumulation in the chamber.

Following pumpdown and baking, the chamber is always leak tested by tuning the mass spectrometer to the He mass and blowing He around all the chamber flanges and bellows. We note that for our chamber, this is best performed either very quickly or with the gate valve shut because the diaphragm backing pump allows a slow He leak back through the turbo pump. If this procedure is not followed, a slow He leak will appear to be present.

### 6.3.2 Sample Cleaning

Once UHV is achieved, the sample needs to be cleaned to achieve an atomically clean single-crystal surface. For Si, this procedure only requires a flash anneal (see Chapter

\(^3\)The LEED filament must be at room temperature in order to safely degas it.
3), or for a heterogeneous semiconductor, a cleave of the sample bar. For many metals, including Pt, a number of sputter anneal cycles are required.

Preparation of clean Pt(111) samples in UHV is as follows [3]. A sample that has been exposed to air will have an oxide layer on the surface, plus contamination by carbon, calcium and phosphorous. It has been found that annealing and subsequently cooling the sample in UHV causes contaminants in the near surface region to segregate on the surface. Heating in oxygen ($5 \times 10^{-8}$ torr) further helps accumulate contaminants on the surface as an oxide, preventing them from penetrating back into the sample surface as the sample cools following an anneal. This is useful, because these oxidized contaminants on the surface can then be removed by bombarding the sample (sputtering) with energetic Ne ions from the ion gun. This impact of Ne ions knocks the contaminants off the surface. Typically one cleaning cycle involves an anneal in oxygen to 1100 K for one minute, followed by sputtering with 0.5-kV Ne ions for 5 minutes (99.999% pure Ne; chamber backfilled to $5\times10^{-5}$ torr; 25-mA gun emission current, giving a $6\mu$A current to the sample). Sputtering the sample for a long time is thought to produce surface damage which can be annealed out; however longer sputters (10 minutes) are performed while the sample is hot (900–1000 K) to help reduce surface damage. Multiple cycles (on the order to 20 to 100) are required to be able to observe a clean Pt surface following a vent. A clean Pt(111) surface is characterized in our chamber by a sharp (111) LEED pattern and a good O$_2$ TPD spectrum (150 K and high temperature peaks visible and highly reproducible between cleaning cycles; see Ch. 4 Fig. 4.1).
References:

I learned this, at least, by my experiment; that if one advances confidently in the direction of his dreams, and endeavors to live the life which he has imagined, he will meet with a success unexpected in common hours. Thoreau, *Walden*

Chapter 7

Conclusions

7.1 Summary of results

In part one of this thesis we presented results from three experiments. In Chapter 2, we described time-resolved vibrational spectroscopy of SO$_2$ and SF$_6$. In SO$_2$ we observe direct $\nu_1$-mode excitation; we are also able to distinguish between excitation of the $\nu_1$-mode and excitation of the nearly resonant $\nu_2$-mode overtone. In SF$_6$, we directly observe $\nu_3$-mode excitation followed by collisional energy redistribution to a heat bath of non-pumped modes. Quantitative modeling of the SF$_6$ spectra yields excited vibrational population distributions and resolves some long-standing inconsistencies between different previously published reports. In Chapter 3 we used time-resolved photoelectron spectroscopy to determine the subpicosecond evolution of an optically-excited hot-electron distribution in silicon. We observe an electron thermalization time of less than 120 fs, electron equilibration with the lattice in 1 ps, and an energy-dependent electron cooling rate consistent with published calculations of the electron-phonon scattering rate. The results
indicate the formation in 1 ps of a surface space-charge electron layer with an electron density two orders of magnitude greater than the bulk electron density. In Chapter 4 we presented the results of 100-fs laser-pulse-induced desorption of O₂ and reaction of O₂/CO to form CO₂. We presented desorption and reaction data obtained over an absorbed fluence range of 1–20 mJ/cm² at wavelengths of 800, 400, and 266 nm. We report the desorption and reaction fluence dependence at 800 nm and 400 nm, and the ratio of O₂ to CO desorption at all three wavelengths. At 800 nm, the desorption and reaction are independent of laser pulsewidth in the range 100 fs to 3.6 ps.

