

Ultrafast Dynamic Ellipsometry and Spectroscopy of Laser Shocked Materials

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Abstract. Shock waves create extreme states of matter with very high pressures, temperatures, and volumetric compressions, at an exceedingly rapid rate of change. We review how to use a beam splitter and a note card to turn a typical chirp pulse amplified femtosecond laser system into an ultrafast shock dynamics machine. Open scientific questions that can be addressed with such an apparatus are described. We report on the development of several single shot time resolved diagnostics needed to answer these questions. These single shot diagnostics are expected to be broadly applicable to other types of laser ablation experiments. Experimental results measured from shocked material dynamics of several systems are detailed. Finally, we report on progress towards using transient absorption as a measure of electronic excitation and coherent Raman as a picosecond probe of temperature in shock compressed condensed matter.

Keywords: ultrafast, shock, dynamic ellipsometry, spectroscopy

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INTRODUCTION

A shock wave can uniaxially compress a material by tens of percent, raise the temperature by several hundred to a few thousand Kelvin, and create molecular level distortions that alter electronic structure.¹⁻⁴ This drastic change occurs in the time it takes the shock front to traverse the molecule at speeds approaching 10 nm/ps. The broad and diverse applications of shock physics has led to extensive continuum level theoretical understanding, engineering level calculations, and databases of empirical knowledge. However, most of the molecular level physics and chemistry detail remains invisible. How does a shock affect a molecule in a solid? How is the energy of the shock coupled into the molecule?⁵ What chemical reactions occur? How fast do they occur? What is the molecular temperature? Are the molecules in their ground electronic state? Are the electronic states seriously distorted, excited, or ionized at the shock front?¹⁻⁴ What is the effect of shock orientation relative to the molecular structure?⁶ What scientific tools are available to address these questions, and what benefits can we expect from knowing the answers?

These types of molecular level phenomena are typical of observations accessible to ultrafast laser spectroscopies. We simply need a method of generating appropriate shock states synchronized to single shot spectroscopies capable of dealing with the destructive nature of the shock process. Herein, we discuss our (nonunique)⁷⁻⁹ solutions to these experimental problems, and demonstrate the results on several material systems.

EXPERIMENTAL

Ultrafast Shock Generation

While focusing a high energy laser onto any material may generate a shock wave, we are particularly interested in simple shock waves structures that allow more detailed understanding of material response. We also seek comparison to techniques accessible to larger scale shock experimentation. Our goal is to produce a sudden transition to a sustained high pressure state. While femtosecond laser ablation can create a shock wave, a longer temporally supported structure is needed to maintain this high pressure state. By focusing a laser onto a metal drive layer through a tamper material, a shock wave is generated by frustrated laser ablation. The resulting shocks can be probed through the non-laser driven side of the metal. Shocks driven by a femtosecond pulse and a temporally supported pulse are contrasted in Fig. 1(a). Far greater motion is achieved with the chirped pulse drive, with no loss of time resolution at short times.

