# Ultrafast Dynamics and Optical Control of Coherent Phonons in Tellurium

A thesis presented

by

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 $\operatorname{to}$ 

The Department of Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the subject of

Physics

Harvard University Cambridge, Massachusetts December 2003 C2003 by Christopher Allan Dewald Roeser

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# Ultrafast Dynamics and Optical Control of Coherent Phonons in Tellurium Eric Mazur Christopher A. D. Roeser

#### Abstract

This dissertation reports the ultrafast dynamics of tellurium after excitation by one or more intense femtosecond laser pulses. Irradiation of tellurium by femtosecond pulses is known to excite coherent phonons, but the nature of the excitation process and the details of the material dynamics under intense excitation are, as of yet, not precisely determined. We investigate these dynamics by monitoring the response of tellurium using an optical pumpprobe technique designed to measure the dielectric tensor across the visible spectrum with femtosecond time resolution.

The observed dynamics are similar to the ultrafast dynamics of molecules, where photoexcitation of electrons establishes a new potential surface on which the nuclei move. The time-resolved dielectric tensor measurements provide a "snapshot" of the material in a particular lattice configuration. From the observed changes in the optical properties, we infer the underlying changes in the lattice, and thereby develop a picture of the nuclear motion.

We find that the main resonance for interband electronic transitions in tellurium shifts to lower photon energy due to the lattice displacement that results from photoexcitation. Under single pulse excitation, a rapid change in the equilibrium lattice configuration leads to a long-lived shift in the resonance energy along with fast oscillations around this value. Under double pulse excitation, the lattice dynamics can be controlled; we achieve both enhancement and cancellation of coherent phonons for excitation strengths up to the damage threshold.

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# Acknowledgements

I write these acknowledgements ten days after my defense and nearly a month after completing the dissertation itself. While my time as a graduate student has come to an end, tradition and my own appreciation urge me to thank those people that made my graduate life fulfilling and my post-graduate life promising. My advisor, Eric Mazur, is the architect of a research group that functions like no other group I have seen. He creates an atmosphere of collegiality among students, post-docs, and visiting scholars where new ideas are welcome, where discussion is paramount, and where responsibility is shared. From experience I can say that students mature quickly, the independence afforded not unlike a "trial by fire" at times and the result being that no one is left feeling ill-prepared for their next step. I also wish to thank my fellow graduate students and the other members of the Mazur group — both here in Cambridge and abroad — for their support and friendship. Their respect means more to me than they probably know, and that respect is returned one hundred fold. I measure the value of the completion of my dissertation by the promise of my post-graduate life, both personal and professional. Over the past few years I have been fortunate to have the time to live a life outside of research. That life includes two loving parents, a brother that I would love to know better, a wife that I love more and grow to know better every day, and a host of dear friends. Words cannot convey the importance of those relationships — my life would be incomplete without them.

Chris Roeser Cambridge, Massachusetts December, 2003

### Acknowledgements of Financial Support

This thesis is based on work supported by the Army Research Office under contract DAAG55-98-1-0077 and by the National Science Foundation under contracts DMR-9807144 and DMR-0303642.

# **Citations to Published Work**

Parts of this dissertation cover research reported in the following articles:

- C. A. D. Roeser, M. Kandyla, A. Mendioroz, and E. Mazur, "Optical control of coherent phonons in Te," *submitted to PRL*, 2004.
- [2] C. A. D. Roeser, A. M.-T. Kim, J. P. Callan, L. Huang, E. N. Glezer, Y. Siegal, and E. Mazur, "Femtosecond time-resolved dielectric function measurements by dual-angle reflectometry," *Rev. Sci. Instrum.*, vol. 74, p. 3413, 2003.
- [3] A. M.-T. Kim, C. A. D. Roeser, and E. Mazur, "Modulation of the bonding-antibonding splitting in Te by coherent phonons," *Phys. Rev. B*, vol. 68, p. 012301, 2003.
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For Therese — and everyone else —

who has made me who I am.

I will be so brief I have already finished.

SALVADOR DALI

# Chapter 1

# Introduction

The work presented in this dissertation, while focused specifically on the dynamics of tellurium, falls within the scope of ultrafast materials science. An emerging field at the time of writing, ultrafast materials science lies at the crossroads of femtosecond optics and condensed matter physics. At its most basic level, the research carried out in this field involves using femtosecond laser pulses to initiate and probe (with sub-picosecond time resolution) phase transitions already known to traditional condensed matter physicists and materials scientists. The transition from a metal to an insulator with decreasing temperature or with increasing disorder is known to occur for many materials, but the rapidity with which these transitions can occur has only recently been observed.<sup>1</sup>

The recent emergence of ultrafast materials science as a *bona fide* field of research is partly due to the development and commercialization of reliable femtosecond laser systems. In the early days of femtosecond optics, the sought-after phase transition was not unlike the speech by Salvador Dali on the previous page: it is finished too quickly to be dissected. The push toward laser pulses of ever-shorter duration eventually provided researchers with

<sup>&</sup>lt;sup>1</sup>See, for example, the dynamics of GaAs in Section 3.3, where the semiconductor becomes metallic within a few picoseconds.

the tools to observe a material *during* its phase transition, rather than simply before and after. The commercialization of these laser systems will alleviate the requirement that one be a true "laser jock" in order to produce cutting-edge research, although that requirement remains for the most part today.

Although the dynamics we initiate in tellurium with femtosecond laser pulses do not lead to a phase transition, the material does approach a semiconductor-semimetal transition, *i.e.*, an indirect band crossing. Photoexcitation of tellurium excites coherent symmetry-preserving  $(A_1)$  phonons and the lattice displacement associated with this phonon mode drives the material toward a semimetallic state. Theoretical calculations of the tellurium band structure for lattice displacements along the  $A_1$  mode allow us to link the observed changes in optical properties with the underlying changes in the material. Thus, while in many ways a typical study in ultrafast materials science, the work presented here is atypical in the sense that theoretical and experimental results join together to an unprecedented degree.

### **Organization of the Dissertation**

Chapter 2 is a review of selected topics in optics and condensed matter, whose aim is to familiarize the reader with the central issues of ultrafast materials science. We discuss the relationship between the linear optical properties and the band structure of solids, the dynamics known to occur in molecules and the analogous dynamics in solids, and some nonlinear optical processes.

Chapter 3 describes the details of the experiment. This chapter leads the reader through the process of measuring the time-resolved dielectric tensor of a solid, from determining the time resolution of the setup to how the error in our measurements is minimized. We discuss examples of how our technique is used to investigate phase transitions in semiconductors.

Chapter 4 reviews recent work on tellurium that is relevant to our results. The information obtained through analysis of our dielectric tensor data is amplified in the context of previous theoretical and experimental results, particularly the density function theory calculations of tellurium with a displaced lattice.

Chapters 5 and 6 present the dynamics of tellurium under intense femtosecond pulse excitation. We observe oscillations in the dielectric tensor that are mainly described by a redshift and oscillation of the main resonance at the frequency of the  $A_1$  phonon mode. Using two pump pulses, we demonstrate both enhancement and cancellation of the coherent lattice vibrations, so-called "coherent control."

# Chapter 2

# **Optical Properties of Solids**

The subject of electromagnetism in the presence of matter is both extensively studied and rich in diverse phenomena. It spans such topics as the quantization of the electromagnetic field to the semiclassical treatment of light-matter interactions to the derivation of the Fresnel reflectivity formulas. The justification for presenting an overview of the subject is somewhat obvious — the theoretical foundations that support the interpretation of experimental results should be made clear, however the long history of optics and condensed matter physics preclude any sort of comprehensive review. Accordingly, this chapter presents a distillation of the theoretical origins of the optical properties of solids.

## 2.1 Light-matter interactions

Fundamental to any description of light–matter interactions are Maxwell's equations [1],

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{2.1}$$

$$\nabla \times \mathbf{H} = -\frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$$
(2.2)

$$\nabla \cdot \mathbf{D} = \rho \tag{2.3}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{2.4}$$

where, along with the usual field terms,  $\mathbf{E}, \mathbf{D}, \mathbf{B}$ , and  $\mathbf{H}$ , are the source terms of charge  $\rho$ and current  $\mathbf{J}$ . The influence of matter is cast in terms of constitutive relations among the fields,

$$\mathbf{B} = \mu_0 \mu \mathbf{H} \tag{2.5}$$

$$\mathbf{D} = \epsilon_0 \epsilon \mathbf{E} \tag{2.6}$$

$$\mathbf{J} = \sigma \mathbf{E} \tag{2.7}$$

for which the vacuum (matter-less) conditions are  $\mu \to 1$ ,  $\epsilon \to 1$ , and  $\sigma \to 0$ . As written, the equations are essentially linear, in that an applied **E** field of frequency  $\omega$  generates a **D** field in the bulk of a material at  $\omega$  and no other frequency. To isolate the response of the material, we introduce the polarization **P**,

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \tag{2.8}$$

$$\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E} \tag{2.9}$$

where the (linear) susceptibility  $\chi^{(1)}$  is related to the dielectric constant by  $\epsilon = (1 + \chi^{(1)})$ . Linear optical properties are fully described by either  $\epsilon$  or  $\chi^{(1)}$ , which are complex, or by the complex index of refraction  $\eta + i\kappa$ .<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>Although it seems obvious that transmission and absorption are determined by the "bulk" properties

### 2.1.1 Relationship between linear optical properties and band structure

A detailed description of light-matter interactions, from a semiclassical or a quantum mechanical point of view, is quite satisfying when executed well and abysmal when not. Fortunately, we need not try to improve on success, and refer the reader to Refs. [2] and [3]. Our task, then, is to highlight the aspects of the semiclassical desciption of light-matter interactions that are of particular relevance for this thesis.

While the electromagnetic field is treated classically, the electrons are governed by the Hamiltonian [2]

$$\mathcal{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}) + \frac{e}{mc} \mathbf{A} \cdot \hat{\mathbf{p}}$$
(2.10)

where the first term is a kinetic energy term involving the momentum operator  $\hat{\mathbf{p}}$ , the second term is the electron-ion Coulomb interaction, and the third term encompasses the coupling between the applied field (represented by the vector potential  $\mathbf{A}$ ) and the electrons.<sup>2</sup> The eigenstates of the above system in the absence of the perturbing field  $\mathbf{A}$  are the well-known Bloch wavefunctions  $|n, \mathbf{k}\rangle$ , which in the position representation take the form

$$\langle \mathbf{r}|n,\mathbf{k}\rangle = u_{n,\mathbf{k}}(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r})}.$$
(2.11)

Here,  $u_{n,\mathbf{k}}(\mathbf{r})$  is a function with the periodicity of the lattice potential  $V(\mathbf{r})$ , and n and  $\mathbf{k}$  corresponds to the band index and crystal momentum, respectively, in the reduced-zone scheme [4]. The energy eigenvalues  $E_n(\mathbf{k})$  constitute the band structure of the crystal.<sup>3</sup> The difference between the band structures of different materials arises from differences in their lattice potentials, due to variations in composition, lattice configuration, or both. Of

of a solid, this is also true of reflection. While surface quality affects the amount of scattered light, bulk properties determine the amount reflected. This is emphasized in Eq. (2.8), where a driving term for the generated **D** field is the material polarization created by the applied **E** field.

 $<sup>^{2}</sup>$ It is apparent from the form of Eq. (2.10) that electron–electron, electron–phonon, electron–hole, and other multibody interactions are not considered here.

 $<sup>^{3}</sup>$ The Hamiltonian of Eq. (2.10), while ignoring important contributions from multibody interactions, captures many of the essential characteristics of semiconductor band structures.

particular interest to our experiments is the fact that a lattice potential that is changing in time gives rise to a time-varying band structure. Ultrashort laser pulses allow one to track the major features of the band structure via their manifestation in the linear optical properties of the material.

To investigate the interaction of light with the system described by Eq. (2.10), we consider the situation where the applied field excites electrons from an occupied (valence band) state to an unoccupied (conduction band) state. The number and energy distribution of such transitions give rise to the optical properties of a solid. Specifically, the imaginary part of the dielectric tensor can be written as [2, 3]

$$\operatorname{Im}\left[\epsilon_{i}(\omega)\right] \sim \frac{1}{\omega^{2}} \sum_{n_{c}, n_{v}, \mathbf{k}} \delta\left(E_{n_{c}}(\mathbf{k}) - E_{n_{v}}(\mathbf{k}) - \hbar\omega\right) \left|\langle n_{c}, \mathbf{k} | \hat{\mathbf{p}}_{i} | n_{v}, \mathbf{k} \rangle\right|^{2}.$$
 (2.12)

The momentum matrix element quantifies the strength of the coupling for vertical transitions between various conduction and valence band states.<sup>4</sup> The dependence of the momentum matrix element on the direction of the applied field, denoted by the subscript i = x, y, z, allows for an anisotropic optical response (*e.g.*, birefringence). The term common to all elements of the dielectic tensor is the joint density of states (JDOS)

$$JDOS = \sum_{n_c, n_v, \mathbf{k}} \delta \left( E_{n_c}(\mathbf{k}) - E_{n_v}(\mathbf{k}) - \hbar \omega \right), \qquad (2.13)$$

which depends solely on the shape of the band structure. The JDOS peaks at photon energies equal to the transition energy between many different states in  $\mathbf{k}$  space. The fact that parallel conduction and valence bands produce a large peak in  $\text{Im}[\epsilon(\omega)]$  is a direct consequence of the form of the JDOS in Eq. (2.13). In fact, the linear optical response of many solids is dominated by only a few peaks in their JDOS — that is, by resonances at a small number of photon energies produced by only a few regions of parallel bands.

<sup>&</sup>lt;sup>4</sup>Although the coupling term of the Hamiltonian in Eq. (2.10) is proportional to the field **A**, the material properties experienced by the applied field depend on its direction rather than its magnitude. Any field-strength dependence of the susceptibility results in a fundamentally nonlinear system.



Figure 2.1: (a) Band structure [3] and (b) dielectric function [5] of GaAs.

It is important to note that the correspondence between band structure and dielectric function is not one-to-one. Many band structures can produce the same dielectric function,<sup>5</sup> which means that the interpretation of optical properties must be done cautiously. Changes in the linear optical properties can be used to make general statements about the changes in band structure, but additional information is often required to localize the dynamics in **k** space.

As an example of the direct relationship between band structure and dielectric function, Figure 2.1 shows the band structure and the dielectric function of GaAs. The characteristic absorption peaks in  $\text{Im}[\epsilon(\omega)]$  at 3.1 eV ( $E_1$ ) and 4.7 eV ( $E_2$ ) are due in part to a large joint densities of states around the L and X valleys, as indicated by the shaded regions in Figure 2.1(a). The real part shows the characteristic dispersive structure for each absorption peak, in agreement with the Kramers–Kronig relations.

<sup>&</sup>lt;sup>5</sup>The dependence of the dielectric function on the JDOS (Eq. (2.12)) illustrates how the essential distinction among band structures — their **k**-dependence — is lost in the summation.

### 2.1.2 The Drude–Lorentz model

The Drude–Lorentz model, also known as the Lorentz oscillator model when applied to semiconductors and as the Drude model when applied to metals, attempts to describe the optical response of a material as that of a classical harmonic oscillator. While simple, involving only a few free parameters, the Drude–Lorentz model is surprisingly good at describing the optical properties of many semiconductors and metals.

The Lorentz model describes, in a phenomenological way, the polarization induced in a material by the applied **E** field. The situation we consider is that of an electron in a solid that is described by its displacement x from its equilibrium position.<sup>6</sup> The equation of motion for the displacement x is taken to be that of a harmonic oscillator,

$$\frac{d^2}{dt^2}x + \Gamma \frac{d}{dt}x + \omega_0^2 x = F(t)$$
(2.14)

where  $\Gamma$  is a phenomenological damping coefficient,  $\omega_0$  is the resonance frequency of the oscillator (a real resonance in the material), and the driving force is due to the applied field,

$$F(t) = \frac{e}{m} \left[ Ee^{-i\omega t} + E^* e^{i\omega t} \right].$$
(2.15)

Without loss of generality, the equation of motion for x(t) can be solved by neglecting the second driving term above and considering a trial solution of the form  $x(t) = Ce^{-i\omega t}$ ...

$$C[-\omega^2 - i\Gamma\omega + \omega_0^2]e^{-i\omega t} = \frac{e}{m}Ee^{-i\omega t}$$
(2.16)

$$\Rightarrow C = \frac{e}{m} E \frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega}$$
(2.17)

$$\Rightarrow x(t) = \frac{e}{m} E \frac{e^{-i\omega t}}{\omega_0^2 - \omega^2 - i\Gamma\omega}.$$
 (2.18)

While x(t) describes the motion of a single electron, it is often the case that many electrons in a solid respond in the same fashion. Thus, if N electrons respond as x(t), then the total

 $<sup>^{6}</sup>$ We take the ions to be fixed in this derivation.

polarization is given by

$$P(t) = Nex(t) = \epsilon_0 \chi^{(1)} E(t), \qquad (2.19)$$

where Eq. (2.9) is used to relate the applied field E(t) to the polarization P(t) and to introduce the linear susceptibility. Hence,

$$\chi^{(1)} = \frac{Ne}{\epsilon_0} \frac{x(t)}{E(t)} = \frac{Ne^2}{\epsilon_0 m} \frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega} \,. \tag{2.20}$$

For our purposes, the dielectric function is more useful than the susceptibility, and takes the form,

$$\operatorname{Re}[\epsilon(\omega)] = 1 + f \frac{E_{\operatorname{res}}^2 - (\hbar\omega)^2}{(E_{\operatorname{res}}^2 - (\hbar\omega)^2)^2 + (\Gamma \cdot \hbar\omega)^2}$$
(2.21)

$$\operatorname{Im}[\epsilon(\omega)] = f \frac{\Gamma \cdot h\omega}{(E_{\operatorname{res}}^2 - (\hbar\omega)^2)^2 + (\Gamma \cdot \hbar\omega)^2} \,.$$
(2.22)

There are two methods by which the Lorentz model is applied to real absorbing materials. First, because the Lorentzian shape of  $\text{Im}[\epsilon_{\text{Lorentz}}(\omega)]$  is similar to a  $\delta$ -function, materials can be modeled by a distribution of Lorentz oscillators, analogous to the distribution of  $\delta$ -function contributions to the JDOS in Eq. (2.13). The sum of many oscillators would produce a "single resonance" in the material (*e.g.*, the  $E_2$  peak in GaAs). However, for modeling changes in the dielectric function on a femtosecond time scale, this technique is numerically challenging to implement (due to noise in the data) as well as physically unsatisfying in the interpretation of its results.

A second method of applying the Lorentz model to real materials is to describe an entire resonance by the three free parameters of a single oscillator; the resonant frequency  $\omega_0$ , the linewidth  $\Gamma$ , and the oscillator strength  $f = Ne^2/\epsilon_0 m$ . Each parameter is connected to features of the band structure. The resonant frequency  $\omega_0$  corresponds to the position of the peak in the JDOS. The linewidth  $\Gamma$  is related to the distribution of energy levels around



Figure 2.2: Lorentz oscillator model fits to (a) Te and (b) GaAs. Black lines represent literature values of  $\text{Re}[\epsilon]$  (solid) and  $\text{Im}[\epsilon]$  (dashed) [5], while gray lines represent the best-fit values of  $\text{Re}[\epsilon_{\text{Lorentz}}]$  (solid) and  $\text{Im}[\epsilon_{\text{Lorentz}}]$  (dash-dotted).

the resonant frequency — sharper absorption lines correspond to smaller values of  $\Gamma$ , arising from regions of parallel bands. Lastly, the oscillator strength f carries information about the number of states contributing to the resonance at  $\omega_0$ .

As an example of the success of the Lorentz model in describing real materials, Figure 2.2 shows fits to Te and GaAs. In each case, the fit is the sum of two Lorentz oscillators with different values of  $\omega_0$ ,  $\Gamma$ , and f for each term. This two-oscillator model follows the major features of the literature optical properties in each case, but fails to capture smaller features. For example,  $\text{Im}[\epsilon_{\text{Lorentz}}(\omega)]$  does not vanish for photon energies below the band gap, nor is it sensitive to sharp features near other critical points. Nevertheless, the Lorentz model is sensitive to large resonances in a material — the parameters of the fit to GaAs in Figure 2.2(b) indicate resonances at 3.18 eV ( $E_1$  peak) and 4.67 eV ( $E_2$  peak).<sup>7</sup>

The form of the Drude model for metals is

$$\epsilon_{\rm Drude}(\omega) = 1 + \frac{Ne^2}{\epsilon_0 m} \left(\frac{i\tau}{\omega(1 - i\omega\tau)}\right), \qquad (2.23)$$

<sup>&</sup>lt;sup>7</sup>For completeness, the parameters of the fit to Te are  $\omega_1 = 2.37 \text{ eV}$ ,  $\Gamma_1 = 1.28 \text{ eV}$ ,  $f_1 = 105 \text{ eV}^2$ ,  $\omega_2 = 9.39 \text{ eV}$ ,  $\Gamma_2 = 4.43 \text{ eV}$ ,  $f_2 = 170 \text{ eV}^2$ , and an additive constant to the real part of 3.66. The parameters of the fit to GaAs are  $\omega_1 = 3.18 \text{ eV}$ ,  $\Gamma_1 = 0.75 \text{ eV}$ ,  $f_1 = 38.7 \text{ eV}^2$ ,  $\omega_2 = 4.67 \text{ eV}$ ,  $\Gamma_2 = 1.14 \text{ eV}$ ,  $f_2 = 125 \text{ eV}^2$ , and an additive constant to the real part of 1.85. The real additive constant arises from Kramers–Kronig-type contributions from resonances outside the spectral range of the fit, as discussed in Section 2.1.3.