In part two of the thesis we described the design and operation of an amplified femtosecond Ti:sapphire laser (Chapter 5), and an ultrahigh-vacuum surface-science chamber (Chapter 6). In both chapters we discussed how specific design features necessary for laser studies of surface reactions in ultrahigh vacuum were incorporated.

### 7.2 Future prospects

In Chapter 1 of this thesis, we showed that all three of the experiments described here are part of a larger experimental goal: the characterization of the intermediate state(s) of a surface reaction. In this final section of the thesis, we discuss how the results presented here may help lead to the realization of time- and state-resolved surface reactions.

Chapter 4 showed that 100-fs laser pulses initiate surface reactions by a substrate-electron mediated excitation mechanism. We demonstrated the use of 100-fs pulses to initiate the reaction O₂+CO→CO₂ on a Pt(111) surface. As discussed in Chapter 4, this reaction proceeds either (1) via dissociation of adsorbed O₂ leading to hot O reaction with adsorbed CO, or alternatively, (2) via excited molecular O₂ reacting with CO. In case (1) dissociation of O₂ creates a hot O atom which translates along the surface and collides with an adsorbed CO to form an O–CO intermediate, which then desorbs as CO₂. This possibility is discussed in Ref. [1]. In case (2) an electronically or vibrationally excited O₂
molecule reacts with a neighboring CO molecule. We believe that in this case the reaction proceeds via an \((\text{O}_2)\)–CO intermediate from which \(\text{O}_2\) dissociates and \(\text{CO}_2\) desorbs, as suggested in Ref. [2]. In either case, the vibrational energy of the adsorbed CO molecule’s C–O stretching mode will change during the reaction on a ps timescale.

Time-resolved spectroscopy can be used to identify the intermediate state. Chapter 2 showed that multiplex coherent Raman spectroscopy can time-resolve the vibrational excitation of a molecule in the gas phase. It has been demonstrated that coherent Raman spectroscopy is applicable to state-resolved detection of surface species [2]. The question that arises is: can time-resolved multiplex CARS be performed with 100-fs time-resolution and with sufficient sensitivity to detect a monolayer surface coverage of CO on Pt(111), and can such a measurement detect the changes in the C–O stretching mode as a reaction occurs? We estimate the surface multiplex CARS signal level to be within a few orders of magnitude of the CARS signal levels obtained in the SF\(_6\) experiments\(^1\); such signal levels are measurable using existing detection techniques. Note that coherent Raman spectroscopy on metal surfaces produces a large non-resonant background [2, 5] which needs to be reduced in order to detect weak signals. We have planned preliminary experimental tests of the