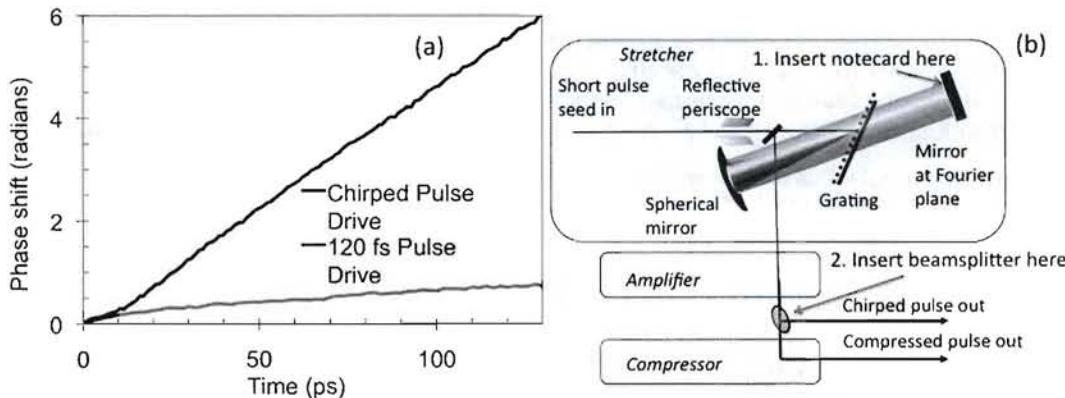


FIGURE 1. Phase shift proportional to surface motion is plotted for frustrated laser ablation driven shocks in an Al film using a chirped pulse and femtosecond pulse drive (a). The chirped pulse exhibits the same risetime and substantially greater sustained motion. Two simple modifications are needed to generate a shock drive pulse from a chirped pulse amplified laser as shown in (b).

The supported pulse can largely be achieved by adding a note card and a beamsplitter to an ultrafast chirp pulse amplified (CPA) laser.¹⁰ The note card at the Fourier plane of the stretcher clips the red edge of the spectrum. The beamsplitter removes most of the amplified energy into the chirped pulse before compression. These simple additions are illustrated in Fig. 1(b). This chirped beam (where the red spectral components temporally precede the blue), is used to drive the shock and to interferometrically measure the shock state. Figure 2 shows the time dependent spectrum and intensity of the chirped pulse.

How well does this simple alteration of a CPA laser achieve our goals? We have measured the shock state, or Hugoniot, of several polymer and liquid materials with our ultrafast laser generated shock system,¹¹⁻¹³ and they match the Hugoniots measured using large scale explosively driven or gas gun driven flyers. To the degree that the Hugoniot parameters of shock velocity and particle velocity specify the shock

state, we are reaching the same shock state and measuring it with diagnostics several orders of magnitude shorter in time duration. We will now describe the diagnostics that allow us to extract information on the shock state and shock dynamics.

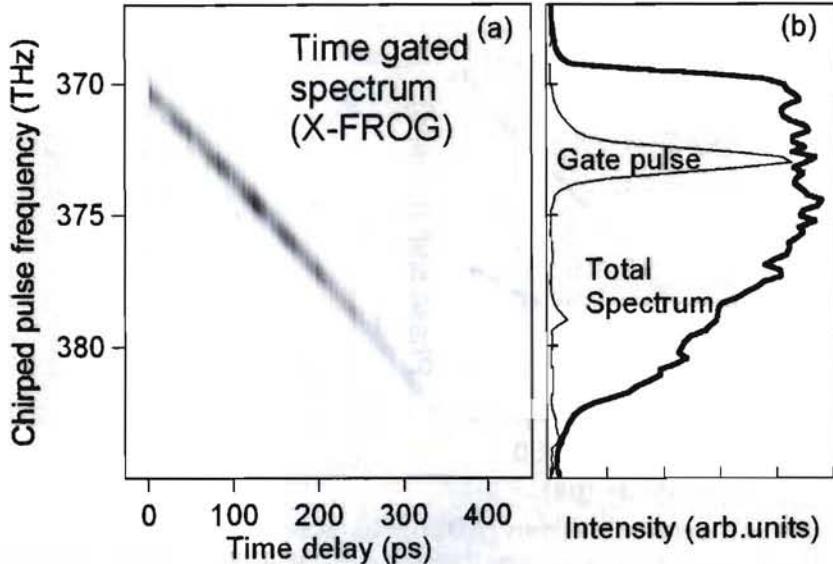


FIGURE 2. The chirped pulse is characterized by cross correlation frequency resolved optical gating (X-FROG). The chirped pulse is crossed in a barium beta borate (BBO) doubling crystal with a spectrally narrow compressed gate pulse that is scanned in time. The spatially isolated sum frequency spectrum is measured as a function of time delay. The X-FROG is shown in (a) and the chirped and gate pulse spectra are shown in (b). Oscillations in the X-FROG are artifacts of the reflection from the thin crystal faces.

