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# UNRAVELING SHOCK-INDUCED CHEMISTRY USING ULTRAFAST LASERS

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**Abstract.** The exquisite time synchronicity between shock and diagnostics needed to unravel chemical events occurring in picoseconds has been achieved using a shaped ultrafast laser pulse to both drive the shocks and interrogate the sample via a multiplicity of optical diagnostics. The shaped laser drive pulse can produce well-controlled shock states of sub-ns duration with sub-10 ps risetimes, sufficient for investigation of fast reactions or phase transformations in a thin layer with picosecond time resolution. The shock state is characterized using ultrafast dynamic ellipsometry (UDE) in either planar or Gaussian spatial geometries, the latter allowing measurements of the equation of state of materials at a range of stresses in a single laser pulse. Time-resolved processes in materials are being interrogated using UDE, ultrafast infrared absorption, ultrafast UV/visible absorption, and femtosecond stimulated Raman spectroscopy. Using these tools we showed that chemistry in an energetic thin film starts only after an induction time of a few tens of ps, an observation that allows differentiation between proposed shock-induced reaction mechanisms. These tools are presently being applied to a variety of energetic and reactive sample systems, from nitromethane and carbon disulfide, to micro-engineered interfaces in tunable energetic mixtures.

**Keywords:** Shock-induced chemistry, ultrafast spectroscopy, laser driven shocks, pulse shaping, ellipsometry

**PACS:** 42.65.Re, 42.62.Fi, 62.50.Ef, 82.40.Fp

## INTRODUCTION

We have been studying shock induced chemical reactions using ultrafast laser drive and diagnostics since 1998, when the High Explosives Reaction Chemistry via Ultrafast Laser Excited Spectroscopies (HERCULES) project was begun at Los Alamos. From the SCCM2001 proceedings, we find the questions asked then are still relevant: 1) Is the initiating shock impulsive or more gradual (i.e., what is the rise time of the shock wave stress); 2) Is a process like multi-phonon up-pumping necessary to excite reaction; 3) Are the observed kinetics in accord with standard transition state theory; 4) Are the reactants and/or products ever in thermodynamic equilibrium on time scales important to the usual HE applications; and 5) Is non-equilibrium temperature (vibrationally hot

products) essential to sustaining a detonation wave? We have recently made some progress towards answering these questions, which will be outlined, particularly the methodologies used, in the remainder of this paper.

## SHAPED ULTRAFAST LASER DRIVE

We found early on that shocks driven with ultrafast laser pulses had a very short risetime, but decayed rapidly [1]. One option is to drive with a longer laser pulse, but the sample must then be thicker to allow the wave to shock up. Instead, we shape the ultrafast drive laser as outlined in Ref. 1. Briefly, we chirp the ultrafast laser in a standard stretcher [2], and remove part of the red (leading temporal) end of the pulse with a sharp edge. The resulting pulse shape has a very fast rise followed by a few hundred picoseconds of reasonably

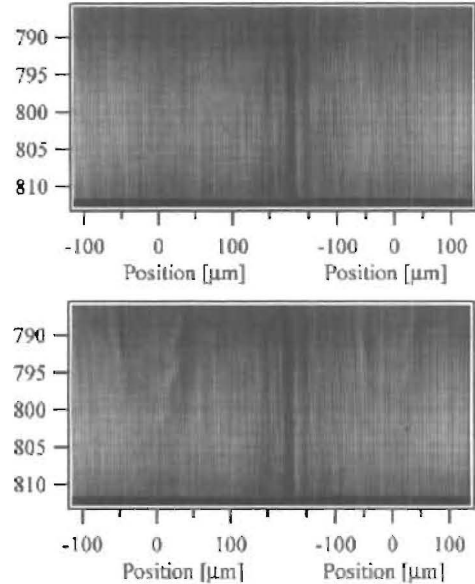
constant intensity. We have shown this kind of laser pulse can produce shock rise times of the order of 10 ps followed by 200-300 ps of constant pressure [ref] in a target consisting of a thin ( $\sim 2 \mu\text{m}$ ) layer of aluminum, optionally capped with a thin layer of a dielectric material. Longer times could be produced using further pulse stretching and thicker targets.

#### ULTRAFAST DYNAMIC ELLIPSOMETRY

The progress of a shock wave through a dielectric layer can be followed using the partial reflections from refractive index discontinuities at the layer transitions. Thin film interference arises when multiple reflections overlap in space and time on a detector. By placing the sample in one arm of a Mach-Zehnder interferometer, and crossing the sample and reference beams at a small angle at the beam combiner, a linear interferogram is produced, which is recorded by a CCD camera. As the shock wave travels through the sample, the thicknesses of shocked and unshocked layers change, changing the thin film interference and therefore the phase and amplitude of the interferogram.