\(^{1}\)In the CARS measurements of SF\(_6\), the weakest multiplex CARS spectrum was obtained integrating 1000 laser shots at position \(z/D = 4.1\) in the free jet expansion. From Lubman, et al. Eq. 26 [3], the number density in the jet at this position was \(10^{17}\) cm\(^{-3}\) for our apparatus (see Ch. 2, p. 15). For an \((80-\mu\text{m})^2 \times 0.1\text{-cm}\) interaction volume, this implies a sample of \(10^{12}\) molecules. The CARS signal power, \(P\text{CARS}\), in watts goes as \(P\text{CARS} \propto (n\chi^{(3)})^2P^3/A^2\) (see Ref. [4]) where \(n\) is the number of molecules, \(\chi^{(3)}\) is the Raman susceptibility, \(P\) is the probe power, and \(A\) is the probed area. Scaling the probe beam intensities from the SF\(_6\) experiment (\(10^6\) W incident on a \(10^{-4}\) cm\(^2\) spot), we see that for a 1-cm\(^2\) spot, one needs \(10^8\) W to achieve the same signal power. This probe power is easily reached with femtosecond pulses (\(10^8\) W = \(10\) \(\mu\text{J}\)/100 fs). An adsorbate coverage of \(10^{12}\) molecules/cm\(^2\) corresponds to \(10^{-3}\) monolayer. Thus if the adsorbate has the same Raman cross-section as SF\(_6\) we should be able to detect the CARS spectrum of \(10^{-3}\) monolayers of reaction product using a room-temperature CCD detector by integrating 1000 shots. If the reaction product has an order of magnitude smaller cross-section than SF\(_6\), the signal will be \(100\times\) smaller, requiring integration for \(10^3\) shots, or 100 seconds at a 1-kHz repetition rate. Using a cooled CCD array or photomultiplier tube would allow detection of even weaker signals.
sensitivity of surface-CARS. In these upcoming experiments, we will investigate small-signal detection techniques and methods to reduce the non-resonant background.

If multiplex-CARS can time-resolve changes in the C–O stretching-mode frequency in an adsorbate monolayer, then the goal of time-and state-resolving the O₂+CO reaction can be realized. The experiment requires initiating the reaction with a pump laser pulse, preferably at a wavelength which favors CO₂ production over O₂ desorption. Chapter 4 showed that using UV wavelengths optimizes the CO₂ yield. The reaction products would be probed by multiplex CARS in order to observe the CO vibrational excitation. As the reaction proceeds, the vibrational frequencies will shift and new modes will appear. If for example, the \( \omega_1 \) and \( \omega_2 \) CARS beams are tuned to detect the C–O stretching frequency of gas-phase CO₂, no signal would be observed until CO₂ begins to form and desorb. Complementary data can be obtained by tuning the CARS frequencies to the C–O stretch energy of adsorbed CO and observing the frequency shift or decay of the CARS signal as CO+O reacts and desorbs. For both measurements, the \( \omega_2 \) beam must be shifted by tens of nanometers from the fundamental 800-nm wavelength; we are in the process of building an optical parametric amplifier which will generate tunable 100-fs pulses suitable for this experiment.

As suggested in Chapter 4, observing the ‘birth of a surface molecule’ would be greatly facilitated if a co-adsorbate system can be found that has a reversible reaction process. This would allow repeated laser probing of the same spot on the sample, with each probe pulse measuring the same initial conditions. For example, a system A+BA in which an A–B–A intermediate forms, but then relaxes back to the original A+BA state within a few hundred ps would allow repeated probing of the reaction intermediate at kHz–MHz rates so that signal averaging techniques can be used to improve the signal-to-noise ratio. While
the CO/O\textsubscript{2}/Pt(111) system is not ideal in this case, no reversible reaction system has been identified so far that is suitable.\textsuperscript{2}

Interpretation of time-resolved CARS spectra of the O\textsubscript{2}+CO reaction requires additional experimental and theoretical work. Theoretical estimates of the intermediate state C–O mode frequencies will be useful for analyzing the CARS spectra. Also, it will be necessary to model the process by which the laser initiates the reaction, as discussed in Chapter 4. To fully understand a substrate-electron-mediated reaction mechanism, the substrate electron energy distribution must be characterized. Time-resolved photoemission, discussed in Chapter 3, has been used to measure electron distributions in a metal [6]; this technique could be applied to characterize the electron distributions created by our 100-fs pump pulses.

We conclude therefore that while experimental and theoretical challenges remain, the results presented in this thesis indicate that work already set in motion will successfully apply time-resolved spectroscopy to directly observe a surface reaction intermediate.

References:


\textsuperscript{2}We note that one advantage of the CO/Pt(111) system (no O\textsubscript{2} co-adsorbed) is that CO does not desorb upon photoexcitation, making it a useful, stable, test case for measuring surface-CARS sensitivity.