Ultrafast Dynamic Ellipsometry

Ultrafast dynamic ellipsometry (UDE)¹³ is used to measure the shock and refractive index dynamics. To specify the shock state, we need to know the particle and shock velocity. The particle velocity is the velocity of the metallic drive layer pushing the material of interest. The shock velocity is the speed at which the mechanical disturbance propagates into the material of interest. Both of these are measured by placing the sample in one arm of a Mach-Zender interferometer. Motion of the metal surface induces time dependent phase shifts, as shown in Fig. 3(a). However, motion of the shock through a transparent material changes the refractive index, leading to a partial reflection off the shock front. This reflection interferes with the reflection off the metal drive layer and alters the phase shifts, as shown in Fig. 3(b). All of these effects are mathematically described by thin film interference equations, and we use simultaneous measurements at multiple polarizations and multiple angles to aid in the separation of derived physical parameters from the data. Several different implementations of these interferometric measurements are possible, our current implementation records 2 orthogonal polarizations at 2 angles with one spatially resolved dimension and one temporally resolved dimension in a single shot, as shown in Fig. 4. The temporal dimension simply uses a spectrometer as a streak camera for the chirped pulse, converting wavelength into time using the XFRG as calibration.

UDE has been used to measure Hugoniots,^{11, 12, 14} isolated shock states, laser excited melting,^{15, 16} and other transient phenomena.¹⁷⁻²¹

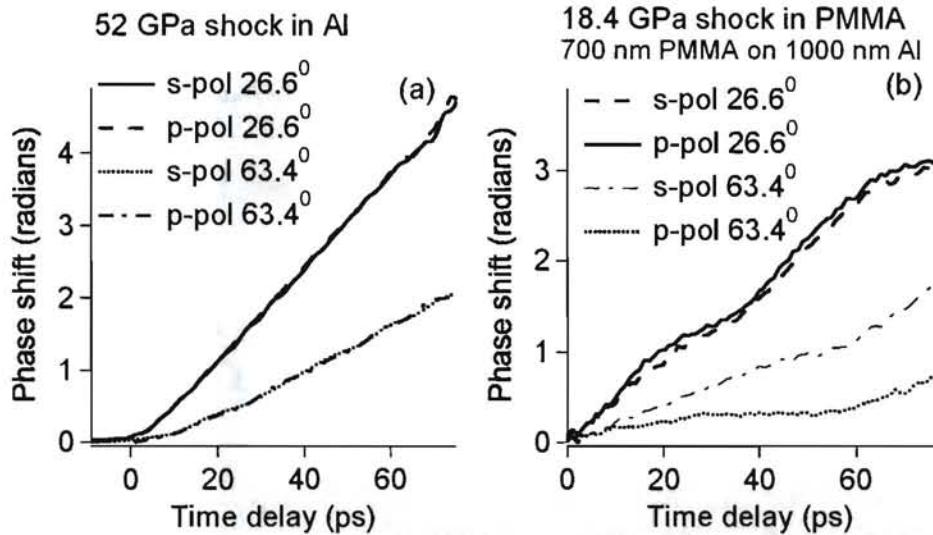


FIGURE 3. Ultrafast dynamic ellipsometry (UDE) measures the shock state. A chirped pulse is used so that spectral data can be converted to a time trace in a single shot. Note that in (a) the surface motion of the metal drive layer shows no polarization effects. In contrast, the shocked transparent film shown in (b) exhibits oscillations and an influence of polarization effects due to thin film interference caused by reflection from the shock front. Fits to thin film interference equations allow determination of shock velocity, particle velocity, and shocked refractive index. Incident angles and polarizations are noted.