Figure 2.3: Drude model fit to Ag. Black lines represent literature values of  $\operatorname{Re}[\epsilon]$  (solid) and  $\operatorname{Im}[\epsilon]$  (dashed) [5], while gray lines represent the best-fit values of  $\operatorname{Re}[\epsilon_{\operatorname{Drude}}]$  (solid) and  $\operatorname{Im}[\epsilon_{\operatorname{Drude}}]$  (dash-dotted).

which is equivalent to Eqs. (2.21) and (2.22) with  $\Gamma \to 1/\tau$  and  $\omega_0 \to 0$ . By convention, a plasma frequency is defined  $\omega_p^2 = Ne^2/\epsilon_0 m$  to play the role of the oscillator strength above. The classical derivation of  $\epsilon_{\text{Drude}}(\omega)$  is analogous to the above derivation for  $\epsilon_{\text{osc}}(\omega)$ , except that an induced current **J** rather than an induced polarization **P** results in a differential equation that lacks a harmonic potential term [4]. The optical properties of many metals consist of a Drude (intraband) contribution from "free" electrons in half-filled bands in addition to Lorentz oscillator (interband) contributions from available vertical transitions. That is, even good metals are rarely described by the Drude model alone. To illustrate this fact, Figure 2.3 shows a Drude model fit to Ag, with  $\omega_p = 8.3 \text{ eV}$  and  $\tau = 50 \text{ fs}$ . While the fit describes low-photon-energy behavior well, it is not accurate near 4 eV due to resonance contributions to  $\epsilon(\omega)$ .

### 2.1.3 The Kramers–Kronig relations

Thus far we have discussed both the real and the imaginary part of the dielectric function as if the two quantities were independent. In reality,  $\operatorname{Re}[\epsilon(\omega)]$  and  $\operatorname{Im}[\epsilon(\omega)]$  are

linked through the Kramers–Kronig relations [6]

$$\operatorname{Re}[\epsilon(\omega)] = 1 + \frac{2}{\pi} \mathcal{P} \int_0^\infty \mathrm{d}\nu \, \frac{\nu \operatorname{Im}[\epsilon(\nu)]}{\nu^2 - \omega^2}$$
(2.24)

$$\operatorname{Im}[\epsilon(\omega)] = \frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \mathrm{d}\nu \, \frac{1 - \operatorname{Re}[\epsilon(\nu)]}{\nu^2 - \omega^2} \tag{2.25}$$

where  $\mathcal{P}$  represents the principal value of the integral. It is worth noting that the Kramers– Kronig relations follow from the fact that the electric field **E** drives the material polarization **P**, as in Eq. (2.9) [6]. Interestingly, the availability of transitions at a single photon energy contributes locally to Im[ $\epsilon(\omega)$ ] (see Eq. (2.12)) but affects Re[ $\epsilon(\omega)$ ] globally according to the Kramers–Kronig relations. For fitting dielectric function data to the Lorentz model when some of the material resonances lie outside the measured spectal range, the expression for the imaginary part will fit the data correctly due to the local contribution of transitions, but the real part will have unaccounted-for global contributions. It is often the case that an additive constant to the real part can dramatically improve the fit by playing the role of these Kramers–Kronig-type contributions from resonances outside the detected spectral range. Since the real part of the Lorentz model is mostly constant far from a resonance,<sup>8</sup> a single additive-constant free parameter is often sufficient to capture all the resonance contributions to Re[ $\epsilon(\omega)$ ] from outside the spectral range of the data.

# 2.2 Ultrafast dynamics of solids under intense photoexcitation

Despite the broad array of topics that fall under the title "ultrafast dynamics of solids," the discussion below is of limited range. For instance, we do not discuss the myriad of electronic phenomena that have been observed at low excitation densities of  $10^{14}$  to  $10^{18}$  cm<sup>-3</sup>, a review of which can be found in Ref. [7]. The reason for this omission is that such

<sup>&</sup>lt;sup>8</sup>The real part varies significantly within a linewidth  $\Gamma$  of the resonance frequency  $\omega_0$ .

phenomena are rarely observed in experiments where the excited carrier density is on the order of  $10^{22}$  cm<sup>-3</sup>. Although excited carrier effects are present and are more pronounced than at lower densities, the material dynamics are often dominated by the ionic motion that results from excitation of a significant fraction of the valence electrons. The text that follows is an attempt to present the framework in which these dynamics are understood.

### 2.2.1 Molecular dynamics and coherent control

The idea that solid dynamics are determined by ionic motion is rooted in the microscopic picture of molecular electronic transitions and molecular dynamics. In fact, the molecular case is even more extreme than the solid one — photoexcitation in molecules often results in dissociation, whereas the sharing of electrons in a solid leads to only a partial weakening of bonds under photoexcitation.<sup>9</sup> Consider a diatomic sodium molecule, where the energy of the system as a function of nuclear displacement is as shown in Figure 2.4. The curves in this figure show the energy of the system in different electronic configurations as a function of ionic separation. Often, the excited state potentials have a shape that results in dissociation (no minimum at finite separations) or bond stretching (a minimum at a different separation than the ground state). When this is the case, electronic transitions are coupled to molecular vibrational transitions [8], where our intuition predicts that the ensuing nuclear motion is determined by the new potential in a classical way — an excitation from the ground  $X^{1}\Sigma_{q}^{+}$  state to the  $2^{1}\Pi_{g}$  state of Figure 2.4 would leave the nuclei displaced from equilibrium and they will thus begin to oscillate. The idea that the nuclei remain fixed during the electronic transition<sup>10</sup> is equivalent to the approximation of vertical transitions in crystals and is known as the Franck-Condon principle [8].

 $<sup>^{9}</sup>$ It is rarely the case that a pump pulse is intense enough to provide one photon for every valence electron in the pumped volume of the solid.

<sup>&</sup>lt;sup>10</sup>This is also representative of the Born-Oppenheimer approximation, where the electronic quantum numbers are the so-called "fast variables" and the nuclear positions are the "slow variables."



Figure 2.4: Potential energy curves for a diatomic sodium molecule, showing bond stretching or dissociation for different excited state potentials. Numbers 1, 2 and 3, indicate the possible transitions to products in a two-pulse excitation scheme after the first pulse excites the electronic system to  $2\,{}^{1}\Pi_{g}$ . After Ref. [9].

The quantum mechanical derivation of molecular excited state dynamics was first provided by Heller [10, 11]. To summarize, immediately after photoexcitation, the ground nuclear eigenstate evolves on the excited state potential surface following the classical trajectory. The anharmonicity of the excited state potential determines the rate at which the nuclear wavepacket spreads and leads to deviations from the classical trajectory. Of primary interest in our case is understanding the way in which the resulting nuclear dynamics can affect properties such as the dielectric function. Heller points out the lack of such a description at the time, stating

After the electrons have made a transition, the nuclei experience new forces; they find themselves displaced relative to the equilibrium geometry of the new potential surface, and interesting dynamics should ensue. Unfortunately, most discussions of electronic transitions cut short any allusions to dynamics and explain the absorption spectrum in terms of Franck-Condon overlaps of the initial nuclear wavefunction with a time-independent vibrational *eigenfunction*  of the upper electronic potential surface. We (and the nuclear wave function) are left hanging; we are given no explanation of the time evolution of the hapless nuclei which, once the photon is absorbed, are ready to move in ways that *determine* the spectra [11].

Before making the connection between molecular and crystal dynamics, we discuss an important application of Heller's work — the coherent control of molecular dissociation. Tannor, Kosloff, and Rice devised a scheme under which the dissociation dynamics of a hypothetical molecule can be controlled simply by varying the time delay between two femtosecond pulses [12, 13]. They considered a ground state potential energy surface with one bound state (ABC) and two dissociated states (AB + C, A + BC), along with different excited state potential surfaces. They demonstrated that by allowing the nuclear wave function to propagate on the excited state potential for specific (different) lengths of time before the second pulse arrives, the "final product" of the two-pulse excitation can be controlled.<sup>11</sup> Experimental realizations of end-product control in molecular dissociation (in systems such as that of Figure 2.4) have been achieved with multiple-pulse and shaped-pulse excitations [9, 14].

### 2.2.2 The molecular picture of crystal dynamics

Many of the features of the dynamics of solids can be understood within the framework described above, albeit with some extensions. Photoexcitation of a large density of electrons establishes a new potential energy surface on which the ions move. The new potential may have no minimum near the initial lattice configuration, resulting in large nuclear displacements, disordering, and often "damage." If a new potential minimum is established, then the ions can respond to the new potential in a more controlled fashion.

<sup>&</sup>lt;sup>11</sup>For an anharmonic excited state potential, the ability to control the end products is reduced, essentially because the projection of a spread nuclear wave function onto the ground state potential can "split" the wave function between the two end products.

Nuclear motion on the new potential energy surface leads to commensurate changes in the band structure, and, in turn, in the optical properties of the solid. That is, the available transitions for the electrons are determined by the lattice configuration, the dynamics of which are determined by the excited electrons.

Additional considerations when discussing solids concern the treatment of the "excited electronic state." First, the manifold of excited energy states is virtually a continuous function of the excited electron density. In general, the excited electron density cannot specify an unique potential because of the possible permutations of transitions among the  $10^{23}$  $\mathrm{cm}^{-3}$  valence electrons. The idea that material dynamics depend on the excited electron density alone is an approximation that holds when the carriers can thermalize before any significant nuclear motion occurs. Excited electrons (holes) thermalize within 10 fs at densities of  $10^{21}$  cm<sup>-3</sup> or more.<sup>12</sup> leading to a Fermi-Dirac distribution within the conduction (valence) band and a loss of memory of the initial excited carrier configuration. Because the ions spend most of their time (all but 10 fs) evolving on a potential determined by a Fermi-Dirac distribution of carriers, the excited electron density is often sufficient to specify the "excited electronic state." A second concern is that the electronic state and the nuclear state do not evolve independently. A particular excited electron distribution establishes a potential surface to which the lattice responds by deformation. This deformation results in a new band structure, resulting in a redistribution of electrons and, in general, a modified potential. In essence, the excited electron potential becomes a dynamic quantity which depends on the nuclear coordinates. These many-body interactions are more pronounced in solids than in molecules and can dynamically modify the potential energy surface and further perturb the semiclassical trajectories of the ions. Electron-electron interactions of

<sup>&</sup>lt;sup>12</sup>At densities of  $10^{18}$  cm<sup>-3</sup>, carrier thermalization occurs within hundreds of femtoseconds [15]. Extrapolation of the results of Becker *et al.* [15] to  $10^{21}$  cm<sup>-3</sup> gives a thermalization time on the order of 10 fs.

exchange and correlation, electron-phonon interactions, and other many-body interactions offer avenues by which the electron distribution within a band can exert a force on the ions.

Even with the further complications of dealing with solids, nuclear dynamics can still be treated with excited state potential surfaces. The accuracy of "exact" calculated results for solids will be less than for molecules, simply due to the increased complexity of a condensed system. Usually, approximations to reduce the complexity of the system make the problem tractable and model a specific experimental situation. We present an example of such a treatment in the following section.

### 2.2.3 Ultrafast disordering of zincblende semiconductors

The observation of laser-induced disordering on a time scale shorter than the thermalization time between excited carriers and the lattice was observed by a number of groups working with semiconductors [16, 17, 18, 19, 20]. Although the disordering of solids via thermal processes (*i.e.*, melting) has been known for a long time, a theoretical description of lattice instability as a result of photoexcitation was first provided by Stampfli and Bennemann [21, 22]. Apparently derived independently from the work described above, their treatment of zincblende semiconductors shares many features with the molecular description of nuclear motion on an excited state potential.

Stampfli and Bennemann consider a tight-binding Hamiltonian that includes nearestneighbor interactions only. A calculation of the potential surface for the lattice in the ground electronic state configuration is shown for silicon in Figure 2.5(a). A clear minimum exists as a function of transverse acoustic ( $\delta_t$ ) and longitudinal optical ( $\delta_l$ ) lattice distortions, indicating a stable lattice. The band structure and optical properties of the calculated ground state configuration agree well with the known properties of Si. After photoexcitation, the



Figure 2.5: Potential energy surface as a function of transverse acoustic ( $\delta_t$ ) and longitudinal optical ( $\delta_l$ ) lattice displacements for silicon (a) in the ground state electronic configuration and (b) when 15% of valence electrons are excited to the conduction band. The stable minimum at  $\delta_t = \delta_l = 0$  becomes unstable for sufficient excitation densities, as shown here. After Ref. [22].

excited electrons rapidly take on a Fermi-Dirac distribution<sup>13</sup> and the lattice potential is recalculated with the different band-filling. As shown in Figure 2.5(b), when 15% of valence electrons are excited to the conduction band,<sup>14</sup> the lattice potential no longer displays a stable minimum at the ground state lattice configuration. The calculated trajectory of the ions is shown in Figure 2.6, displaying oscillations and translation in one direction and pure translation in another, following the shape of the potential in Figure 2.5(b). The significant motion of ions on a time scale of 100 fs agrees with the experimental results of many groups [16, 17, 18, 19, 20], and the onset of metallic behavior on this time scale has also been observed [23, 24].

The main difference between the response of silicon and that of Na<sub>2</sub> molecules

<sup>&</sup>lt;sup>13</sup>Immediately after photoexcitation, the excited electrons are distributed in the conduction band according to the pump spectrum.

<sup>&</sup>lt;sup>14</sup>In practice, the excitation of 15% of valence electrons to the conduction band is rarely achieved in pump–probe experiments. Excitation of a few percent of valence electrons is both more common and often sufficient to initiate phase transitions.



Figure 2.6: Trajectory of ionic motion on the potential shown in Figure 2.5(b). Significant nuclear displacements are predicted to occur within 100 fs. After Ref. [22].

to photoexcitation is that an ensemble of ions, rather than two, are set in motion on a new potential surface. As shown in Figure 2.6, the ionic motion is confined to a certain path for all initial conditions (within a certain range). The physical mechanisms underlying the response of tellurium to intense photoexcitation are similar to those that govern the response of silicon. Whereas nuclear motion in silicon develops along two directions, the photoinitiated nuclear motion in tellurium affects only a single lattice parameter. Moreover, the excited state potential in tellurium has a minimum near the initial lattice configuration, which leads to lattice vibrations that are analogous to the vibrations observed in Na<sub>2</sub>.

## 2.3 Nonlinear optical properties

Although the majority of this thesis concerns linear optics in solids, nonlinear optical processes are encountered as well. A nonlinear optical response occurs when fields of frequency different than that of the applied field are generated. The nonlinear response is usually isolated from the linear one, and Eq. (2.9) becomes

$$\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E} + \mathbf{P}^{NL} \tag{2.26}$$

$$\mathbf{P}^{NL} = \epsilon_0 \chi^{(2)} : \mathbf{E} \cdot \mathbf{E} + \epsilon_0 \chi^{(3)} :: \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \cdots .$$
(2.27)

Essentially, the material response is expanded in powers of the applied  $\mathbf{E}$  field. Note that the total field is involved in driving the polarization and this total field may involve contributions from laser pulses of different frequency travelling in different directions with different field polarizations. The total polarization then acts as a driving term, as in Eq. (2.8), to radiate fields at the fundamental frequency<sup>15</sup> as well as at the frequency of the nonlinear polarization.

Broadly speaking, there are two criteria which must be satisfied in order to generate nonlinear radiation. For a nonlinear process involving n fields of the form<sup>16</sup>

$$E_j(t) = \frac{1}{2} \left( E_j e^{i(\vec{k}_j \cdot \mathbf{r} - \omega_j t)} + E_j^* e^{-i(\vec{k}_j \cdot \mathbf{r} - \omega_j t)} \right), \qquad (2.28)$$

for  $j = 1 \dots n$ , these criteria are

$$\omega_{NL} = \sum_{i=1}^{n} \pm \omega_i \tag{2.29}$$

$$\vec{k}_{NL} = \sum_{i=1}^{n} \pm \vec{k}_i$$
 (2.30)

where the choice of sign indicates whether the " $\omega$ " or the " $-\omega$ " term of a particular field contributes, as determined by the particular nonlinear process considered and the experimental arrangement. Equation (2.29) is always satisfied in a nonlinear process and specifies the nonlinear frequency generated. Equation (2.30) is the "phase-matching" condition and determines the direction of the radiated nonlinear field.<sup>17</sup> In the remainder of this Section, we present an overview of second- and third-order nonlinearities and refer the interested reader to Ref. [25] for further details.

 $<sup>^{15}\</sup>mathrm{The}$  "fundamental" frequency refers to the center or carrier frequency of the applied  $\mathbf E$  field.

 $<sup>^{16}</sup>$ Here and for the remainder of the discussion we ignore the polarization of the applied **E** field.

<sup>&</sup>lt;sup>17</sup>Many details of phase-matching are omitted here because they are beyond the scope of this thesis. See Refs. [25] and [26].

### 2.3.1 Second-order nonlinearities

The type of second-order nonlinear process most often encountered in the lab is second harmonic generation (SHG), which involves two degenerate driving fields ( $\omega_1 = \omega_2$ ) of the form in Eq. (2.28). The nonlinear polarization generated by SHG is

$$P^{(2)}(2\omega_1) = \epsilon_0 \chi^{(2)}(2\omega_1 : \omega_1, \omega_1) E_1 E_1 e^{i(\vec{k}(2\omega_1) \cdot \mathbf{r} - 2\omega_1 t)}$$
(2.31)

where the criteria of Eqs. (2.29) and (2.30) involve only positive terms (e.g.,  $\omega_{NL} = \omega_1 + \omega_1$ ). We have allowed for less-than-perfect phase matching because the dispersion of the material determines whether  $\vec{k}(2\omega_1) = 2\vec{k}(\omega_1)$ . When the phase matching is not perfect, the nonlinear field generated at different positions in the crystal intefere somewhat destructively, reducing the total radiated nonlinear field.

The most common application of SHG is in measuring the duration of a femtosecond pulse via autocorrelation. In practice, two copies of the same pulse are overlapped in a nonlinear crystal with a controllable delay  $\tau$  between the two pulses. Because the nonlinear field depends on the total intensity, the SHG signal S varies with the temporal overlap of the pulses. One can extract the pulse duration from the shape of  $S(\tau)$ .<sup>18</sup> An example of autocorrelation is given in Section 3.1.1.

### 2.3.2 Third-order nonlinearities

In general, third-order nonlinearities require three driving fields. In practice, two or even all three fields are degenerate. One situation of particular interest is the following

<sup>&</sup>lt;sup>18</sup>The ease of such a measurement makes it attractive, but it does not fully characterize the temporal profile of the laser pulse [27].

interaction between two fields of frequency  $\omega_1$  and  $\omega_2$ 

$$P^{(3)}(\omega_{NL}) = \frac{1}{2} \epsilon_0 \chi^{(3)}(\omega_{NL} : \omega_1, -\omega_1, \omega_2) E_1 E_1^* E_2 e^{i(\vec{k}_2 \cdot \mathbf{r} - \omega_2 t)}$$
(2.32)

$$\omega_{NL} = \omega_1 - \omega_1 + \omega_2 \tag{2.33}$$

$$\vec{k}_{NL} = \vec{k}_1 - \vec{k}_1 + \vec{k}_2 \tag{2.34}$$

This particular nonlinear mixing can result in intensity-dependent effects. For  $\chi^{(3)}$  real, an intensity-dependent index of refraction leads to self-focussing of a gaussian beam.<sup>19</sup> An imaginary  $\chi^{(3)}$  produces intensity-dependent absorption (*i.e.* two-photon absorption). Both phenomena are widely applied in the field of optics. Self-focussing, or Kerr lensing, is used to mode-lock oscillators and contributes to the generation of white-light femtosecond pulses. Two-photon absorption (TPA) is commonly used for cross-correlation of ultrashort pulses<sup>20</sup> because it is automatically phase-matched and produces a field at the fundamental.