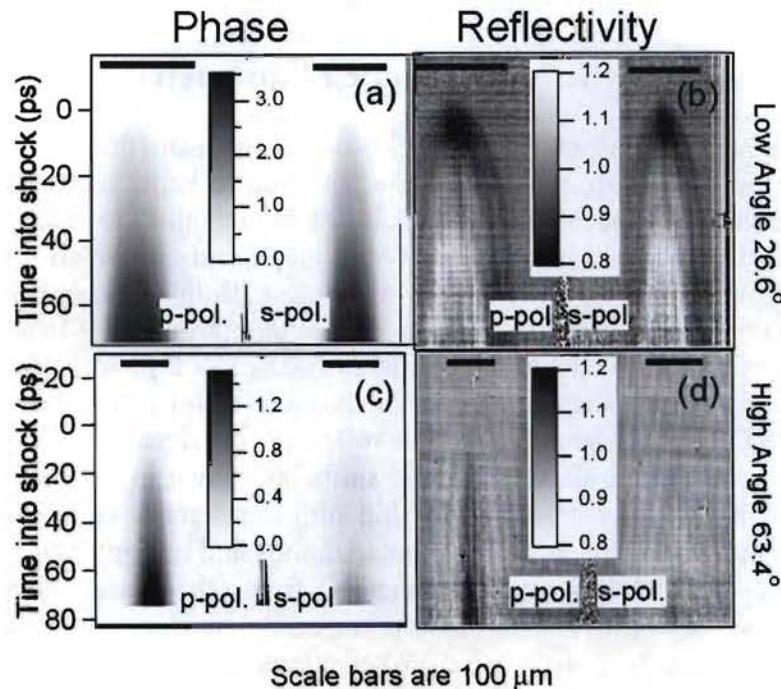


FIGURE 4. Full 2-dimensional UDE data shows phase and reflectivity changes as a function of pressure along the Gaussian shaped shock. The lineouts shown in Fig. 3 are from the center of these complete data sets of shocked PMMA on Al.

Transient electronic absorption spectroscopy

The Hugoniot is a very gross measure of shock dynamics. Most molecular phenomena are washed out in ensemble measures of shock and particle velocity. Molecular excitations, chemical reactions, or phase transition are often implicated by small nonlinearities in the Hugoniot, but this is by no means a direct measure. While shock physics would be ill defined without a measurement of the shock, spectroscopic observations hold great promise for providing supplementary understanding and eventually optimization of the molecular response to shock loading.

We have been coupling transient electronic absorption spectroscopy to the ultrafast laser shock and UDE measurements. Our goal is to address questions regarding the effect of extreme nuclear distortion accompanying shock wave passage on the electronic structure of organic solids.

Experimentally, transient absorption in the near ultraviolet to near infrared is trivial. Focusing a few microJoules of femtosecond near-infrared light into a few millimeters of calcium fluoride produces a broadband continuum from 375-850 nm. Reflective mode linear absorption spectroscopy is performed by focusing onto the shocked region and either scanning the time delay between the shock pump and absorption probe, as shown in Fig. 5, or by measuring several time delays in a single shot, shown in Fig. 6.

While the data of Fig. 5 are preliminary and not fully analyzed, several features are readily apparent. The increased refractive index behind the shock front that is responsible for the oscillations in phase shift versus time in the UDE data also leads to oscillations in reflectivity as a function of wavelength at a single time. The same thin film equations used to analyze UDE are used to model the transient absorption data.

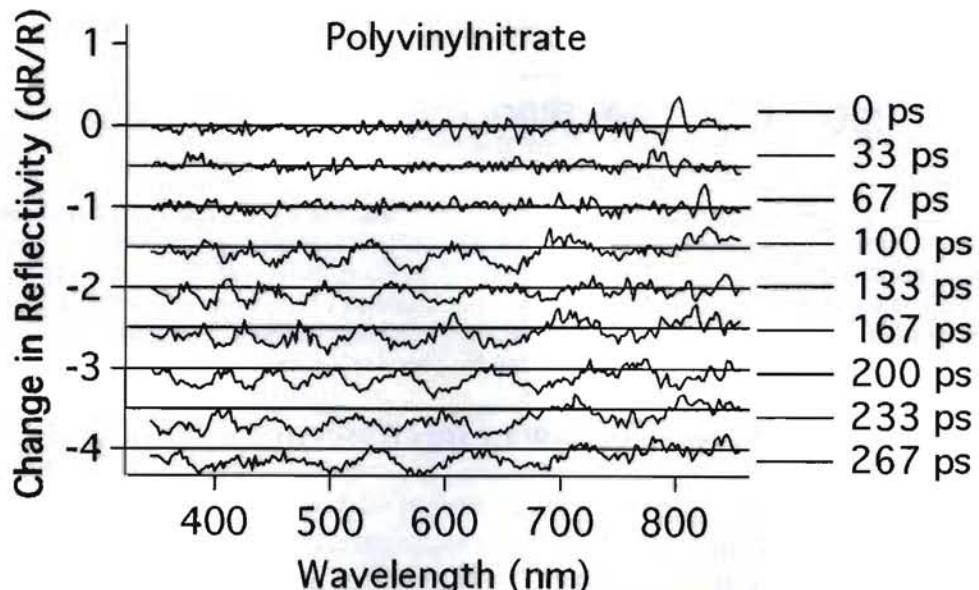


FIGURE 5. A shocked 1200 nm polyvinylnitrate film exhibits oscillations as a function of wavelength and broadband suppression in reflectivity at snapshots in time. The oscillations originate in the change in refractive index of the shocked layer. Each time trace is offset by -0.5.

We have learned from the UDE experiments that dramatically better data can be obtained with lessened sample requirements if all data can be taken in a single shock event. The simplest manner of multiplexing the transient absorption data are to spatially separate several different time delays²² and record all the spectra in a single shot on a 2-dimensional CCD camera. We double pass a 1.5" diameter pulse through a stack of staggered transparent windows. Each component of the pulse transits a different number of windows, and hence has a different time of arrival at the sample. Care is taken to focus tightly at the shocked region, and to image the window stack onto the spectrometer slit. Fig. 6 shows that the large changes in absorption typical of these shock experiments can be seen even in the raw data. Further data analysis is required to correct for the imaging aberrations across the broad spectral range and to accurately normalize the spectra at each time delay. Comparison to theoretical modeling suggests that increased absorption (increase in the imaginary part of the refractive index) is occurring in the shocked PVN along with the oscillations due to increased refractive index.

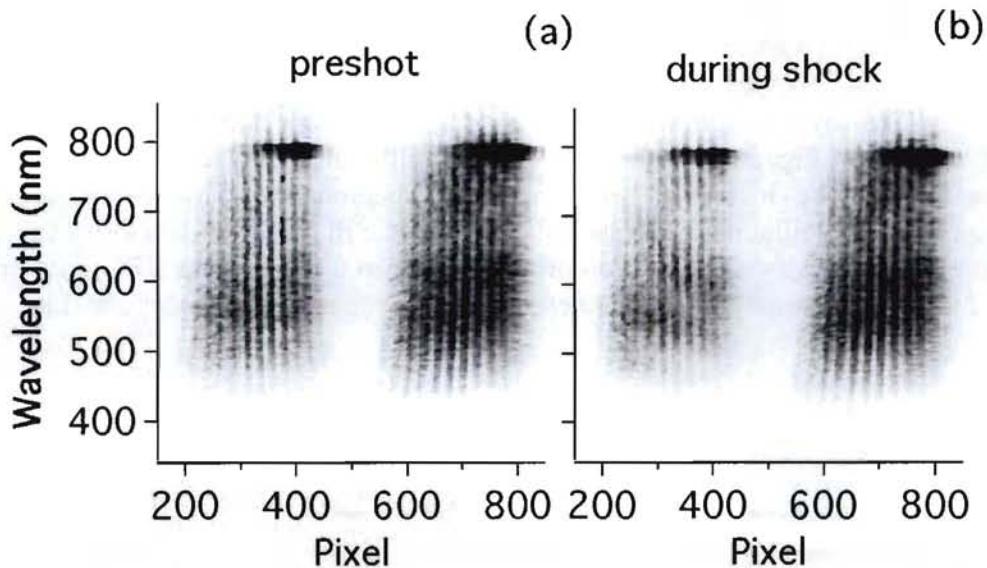


FIGURE 6. 2-dimensional transient absorption data are shown, with the sample on the left of each picture and a reference pulse on the right. A series of spectra at discrete time steps can be measured by adding a stack of transparent windows into the beam. There is an additional 13.9 ps of delay per window from left to right. The edge of each window (vertical stripe of low intensity) clearly delineates each time delay. The raw data exhibit decreased reflectivity and time dependent spectral oscillations in the shocked film of 1200 nm polyvinylnitrate.