Of particular interest to researchers is how nonlinear susceptibilities are related to (and can reveal) material properties. For instance, the process of two-photon absorption described in Eq. (2.32) does not occur unless a photon of energy  $\hbar(\omega_1 + \omega_2)$  would be absorbed linearly. This is not to say that  $\text{Im}[\chi^{(3)}]$  depends on  $\text{Im}[\chi^{(1)}]$ . Rather, both depend on the availability and distribution of, in this case, vertical electronic transitions.

In addition to electronic transitions, the existence of lattice vibrations (phonons) serves to enhance nonlinear susceptibilities, in particular  $\chi^{(3)}$ , via the change in linear optical properties with lattice distortion. When the interaction in Eq. (2.32) is used to probe (or excite) a phonon  $\omega_v$  of a solid where  $\omega_1 - \omega_2 = \omega_v$ , it is called a Raman interaction. The form of the phonon contribution to the nonlinear susceptibility is given by [25]

$$\chi_{\text{Raman}}^{(3)}(\omega_2:\omega_1,-\omega_1,\omega_2) \sim \left(\frac{\partial\alpha}{\partial q}\right)^2 \frac{1}{\omega_v^2 - (\omega_1 - \omega_2)^2 + 2i(\omega_1 - \omega_2)\gamma}, \qquad (2.35)$$

<sup>&</sup>lt;sup>19</sup>For self-focussing, and any other self-action effects,  $\omega_1 = \omega_2$ .

 $<sup>^{20}</sup>$ See Section 3.1.1.
where q is a displacement of the lattice associated with the phonon and  $\gamma$  is the associated damping constant. By convention,  $\omega_2$  is referred to as the Stokes frequency when  $\omega_2 < \omega_1$ and as the anti-Stokes frequency otherwise. The quantity  $\alpha$  is the polarizability of the material, which changes as the lattice is distorted. Note that  $\chi^{(3)}_{\text{Raman}}$  contains a resonance denominator of similar form to the linear susceptibility in Eq. (2.20), however the "strength" of the Raman process depends on the sensitivity of the polarizability to lattice displacement. Analogous to the electronic case, where an applied field induces an oscillating electronic polarization that leads to excitation of an electron, Raman interactions lead to the excitation of phonons.

## 2.4 Summary

The availability of electronic transitions, the existence of vibrational modes, and the dynamics of nuclei all influence the optical properties of solids. In this chapter we have laid the foundation for the discussion of the properties of tellurium in Chapter 4 and for the interpretation of the time-resolved dielectric function data in Chapters 5 and 6.

## Chapter 3

# **Experimental Method**

Ultrafast optics has blossomed into a mature but still rapidly developing field of science since subpicosecond pulses were first generated in 1976 [28]. The variety of ultrafast spectroscopy techniques has grown with the development of ultrafast laser sources [29]. Many of these techniques [7, 30] are exquisitely sensitive to the pertubations induced by specific excitations in material systems. At the same time, significant advances have been made in the development and commercialization of ellipsometers, a review of which is given by Collins [31]. Materials scientists have used ellipsometry as a tool to study the electronic structure of metals [32], as a noninvasive probe of layer thicknesses and composition in multi-layer stack systems [33], and as an *in situ* monitor of thin film growth rates [34].

Recent interest in the dynamics of highly photoexcited materials<sup>1</sup> calls for measurement techniques that function as monitors of both electron and lattice dynamics. Highly excited solid state materials, especially semiconductors, are of interest for industrial applications as well as for fundamental scientific reasons. Potential applications include micromachining using femtosecond laser pulses and developments in modern high power laser

<sup>&</sup>lt;sup>1</sup>Here, highly photoexcited refers to excitation near or above the threshold for permanent damage, where the excited electron density is  $10^{20}$  cm<sup>-3</sup> or greater.

diodes, in which the injection currents generate very high carrier densities. The challenge in understanding the physics of high carrier densities lies in determining the dominant process among the many that occur and in tracking the phase state of the material.

To meet this challenge, we have developed a technique that measures the dielectric function of a material with femtosecond time resolution. By measuring  $\epsilon(\omega)$  with femtosecond time resolution, we can infer the structural and electronic dynamics that occur during a photoinduced phase transition from the direct relationship between band structure and electron occupation and  $\epsilon(\omega)$ . Using a probe with a broad spectral range provides information at many transition energies, which reveals the redistribution of bonding strengths as the material changes phase. The dielectric function can also be used to determine the density of excited carriers and even transient carrier distributions in **k** space.

In this chapter we present a dual-angle-of-incidence pump-probe reflectometry technique for measuring the femtosecond time-resolved dielectric tensor of a solid. In Section 3.1, we discuss the experimental details of white-light pump-probe spectroscopy. In Section 3.2, we discuss how this reflectometry technique can be used on various solid materials. In Section 3.3, we show femtosecond time-resolved measurements of the dielectric function of GaAs and *a*-GeSb, and discuss them in relation to previous pump-probe reflectivity results.

## 3.1 Pump–probe methods

#### 3.1.1 Measuring laser pulse durations

Before a femtosecond pulse is used in any experiment, its pulse duration must be measured. Pulsed laser damage thresholds of solids vary with pulse duration, and the ultimate time resolution of a pump-probe experiment is directly derived from pulse duration. For the experiments presented here, the latter issue is of paramount importance and is the



Figure 3.1: A schematic representation of an autocorrelation measurement (left) and a typical autocorrelation trace where two photon absorption is the interaction mechanism (right).

subject of this section.

The most common method of ultrashort pulse measurement is the autocorrelation, depicted in Figure 3.1. Replicas of the same femtosecond pulse are overlapped in a nonlinear crystal after one of the pulses traverses a path of variable optical delay. The photodiode (PD) in Figure 3.1 measures a time-integrated signal  $S(\tau)$  that depends on the delay  $\tau$  between the two pulses. The nonlinear interaction mechanism (described in Section 2.3) allows one pulse to optically "gate" the other — deviations in the signal depend on the degree of temporal overlap between laser pulses.<sup>2</sup> Precisely how the signal trace is interpreted depends on the type of nonlinearity that couples the two laser pulses.

Any further discussion of pulse duration measurements at this point would suffer from the lack of a mathematical description of the pulse itself, which we rectify below. A laser pulse of duration T and of center frequency  $\omega_0$  can be described by<sup>3</sup>

$$E(t) \sim E_{\rm env}(t)e^{i\omega_0 t - i\phi(t)}$$
 (3.1)

$$E_{\rm env}(t) \sim e^{-2\log[2]\left(\frac{t}{T}\right)^2} \tag{3.2}$$

 $<sup>^{2}</sup>$ The bandwidth of electronic devices is insufficient for measuring femtosecond pulses, and thus measurements must be done optically. Similarly, investigations of ultrafast processes in solids cannot be done electronically.

<sup>&</sup>lt;sup>3</sup>The envelope of femtosecond laser pulses are approximately gaussian or  $1/\cosh^2$  in shape. Gaussian pulses are discussed because they allow analytical expressions of the autocorrelation trace to be derived.

where  $\phi(t)$  is the phase of the pulse and log is  $\log_e$  unless otherwise indicated. By convention, the pulse duration T is the FWHM of the intensity  $I(t) \sim |E(t)|^2$ . The *local* frequency is defined as

$$\omega(t) = \omega_0 - \frac{d\phi}{dt}.$$
(3.3)

The inclusion of the time-dependent phase can result in a chirped pulse, which we discuss in Section 3.1.3. For now, we take  $\omega(t) = \omega_0$ .

As mentioned above, the nonlinear interaction in the material determines the precise shape of the autocorrelation trace. Producing a catalog of autocorrelation traces for various types of nonlinearities would try the patience of both the reader and the author, so we consider the particular case of two-photon absorption. From the form of this  $\chi^{(3)}$ nonlinearity (see Eq. (2.32)), the photodiode in Figure 3.1 detects the signal  $S(\tau)$ 

$$S(\tau) \sim S_{\rm bkg} - \left| \int \mathrm{d}t \, E(t) I(t-\tau) \right|^2. \tag{3.4}$$

The background signal  $S_{bkg}$  arises from transmission of the detected pulse in the absence of the second pulse. The transmitted field decreases in the presence of the second pulse because one photon from each pulse is destroyed to excite an electron. Substituting the expression for the electric field given above and carrying out the integration yields

$$S(\tau) \sim S_{\rm bkg} - e^{-4\log[2]\left(\frac{\tau}{\sqrt{3/2T}}\right)^2}$$
 (3.5)

A typical autocorrelation trace of this kind is shown in Figure 3.1. The FWHM of the trace is directly related to the pulse duration T by the numerical factor  $\sqrt{3/2}$ .

Related to the autocorrelation measurement is the cross-correlation, where the two interacting pulses are of different pulse durations, say  $T_1$  and  $T_2$ . Usually, the pulse duration of one is known or measurable via autocorrelation (*e.g.*, the pump of a pump-probe experiment) and the other is not because of the dispersive effects of transmissive optics or



Figure 3.2: Schematic representation of white-light pump-probe setup. BS = polarizing beam splitter; M = flat mirror; PM = parabolic mirror; L = lens; P = polarizer;  $\lambda/2$  = half-wave plate.

because the pulse energy is too low to perform an autocorrelation (*e.g.*, the probe). The shape of the cross-correlation trace is again gaussian, and performing an integral similar to Eq. (3.4) yields the unknown pulse duration  $T_1$ ,

$$T_1 = \sqrt{(\text{FWHM})^2 - \frac{T_2^2}{2}}.$$
 (3.6)

Note that the degenerate case  $(T_1 = T_2)$  corresponds to an observed FWHM of  $\sqrt{3/2}T_2$ .

#### 3.1.2 White-light pump–probe setup

Figure 3.2 shows a schematic representation of the experimental setup. We use a commercially available Ti:sapphire oscillator to seed a home-built, 1-kHz repetition rate, Ti:sapphire multipass amplifier which produces 40-fs, 0.5-mJ pulses at 800 nm. The design of the amplifier follows that of Backus *et al.* [35].

As Figure 3.2 shows, a femtosecond pulse is split into a pump and a probe pulse at

the beamsplitter (BS). The pump pulse is directed to the sample via a variable delay stage, allowing for adjustable time delays between the pump and the probe pulse. The pump pulse is focused onto the sample using a slowly focusing lens (0.20-m focal length). The pump spot size can be adjusted according to specific experimental requirements by varing the distance from the lens to the sample, but remains at least four times larger than the probe spot to ensure probing of a homogenously excited region. After the beamsplitter, the probe and the pump pulses pass through waveplate–polarizer combinations. The polarizer in the probe line is crossed to that of the pump line, and the waveplate–polarizer combination in each arm allows for adjustment of the probe- and pump-pulse energies.

A white-light probe pulse is generated by focusing the 800-nm pulse into a 3mm thick piece of CaF<sub>2</sub>. A number of nonlinear optical processes, including self-focusing and self-phase modulation, contribute to the generation of this white-light continuum [36]. Due to the 10.2-eV band gap of CaF<sub>2</sub>, the broadband continuum extends from the near infrared to the near ultraviolet [37]. As shown in Figure 3.3, the majority of the probe pulse energy remains at the seed wavelength of 800 nm. A 1.5-mm Schott BG-40 filter is used to flatten the spectrum, making it suitable for charge-coupled-device spectrometer detection and preventing damage of the sample.

The white-light pulse is split into a probe and a "reference" pulse by a 1-mm thick piece of sapphire. The probe pulse is focused on the sample with a parabolic mirror and recollimated with an acromatic lens. Both the probe and reference pulses are directed into a 1-to-1 imaging spectrometer. A broadband polarizer is inserted between the sample and the spectrometer to prevent scattered pump light from reaching the detector and to ensure that only p polarized light is measured. We monitor the reference pulse spectrum to correct for shot-to-shot probe fluctuations, as discussed in Section 3.2.4.

Maintaining femtosecond time resolution with the large bandwidth of the white-



Figure 3.3: Spectrum of the white-light pulse generated in  $CaF_2$ . The solid and dashed curves show the spectrum of the white-light pulse before and after passing through the BG-40 filter, respectively.

light probe pulses requires specific attention. While reflective optics are used to deliver the white-light pulse from the CaF<sub>2</sub> to the sample, the BG-40 filter, the sapphire beam splitter, and the CaF<sub>2</sub> itself contribute to dispersive stretching (chirp) of the probe. In order to regain the original time resolution, the measured reflectivity transients at each wavelength are time shifted to correct for this chirp. The chirp of our white-light probe pulse is shown in Figure 3.4. The data in Figure 3.4 correspond to a spectrally-resolved "time zero" between the pump and white-light probe, measured by pump-probe cross-correlations using two-photon absorption [38]. We obtain traces similar to the autocorrelation trace of Figure 3.1, where the maximum dip marks "time zero" for that photon energy. The width of the cross-correlations indicate that the time resolution of the apparatus is better than 50 fs for all wavelengths of the probe.<sup>4</sup>

<sup>&</sup>lt;sup>4</sup>Two-photon-absorption-based cross-correlations have the disadvantage of being asymmetric: the intense pump pulse alone promotes carriers via two-photon absorption and, subsequently, free carrier absorption of the probe causes the trace to be asymmetric. Hence, this technique can be used to estimate time resolution using only the rising edge of the cross-correlation trace.



Figure 3.4: Temporal chirp of the white-light pulse. The full circles indicate data points measured using two-photon absorption. The solid curve is a second order polynomial fit through the data.

#### 3.1.3 Calculated time resolution of white light probe

The chirp of the white-light probe significantly affects the time resolution of our experimental apparatus. In fact, the probe would be only a few femtoseconds long if the chirp were removed. In our experiment, the probe is chirped to about 1 ps in duration, yet the actual time resolution is much shorter due to the shape of the chirp. To understand why, we develop a method for calculating the time resolution for each spectral component of the probe, which draws from the work of Kovalenko *et al.* [39].

We take the white-light probe to have the spectrum and chirp shown in Figure 3.5(a). The chirp shown here is the time of arrival, at an arbitrary point in space, of each spectral component of the probe. From the spectrum and chirp, the pulse is constructed from a Fourier transform via

$$E(t) = \frac{2}{\sqrt{2\pi}} \int_0^\infty \mathrm{d}\omega' \, E(\omega') e^{-i\omega' t} \tag{3.7}$$

where

$$E(\omega) = \sqrt{I(\omega)}e^{i\phi(\omega)} \tag{3.8}$$



Figure 3.5: (a) Spectrum and chirp of white-light probe pulse. (b) Pulse intensity I(t) constructed from data in (a).

and

$$\phi'(\omega) = -t_0(\omega). \tag{3.9}$$

A given chirp  $t_0(\omega)$  produces a frequency-dependent phase-delay in  $E(\omega)$ , which in turn creates a time-varying local frequency in E(t). In our case, the chirp is mostly linear, so the pulse I(t) in Figure 3.5(b) looks similar to "a spread out version" of the spectrum. Notice, however, that the sharp features near 1.55 eV are smoothed out in the process of constructing the pulse.

Once the E field of the white-light pulse is calculated, the time resolution of our pump-probe experiment can be determined. The experimental situation we consider is a pump-probe cross-correlation using two-photon absorption, where the photodiode in Figure 3.1 is replaced by a spectrometer. The observed spectrogram  $S(\omega, \tau)$ , analogous to the trace  $S(\tau)$  in Eq. (3.4), is

$$S(\omega,\tau) \sim S_{\rm bkg} - \left| \int dt \, e^{i\omega t} E(t) I(t-\tau) \right|^2 \tag{3.10}$$

where E(t) is the white-light probe pulse and I(t) is taken to be a 31.5 fs transform-limited pump pulse centered at 800 nm to simulate our experimental conditions. The procedure for determining the time resolution of each spectral component of the probe is as follows. At



Figure 3.6: Time resolution as a function of photon energy for the chirped white-light probe. For reference, the spectrum (arbitrary units) and chirp is also shown.

each frequency, the cross-correlation trace  $S(\omega, \tau)$  is calculated by numerically performing the integral in Eq. (3.10). The trace is then fit to a gaussian in order to extract the FWHM. Using Eq. (3.6), the FWHM of the trace, and  $T_2 = 31.5$  fs, we determine the probe pulsewidth  $T_1$  at each frequency of the probe. The results of this calculation are shown in Figure 3.6. The variation in the time resolution with photon energy results from the *curvature* of the chirp — a steeper slope in the near UV than in the near IR results in 60 fs rather than 20 fs time resolution. Of course, the shape of the spectrum is important as well, and the almost linear downward trend in pulse duration toward the IR is halted by the structure in the white-light spectrum between 1.4 eV and 1.7 eV.

## 3.2 Dual-angle reflectometry method

The dielectric function fully describes the linear optical properties of a material. In general,  $\epsilon(\omega)$  consists of a real and an imaginary part. The imaginary part peaks at energies where the joint density of states is large, *i.e.*, where a large number of electronic transitions are available (see Section 2.1.1). The real part is related to the imaginary part through the Kramers–Kronig relations and exhibits a dispersive "wiggle" at each absorptive peak in the imaginary part (see Section 2.1.3).

The most widespread method of measuring  $\epsilon(\omega)$  is ellipsometry [40]. In standard continuous wave (cw) ellipsometry, reflectivity values are typically measured at a fixed angle of incidence while the polarization of the incident light (or the orientation of a polarization analyzer) is rotated through 180°. A large number of data points allows an accurate determination of the real and imaginary part of  $\epsilon(\omega)$  by inverting the Fresnel reflectivity formulas. Alternatively, the Kramers–Kronig relations between  $\text{Re}[\epsilon(\omega)]$  and  $\text{Im}[\epsilon(\omega)]$  can be used to determine the full dielectric function from the measurement of just one part. Previous experiments have measured the real part of the refractive index over a very wide frequency range [41], and determined the imaginary part using the Kramers–Kronig relations. For an accurate calculation of the unknown quantity, it is necessary to measure the known quantity from dc to infinite frequency.

In order to measure the dielectric function of highly excited materials, we employ a dual-angle-of-incidence reflectometry technique. The finite bandwidth of the femtosecond probe prohibits using the Kramers–Kronig relations, requiring measurement of at least two quantities to determine  $\operatorname{Re}[\epsilon(\omega)]$  and  $\operatorname{Im}[\epsilon(\omega)]$ . If one knows the geometry of the sample to be investigated, two measurements are sufficient to determine  $\epsilon(\omega)$ . This should be contrasted with ellipsometry, where no prior knowledge of the sample is assumed and where at least three measurements are needed to determine its optical properties [42]. Although a true ellipsometry-type technique could produce results with smaller error than the technique described here, changes in the dielectric function of highly excited materials (see Section 3.3) can exceed 50% in both the real and imaginary part, which is an order of magnitude greater than the error in our apparatus. In addition, studying highly excited materials often involves pump fluences above the threshold for permanent damage of the material, where sample size limits the number of measurements that can be made. Thus, the two-angle reflectometry technique permits measurement of the dynamics of highly excited materials over a wider range of excitation fluences and time delays than true ellipsometry without a significant sacrifice in accuracy.

In the remainder of this section, we discuss how to design a two-angle-of-incidence reflectometer. First, we consider the case of an isotropic material, then expand the discussion to include multilayer systems and anisotopic materials.

#### **3.2.1** Determining $\epsilon(\omega)$ of isotropic materials

Because the dielectric function of a material is not directly measurable, constitutive equations are necessary to relate measurable quantities, such as reflectivity and transmissivity, to  $\epsilon(\omega)$ . In cw multiple-angle-of-incidence ellipsometry, measurements are performed over a range of incident angles, and  $\epsilon(\omega)$  is found by numerical inversion of the appropriate constitutive equation with high accuracy and precision. For an isotropic material, the Fresnel formulas [43] are used to relate reflectivity to  $\epsilon(\omega)$ :

$$r_p = \frac{\epsilon \cos \theta - \sqrt{\epsilon_0} \sqrt{\epsilon - \epsilon_0 \sin^2 \theta}}{\epsilon \cos \theta + \sqrt{\epsilon_0} \sqrt{\epsilon - \epsilon_0 \sin^2 \theta}},$$
(3.11)

$$r_s = \frac{\sqrt{\epsilon_0}\cos\theta - \sqrt{\epsilon - \epsilon_0}\sin^2\theta}{\sqrt{\epsilon_0}\cos\theta + \sqrt{\epsilon - \epsilon_0}\sin^2\theta},$$
(3.12)

where  $r_p$  and  $r_s$  are the field reflectivities — the ratios of the reflected and incident complex E fields — for p and s polarization, respectively, and  $\theta$  is the angle of incidence from medium "0." The power reflectivity R is given by the absolute square of the Fresnel factors, *e.g.*,  $R_p = |r_p|^2$ . We extract both  $\operatorname{Re}[\epsilon(\omega)]$  and  $\operatorname{Im}[\epsilon(\omega)]$  from two measurements of the absolute reflectivity. Using the minimum number of measurements to determine  $\epsilon(\omega)$  by numerical inversion requires a careful choice of operating parameters — namely, the polarization and angle of incidence.