Coherent Raman spectroscopy

Temperature is a very important parameter of shock experiments that is very difficult to measure. This difficulty is further exacerbated by the small sample size and short time durations of ultrafast laser shocks. While there have been occasional measurements of temperature using nanosecond lasers and spontaneous Raman,^{23, 24} there have been no clear paths to measure temperature in condensed phases with coherent Raman. While CARS is frequently used for thermometric measurement in the gas phase, the inherently broad spectra of condensed phase vibrations, particularly

when shocked into a hot, dense state, do not allow resolution of overtones in most molecule. A notable exception is shocked diatomics.²⁵ A method similar to the Stokes/anti-Stokes ratio of spontaneous Raman will be needed for shocked condensed phase polyatomic molecules.

We have been pursuing femtosecond stimulated Raman scattering²⁶ (FSRS) as a potential single shot temperature diagnostic. Theoretical formulae for temperature dependence have been worked out long ago,²⁷ but have been overlooked experimentally since they are only relevant at high temperatures, or for very low frequency modes.

While our real interest is in transient high temperatures, a simple test of these ideas can be experimentally shown by measuring low frequency vibrations from cryogenic to room temperature. The use of low frequencies and low temperatures for a proof of principle experiment allows the intrinsic bandwidth of the femtosecond pulse to serve as the Raman probe, while a spectrally filtered version serves as the pump. The FSRS pump and probe pulses are shown in Fig. 7(a). Figure 7(b) presents simultaneous Stokes and anti-Stokes FSRS of a 2.2 mm thick silicon dioxide (quartz) crystal. These data were recorded averaging a 1 kHz laser, but spectra have also been recorded in a single laser shot.

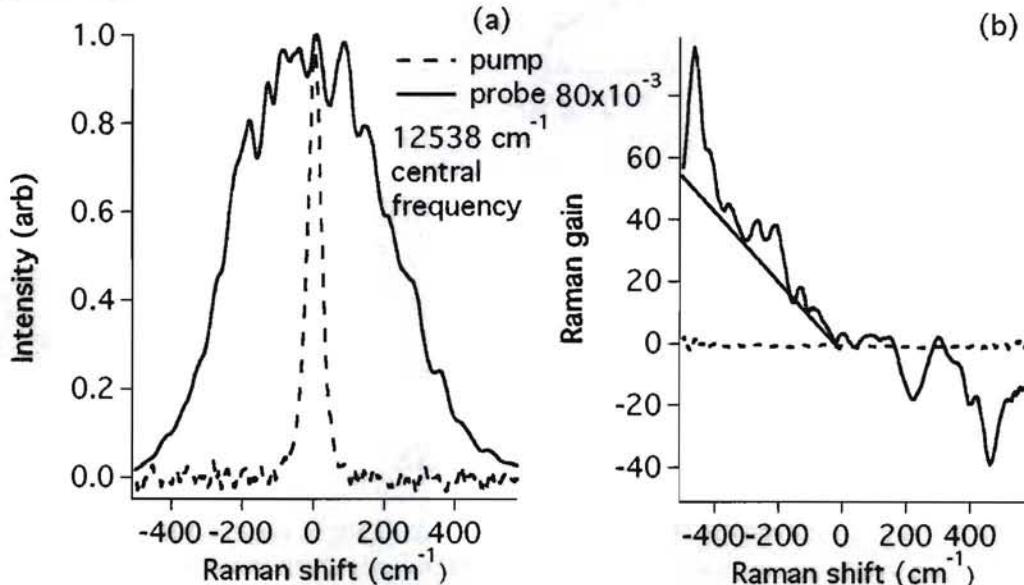


FIGURE 7. Femtosecond stimulated Raman spectroscopy (FSRS) is performed in simultaneous Stokes and anti-Stokes configuration attempting to obtain picosecond temperature measurements in condensed phases. The excitation spectra are shown in (a), and the FSRS spectrum of a 2.2 mm thick SiO₂ crystal is shown in (b). The line near zero is the background noise with the pump blocked. The broadband feature on the Stokes side shown by the solid line is attributed to stimulated emission of impurities, and subtracted to determine Raman gain intensities. The pump was attenuated to keep the gain below 0.05, excluding the stimulated emission.