To determine the optimum polarization and angle of incidence for the two mea-

surements, we calculate reflectivity pairs over a range of dielectric constant values using Eqs. (3.11) and (3.12). Figure 3.7(a) shows a grid of dielectric constant values as well as the dielectric functions of four materials (Te, Si, GaAs, and Sb) over the spectral range of our probe (1.5 - 3.5 eV). If we choose to perform measurements at a 45° angle of incidence, p and s polarization, this grid of values is mapped into the reflectivity space shown in Figure 3.7(b). With this choice of operating parameters, the grid of dielectric values collapses onto a line, and so the experimental uncertainty in the measurement of absolute reflectivities will translate into a large uncertainty in dielectric constant values after numerical inversion. Although shown for a 45° angle of incidence, the same problem occurs when the s and p polarized reflectivity are measured at any single angle of incidence.

When both measurements are taken with p polarized light at different angles of incidence, the uncertainty in extracting  $\epsilon(\omega)$  can be reduced to reasonable levels. Figures 3.7(c), 3.7(d), and 3.7(g) show the mapping of the grid of dielectric constant values into reflectivity space for  $45^{\circ}$  angle of incidence paired with  $60^{\circ}$ ,  $75^{\circ}$ , and  $83^{\circ}$ , respectively. As the second angle is increased, the grid of points in (a) spreads over a larger range of reflectivities because the pseudo-Brewster angle<sup>5</sup> is approached for many of the dielectric constant values.

With the general notion of "a good spread" in reflectivity space in mind, we wish to fine-tune our choice of angles. In addition, we desire a sense of "how good" our technique can be, given a certain amount of uncertainty in measuring each reflectivity. If f is the constitutive relation between reflectivity and dielectric constant,  $R = f(\epsilon, \theta)$ , then

$$\begin{pmatrix} \Delta R(\theta_1) \\ \Delta R(\theta_2) \end{pmatrix} = \mathbf{J} \begin{pmatrix} \Delta \epsilon_1 \\ \Delta \epsilon_2 \end{pmatrix}, \qquad (3.13)$$

<sup>&</sup>lt;sup>5</sup>Absorbing materials do not possess a Brewster angle because the p polarized reflectivity is non-zero for all angles of incidence. The pseudo-Brewster angle is defined as the angle for which the p polarized reflectivity is minimized.



Figure 3.7: (a) The dielectric functions of Si, GaAs, Sb, and Te (from 1.5 to 3.5 eV) are plotted over a grid of dielectric constant values. In (b), (c), (d), and (g), the Fresnel formula are used to calculate reflectivity pairs at the angles and polarizations indicated for each of the points in (a). In (e) and (f), contour plots represent the uncertainty in extracting  $\operatorname{Re}[\epsilon(\omega)]$  and  $\operatorname{Im}[\epsilon(\omega)]$ , respectively, given a 1% error in measuring the reflectivity for the parameters indicated in (d). Plots (h) and (i) are analogous to (e) and (f), but are calculated for the parameters indicated in (g). In all four contour plots, the representative materials are overlayed as a reference.

where

$$\mathbf{J} = \begin{bmatrix} \frac{\partial f(\theta_1)}{\partial \epsilon_1} & \frac{\partial f(\theta_1)}{\partial \epsilon_2} \\ \frac{\partial f(\theta_2)}{\partial \epsilon_1} & \frac{\partial f(\theta_2)}{\partial \epsilon_2} \end{bmatrix}, \qquad (3.14)$$

is a Jacobian matrix and  $\epsilon = \epsilon_1 + i\epsilon_2$ . Inverting Eq. (3.13) yields the uncertainty in the dielectric constant as a function of the uncertainty in reflectivity,

$$\begin{pmatrix} \Delta \epsilon_1 \\ \Delta \epsilon_2 \end{pmatrix} = \mathbf{J}^{-1} \begin{pmatrix} \Delta R(\theta_1) \\ \Delta R(\theta_2) \end{pmatrix}.$$
 (3.15)

Assuming a 1% uncertainty in each reflectivity measurement,  $\Delta R/R = 0.01$ , Eq. (3.15) predicts the uncertainty in extracting the real or imaginary dielectric constant as a function of  $\epsilon_1$  and  $\epsilon_2$ . Figures 3.7(e) and 3.7(h) are contour plots of the relative uncertainty ( $\Delta \epsilon_1/\epsilon_1$ ) in the real part of the dielectric constant for the angles and polarizations in Figures 3.7(d) and 3.7(g), respectively. The dielectric functions of the three reference materials are overlayed to show the resulting uncertainty in the dielectric functions of these materials. The decrease in error at 83° vs. that at 75° is more apparent in these figures than in Figures 3.7(d) and 3.7(g). At 75°, the uncertainty in  $\text{Re}[\epsilon(\omega)]$  of silicon is as much as 20%, but remains below 2% at 83°. Similar improvements are seen for the other reference materials. The uncertainty in the imaginary part of the dielectric constant also improves in going from 75° to 83°, as shown in Figures 3.7(f) and 3.7(i). While the uncertainty is generally lower at 83° than at 75°, it does increase for certain values of ( $\epsilon_1, \epsilon_2$ ), illustrating the fact that different angle-of-incidence pairs are optimal for different materials.

In order to find  $\epsilon(\omega)$  after performing pump-probe reflectivity measurements at the chosen angles of incidence, we numerically invert the constitutive equations (in the case of an isotropic material, the Fresnel formulas). The numerical inversion algorithm is based on the simplex downhill method [44], which minimizes the difference between the measured reflectivities and the reflectivities calculated via the constitutive equations for trial values of  $\operatorname{Re}[\epsilon(\omega)]$  and  $\operatorname{Im}[\epsilon(\omega)]$  at each wavelength and time delay.

#### 3.2.2 Extension to oxide layers, thin films, and uniaxial materials

To obtain the dielectric function of an isotropic material, Eqs. (3.11) and (3.12) are required to relate  $\epsilon(\omega)$  to the sample reflectivity. In practice, a single interface between the vacuum and a semi-infinite isotropic sample is rare. In this section, we introduce constitutive equations that relate the observed reflectivity to the dielectric functions of multi-layer and anisotropic materials.

#### Multilayer systems

Many solid materials develop a native oxide layer when exposed to air. Typically, native oxide layers are 1 – 10 nm thick with  $\epsilon(\omega)$  a real constant ranging from 4 to 10 in the visible [45]. For optical experiments, especially at high angles of incidence, the native oxide layer greatly affects the reflectivity of the sample.

A general procedure for calculating the reflectivity of a multilayer stack is the matrix method described by Born and Wolf [43]. The system of interest is the multilayer stack depicted in Figure 3.8. We define a characteristic matrix for each layer l,

$$M_{l} = \begin{bmatrix} \cos \beta_{l} & -\frac{i}{q_{l}} \sin \beta_{l} \\ -iq_{l} \sin \beta_{l} & \cos \beta_{l} \end{bmatrix}, \qquad (3.16)$$

where

$$q_l = \frac{1}{\epsilon_l} \sqrt{\epsilon_l - \epsilon_0 \sin^2 \theta_0} \tag{3.17}$$

and

$$\beta_l = \frac{\omega}{c} h_l q_l. \tag{3.18}$$

Variables  $\epsilon_l$  and  $h_l$  denote the dielectric constant and thickness of layer l, respectively, and  $\theta_0$  is the angle of incidence of p-polarized light to the stack. If there are N layers between the incident medium (labeled "0") and the substrate (labeled "N + 1"), the characteristic matrix for the entire stack of layers is the matrix product

$$M = \prod_{l=1}^{N} M_l. \tag{3.19}$$

The reflectivity of the sample is calculated from the elements of the  $2 \times 2$  matrix M and



Figure 3.8: A multi-layer stack of N layers between the ambient ( $\epsilon_0$ ) and a semi-infinite substrate ( $\epsilon_{N+1}$ ).

the optical properties of the incident medium and the substrate [43]:

$$R = |r|^{2} = \left| \frac{(M_{11} + M_{12} q_{N+1}) q_{0} - (M_{21} + M_{22} q_{N+1})}{(M_{11} + M_{12} q_{N+1}) q_{0} + (M_{21} + M_{22} q_{N+1})} \right|^{2}.$$
(3.20)

Equation (3.20) is the constitutive equation that relates the sample reflectivity to the dielectric function and thickness of each layer. For choosing angles of incidence and numerically extracting the dielectric function of a thin film or substrate, the role of Eq. (3.20) is identical to that of the Fresnel equations for isotropic materials, as described in Section 3.2.1. The layer thickness is determined by continuous wave ellipsometry or in the manner described in Section 3.2.3; the thickness is not determined from the numerical inversion.

#### Uniaxial materials

The crystal symmetry of an isotropic material reduces its  $3 \times 3$  dielectric tensor to a single dielectric function times the identity matrix. Uniaxial materials, such as tellurium, have crystal symmetries that distinguish a *c* axis from an *ab* plane. As a result, the dielectric tensor has two independent elements. The ordinary dielectric function  $\epsilon_{\rm ord}(\omega)$  describes the optical properties for **E** fields in the *ab* plane while the extraordinary dielectric function  $\epsilon_{\rm ext}(\omega)$  describes the optical properties for **E** fields along the *c* axis. For these materials, full optical characterization requires measuring four quantities — the real and imaginary parts of  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$ .

Earlier works [46, 47, 48] have derived equations for the reflectivity of uniaxial materials in various geometries. A geometry of particular interest to our technique is the following. Consider a three-medium structure of vacuum–oxide–substrate, where the oxide layer is isotropic but the substrate is uniaxial. The reflectivity is given by [43]

$$R = \left| \frac{r_{01} + r_{12} e^{2i\beta_1}}{1 + r_{01} r_{12} e^{2i\beta_1}} \right|^2, \qquad (3.21)$$

where  $r_{01}$  and  $r_{12}$  are the field reflectivities of the vacuum-oxide and oxide-substrate interfaces, respectively, and  $\beta_1$  is calculated from Eq. (3.18). The vacuum-oxide reflectivity is given by the Fresnel formulas. The reflectivity of the oxide-substrate interface depends on the orientation of the *c* axis. If the *c* axis lies along the interface and is perpendicular to the plane of incidence, as in Figure 3.9(a), the *p* polarized reflectivity is given by Eq. (3.11) with  $\epsilon \rightarrow \epsilon_{\text{ord}}$ . If the *c* axis lies along the interface and in the plane of incidence, as in Figure 3.9(b), the *p* polarized reflectivity is given by

$$r_{12} = \frac{n_{\parallel} n_{\perp} \cos \theta - n_{\rm ox} \sqrt{n_{\perp}^2 - n_{\rm ox}^2 \sin^2 \theta}}{n_{\parallel} n_{\perp} \cos \theta + n_{\rm ox} \sqrt{n_{\perp}^2 - n_{\rm ox}^2 \sin^2 \theta}},$$
(3.22)

where  $n_{\parallel} = \sqrt{\epsilon_{\text{ext}}}$ ,  $n_{\perp} = \sqrt{\epsilon_{\text{ord}}}$ , and  $n_{\text{ox}} = \sqrt{\epsilon_{\text{ox}}}$  is the complex index of refraction of the



Figure 3.9: Reflection configurations where the surface contains the c axis: the c axis is (a) perpendicular or (b) parallel to the plane of incidence. The **E** field is p polarized in both cases.

oxide layer.

Of the possible field polarizations and c-axis orientations, the reflection geometries of Figure 3.9 are the most sensitive for two-angle-of-incidence measurements of  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$ . For the geometry of Figure 3.9(a), the reflectivity depends solely on the ordinary dielectric function because the **E** field is perpendicular to the optic axis. Using the same analysis as in Section 3.2.1, two angles of incidence are chosen and the time-resolved ordinary dielectric function is measured. Then, in the geometry of Figure 3.9(b), the extraordinary part of the dielectric tensor can be extracted using Eqs. (3.22) and (3.21) because the values of  $\epsilon_{\rm ord}(\omega)$  have been measured for each time delay and pump fluence. In addition to being sensitive to the two dielectric functions of interest in each case, these measurement geometries have the practical advantage of being related by a 90° rotation of the sample.

#### 3.2.3 Measuring absolute reflectivities

The constitutive relations in Sections 3.2.1 and 3.2.2 relate the dielectric function to absolute reflectivity. Thus, the experimental challenge lies in measuring the absolute reflectivity of a sample when reflective and transmissive optical elements modify the spectrum of the probe pulse before it reaches the detector. The calibration of the detection system must account for these absorptive losses. Since the probe and reference beams are split from the same pulse, the detected spectra  $[S_{\text{probe}}(\omega)]$  and  $S_{\text{ref}}(\omega)]$  can be used to calibrate our system. For a particular sample, the ratio of the detected spectra is

$$\frac{S_{\text{probe}}(\omega)}{S_{\text{ref}}(\omega)} = \frac{g(\omega)}{h(\omega)} R(\omega), \qquad (3.23)$$

where  $h(\omega)$  accounts for the absorptive losses in the reference beamline and  $g(\omega)$  accounts for the losses in the probe beamline, separate from the sample reflectivity  $R(\omega)$ . In order to calibrate the system we must measure  $g(\omega)/h(\omega)$ , which is independent of the sample under investigation. From the above equation,

$$\frac{g(\omega)}{h(\omega)} = \frac{S_{\text{probe}}(\omega)}{S_{\text{ref}}(\omega)} \frac{1}{R(\omega)}.$$
(3.24)

For a sample of known optical properties, we can calibrate the apparatus by measuring  $S_{\text{probe}}(\omega)$  and  $S_{\text{ref}}(\omega)$  and taking  $R(\omega)$  to be the calculated reflectivity of the sample for a given angle of incidence. When multiple reference samples are used, the quality of the sample of interest can be verified and the confidence in the calibration can be improved.

The above-described method of calibration can also be used to measure the angle of incidence of the white-light probe and the thickness and dielectric constant of any oxide layers. To perform such a measurement, as many reference samples are used as there are unknowns. All reference samples are aligned to the same (possibly unknown) angle of incidence using a HeNe laser. The values of  $S_{\text{probe}}/S_{\text{ref}} \times 1/R(\omega)$  for different samples only



Figure 3.10: A contour plot of the uncertainty in the calibration as a function of photon energy for a range of possible angles of incidence (b) finds the angle of incidence to be  $82.5^{\circ}$  (dotted line). The calibration data is shown in (a) for this angle.

agree when the reflectivity is calculated at the correct angle of incidence and with the correct oxide layer thicknesses and dielectric constant values. Using as many reference materials as unknowns ensures that all curves agree for only the correct values of the unknowns. Figure 3.10(b) is a plot of the uncertainty in the calibration among three reference samples (standard deviation divided by mean) at each photon energy in the probe for a range of possible incident angles. The reference samples are sapphire, GaAs with an oxide layer of known thickness, and Te in the geometry of Figure 3.9(a). The mean uncertainty is lowest for the angle indicated by the dotted line in Figure 3.10(b), marking the actual angle of incidence of the probe  $(82.5^{\circ})$  for the case presented here. Figure 3.10(a) shows the agreement between the three samples for this angle of incidence. The calibration is taken to be the average of the three curves in Figure 3.10(a). Using this method of analysis, the angle of incidence and oxide layer thicknesses can be determined to an accuracy of  $0.1^{\circ}$ and 0.5 nm, respectively. These uncertainties do not significantly affect the final assigned uncertainty in  $\epsilon(\omega)$ . They can be folded into the analysis of Section 3.2.1 to minimize their effects (see Section 3.2.4). Whenever possible, oxide layers are determined in a separate measurement to avoid the effects of parameter correlation [33, 49].

The uncertainty in measurements of the absolute reflectivity depend on both the

accuracy of the calibration and the shot-to-shot fluctuations of the probe. If the experiment is carried out at pump fluences below the threshold for permanent damage, multiple shots can be averaged at the repetition rate of the laser source. We find that the resolution of our setup in this multiple-shot mode is on the order of  $\Delta R/R = 10^{-3}$  when 5000 laser shots are acquired. However, this is not the accuracy in measuring the absolute reflectivity due to the approximate 1% uncertainty in the calibration. For experiments at pump fluences near or above the damage threshold, the sample must be translated between shots so that each pulse strikes a new spot on the sample. The single-shot operation mode carries larger uncertainties ( $\Delta R/R \approx 5\%$ ) than that of the calibration because sample area limits the number of spectra that can be accumulated at each time delay and pump fluence. On the other hand, the dynamics of highly excited materials (*e.g.*, the semiconductor-to-metal transitions in GaAs) are accompanied by signal variations of  $\Delta R/R \approx 200\%$ , so the signalto-noise ratio is still high.

To calculate the uncertainty in  $\epsilon(\omega)$ , dielectric constant values for the four pairs of reflectivities  $[R(\theta_1) \pm \Delta R(\theta_1), R(\theta_2) \pm \Delta R(\theta_2)]$  are extracted from the numerical inversion algorithm. Error bars are taken from the two values maximally displaced from the dielectric constant value associated with  $[R(\theta_1), R(\theta_2)]$ .

#### 3.2.4 Estimate of total experimental error

The analysis of Section 3.2.1 handles the estimation of error in extracting the dielectric function on a somewhat superficial level. In particular, the assumed accuracy of  $\Delta R/R = 0.01$  disregards the angular dependence of the accuracy of calibration. Each reference material is aligned to the sample with 0.1° accuracy, and the effect of this uncertainty on the uncertainty of the calibration changes with the angle of incidence. Below we present a correction to the error calculation of Section 3.2.1, resulting in clear choices for

the optimum angles of incidence for a given sample material.

In order to provide a better estimate of the uncertainty in reflectivity ( $\Delta R$  of Eq. (3.15)), consider the following expression, which is the "experimental version" of Eq. (3.23),

$$R = C \times \frac{\bar{S}_{\text{probe}}}{\bar{S}_{\text{ref}}} \tag{3.25}$$

where C is the measured calibration (h/g in Eq. (3.23)), and  $\overline{S}$  is an average spectrum of N white-light pulses (typically, N = 5000).<sup>6</sup> Formally, the relative uncertainty in reflectivity can be written in terms of two contributions

$$\left[\frac{\Delta R}{R}\right]^2 = \left[\frac{\Delta C}{C}\right]^2 + 2\left[\frac{\Delta \bar{S}}{\bar{S}}\right]^2.$$
(3.26)

The error term  $\Delta \bar{S}/\bar{S}$  results from shot-to-shot fluctuations in white-light intensity when taking measurements of the sample. The values of  $S_{\text{probe}}$  and  $S_{\text{ref}}$  fluctuate by as much as 25% due to the nonlinear mechanisms of white-light generation. However, the uncertainty  $(\Delta \bar{S}/\bar{S})^2$  decreases with averaging over many laser pulses and is no worse than  $0.25^2/N$ . The factor of 2 in Eq. (3.26) accounts for fluctuations in both probe and reference beams, which tends to over-estimate the actual uncertainty because it ignores the fact that these fluctuations are not independent.

The error term  $\Delta C/C$  represents uncertainty in the value of the calibration, which arises from errors in the alignment of reference materials as well as from fluctuations in white-light intensity during the calibration process. From an expression for the calibration

<sup>&</sup>lt;sup>6</sup>It is usually the case that a mixture of on-CCD-chip averaging of  $S_{\text{probe}}$  and  $S_{\text{ref}}$  and an averaging of sets of  $\bar{S}_{\text{probe}}/\bar{S}_{\text{ref}}$  occur in a given experiment. In general, the smallest errors occur when on-chip averaging is kept to a minimum.

C, we derive an expression for the uncertainty...