While the analysis of the Stokes to anti-Stokes ratio of FSRS as a function of temperature is ongoing, Fig. 8 shows that the Stokes Raman gain may serve as a temperature measure. The data clearly follow the expected temperature dependence,²⁷ although the stimulated emission feature seen in Fig. 7(b) adds noise and uncertainty to the data. Additionally, it is noted that we purposefully kept the Raman gain at about

5% to remain in the small gain regime, since FSRS is exponential in Raman cross section. Figure 8(b) shows that if we increased the Raman gain, we would have a much larger slope of gain versus temperature, increasing our sensitivity. Larger gains are also easier to measure. One limitation of the approach of using the temperature dependence of the Stokes peaks is that the interpretation relies on the peak maintaining its identity and oscillator strength throughout the temperature range of interest. While this is true for cryogenic experiments, it is not true in the interesting cases of shock induced chemistry or phase transitions. Reactive conditions will require a means of normalizing the Stokes peaks to the anti-Stokes peak intensities.

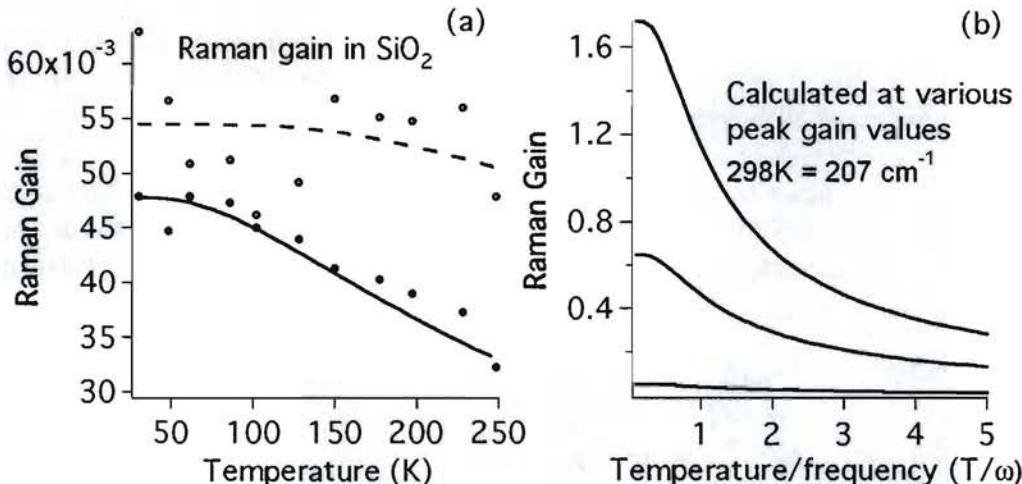


FIGURE 8. The measured Raman gain versus temperature for modes at ~ 200 (solid) and 450 (open) cm^{-1} are shown in (a) along with the theoretical predictions. The only parameter used to fit is the low temperature Raman gain. The predicted Stokes Raman gain temperature dependence is shown for several peak gain values (b). The temperature is normalized to the vibrational frequency to generate universal curves. Note that the data in (a) were taken in the low gain limit (bottom curve of (b)), but will be a far more sensitive measure of temperature in the large gain limit, where the gain versus temperature slope is greater.

CONCLUSIONS

Ultrafast shock dynamics is a field with many open questions that are readily accessible through trivial modifications to a standard chirp pulse amplified laser. Ultrafast dynamic ellipsometry is a well-developed technique that can characterize shock states, as well as provide useful data on other transient processes. Electronic transient absorption spectroscopy of shocked materials is beginning to produce useful information, but experimental refinement is called for to enable single shot spectra at multiple time delays. Similarly, femtosecond stimulated Raman spectroscopy is beginning to show promise as a picosecond temperature diagnostic in condensed phases, but further advances will be needed to broaden its range of applicability.

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