=

$$C = \frac{1}{n} \sum_{j=1}^{n} C_j = \frac{1}{n} \sum_{j=1}^{n} R_j \frac{\bar{S}_{\text{ref},j}}{\bar{S}_{\text{probe},j}}$$
(3.27)

$$\Rightarrow \Delta C^2 = \frac{1}{n} \sum_{j=1}^n \left( \left[ \frac{\Delta R}{R} \right]_j^2 + 2 \left[ \frac{\Delta \bar{S}}{\bar{S}} \right]_j^2 \right) C_j^2 \tag{3.28}$$

$$\Rightarrow \left[\frac{\Delta C}{C}\right]^2 \approx \frac{1}{n} \sum_{j=1}^n \left( \left[\frac{\Delta R}{R}\right]_j^2 + 2\left[\frac{\Delta \bar{S}}{\bar{S}}\right]_j^2 \right)$$
(3.29)

where *n* is the number of materials used in measuring the calibration,  $\bar{S}_j$  is the average of N spectra collected for the *j*th material, and  $R_j$  is the reflectivity of the *j*th material as calculated from literature values of its optical properties. The uncertainty in the calculated reflectivity arises from alignment errors ( $\Delta \theta = 0.1^{\circ}$ ), and the  $\Delta S/S$  term is described above. The approximation step is an important one, where we take  $C_j \approx C$  for all materials. Without such a step, values of the measured spectral intensity must be provided, which is usually difficult to do before an experiment begins. Using Eq. (3.29) and rewriting  $[\Delta R/R]_j$  in terms of  $\Delta \theta$ , Eq. (3.26) becomes

$$\left[\frac{\Delta R}{R}\right]^2 = 2\frac{(0.25)^2}{N} + \frac{1}{n}\sum_{j=1}^n \left( \left[\frac{1}{R_j}\frac{\partial R_j}{\partial \theta}\Delta\theta\right]^2 + 2\frac{(0.25)^2}{N}\right).$$
(3.30)

While Eq. (3.30) does not take into account every source of error in the experiment,<sup>7</sup> it does reveal significant sources of error beyond the analysis of Section 3.2.1. Figure 3.11 shows the result of using Eqs. (3.15) and (3.30) to determine the ideal angles of incidence for measuring the ordinary dielectric function of tellurium. The uncertainty in  $\text{Re}[\epsilon]$ or  $\text{Im}[\epsilon]$  shown in Figure 3.11 is the average uncertainty over the spectral range of the probe (1.5 eV to 3.5 eV). The reference materials used for this calculation are sapphire, GaAs, and Si. The conclusion from Figure 3.7 that smaller uncertainties occur when one angle is close to the pseudo-Brewster angle of the sample is reproduced in this analysis — the error

<sup>&</sup>lt;sup>7</sup>For instance, uncertainty in the angle of incidence as determined by the methods of Section 3.2.3 alters the mapping of reflectivity pairs to dielectric function.



Figure 3.11: Contour plots of the average uncertainty in (a)  $\operatorname{Re}[\epsilon]$  and (b)  $\operatorname{Im}[\epsilon]$  for possible angle-of-incidence pairs.

decreases as one angle approaches  $80^{\circ}$ .<sup>8</sup> The insight gained from this analysis is the degree to which the choice of reference material affects the uncertainty. As one of the angles of incidence approaches the Brewster (or pseudo-Brewster) angle of one of the reference materials, the uncertainty greatly increases. As shown in Figure 3.11, one such increase occurs at the Brewster angle of sapphire (~ 60.6°). The effects of choosing the semiconductors Si and GaAs are distributed across multiple angles because each material has a different pseudo-Brewster angle for each color of the probe, although the feature at 75° results from their inclusion. While it is always possible to use certain reference materials for calibration at low angles of incidence and others at high angles, Figure 3.11 shows that this is certainly not necessary. Good accuracy in extracting the dielectric function occurs when the first angle of incidence is near the pseudo-Brewster angle of the sample, the second angle is at least 10° away from the first, and neither angle is very close to the Brewster angle of any of the reference materials (in particular, transparent materials).

<sup>&</sup>lt;sup>8</sup>The pseudo-Brewster angle of  $\epsilon_{ord}$  of tellurium varies from 80° at 1.5 eV to 81.5° at 2eV to 72° at 3.5 eV.

#### **3.3** Time-resolved dielectric function measurements

As an illustration of our technique, we present measurements of the femtosecond time-resolved dielectric function of an isotropic material (GaAs) and a thin film (*a*-GeSb). Discussion of measurements of an anisotropic material (Te) are reserved for Chapters 5 and 6. We briefly discuss the importance of these results and compare them to other measurements of the material dynamics.

#### 3.3.1 Ultrafast carrier and lattice dynamics in GaAs

Shortly after the introduction of femtosecond laser sources, numerous experiments were conducted on semiconductors where a transition to a metallic state was observed upon laser irradiation. Experimental techniques included pump-probe reflectivity measurements [16], both reflectivity and second harmonic measurements [50, 19, 17, 18], and pump-probe microscopy [51, 52]. While a laser-induced phase transition was observed in each experiment with high precision, the nature of the resulting phase and the changes in the band structure were difficult to determine. This difficulty is due to the fact that many different values of  $\epsilon(\omega)$ , and hence many different band structures and material phases, can yield the same reflectivity at a particular angle of incidence.

We performed single-shot femtosecond time-resolved dielectric function measurements of GaAs to investigate carrier and lattice dynamics associated with its ultrafast semiconductor-to-metal transition under intense photoexcitation [23, 53]. Figure 3.12 shows dielectric function measurements of GaAs. Without excitation of the sample,  $\epsilon(\omega)$  matches literature values of the dielectric function [5], confirming that our technique measures the dielectric function correctly. Figure 3.12(b) shows  $\epsilon(\omega)$  500 fs after excitation below the threshold for permanent damage ( $F_{\rm th} = 1.0 \text{ kJ/m}^2$ ). Shortly after excitation, before the ions of the lattice can move, changes in  $\epsilon(\omega)$  are due to the presence of excited carriers in



Figure 3.12: Dielectric function data for GaAs — • =  $\operatorname{Re}[\epsilon]$ , • =  $\operatorname{Im}[\epsilon]$ . (a) Under no excitation,  $\epsilon(\omega)$  matches literature values of the dielectric function, represented by the solid and dashed curves [5]. An example of changes in  $\epsilon(\omega)$  due to the presence of excited carriers is shown in (b). (c) At sufficiently high pump fluences, a semiconductor-to-metal transition is observed, as evidenced by the fit to the Drude model ( $\omega_{\rm p} = 13.0$  eV and  $\tau = 0.18$  fs).

the conduction band. The decrease of  $\text{Im}[\epsilon(\omega)]$  around the  $E_1$  critical point (near 3 eV) is likely due to Pauli blocking of the transition by electrons in the conduction band. At higher excitation fluences, a transition to a metallic state is observed, an example of which is shown in Figure 3.12(c). This data is well fit by the Drude model, which describes freeelectron (metallic) behavior. The parameters of the fit (a plasma frequency of 13 eV and a relaxation time of 0.18 fs) reveal that virtually all of the valence electrons are free and that the band gap has completely collapsed. Theoretical calculations of the evolution of the dielectric function of GaAs after femtosecond-pulse excitation agree with our experimental results [54, 55, 56].

#### 3.3.2 Ultrafast phase changes in *a*-GeSb

The speed of ultrafast phase transitions and the large reflectivity variations associated with them make materials that display such transitions good candidates for optical switches and high speed optical data storage. Thin films of *a*-GeSb allow optically induced, optically reversible amorphous-to-crystalline transitions. In 1998, Sokolowski-Tinten and co-workers presented normal-incidence reflectivity measurements which suggested that femtosecond pulses above the threshold for permanent crystallization can induce an ultrafast *disorder-to-order* transition in amorphous  $Ge_{0.06}Sb_{0.94}$  films within 200 fs [57]. The suggestion of a subpicosecond amorphous-to-crystalline phase transition raises an important question: how can lattice ordering occur in less time than it takes to establish thermal equilibrium between the laser-excited electrons and the lattice?

We performed single-shot dielectric function measurements of a 50-nm thin film of a-Ge<sub>0.06</sub>Sb<sub>0.94</sub> to determine the nature of the phase during its ultrafast phase transition [58]. Figure 3.13(a) shows the agreement between  $\epsilon(\omega)$  obtained at a time delay of -1 ps and literature values of the dielectric function [5]. As a reference, the dielectric function of the crystalline phase is also shown.<sup>9</sup> Because the film was optically thin and covered by a 1.25-nm SbO<sub>2</sub> oxide layer [59], this sample is considered a four-medium system: air, oxide, *a*-GeSb thin film, and fused silica substrate.

Figure 3.13(b) shows the response of the dielectric function 200 fs after arrival of a pump pulse of fluence  $F = 320 \text{ J/m}^2$ , which is 60% above the threshold for permanent crystallization ( $F_{cr}$ ). At this excitation fluence, the dielectric function remains unchanged from 200 fs to 475 ps. The same dielectric function is observed on subpicosecond time scales for all fluences above  $F_{cr}$ , indicating the existence of a nonthermal phase after femtosecond-

<sup>&</sup>lt;sup>9</sup>Literature values of  $\epsilon(\omega)$  for c-Ge<sub>0.06</sub>Sb<sub>0.94</sub> are not available. The data presented are measurements taken in our apparatus of a region of the sample that was permanently crystallized by laser irradiation.

pulse excitation. The existence of a new phase at ultrashort time delays for all fluences above  $F_{\rm cr}$  was correctly identified by the authors of Ref. [57], however, the material is not crystalline, as evidenced by the discrepancy between the measured dielectric function and that of the crystalline phase (see Figure 3.13(b)). This discrepancy is brought out by Figure 3.13(c), which shows the normal-incidence reflectivity as calculated from our time-resolved dielectric function measurements. Only at the 2.01-eV photon energy of the experiments in Ref. [57] does the reflectivity at 200 fs after excitation above  $F_{\rm cr}$  match that of the crystalline phase. Furthermore, even at 2.01 eV, we find that for angles of incidence near or above the pseudo-Brewster, the reflectivity does not go to the crystalline level for pump fluences above  $F_{\rm cr}$ . Our measurements thus show that broadband measurements of  $\epsilon(\omega)$  enable one to distinguish phases that may appear the same based on reflectivity or transmission for a single photon energy at a single angle of incidence.

## 3.4 Summary

The time-resolved dielectric function measured with this reflectometry technique provides the most information of any linear optical probe, revealing changes in the lattice bonding, carrier distribution, and phase of a material. We avoid the necessity of assuming a particular model of the material dynamics as well as the potential pitfalls of other methods that measure changes in reflectivity at a single photon energy. While a representative set of sample types is presented, this technique can be extended to any sample geometry, provided a constitutive relation between reflectivity and dielectric tensor exists.

An extension of this technique would be useful as a probe of the interaction between substrate and oxide layer. Under intense excitation, both above and below the threshold for permanent damage, the substrate can alter its lattice configuration or lose order completely.



Figure 3.13: (a),(b) Dielectric function data for *a*-GeSb thin films — • = Re[ $\epsilon(\omega)$ ], • = Im[ $\epsilon(\omega)$ ]: (a)  $\epsilon(\omega)$  under no excitation (-1 ps time delay), and (b)  $\epsilon(\omega)$  200 fs after excitation of 320 J/m<sup>2</sup>. In both plots, the solid and dashed curves show the real and imaginary parts of  $\epsilon(\omega)$  for the amorphous phase from previous measurements,[60] and the dotted and dash-dotted curves show the real and imaginary parts of  $\epsilon(\omega)$  of the crystalline phase. (c) Normal-incidence reflectivity calculated from the time-resolved  $\epsilon(\omega)$  data. The reflectivity of the amorphous, crystalline, and liquid phases are shown for reference.

Yet, the dynamics of the oxide layer during the phase transition of the substrate are often ignored. Additional measurements at other angles of incidence could enable monitoring the substrate along with the thickness of the oxide layer and its optical properties. Given the accuracy of spectroscopic ellipsometry in measuring thin film characteristics, a pump–probe ellipsometer may be the ideal device for such an application because any change in oxide layer thickness, dielectric function, or in the oxide–substrate interface, is likely to be small on the picosecond time scale.

## Chapter 4

# **Previous Work on Tellurium**

In order to provide the reader a context in which to view the results presented in Chapters 5 and 6, we present a review of the relevant work on tellurium that has preceded this thesis. In this chapter we discuss the crystal structure, optical properties, and calculated band structure of tellurium, as well as the results of several groups that have performed experimental and theoretical investigations of the dynamics under femtosecond pulse excitation.

## 4.1 Structural and optical properties of tellurium

The crystal structure of tellurium is that of three-atom per turn helices arranged in a hexagonal array. In crystallographic terms, tellurium is trigonal with space group P3<sub>1</sub>21–D<sup>4</sup><sub>3</sub> and a three-atom basis at  $(u0\frac{1}{3},0u\frac{2}{3},\bar{u}\bar{u}0)$  [61]. Figure 4.1 shows the structure of tellurium viewed down the *c* axis. The equilibrium lattice constants are a = 0.4456 nm and c = 0.5927 nm, the ratio of the helical radius to the interhelical spacing *a* is u = 0.2633, and each atom is spaced vertically by c/3 [61]. Each tellurium atom has two nearest neighbor bonds of length r = 0.2834 nm and four second nearest neighbor bonds of length R = 0.3494



Figure 4.1: Crystal structure of tellurium viewed down the c axis. Ions of the same shading are in the same plane (black-shaded ions are below the page, white-shaded above). Solid lines indicate nearest neighbor bonds, dashed lines indicate second nearest neighbor bonds, and dash-dotted lines indicate bonds to ions in planes not shown here. In the equilibrium configuration, helices are formed with radius u = 0.2633a, the lattice constant of the trigonal arrangement of helices is a, and the spacing between planes is c/3.

nm [61].

The lattice structure of tellurium has many normal modes of vibration, that is, many phonon modes.<sup>1</sup> Although all of the six optical phonon modes in Te have been excited coherently and detected, the symmetry-preserving  $A_1$  mode is dominant as a result of the efficiency of its excitation or its efficiency in modulating the dielectric function or both, which we discuss later. For now, we simply describe the  $A_1$  mode as a "breathing mode," where the value of the helical radius u changes but the lattice constants a and c remain fixed.

Tellurium is optically anisotropic due to its crystal structure. For electric fields directed parallel (perpendicular) to the *c* axis, the material response is governed by the extraordinary (ordinary) dielectric function  $\epsilon_{\text{ext}}(\omega)$  ( $\epsilon_{\text{ord}}(\omega)$ ). As shown in Figure 4.2,  $\epsilon_{\text{ord}}(\omega)$ and  $\epsilon_{\text{ext}}(\omega)$  display many of the same features. This similarity results from the fact that, at

<sup>&</sup>lt;sup>1</sup>For a complete listing of the phonon modes of tellurium, see the german text Ref. [62].



Figure 4.2: Linear optical properties of tellurium. The ordinary part of the dielectric tensor is shown in black, the extraordinary part in gray. In both cases, solid lines show the real part and dashed lines the imaginary part of the function.

optical frequencies, both dielectric functions represent the same set of electronic transitions in the crystal, the same JDOS.<sup>2</sup> However, as Figure 4.2 shows, the optical properties are different along different directions in the crystal. These differences come from variations in the value of the matrix elements that quantify the strength of those transitions as the direction of the applied field changes the coupling  $\mathbf{A} \cdot \hat{\mathbf{p}}$  (see Eq. 2.12).

Tellurium is a Group VI element and each atom in the crystal contributes six valence electrons to form the bonds that hold the lattice intact. The density of valence electrons in tellurium is  $1.77 \times 10^{23}$  cm<sup>-3</sup>.<sup>3</sup> In experiments where the excitation strength approaches the threshold for permanent damage of the crystal, the excited electron density is equal to or greater than 1% of the valence electron density. Although this excitation is not as strong as that which leads to disordering of a zincblende semiconductor,<sup>4</sup> it still breaks a significant number of bonds in the material. The effects of this bond-breaking are described in the following sections.

 $<sup>^{2}</sup>$ See Section 2.1.1.

 $<sup>^{3}</sup>$ The density of valence electrons is calculated from the mass density of tellurium and the fact that each tellurium atom contributes six valence electrons.

<sup>&</sup>lt;sup>4</sup>See Section 2.2.3.

### 4.2 Time-domain experiments

Coherent lattice vibrations in tellurium were first reported by a group at MIT [63]. Using a single-color pump-probe reflectivity setup, oscillations in the reflectivity were observed at the frequency of the symmetry-preserving  $A_1$  phonon mode and at no other after excitation by a 60 fs pulse of fluence 2.5 J/m<sup>2</sup>. Figure 4.3(a) shows the oscillations observed, and the inset shows the peak in the Fourier transform that corresponds to the phonon mode excited (the arrows indicate the frequency of other known phonon modes that were not observed). The researchers also observed oscillations in the reflectivity of Sb, Bi, and Ti<sub>2</sub>O<sub>3</sub>, at the frequency of their respective  $A_1$  modes. Based on these observations, they propose a generation mechanism called displacive excitation of coherent phonons (DECP). According to DECP theory, the excitation of carriers by a femtosecond pulse establishes new equilibrium positions before the lattice has significantly deformed, allowing all ions to move in concert if the new equilibrium lattice configuration has the same symmetry as the undisturbed lattice. This argument is very similar to the discussion of the dynamics of Si in Section 2.2.3, although in DECP the new lattice potential is required to have a stable minimum after excitation.

Further investigation of the coherent phonon dynamics in tellurium revealed a variation in the  $A_1$  phonon frequency with pump intensity [65, 66, 67]. At excitations up to 130 J/m<sup>2</sup>, the coherent phonon frequency is observed to decrease roughly linearly with increasing excitation strength. The maximum change in reflectivity also increases with excitation strength, linearly for small fluences, and asymptotically approaches a maximum change of  $\Delta R/R \approx 0.1$  under the highest excitations. Under increasing excitation, the lifetime of the coherent phonon oscillations decreases. In addition to physical mechanisms that "dephase" the lattice vibrations, such as phonon-phonon scattering, the researchers



Figure 4.3: (a) Transient reflectivity of tellurium at 2 eV and (inset) Fourier transform of the signal, after Ref. [63]. (b) Transient isotropic and anisotropic reflectivity of tellurium at 2 eV, after Ref. [64].

argue that the variation in excited electron density with depth in the sample, coupled with the dependence of the phonon frequency on the excited electron density, leads to a decrease in the lifetime of the reflectivity oscillations [67].<sup>5</sup>

Although the excitation of the symmetry-preserving  $A_1$  phonon mode in tellurium dominates the optical response, the coherent excitation of other phonon modes has also been observed [64, 68]. The observation of oscillations at 2.77 THz and 4.2 THz in the anisotropic reflectivity,<sup>6</sup> precisely the frequency of the two  $E_{TO}$  phonon modes in tellurium, suggests that other modes can be excited (see Figure 4.3(b)). Anisotropic reflectivity changes in other geometries as well as the detection of THz emission from tellurium under short-pulse excitation reveals that coherent  $E_{LO}$  phonons can be excited as well. The researchers recognized that the excitation of all possible Raman modes (not just the  $A_1$  mode) does not fit the DECP scheme and suggested a mismatch in the diffusion rates of photoexcited

<sup>&</sup>lt;sup>5</sup>Calculations show that the observed oscillations decay because, within a few cycles, lattice vibrations near the surface and deep in the sample are out of phase.

<sup>&</sup>lt;sup>6</sup>The anisotropic reflectivity change is given by, *e.g.*  $\Delta R_a - \Delta R_b$ , where *a* and *b* refer to crystal axes perpendicular to the optic axis. Only phonon modes not symmetric in the *ab* plane can contribute to  $\Delta R_a - \Delta R_b$ .
electrons and holes<sup>7</sup> as a potential excitation mechanism [68].

## 4.3 Theories of coherent phonon excitation

Experimental observation often precedes theoretical understanding of physical phenomena, and the phenomena of coherent phonon generation in solids is no exception. The debate surrounding the physical mechanism responsible for excitation of coherent phonons in absorbing solids centers on two main theories. One is an outgrowth of the phenomenological DECP, the other an extension of the theory describing coherent phonon generation in transparent materials. We discuss both these theories below.

The DECP theory proposed by Zeiger *et al.* [63] involves a phonon amplitude Q(t)that is driven by a displacement  $Q_0(t)$  of its equilibrium lattice coordinate from its initial value. The equation of motion describing the amplitude of the lattice vibration is that of a harmonic oscillator

$$\ddot{Q} + \Gamma \dot{Q} + \Omega^2 Q = \Omega^2 Q_0(t) \tag{4.1}$$

where  $\Omega$  is the phonon frequency and  $\Gamma$  is a phenomenological damping constant. According to the initial theory,  $Q_0(t)$  is determined by quantities such as excited electron temperature or density. Other researchers applied the ideas of DECP to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and claimed the breaking of superconducting electron pairs was yet another means by which to drive coherent lattice vibrations because the superconducting state has a different lattice configuration than the non-superconducting state [69]. Regardless of the mechanism responsible for displacing the equilibrium positions of the ions, the key feature of DECP is that the change in equilibrium position provides an impulsive "kick" to the system.

<sup>&</sup>lt;sup>7</sup>In highly excited materials, diffusion of a significant density of carriers can occur within a few hundred femtoseconds. Unequal diffusion rates between electrons and holes can create an electric field due to this charge separation, the so-called Dember field, giving an impulsive kick to polar phonon modes.

A microscopic (read: quantum mechanical) description of DECP is presented by Kuznetsov and Stanton [70]. The Hamiltonian they consider is

$$\mathcal{H} = \sum_{n,\mathbf{k}} E_n(\mathbf{k}) c_{n,\mathbf{k}}^{\dagger} c_{n,\mathbf{k}} + \sum_{\mathbf{q}} \hbar \Omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \sum_{n,\mathbf{k},\mathbf{q}} M_{n,\mathbf{k},\mathbf{q}} \left( b_{\mathbf{q}} + b_{-\mathbf{q}}^{\dagger} \right) c_{n,\mathbf{k}}^{\dagger} c_{n,\mathbf{k}+\mathbf{q}} , \qquad (4.2)$$

where the "single-particle" energies of the electrons and phonons is accounted for in the first and second terms using creation and annihilation operators  $c_{n,\mathbf{k}}, c_{n,\mathbf{k}}^{\dagger}$ , and  $b_{\mathbf{q}}^{\dagger}, b_{\mathbf{q}}$ , respectively, and the interaction between electrons and phonons is described by the deformation potential matrix elements  $M_{n,\mathbf{k},\mathbf{q}}$  that give the change in energy of state  $|n,\mathbf{k}\rangle$  due to lattice displacement  $\mathbf{q}$ . In this system, the coherent phonon amplitude can be expressed in terms of expectation values for the phonon creation and annihilation operators,  $D_{\mathbf{q}} = \langle b_{\mathbf{q}} \rangle + \langle b_{-\mathbf{q}}^{\dagger} \rangle$ , and the microscopic equation of motion for  $D_{\mathbf{q}}$  (analogous to the phenomenological equation of motion Eq. (4.1)) is

$$\ddot{D}_{\mathbf{q}} + \Omega^2 D_{\mathbf{q}} = -2\Omega_{\mathbf{q}} \sum_{n,\mathbf{k}} M_{n,\mathbf{k},\mathbf{q}} \langle c_{n,\mathbf{k}}^{\dagger} c_{n,\mathbf{k}+\mathbf{q}} \rangle .$$
(4.3)

Comparing Eqs. (4.1) and (4.3), we see that the coherent lattice vibrations are driven by changes in the total energy of the system due to electron occupation (*i.e.*, deformation coupling). Because linear absorption prepares the system in a diagonal state  $\langle c_{n,\mathbf{k}}^{\dagger}c_{n,\mathbf{k}'}\rangle \sim$  $\delta_{\mathbf{k},\mathbf{k}'}$ , only  $\mathbf{q} = 0$  modes can be driven coherently. This treatment of phonon excitation shares many similarities with the description of molecular dynamics in Section 2.2.

Soon after coherent phonon modes other than the symmetry-preserving  $A_1$  mode were observed, Merlin and coworkers developed a general theory of coherent phonon excitation which they refer to as light excitation of coherent phonons (LECP) [71, 72]. Starting with the same Hamiltonian as in Eq. (4.2), they performed a second-order pertubation calculation of the driving term in Eq. (4.3), and discussed the electron-phonon coupling in terms of the Raman tensor  $\partial \chi^{(1)}/\partial Q$ . They go on to argue that LECP is related to resonance Raman scattering, which is discussed in Refs. [73] and [74]. The important result is that the theory provides a framework in which coherent phonon generation can be understood for transparent materials<sup>8</sup> as well as for opaque materials. The main differences between this theory and DECP include the possibility of coherently exciting non-symmetric phonon modes and the requirement of phase matching during the generation process.

The task of settling the question as to which excitation mechanism (DECP or LECP) is the dominant one in the case of tellurium is not undertaken in this thesis. The theoretical results in molecules (see Section 2.2) and the theoretical calculation discussed in Section 4.5 support the DECP picture with respect to the  $A_1$  mode, but the LECP framework is required to account for the excitation of non-symmetry preserving coherent phonons. It is more enlightening to consider the similarities of the underlying physics in each case. The Raman tensor simply represents changes in the linear susceptibility  $\chi^{(1)}$ with lattice displacement, changes that result from pertubations of electronic energy levels via the deformation potential, namely M. Neither  $M_{n,\mathbf{k},\mathbf{q}}$  nor  $\partial\chi^{(1)}/\partial Q$  exactly describes a material: the former treats each excited electron separately while the latter represents the first order approximation to the relationship between lattice displacement and change in susceptibility. However, both quantities reflect the fact that electron occupation can exert a force on the ions, causing lattice distortions that shift electron energy levels.

## 4.4 Experiments in coherent control

The objective of studies in optical control over coherent optical phonons is to prepare a solid in a nonequilibrium state and investigate its evolution on femtosecond time scales. The earliest experiments were performed on transparent materials (via the ISRS generation mechanism) [75, 76]. Soon after the observation of coherent phonons in absorbing

<sup>&</sup>lt;sup>8</sup>In transparent materials, this process is known as impulsive stimulated Raman scattering (ISRS), where laser frequencies within the bandwidth of a single laser pulse generate coherent phonons through the same  $\chi^{(3)}_{Raman}$  process as described in Section 2.3.2.

solids, attempts were made to control the amplitude of the oscillations.

Hase et al. [77] performed pump-probe reflectivity experiments on Bi films and observed that the reflectivity oscillations due to coherent  $A_1$  phonons can be modified by a second pump pulse. A time delay of nT between the two pump pulses, where n is an integer and T is the phonon period, results in enhancement while a time delay of (n+1/2)T results in cancellation. Although Hase et al. make no reference to the complimentary studies of controlled dissociation performed on molecules, they discuss the process of coherent phonon excitation in terms of DECP. Curiously, however, the process of control is described as the sum of two sets of coherent phonons whose motion was initiated at different times and that now interfere. The formulation described by Hase *et al.* is incorrect because they model the observed traces as the sum of two single-pump reflectivity traces  $(R_1(t) + R_2(t))$  rather than as the reflectivity that derives from the sum of two oscillating susceptibilities  $(\chi_1(t) + \chi_2(t))$ . In fact, the latter (correct) treatment results in measurable reflectivity oscillations even when the "cancellation" criterion of equal amplitude, out-of-phase oscillations is satisfied.<sup>9</sup> When the change in susceptibility is small enough, this model predicts that the reflectivity approaches  $R_1(t) + R_2(t)$ . Indeed, this was the case in Ref. [77], where experiments involved low-energy pump pulses.<sup>10</sup>

DeCamp *et al.* [78] investigated the dynamics of single-crystal Bi for laser excitation near the damage threshold. They observed that the oscillations can be cancelled near the peak lattice displacement by a second pump pulse. Although they do not present as comprehensive a study as that of Hase *et al.*, it is interesting to note that the time delay of the second pump that cancels the oscillation is not precisely (n + 1/2)T. The second pump arrives 500 fs after the first, which is approximately 35 fs earlier than the (n + 1/2)T crite-

<sup>&</sup>lt;sup>9</sup>This perhaps unexpected outcome is due to the photodiode detector measuring, essentially,  $|\chi_{tot}(t)|^2$ , which involves cross-terms with oscillatory components

 $<sup>^{10}</sup>$ In discussing the claims of Hase *et al.*, we have ignored the issue of how two independent sets of coherent vibrations are excited within a crystal.

rion predicts. The authors provide no explanation for this result. In Chapter 6, we discuss similar observations concerning coherent control of large-amplitude phonons in tellurium.

## 4.5 Density functional theory calculations

In Sections 4.2 and 4.3 we discuss the experiments that confirm the excitation of coherent phonons by a femtosecond laser pulse and the theories of how the excitation takes place. In this section, we present theoretical work that calculates how the lattice changes that occur during the coherent phonon motion affect the band structure and optical properties of tellurium, as a prelude to the discussion of our time-resolved dielectric function measurements in Chapters 5 and 6. Currently, the primary theoretical tool for calculating the electronic and optical properties of solids is density functional theory.

The objective of density functional theory (DFT) is to remedy the shortcomings of the non-interacting electron picture of Eq. (2.10). Because solving a Hamiltonian that includes exchange and correlation effects is an intractable many-body problem, the use of electron density to somewhat ignore, yet still take account of, these effects was shown to be a useful model of physical systems [79, 80]. In the framework of DFT, exchange and correlation effects are calculated by computing interaction energies between single electron wavefunctions and the overall electron density rather than computing a sum of these interactions between every pair of electron wavefunctions. A DFT calculation is said to have converged to a particular electron density  $n(\mathbf{r})$  when filling the band structure predicted by  $n(\mathbf{r})$  returns the electron density  $n(\mathbf{r})$  itself.

Theoretical investigations of tellurium using DFT and other self-consistent calculations began in the 1970's and continue today. Experimental observations of pressure-induced semiconductor-to-metal transitions [81, 82] prompted theorists to model the pressure-induced structural and electronic changes in tellurium. More recently, lattice shifts as a result of femtosecond pulse excitation have revived the subject among theorists, yielding a similar set of calculations for a slightly different lattice distortion. In this section, we review the relevant theoretical work and draw parallels between two generations of DFT calculations.

### 4.5.1 Tellurium under short pulse excitation

The majority of DFT calculations for tellurium under femtosecond pulse excitation were performed by Tangney and Fahy [83, 84, 85].<sup>11</sup> Their goal was to model the softening of the  $A_1$  phonon mode, as observed by Hunsche *et al.* [65], and to investigate the generation mechanisms of coherent phonons.

Figure 4.4 shows DFT calculations of the band structure of Te in the u = 0.2686ground state lattice configuration. As shown, tellurium is semiconducting with an indirect band gap between the valence band at H and the conduction band at A, although the size of the indirect gap is nearly that of the smallest direct gap at H. The band gap is found to be 0.253 eV and agrees fairly well with the experimentally determined value of 0.33 eV [83]. The main feature in the linear optical properties of tellurium (the resonance near 2 eV, as shown in Figure 4.2) arises mostly from vertical transitions around the A point, evidenced by the regions of parallel valence and conduction bands. Other self-consistent theoretical calculations support this interpretation and go on to claim that the peak near 2 eV is due to available transitions from the uppermost valence band to the lowermost conduction band [86, 87].

As the size of the helical radius increases, tellurium goes through various electronic transitions. An indirect band-crossing transition occurs at u = 0.286. Figure 4.5 shows the semimetallic band structure calculated for u = 0.31, where the conduction band at A is

<sup>&</sup>lt;sup>11</sup>Throughout this section, references are made to specific papers by Tangney and Fahy only in cases where the information is not available in Ref. [85].



Figure 4.4: DFT band structure calculations of tellurium in the ground state lattice configuration u = 0.2686 (after Ref. [85]).

significantly below the valence band at H. Comparing Figures 4.4 and 4.5, one can see that the uppermost valence band remains roughly fixed around A and H, but that the conduction band drops significantly around A. Thus, as the helical radius increases, one would expect the resonance near 2 eV in  $\epsilon(\omega)$  to move toward lower photon energy, and the size of this shift will be comparable to the decrease in the indirect band gap. Using DFT, Choly and Kaxiras calculate the band structure and linear optical properties of tellurium for different values of u, and find that the resonance in the dielectric tensor redshifts with increasing uand that the main contribution to the resonance for all values of u arises from transitions near the A point [88]. Tellurium becomes metallic at u = 0.33, where the first and second nearest neighbor distances become equal and the crystal takes on higher symmetry.

It is important to note that the size of the helical radius is not determined by the crystal symmetry — it takes a value that minimizes the free energy of the system, as shown in Figure 4.6.<sup>12</sup> Minima in the total energy indicate the value of the equilibrium helical radius for various excited electron densities.<sup>13</sup> The shift in equilibrium position is

 $<sup>^{12}</sup>$ This fact reminds us that electrons and ions *together* determine the lattice configuration and band structure.

<sup>&</sup>lt;sup>13</sup>The shape of the minimum reveals a decrease in the (coherent) phonon frequency as the excited carrier density increases because shallower minima correspond to smaller restoring forces when the ions move along



Figure 4.5: DFT band structure calculations of tellurium for the lattice displacement u = 0.31 (after Ref. [83]).



Figure 4.6: Calculations of the energy per unit cell (zero is chosen arbitrarily) as a function of lattice displacement for different excitation densities. The position of the minimum at u = 0.2686 moves toward larger values of u as the excitation density increases from 0% (lowest curve) to 1.25% (highest curve) of valence electrons (after Ref. [85]).

due to the fact that, under photoexcition, carriers are removed from states that hold the lattice near the minimum at u = 0.2686 and are placed in states that push the lattice toward the minimum at u = 0.365. Figure 4.7 shows the calculated lattice shift and phonon frequency as a function of carrier excitation. Equally large lattice displacements as a result of photoexcitation (up to 10% change in a lattice parameter) have been observed in bismuth [89].



Figure 4.7: (a) Equilibrium helical radius as a function of excitation density. The curve is a guide to the eye. (b) Phonon frequency as a function of excitation density, showing both initial large amplitude frequency (open squares) and small amplitude motion (filled circles). A linear fit to the small amplitude motion is shown (after Ref. [85]).

## 4.5.2 Tellurium under pressure

DFT calculations of tellurium in the ground state and under 8 kbar hydrostatic pressure were performed by Starkloff and Joannopoulos [90]. The calculated band structure is shown in Figure 4.8. Discrepancies between these results and those of Tangney and Fahy can be attributed to the sensitivity of DFT to the choice of pseudopotential and to two decades of improvement in numerical techniques. Except for the fact that this calculation predicts that tellurium has a direct band gap, the general shape of the bands is reproduced.

The researchers repeated the calculation for the lattice configuration as determined experimentally under 8 kbar hydrostatic pressure. For this lattice distortion, the band structure changes in such a way that the highest-valence-band-to-lowest-conduction-band resonances shift by -0.0062 eV/kbar. In the Section 4.5.3, we discuss the similarities between application of pressure and excitation of carriers for the response of tellurium.



Figure 4.8: DFT band structure calculations of tellurium at ambient pressure (after Ref. [90]).

#### 4.5.3 Comparison of pressure and photoexcitation calculations

The link between pressure and photoexcitation in tellurium can be established within the formalism of continuous phase transitions [91]. In the case of tellurium, the phase transition of interest is that when the crystal attains higher symmetry at u = 0.33, accompanied by a transition to a metallic state. The lattice displacements associated with the application of pressure and with photoexcitation are different, but both can lead to the same insulator-to-metal phase transition.<sup>14</sup> The degree of proximity to such a phase transition is measured by a continuous variable called the order parameter  $\eta$ , and the transition from a phase of lower symmetry to one of higher symmetry occurs when  $\eta$  vanishes. Thus, the physical properties of tellurium, such as the photon energy of the main resonance, should behave similarly under pressure and under photoexcitation when the lattice displacements are recast in terms of the order parameter.

The order parameter for tellurium can be either R/r - 1 [92], where r(R) is the first (second) nearest neighbor bond length, or simply 1 - 3u. The expression R/r - 1

<sup>&</sup>lt;sup>14</sup>Under pressure, the helices of the crystal structure are squeezed closer to one another but the helical radius does not change significantly. So, application of pressure leads to u = 0.33 by varying the spacing between helices while photoexcitation induces a increase in the helical radius itself.

has greater physical significance because the interplay between nearest and second nearest neighbor bonding is believed to be a determining factor in the lattice dynamics of tellurium [83]. In reality, both  $\eta = R/r - 1 = 0$  and  $\eta = 1 - 3u = 0$  describe the same lattice, so it is expected that both are good order parameters.

The final step in linking the resonance shift in tellurium under pressure and under photoexcitation is to recast the response in terms of changes in the order parameter. For the calculations of Tangney and Fahy, the resonance shift is taken to be the change in the separation between the highest valence band and the lowest conduction band states at the Apoint (0.89 eV) as the lattice is displaced from the ground state configuration to the u = 0.31configuration [83]. The result of Starkloff and Joannopoulos, that the resonance shifts at a rate of -0.0062 eV/kbar, is expressed in terms of the order parameter using the known lattice displacements under pressure. For the order parameter  $\eta = 1 - 3u$ , we find that the photon energy of the main resonance in tellurium shifts by 4.7 eV/ $\delta\eta$  under pressure and by 7.2 eV/ $\delta\eta$  under photoexcitation. Similarly, for  $\eta = R/r - 1$ , we calculate a shift of 2.9  $eV/\delta\eta$  under pressure and 6.2  $eV/\delta\eta$  under photoexcitation. The quantitative agreement (within a factor of 2) between these independent numerical results in different physical situations (using different pseudopotentials, no less) justifies the notion that very different lattice distortions can be treated in one framework. In Chapter 5, we use these calculations and the measured resonance shifts to estimate the size of the lattice displacement and the coherent phonon amplitude in tellurium.

## 4.6 Summary

Previous experimental and theoretical work on tellurium indicate that the phonon mode that is predominantly excited is the symmetry-preserving  $A_1$  mode. The DFT calculations of Tangney and Fahy support the notion that the dynamics of tellurium are analogous to the dynamics of excited molecules (discussed in Section 2.2). In the following chapters, we discuss our measurements of the time-resolved dielectric tensor of tellurium, focusing on how these optical measurements reveal the structural dynamics of tellurium and on the degree to which the material dynamics can be controlled on a femtosecond time scale.

## Chapter 5

# Dynamics of Tellurium under Single Pulse Excitation

In this chapter we present femtosecond time-resolved measurements of the dielectric tensor of tellurium when femtosecond pump pulses excite coherent phonons. Experimental details of how the measurement is performed are described in Chapter 3. The results are discussed in relation to previous investigations of tellurium, which are summarized in Chapter 4.

## 5.1 Dielectric tensor measurements

Experiments were performed in the multiple-shot mode described in Section 3.2.3, where the sample is not translated between laser shots. At normal incidence, the elliptical cross section of the pump beam upon reaching the sample measured 190  $\mu$ m wide by 155  $\mu$ m tall, but the width was increased by the angle of incidence of the pump. The cross section of the probe spot was approximately 10  $\mu$ m in diameter, but the width of the probe spot was also increased due to the angle of incidence. For all data sets, the angle between the pump and probe beams was kept as small as possible (approximately  $13^{\circ}$ ) to minimize the loss of temporal resolution that accompanies non-collinear pump-probe experiments.<sup>1</sup> The two angles of incidence of the probe used for these experiments were  $80.4^{\circ}$  and  $68.4^{\circ}$ .

Under irradiation by a 1-kHz train of 800-nm, 35-fs pulses at ~ 67.5° angle of incidence, the minimum pulse energy at which permanent damage to the sample is observed is 3.4  $\mu$ J. It is believed that no cumulative effects occur from irradiation by a train of pulses due to the 1-ms interval between pulses, although no measurements of the single-shot damage threshold have been performed. Accounting for the reflectivity of the tellurium sample and the 67.5° angle of incidence of the pump, the 3.4- $\mu$ J pulse energy corresponds to a non-reflected threshold fluence of  $F_{\rm th} = 21 \text{ J/m}^2$ . The error in the value of  $F_{\rm th}$  is roughly 30%, owing to the lack of accuracy in measuring the pump spot size.

The excellent agreement between literature values [5] and measured values of the dielectric tensor is shown in Figure 5.1, verifying that our experimental technique is sensitive to each component of the dielectric tensor. The data shown were taken for a time delay of -300 fs, where the probe arrives before the pump. However, with the entire pulse train incident on the sample, the probe arrives about 1 ms after the *prior* pump pulse. Thus, the agreement between measured and literature values of the dielectric tensor in Figure 5.1 is proof that no cumulative effects occur from multiple-pulse irradiation.

Single pulse excitation experiments were performed at pump fluences of  $0.43F_{\rm th}$ ,  $0.57F_{\rm th}$ ,  $0.71F_{\rm th}$ , and  $0.85F_{\rm th}$ . Despite the large error in the measurement of  $F_{\rm th}$ , the coefficients quoted here are accurate to a few percent. The measured dielectric tensor data is shown in Figures 5.2 through 5.9. The data under different excitation conditions share the following features: (1) cosine-like oscillations in both  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$ , (2)

<sup>&</sup>lt;sup>1</sup>Because femtosecond pulses are akin to "photon pancakes" propagating through space, the angle between pump and probe beams leads to a spatial variation of "time zero" across the probe spot. While typically leading to a loss of temporal resolution, the technique of femtosecond microscopy overcomes this problem by imaging the dynamics across the surface of the sample, as in, *e.g.*, Ref. [57].



Figure 5.1: Measured (circles) and literature (curves) values of the dielectric tensor of tellurium.

an apparent shift of optical properties toward lower photon energies, and (3) increasing oscillation amplitude with increasing fluence. In Section 5.2 we quantify the redshift of optical properties by applying the Lorentz model to the data. In Section 5.3 we analyze the frequency of the coherent phonons.



Figure 5.2: Response of (a)  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ord}}(\omega)]$  under  $0.43F_{\text{th}}$ excitation.



Figure 5.3: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under  $0.43F_{\text{th}}$ excitation.



Figure 5.4: Response of (a)  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ord}}(\omega)]$  under  $0.57F_{\text{th}}$ excitation.



Figure 5.5: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under  $0.57F_{\text{th}}$ excitation.



Figure 5.6: Response of (a)  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ord}}(\omega)]$  under  $0.71F_{\text{th}}$ excitation.



Figure 5.7: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under  $0.71F_{\text{th}}$ excitation.



Figure 5.8: Response of (a)  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ord}}(\omega)]$  under  $0.85F_{\text{th}}$ excitation.



Figure 5.9: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under  $0.85F_{\text{th}}$ excitation.

## 5.2 Application of Lorentz model to dielectric tensor data

In order to establish a more quantitative picture of the material dynamics, we apply the Lorentz model to the dielectric tensor data. As discussed in Section 2.1.2, the Lorentz model is useful for describing the general features of a broad resonance in a solid. Thus, we model the data using Eqs. (2.21) and (2.22), and include a real additive constant c to account for the contribution of resonances outside the spectral range of the probe, as discussed in Sections 2.1.2 and 2.1.3. We expect there to be a difference in the parameters of the fit to  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  due to the differences in  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  themselves; the variation in the matrix elements of the dipole interaction that couple the same set of states results in slightly different optical properties.<sup>2</sup>

#### 5.2.1 Fit method

The fitting procedure is designed to minimize the metric

$$\sum_{\hbar\omega_i=1.65}^{3.3} \left( \operatorname{Re}[\epsilon_{\operatorname{Lorentz}}(\omega_i)] + c - \operatorname{Re}[\epsilon(\omega_i)] \right)^2 + \left( \operatorname{Im}[\epsilon_{\operatorname{Lorentz}}(\omega_i)] - \operatorname{Im}[\epsilon(\omega_i)] \right)^2 , \qquad (5.1)$$

which is similar to the common least-squares metric, but extended to complex-valued functions. For the data at each time delay, the initial values of the additive constant c as well as the parameters f,  $\omega_0$ , and  $\Gamma$  of  $\epsilon_{\text{Lorentz}}(\omega)$  (see Eqs. (2.21) and (2.22)) are taken to be those that result from fitting literature values of the dielectric function, as discussed below. The fitting routine uses the Levenberg–Marquardt method [44] to search parameter space for a minimum in the sum-of-squares metric.

The ability of the Lorentz model to describe the optical properties of tellurium is evidenced in Figure 5.10, where both the ordinary and extraordinary dielectric functions are well-reproduced. The parameters of the fits are f = 110,  $\hbar\omega_0 = 2.33$  eV,  $\hbar\Gamma = 1.34$  eV, and

 $<sup>^{2}</sup>$ See Section 2.1.1.



Figure 5.10: Measured values (circles) and Lorentz model fits (curves) of the dielectric tensor of tellurium. See text for details of the fit.

c = 7.34 for the ordinary part and f = 161,  $\hbar\omega_0 = 2.11$  eV,  $\hbar\Gamma = 1.41$  eV, and c = 5.77 for the extraordinary part. Fits to literature values of  $\epsilon_{\rm ord}(\omega)$  using a Lorentz model with two resonances (see Figure 2.2(b)) indicate that approximately half of the real additive constant c is due to the material resonance near 9 eV and that the remaining portion is due to the presence of resonances at greater than 12 eV.

Before discussing specific features of the dynamics, a few general remarks are in order. All four fit parameters deviate from their pre-excitation values for positive time delays (Figures 5.12 though 5.19), although for the data at certain time delays, the value of a fit parameter never deviates from the initial guess during the fitting procedure. Continuity in the minimized value of the sum-of-squares metric (Eq. (5.1)) around these time delays indicates that the fit procedure is robust and that this lack of deviation from initial values is an artifact of the fit precision and iteration limits. Of critical importance is that the physically significant parameter, the resonance energy, is insensitive to the parameters that display these effects. Figure 5.11 shows the change in the fit value of the resonance energy for the  $0.85F_{\rm th}$ -excitation  $\epsilon_{\rm ord}(\omega)$  data (Figure 5.8) when the fit is performed with the oscillator strength f and the additive constant c held fixed at 110 and 7.34, respectively, instead of



Figure 5.11: Change in fit values of the resonance energy when the oscillator strength and additive constant are held fixed at their literature values ( $\epsilon_{\rm ord}(\omega)$ , 0.85 $F_{\rm th}$  excitation).

allowing all parameters to vary. The discrepancy is less than 1% for all time delays, and similar results are found for other data sets, which indicates that the resonance energy is independent of the other parameters of the fit.

## 5.2.2 Fit results

Figures 5.12 though 5.19 show the transient behavior of the best-fit parameters of the Lorentz model when applied to the data in Figures 5.2 through 5.9. The four plots in each Figure display (a) the resonance energy  $\hbar\omega_0$ , (b) the linewidth  $\hbar\Gamma$ , (c) the oscillator strength f, and (d) the additive constant c.



Figure 5.12: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ , 0.43 $F_{\rm th}$  excitation.



Figure 5.13: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ , 0.43 $F_{\text{th}}$  excitation.



Figure 5.14: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ , 0.57 $F_{\rm th}$  excitation.



Figure 5.15: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ , 0.57 $F_{\text{th}}$  excitation.



Figure 5.16: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ , 0.71 $F_{\rm th}$  excitation.



Figure 5.17: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ , 0.71 $F_{\text{th}}$  excitation.



Figure 5.18: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ ,  $0.85F_{\rm th}$  excitation.



Figure 5.19: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ , 0.85 $F_{\text{th}}$  excitation.

#### 5.2.3 Discussion of fit results

The changes in the optical properties of tellurium after photoexcitation is directly related to the changes in the band structure, as discussed in Section 2.1.1. The Lorentz model allows us to determine the ways in which the band structure changes during the photoinitiated lattice dynamics. The data clearly show a shift of the main resonance toward lower photon energies and the shift increases with the excitation strength.<sup>3</sup> This shift indicates that the gap between valence and conduction bands decreases for those states that constitute this resonance. The linewidth of the resonance and the oscillator strength increase slightly after photoexcitation, although their behavior is not consistent across excitation strengths. Changes in the additive constant c show no trend and statistical tests of the fit question the significance of the variation of this parameter.<sup>4</sup>

The qualitative aspects of the dynamics agree well with theoretical calculations of the band structure changes that result from a lattice displacement along the  $A_1$  phonon mode. As discussed in Section 4.5.1, the energy separation between valence and conduction band states around the A point in **k** space decreases as the helical radius increases. Thus, the consistent redshift of the resonance in our data shows that the helical radius increases upon photoexcitation, in contrast to previous work that suggests a decrease of the helical radius [66]. Comparing Figures 4.4 and 4.5, one observes that the size of the region over which the bands remain parallel is roughly the same after the lattice is significantly displaced, which supports the conclusion that the oscillator strength f does not significantly change. Changes in the linewidth  $\hbar\Gamma$  are difficult to predict based on the calculated band structures simply because it is difficult to judge the degree of "parallel-ness" of bands near the A point.

Many researchers have suggested that the material response is composed of two

<sup>&</sup>lt;sup>3</sup>See, also, Figure 6.17.

<sup>&</sup>lt;sup>4</sup>The F test [93] for an additional fit parameter supports the inclusion of c in the model, but questions the inclusion of another parameter that represents the deviation of c from its pre-excitation value.

parts; an oscillatory signal produced by coherent phonons and a "background signal" due to a purely electronic effect, such as a Drude contribution from free electrons or Pauli blocking. Our dielectric tensor measurements indicate that the lattice dynamics are responsible for all components of the signal. Many-body effects, such as Pauli blocking, are typically localized to the pump wavelength, so the existence of a "background signal" at all wavelengths questions the significance of many-body electronic effects. The Drude contribution to  $\text{Im}[\epsilon(\omega)]$  is positive for all wavelengths and is less than 0.5 at the excited electron densities attained in our experiments, whereas  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$  and  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$  increase for some photon energies and decrease for others. Because the dielectric tensor data is well-fit by the Lorentz model and does not indicate the presence of free electron effects, we conclude that the photoinitiated lattice dynamics are entirely responsible for the observed behavior.<sup>5</sup>

We can estimate the size of the overall lattice displacement and the size of the coherent phonon amplitude from the observed resonance shifts using calculations of the redshift of resonances in tellurium due to photoexcitation [83, 84, 85] and due to the application of pressure [90]. We assume that photoexcitation leads to a lattice shift along the  $A_1$  mode only, which allows us to immediately apply the theoretical results of Tangney and Fahy for tellurium under photoexcitation. A linear fit to the change in the energy gap at the A point between the highest valence and the lowest conduction band as a function of the normalized helical radius estimates the resonance to change as  $-21.5 \text{ eV}/\delta u$ . Thus, the maximum redshift of roughly -0.3 eV, observed under  $0.85F_{\text{th}}$  excitation, corresponds to an increase in the helical radius of 0.006 nm, and the maximum peak-to-trough resonance variation of roughly 0.17 eV corresponds to a coherent phonon amplitude of 0.003 nm. The band structure calculations of Starkloff and Joannopoulos must be interpreted through

<sup>&</sup>lt;sup>5</sup>Ruling out electronic effects as a major contributor to the dynamics is made possible by measuring the dielectric tensor over a wide spectral range. Single-color reflectivity transients cannot distinguish between the shifting of a resonance and a Drude contribution, and only in rare cases can they be used to make definitive statements about the material dynamics.

the use of an order parameter<sup>6</sup> because the lattice shifts of tellurium under pressure are not confined to the  $A_1$  mode. The order parameter  $\eta = 1 - 3u$  predicts a maximum lattice displacement and coherent phonon amplitude of 0.009 nm and 0.005 nm, respectively. Similarly, the order parameter  $\eta = R/r - 1$  predicts a maximum lattice displacement and coherent phonon amplitude of 0.013 nm and 0.007 nm, respectively. The estimated magnitude of the lattice displacement in tellurium is similar to the ~ 0.02 nm displacement of the bismuth lattice observed with ultrashort x-ray pulses [89].

## 5.3 Analysis of coherent phonon frequencies

A Fourier analysis of the oscillations in the optical properties of tellurium is useful for understanding the underlying lattice dynamics. By performing Fourier transforms of the entire oscillatory reflectivity signal, researchers observe that the  $A_1$  phonon frequency decreases with increasing excitation [65, 78, 94], suggesting that the shape of the parabolic (harmonic) potential on which the ions move changes upon photoexcitation or that the large amplitude phonons experience the anharmonicity of the original potential to a greater extent as the excitation increases in strength. The former phenomenon is referred to as "softening" of the phonon mode, the latter as simply anharmonicity. Theoretical calculations, such as those of Tangney and Fahy [84], predict a decrease in the coherent phonon frequency based on softening alone, while experimental investigations of bismuth suggest that anharmonicity and softening are necessary to explain the dynamics [94]. It is likely the case that both effects contribute to the dynamics of tellurium.

Because a significant amount of experimental work has been done on coherent phonon frequencies in tellurium, most notably by Hunsche *et al.* [65, 66, 67], we devote little space to the aspects of our results that simply verify previous observations. In Section

<sup>&</sup>lt;sup>6</sup>See Section 4.5.3.

5.3.1 we present results from a Fourier analysis that show a decrease of the coherent phonon frequency with increasing excitation strength and that suggest that nonlinear effects play a role in the absorption of the pump pulse. In Section 5.3.2 we discuss how the phonon frequency changes on a sub-picosecond time scale.

#### 5.3.1 Excitation-strength dependence of the coherent phonon frequency

Fast-Fourier transforms (FFTs) of the reflectivity, the dielectric tensor, and the resonance energy were performed over the  $\sim 3$  ps range of the data. The same peak frequency was observed in the FFT spectrum of the reflectivity transient for all photon energies of the probe, and the same frequency was observed for the reflectivity, dielectric tensor, and resonance energy. We concentrate on the resonance energy because its dependence on the lattice displacement is more linear than that of the reflectivity or dielectric constant.

Figure 5.20 shows the FFT spectrum of the resonance energy of  $\epsilon_{\rm ord}(\omega)$  under  $0.57F_{\rm th}$  excitation.<sup>7</sup> The peak in the FFT spectrum near 3.2 THz is due to the presence of coherent phonons. The low-frequency portion of the spectrum arises from the overall displacement of the resonance energy from its initial value. The FFT spectrum of the oscillatory part of the resonance energy (background displacement removed<sup>8</sup>) lacks these low-frequency contributions and the value of the peak frequency remains approximately the same.

Figure 5.21(a) shows the dependence of the coherent phonon frequency on the strength of the excitation,<sup>9</sup> where the data from  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  are combined. The data show a decrease in the coherent phonon frequency upon increasing excitation. As

<sup>&</sup>lt;sup>7</sup>Data shown in Figure 5.14(a).

<sup>&</sup>lt;sup>8</sup>The background signal was determined by fitting the data to an over-damped oscillator, which tracks the motion of the equilibrium lattice position. The oscillatory part of the resonance energy dynamics is the difference between the data and this fit.

 $<sup>^{9}</sup>$ The incident pulse energy of the  $80.4^{\circ}$  reflectivity data is used in Figure 5.21(a), although the pulse energy of the lower-angle data set shows the same linear trend.



Figure 5.20: FFT spectrum of the resonance energy in Figure 5.14(a) (solid line) and the FFT analysis of the oscillatory component only (dashed line).



Figure 5.21: (a) Dependence of the coherent phonon frequency on pump energy, as observed in oscillations of the resonance energy of  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$ . (b) The ordinary and extraordinary data, plotted as a function of the excited electron density from linear absorption, do not agree.

discussed in a previous publication [95], the observed -0.0025 THz per J/m<sup>2</sup> rate of change of the phonon frequency with incident fluence agrees quantitatively with the results of Hunsche *et al.* [65].

Unexpectedly, the frequency of oscillation seen in the  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  data do not display the same trend when plotted as a function of excited electron density based on linear absorption, as shown in Figure 5.21(b). Tangney and Fahy showed that the excited electron density determines the frequency of the  $A_1$  phonon mode.<sup>10</sup> It is expected that any lattice vibrations will manifest themselves as similar oscillations in  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$ . Thus, we expect the frequency of oscillation observed in the two sets of data to lie on the same line. It is clear from Figure 5.21(b) that they do not.

The reason why the same nominal excitation, say  $0.57F_{\rm th}$ , results in different excited electron densities when probing  $\epsilon_{\rm ord}(\omega)$  or  $\epsilon_{\rm ext}(\omega)$  is due to the skin depth of the sample in the geometry of each measurement. The excited electron density N is given by

$$N = F\alpha \left(\frac{1 \text{ electron}}{1 \text{ photon}}\right) \tag{5.2}$$

where F is the fluence in photons/m<sup>2</sup> and  $\alpha = 4\pi\kappa/\lambda$  is the skin depth of the material. As described in Section 3.1.2, the polarization of the pump is crossed to that of the probe. Thus, when the setup is designed to measure  $\epsilon_{\rm ord}(\omega)$ , the pump reflectivity and absorption is determined by the extraordinary optical properties. Similarly, when the setup is arranged to measure  $\epsilon_{\rm ext}(\omega)$ , the pump sees the ordinary optical properties. Accounting for the difference in reflectivity of the pump between the two cases allowed us to perform measurements of  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  for the same non-reflected pump fluence. Only after the experiment was complete did we discover that the same non-reflected fluence in each case does not correspond to the same excited electron density,<sup>11</sup> due to the factor of ~ 3 difference in the absorption constant  $\kappa$  between ordinary and extraordinary optical properties.

Does the apparent mismatch in excitation strength invalidate the dielectric tensor measurements? While it is true that the method for determining  $\epsilon_{\text{ext}}(\omega)$  depends on previous measurements of  $\epsilon_{\text{ord}}(\omega)$  for the same excitation, the angles of incidence used for the measurements of  $\epsilon_{\text{ext}}(\omega)$  make the numerical inversion fairly insensitive to  $\epsilon_{\text{ord}}(\omega)$ .<sup>12</sup>

 $<sup>^{10}</sup>$ See Section 4.5.1, specifically Figures 4.6 and 4.7(b).

<sup>&</sup>lt;sup>11</sup>During the course of the experiment, we monitored the oscillation frequency of the reflectivity observed when measuring  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  and found that they agreed fairly well for the same non-reflected fluence.

 $<sup>^{12}</sup>$ The numerical inversion routine was performed matching the  $0.85F_{\rm th}$  "extraordinary reflectivities" with

Thus, the measurements of  $\epsilon_{\text{ext}}(\omega)$  are valid, though they may not correspond to the same excitation density as  $\epsilon_{\text{ord}}(\omega)$ .

The mismatch between the phonon frequencies for  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  in Figure 5.21(b) indicates that linear absorption is not the only process by which the pump is absorbed. Tangney and Fahy predict that the phonon frequency depends linearly on the excitation density, however they do not specify the means by which the electrons are excited. While linear reflectivity and linear absorption is most often used by researchers to estimate the photoexcited electron density in absorbing solids, nonlinear effects are known to be important when intense femtosecond pulses interact with solids. The clear discrepancy in the observed phonon frequencies when plotted as a function of excitation density based on linear absorption indicate that the nonlinear optical properties of tellurium play a significant role in the excitation process.

To verify that nonlinear effects are important in our experiments, we estimate the number of electrons available for linear absorption by the pump pulse. The importance of establishing the number of electrons available for linear absorption lies in comparing it to the excited electron density predicted by linear absorption of the entire pump pulse. If the number of electrons available for excitation is on the order of the number of photons to be absorbed, then both saturation of linear absorption and nonlinear effects become important. Inverting Eq. (2.12) and using Eq. (2.13), we estimate the joint density of states to be

$$\text{JDOS}(\omega) \sim \omega^2 \text{Im}[\epsilon(\omega)],$$
 (5.3)

where the matrix elements of the dipole interaction in Eq. (2.12) are taken to be independent of **k**. Between 0.3 eV and 4 eV, the JDOS accounts for all transitions between the three uppermost valence bands and the three lowermost conduction bands in tellurium (see Figure

the  $0.43F_{\rm th}$ -values of  $\epsilon_{\rm ord}(\omega)$ , which correspond to similar excited electron densities. The difference between these extracted values of  $\epsilon_{\rm ext}(\omega)$  and the data shown in Figure 5.9 is significantly less than the error in the numerical inversion itself.

4.4). Thus, the fraction F of these transitions available to a 35-fs, 800-nm laser pulse<sup>13</sup> is

$$F = \frac{\int_{1.52}^{1.58} \mathrm{d}(\hbar\omega) \,\mathrm{JDOS}(\hbar\omega)}{\int_{0.3}^{4} \mathrm{d}(\hbar\omega) \,\mathrm{JDOS}(\hbar\omega)} \,. \tag{5.4}$$

Finally, to convert from transitions to electrons, we notice that each electron in the valence band is likely to have only one transition (if any) within the spectral range of the pump, however all three of its transitions are accounted for in the denominator of Eq. (5.4). This overcounting is remedied by multiplying the above expression by 3 to obtain the fraction of electrons excited from the uppermost valence bands to the lowermost conduction bands. Because the three uppermost valence bands contain 1/3 of all valence electrons, the factors of 3 and 1/3 cancel, so Eq. (5.4) also gives the fraction of all valence electrons available for linear absorption of the pump.

From literature values of  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$ , we calculate the fraction of valence electrons available for linear absorption when the pump is polarized along the optic axis  $(F_{\rm ext})$  and when the pump polarization lies perpendicular to the optic axis  $(F_{\rm ord})$ . Following the above discussion, the pump would see  $F_{\rm ext}$  electrons available for linear absorption for the experimental situation of measuring  $\epsilon_{\rm ord}(\omega)$ , and  $F_{\rm ord}$  when measuring  $\epsilon_{\rm ext}(\omega)$ . We find  $F_{\rm ext} = 0.012$  and  $F_{\rm ord} = 0.005$ . Thus, the pump conditions in our experiment are such that linear absorption of the entire pump pulse requires as many or more electrons than we estimate to be available. In these cases, saturation of linear absorption will occur and it is likely that two-photon absorption of electrons would become important.

In addition to indicating that saturation of linear absorption is an important consideration in our experiments, the above calculation offers a remedy to the discrepancy shown in Figure 5.21(b). The measurements of  $\epsilon_{\rm ord}(\omega)$  were performed for stronger excitations relative to the saturation level  $F_{\rm ext}$  than the measurements of  $\epsilon_{\rm ext}(\omega)$  relative to  $F_{\rm ord}$ .

<sup>&</sup>lt;sup>13</sup>The FWHM of the spectrum of this pulse ranges from 1.52 eV to 1.58 eV. For this calculation, we ignore the gaussian shape when counting transitions and simply use a top hat function.

While saturation of linear absorption will shift both data sets toward lower excited electron densities, the ordinary data will be shifted to a greater extent, bringing the ordinary and extraordinary data closer to falling on the same line.

## 5.3.2 Time- and frequency-resolved phonon dynamics

The question of whether anharmonicity or softening properly describes the change in phonon frequency upon excitation can be addressed using a short term Fourier transform (STFT). A STFT consists of performing a Fourier transform of the measured signal S(t)convolved with a gaussian pulse  $G(t, \tau)$  centered around many time delays  $\tau$ . The peak in the Fourier transform gives the local frequency  $\Omega(\tau)$  of the signal S, which is tracked over the entire signal to yield the time-varying local frequency. Reflectivity-based studies of coherent phonons in Bi reveal that the phonon frequency is initially decreased by up to 10%, but then exponentially decays toward the pre-excitation phonon frequency with time constant of about 2 ps [94]. Hase *et al.* argue that the linear relationship between the local frequency  $\Omega(\tau)$  and the squared amplitude of the oscillations in S(t) at  $\tau$ , which is expected for an anharmonic potential, supports anharmonicity as the dominant source of the change in coherent phonon frequency [94]. Softening is observed as the excitation strength is increased, but the effects are significantly smaller than the effects of amplitude variation.

STFT traces of the dynamics of the resonance energy are shown in Figure 5.22(a) for the ordinary data and in Figure 5.23(a) for the extraordinary data. For this analysis, the FWHM of the windowing function  $G(t, \tau)$  was chosen to be 300 fs.<sup>14</sup> Generally speaking, the traces in both figures show a slow return of the phonon frequency toward the ground state

 $<sup>^{14}</sup>$ We found that a 300 fs width, approximately that of the phonon period, was neither too long to see changes in the frequency over the range of our data nor too short to be overly susceptible to the oscillations in the data itself.



Figure 5.22: Local frequency of the resonance energy of  $\epsilon_{\rm ord}(\omega)$  calculated via the STFT technique (a) for the entire data set and (b) for only the oscillatory part of the data.



Figure 5.23: Local frequency of the resonance energy of  $\epsilon_{\text{ext}}(\omega)$  calculated via the STFT technique (a) for the entire data set and (b) for only the oscillatory part of the data.

value (3.6 THz), while traces corresponding to difference pump fluences are significantly shifted. The sharp trend toward very low frequency at early time delays is an artifact of using data that includes the background signal. Removing this background to analyze only the oscillatory part yields the data of Figures 5.22(b) and 5.23(b), which do not display this trend.

Figures 5.22(b) and 5.23(b) show that the local frequency  $\Omega(\tau)$  does not significantly change over the observed range of our data compared to the change in phonon frequency with excitation strength. The amplitude of the oscillations in the resonance energy are typically reduced by half within 2 ps (see part (a) of Figures 5.12 though 5.19),
however the shift of the phonon frequency is typically small over this same time period. This suggests that, in the case of tellurium, anharmonicity is less important than softening in determining the coherent phonon frequency.

## 5.4 Summary

The ultrafast changes in the main resonance in tellurium provide a means to investigate the lattice and band structure dynamics that result from excitation of coherent phonons. Analysis of the data using the Lorentz model yields a quantitative measure of the resonance shift and an estimate of the size of the lattice distortion. The dependence of phonon frequency on excitation strength reveals that linear and nonlinear interactions between the pump and the material are important. Finally, the transient behavior of the phonon frequency indicates that mode softening is more important than anharmonicity in photoexcited tellurium, in agreement with the theoretical predictions of Tangney and Fahy [84].

# Chapter 6

# Dynamics of Tellurium under Double Pulse Excitation

As an extension of the experiments described in Chapter 5, we investigated the degree to which the lattice dynamics of tellurium can be controlled via double pulse excitation. The experiment was carried out in the same manner as described in Chapter 3 and Section 5.1, with the addition of a second colinear pump pulse. The data presented in this Chapter shows that enhancement and cancellation of coherent phonons is achievable under near-damage threshold excitation. The excitation conditions under which cancellation is achieved is contrasted with previous low-excitation coherent control experiments on bismuth and reveal a departure from the expected behavior.

### 6.1 Dielectric tensor measurements

The key experimental challenge of performing experiments in coherent control, and the primary difference from the single pulse excitation experiments, lies in controlling the time delay between exciting pulses. Precise control of the time delay between pump pulses is required to achieve cancellation of coherent phonons. The common autocorrelation technique<sup>1</sup> proved too difficult to employ: "time zero" between the pulses could be established in a separate autocorrelator, but slight angles between the beams due to daily alignment of the setup caused "time zero on the sample" to occur for a different (random) delay stage position. To establish "time zero on the sample," the two pump pulses were attenuated to the same energy and each was used separately to excite tellurium as the transient reflectivity was recorded. The time shift between the two measured responses yielded the actual time delay between pump pulses. Using this technique, the error in establishing "time zero on the sample" between the two 35 fs pump pulses is  $\pm 7$  fs.

Double pulse excitation experiments to enhance and cancel the coherent vibrations were performed under a variety of pump conditions, as summarized in Table 6.1. Measurements of  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  are shown in Figures 6.1 through 6.8. In the same manner as the single pulse excitation data is analyzed in Chapter 5, the Lorentz model is used to describe the changes in the dielectric tensor. The results of the fitting procedure are shown in Figures 6.9 through 6.16. The results are discussed in Section 6.2.

1 <sup>st</sup> pulse		2 <sup>nd</sup> pulse		$\epsilon_{ m ord}(\omega) \; {f data}$	
energy $(\mu \mathbf{J})$	fluence $(F_{th})$	energy $(\mu \mathbf{J})$	fluence $(F_{th})$	delay (fs)	effect
1.48	0.43	1.14	0.35	127	cancel
1.96	0.57	1.56	0.46	133	cancel
2.43	0.71	1.23	0.43	467	cancel
1.48	0.43	1.14	0.35	267	enhance
1 <sup>st</sup> pulse					
1 <sup>st</sup> ]	pulse	2 <sup>nd</sup>	pulse	$\epsilon_{ m ext}(\omega)$	data
$\begin{array}{c} 1^{\text{st}} \\ \end{array}$ energy ( $\mu$ J)	$\mathbf{pulse}$ fluence $(F_{\mathbf{th}})$	2 <sup>nd</sup> energy (μJ)	pulse fluence $(F_{\rm th})$	$\epsilon_{\rm ext}(\omega)$ delay (fs)	data effect
1 <sup>st</sup> ] energy (μJ) 1.19	pulse fluence $(F_{th})$ $0.43$	2 <sup>nd</sup> energy (μJ) 0.93	pulse fluence (F <sub>th</sub> ) 0.33	$\epsilon_{\rm ext}(\omega)$ delay (fs) $127$	data effect cancel
1 <sup>st</sup> μ energy (μJ) 1.19 1.57	pulse fluence (F <sub>th</sub> ) 0.43 0.57	2 <sup>nd</sup> energy (μJ) 0.93 1.48	pulse fluence (F <sub>th</sub> ) 0.33 0.45	$\epsilon_{\rm ext}(\omega)$ delay (fs) $127$ $133$	data effect cancel cancel
1 <sup>st</sup> ] energy (μJ) 1.19 1.57 1.96	pulse fluence (F <sub>th</sub> ) 0.43 0.57 0.71	2 <sup>nd</sup> energy (μJ) 0.93 1.48 1.06	pulse fluence (F <sub>th</sub> ) 0.33 0.45 0.34	$\epsilon_{\rm ext}(\omega)$ delay (fs) 127 133 467	data effect cancel cancel cancel

Table 6.1: Summary of pump conditions for control of coherent phonons. Cancellation near the first maximum is observed in those data sets with a  $\sim 130$  fs delay between pulses. Cancellation near the second maximum is observed in those data sets with a 467 fs delay.



Figure 6.1: Response of (a)  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ord}}(\omega)]$  under  $0.43F_{\text{th}}-0.35F_{\text{th}}$  excitation with a time delay of 127 fs between pulses.



Figure 6.2: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under under  $0.43F_{\text{th}}$ –  $0.33F_{\text{th}}$  excitation with a time delay of 127 fs between pulses.







Figure 6.4: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under  $0.57F_{\text{th}}$ –  $0.45F_{\text{th}}$  excitation with a time delay of 133 fs between pulses.



Figure 6.5: Response of (a)  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ord}}(\omega)]$  under  $0.71F_{\text{th}} 0.43F_{\text{th}}$  excitation with a time delay of 467 fs between pulses.



Figure 6.6: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under  $0.71F_{\text{th}}$ –  $0.34F_{\text{th}}$  excitation with a time delay of 467 fs between pulses.



Figure 6.7: Response of (a)  $\text{Im}[\epsilon_{\text{ord}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ord}}(\omega)]$  under  $0.43F_{\text{th}}-0.35F_{\text{th}}$  excitation with a time delay of 267 fs between pulses.



Figure 6.8: Response of (a)  $\text{Im}[\epsilon_{\text{ext}}(\omega)]$ and (b)  $\text{Re}[\epsilon_{\text{ext}}(\omega)]$  under  $0.43F_{\text{th}}$ –  $0.33F_{\text{th}}$  excitation with a time delay of 267 fs between pulses.



Figure 6.9: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ ,  $0.43F_{\rm th}-0.35F_{\rm th}$ , oscillations cancelled.



Figure 6.10: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ ,  $0.43F_{\text{th}}$ – $0.33F_{\text{th}}$ , oscillations cancelled.



Figure 6.11: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ ,  $0.57F_{\rm th}-0.46F_{\rm th}$ , oscillations cancelled.



Figure 6.12: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ ,  $0.57F_{\text{th}}-0.45F_{\text{th}}$ , oscillations cancelled.



170 12 (C) (d) oscillator strength additive constant 150 10 130 110 4└\_\_ -0.5 time (ps) 0 time (ps) 0.5 1.5 2 2.5 0 1.5 2 2.5

Figure 6.13: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ ,  $0.71F_{\rm th}-0.43F_{\rm th}$ , oscillations cancelled near 2<sup>nd</sup> maximum.



Figure 6.14: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ ,  $0.71F_{\text{th}}-0.34F_{\text{th}}$ , oscillations cancelled near 2<sup>nd</sup> maximum.



Figure 6.15: Transient behavior of parameters in Lorentz model:  $\epsilon_{\rm ord}(\omega)$ ,  $0.43F_{\rm th}-0.35F_{\rm th}$ , oscillations enhanced.



Figure 6.16: Transient behavior of parameters in Lorentz model:  $\epsilon_{\text{ext}}(\omega)$ ,  $0.43F_{\text{th}}$ – $0.33F_{\text{th}}$ , oscillations enhanced.

#### 6.2 Discussion of double pulse excitation results

Discussion of the data and Lorentz model analysis is separated into three sections. In Section 6.2.1, the measurements of the dielectric tensor under single and double pulse excitation are compared. In Section 6.2.2, we discuss observed trends in the shift of the resonance in  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$ . Finally, in Section 6.2.3, we discuss features of the dynamics under double pulse excitation that show that the process of coherent control is more complicated at high levels of photoexcitation than the low-excitation experiments of other workers indicate.

#### 6.2.1 Qualitative aspects of coherent control dynamics

The variety of phenomena observed under double pulse excitation, as shown in Figures 6.1 through 6.8, are proof that control of large amplitude coherent phonons can be achieved in tellurium. As mentioned above, achieving phonon cancellation is exquisitely sensitive to the arrival time and fluence of the second pump pulse relative to the first. We observe that only a pulse of a certain delay and fluence cancels the oscillations near the first maxima and a different pulse must be used to cancel the oscillations near each maxima. Thus, we believe that the fluence of the first pump pulse uniquely specifies a set of arrival times and fluences of the second pump pulse that cancels the observed oscillations near the local maxima. If the time delay or fluence of the second pulse is not chosen correctly, then oscillations ensue. The data in Figures 6.7 and 6.8 are the most extreme example of such, where the chosen time delay between pump pulses increased the coherent phonon amplitude rather than causing it to vanish. Hase *et al.* observed similar dynamics in low excitation strength experiments on bismuth films [77], as discussed in Section 4.4.

#### 6.2.2 Excitation-strength dependence of resonance redshift

Similar to the discussion of phonon frequencies in Section 5.3.1, we expect that the shift of the resonance measured in the ordinary and extraordinary dielectric functions would agree because the underlying lattice configuration determines the JDOS (or, equivalently, the shape of the band structure), which affects all parts of the dielectric tensor. Theoretical calculations show that the excitation of electrons causes a lattice displacement such that the conduction and valence bands move closer together, resulting in a redshift of the optical properties. We consistently observe this redshift under both single pulse excitation (see Figures 5.12 through 5.19) and double pulse excitation (see Figures 6.9 through 6.16). Moreover, we observe an increasing redshift of the resonance of tellurium at the equilibrium lattice configuration<sup>2</sup> with excitation strength,<sup>3</sup> as shown in Figure 6.17(a). However, the dependence of the resonance shifts observed in  $\epsilon_{\rm ord}(\omega)$  and  $\epsilon_{\rm ext}(\omega)$  on excited electron density based on linear absorption is not the same, as shown in Figure 6.17(b). The divergence of the two data sets in Figure 6.17(b), like the divergence of the data in Figure 5.21(b), is evidence that nonlinear effects play an important role in the interaction between the intense pump pulses and the sample.

It is interesting to note that the maximum change in the resonance energy approaches the size of the band gap as the excitation strength approaches the threshold for permanent damage.<sup>4</sup> As discussed in Section 4.5.1, theoretical calculations indicate that the size of the resonance redshift is approximately equal to the decrease in the indirect band

 $<sup>^{2}</sup>$ The position of resonance of the equilibrium lattice configuration is found from the fit values of the Lorentz model in the following way. For single pulse excitations, the average of the first maximum and the first minimum is taken. For double pulse excitations that cancel the oscillations, the value maximally displaced from the initial resonance energy is taken.

<sup>&</sup>lt;sup>3</sup>The pump pulse energies given are those of the reflectivity data taken at  $80.4^{\circ}$ , although the trend is the same when the pump pulse energy of the data set at  $68.4^{\circ}$  is considered.

<sup>&</sup>lt;sup>4</sup>Under single pulse excitation, damage was observed for an incidence pulse energy of 3.4  $\mu$ J. Under double pulse excitation, the sum of the energies of the two pulses could exceed 3.4  $\mu$ J without leading to permanent damage.



Figure 6.17: Dependence of the change in equilibrium resonance energy under single and double pulse excitation on (a) total incident pump energy and (b) total excited electron density.

gap for a given lattice displacement along the  $A_1$  mode. The fact that the onset of damage and the indirect band-crossing seem to coincide suggests that the mechanism for damage is due in part to the transfer of electrons from the top of the valence band at H to the bottom of the conduction band at A via electron-phonon scattering. If true, this further implies that the scattering process is fast, on the order of 100 fs or less.<sup>5</sup>

#### 6.2.3 Details of coherent control of large lattice displacements

To gain a better understanding of the coherent control dynamics, we compare the changes in the resonance energy under various single and double pulse excitation conditions, as shown in Figure 6.18. In all parts of the figure, pump pulses "1" and "2" (and "3") indicate their time of arrival and their 35 fs pulse duration is drawn to scale. In Figure 6.18(a), the variation in the resonance energy in  $\epsilon_{\rm ord}(\omega)$  is shown under single pulse excitation at  $0.57F_{\rm th}$  and under double pulse excitation at  $0.57F_{\rm th}$  and  $0.46F_{\rm th}$  with a pulse separation of 133 fs. The data show that this double pulse combination leads to cancellation of the

<sup>&</sup>lt;sup>5</sup>To verify that electron-phonon scattering from valence to conduction band leads to permanent damage, one could measure the damage threshold as a function of the pulse duration. Long and short pulses of equal energy excite the same density of electrons, leading to the same displaced equilibrium position, but long pulses excite smaller amplitude coherent phonons than short pulses. If the damage threshold does not depend on pulse duration, then the photoexcitated carrier density is the important parameter.



Figure 6.18: Transient behavior of the main resonance energy determined by Lorentz fits to the data. (a) Pump pulses 1 and 2 lead to cancellation of the oscillations at the first peak. By varying the time delay between the two pump pulses, enhancement (b, "1+3") or cancellation at later peaks (c, "1+3") can be achieved. See text for further details.

coherent phonons. The cancellation of oscillations in the  $\epsilon_{\text{ext}}(\omega)$  data is shown in parts (b) and (c) under different excitation conditions. Figure 6.18(b) shows single pulse oscillations, double pulse cancellation, and double pulse enhancement of the oscillations for a first pump pulse fluence of  $0.43F_{\text{th}}$  and a second pump pulse fluence of  $0.33F_{\text{th}}$ . For cancellation, the time delay between pump pulses is 127 fs, while for maximum enhancement the time delay is 267 fs. Figure 6.18(c) shows cancellation at the first maximum as well as at the second maximum, both leading to roughly the same lattice displacement for different excitations ( $1 = 0.57F_{\text{th}}$ ,  $2 = 0.45F_{\text{th}}$ , 133 fs delay for first-maximum cancellation;  $1 = 0.71F_{\text{th}}$ ,  $2 = 0.34F_{\text{th}}$ , 467 fs delay for second-maximum cancellation).

Many aspects of the current theoretical understanding of coherent phonon exci-

tation in absorbing solids are supported by the results presented here. Both DECP [70] and LECP [71] predict that the excitation of electrons to the conduction band couples to the lattice via the deformation potential. In essence, photoexcitation breaks a number of bonds in the material and the nuclear motion that ensues follows a classical trajectory on the potential energy surface determined by the number (and distribution) of the excited carriers. In zincblende semiconductors, calculations show that the absorption of intense femtosecond pulses can produce a potential surface with no minimum, leading to disorder within hundreds of femtoseconds [22]. In tellurium, density functional theory calculations show that transferring electrons from the valence band to the conduction band changes the potential surface so that a larger equilibrium helical radius is established [85]. The cosine-like response of our single pulse data supports the notion that the transfer of carriers, which occurs within the pump pulse duration, establishes a new equilibrium lattice configuration to which the ions, initially at rest, respond.

Within the theoretical framework described above, the process of coherent control can be thought of in the following way. The first pump pulse establishes a new potential surface on which the nuclei move. Initially displaced from the newly established equilibrium configuration, the lattice achieves this configuration in approximately one quarter of a phonon period, but the nuclei have momentum at that point. When the nuclei reach the classical turning point of their motion, a second pump pulse can excite the precise density of carriers to shift the equilibrium position to the current position of the ions, stopping the oscillatory motion. Because photoexcitation of additional electrons can only increase the equilibrium helical radius, the vibrations can only be stopped at the maximum displacement, or for time delays of n + 1/2 phonon periods between pump pulses. Under weak excitation, this n + 1/2 criterion has been verified experimentally in bismuth films [77].

Our experiments reveal that the strong excitation conditions that result in can-

cellation do not support this n + 1/2 criterion and that the vibrations do not stop at the maximum displacement. The 127 fs and 133 fs time delays that achieve cancellation as shown in Figure 6.18 do not coincide with the time to reach the maximum displacement in the single pump case, which is approximately 220 fs. The 467 fs time delay between pulses that results in cancellation near the second maximum is also smaller than the 520 fs it takes for the ions to reach the second maximum under single pulse excitation. Similar results occur in bismuth under strong excitation, where a 500 fs delay between pump pulses cancelled the lattice vibrations near the second maximum, while the second maximum is reached 600 fs after single pulse excitation [78], but the authors do not comment on the discrepancy. Our dielectric tensor data reveal that the resonance energy redshifts beyond the single pump maximum for phonon-cancelling excitations, as shown in Figure 6.18. Thus, the nuclei do not stop their coherent oscillations at the classical turning point, which is different from the low-excitation strength behavior of other materials [77].

The fact that the second pump pulse causes the ions to move past the classical turning point without resulting in oscillations indicates that the value of the equilibrium helical radius continues to change after the second pump has been fully absorbed. One possibility is that the establishment of a new equilibrium radius by the second pump pulse takes some time, allowing the lattice to track the equilibrium configuration adiabatically. The physical origin of such a phenomenon would likely involve many body effects, such as a deformation coupling that changes with lattice configuration. For a sufficiently large displacement of the lattice, a further increase in the helical radius may allow the excited electrons to redistribute in such as way as to increase the equilibrium helical radius. In this way, the lattice essentially "pulls" the equilibrium position along until it costs too much energy to displace the lattice further, at which point the helices stop their expansion and slowly return to their unexcited configuration.

## 6.3 Summary

The results presented in this chapter show that optically excited coherent phonons in tellurium can be controlled at excitation strengths near the threshold for permanent damage. The time delay between pump pulses that achieves cancellation or maximum enhancement of coherent phonons is earlier than what is expected based on low excitation experiments and reveals a departure from classical harmonic motion that is not apparent from the single pulse excitation data. Similar observations in other materials for strong optical excitation [78] suggest that this departure from damped harmonic motion may be a trait common to coherent phonons in all materials. In addition to revealing the importance of many-body effects on the post-second pulse dynamics, our results show that saturation of linear absorption and nonlinear optical effects play a role in the interaction between the pump pulse and the sample.

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