We implement ellipsometry by using two portions of a single ultrafast laser beam to probe the sample at two different angles of incidence (near  $30^\circ$  and  $60^\circ$ ), and rotate the electric field of each beam to allow simultaneous visualization of both s and p polarizations. If a single 100 fs pulse is used, an ellipsometric version of the interferometric microscopy method [3] results, but multiple laser shots on different regions of a target using different shock drive pulse/interferometry pulse time delays are necessary to build up a time history [4]. A single shot version of this method can be constructed using a chirped laser for the probe and spectrally dispersing the interferogram to extract the time dependence [5]. We have used part of our shock-drive chirped laser pulse for this purpose. We measure the chirp (time versus frequency) using cross correlation frequency resolved optical gating (XFROG) [6]. The image of the interferometer fringes is optically transferred onto the slit of the spectrograph (one each in both high and low angle interferometers). The slit image is aligned to the center of the emerging shock wave at the sample, giving a line of spatially-resolved (to a few  $\mu\text{m}$ ) interferometric information. The XFROG calibration provides the means to extract

the times along the spectrometer wavelength axis. With 300 resolution elements along the wavelength axis, we achieve ps time resolution over the 300 ps time duration of our chirped probe pulse. An example is given in Figure 1.



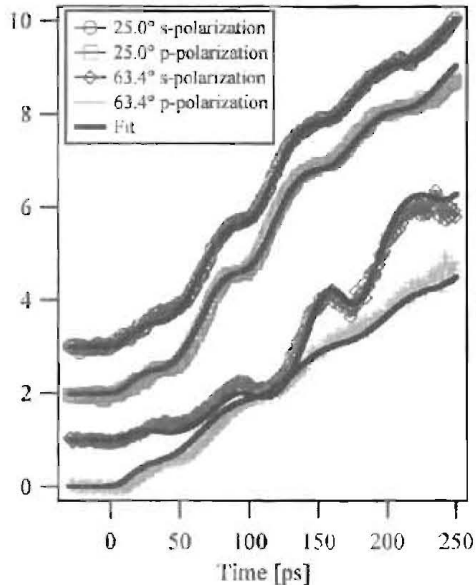
**Figure 1.** Interferograms for a  $25.0^\circ$  incidence probe with the p-polarized light on the left and the s-polarized light on the right; recorded (top) before and (bottom) during a  $8.7 \pm 0.2 \text{ GPa}$  shock in 1530 nm of polycarbonate on  $2 \mu\text{m}$  of Al. The ordinate is wavelength in nm. XFROG calibration gives the wavelength to time conversion.

The interferometric data is analyzed using an inverse fast Fourier transform (IFFT) along the spatial axis, followed by isolation of the relevant signal peak using a cosine tapered filter mask, and finally an FT to return the phase shift and reflectivity data [7]. The phase shift (or reflectivity) at a given spatial location versus time is obtained using a vertical lineout through the data, as shown in Figure 2. This data is then analyzed using the thin film interference equations, where the thicknesses of the layers change with time (ignoring the shock rise time) as:

$$d_u(t) = u_s t \text{ and } d_s(t) = (u_s - u_p)t$$

where  $d_u$  is the thickness of the unshocked layer and  $d_s$  is the thickness of the shocked layer and  $u_s$

and up are the shock and particle velocities of the shocked material. These velocities are determined concurrently without the need for reference experiments.

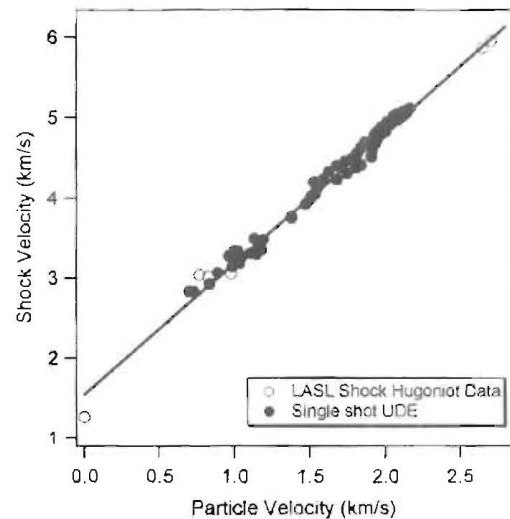


**Figure 2:** Phase shift versus time of a shock passing through a thin polycarbonate (PC) film on an Al shock drive layer. The positive phase shift with time is due to movement of the Al/PC interface (up). The oscillations arise from the thin film interference effects caused by the time-dependent thicknesses of the shocked and unshocked PC layers. A similar plot is obtained for the reflectivity data [ref].

The phase shift and reflectivity data at two angles and two polarizations (eight data sets) are simultaneously fit using the matrix formalism for light propagating in stratified media, this being the time-dependent thin film structure of the shocked PC layer (as well as the shocked Al and  $\text{Al}_2\text{O}_3$  layers of the shock drive material). After obtaining data at a number of different drive laser energies, we obtain the plot given in Figure 3. Note the scatter, which we determined were caused primarily from small variations in the thickness and density of the spin cast PC film on the micron spatial scale.

Finally, we are taking advantage of the smoothly varying spatial energy distribution of our shock laser to provide a range of stresses in a single shot. Figure 1 shows that we already have spatial resolution along a line through the center of our

laser-shocked region. For a shock drive laser focal diameter of  $100\text{ }\mu\text{m}$  and spatial resolution of  $2\text{ }\mu\text{m}$ , we have up to 50 different shock pressures, as long as the experiment is essentially one-dimensional. Figure 3 shows the Hugoniot points obtained from a single laser shot in cyclohexane using this methodology and the bulk Hugoniot for comparison. We used CTH simulations to determine that the maximum error in our assumptions that the flow was essentially 1-D was less than 2% after 200 ps of shock travel for our 100:1 aspect ratio shocks ( $1\text{ }\mu\text{m}$  of travel for a  $100\text{ }\mu\text{m}$  diameter shock).



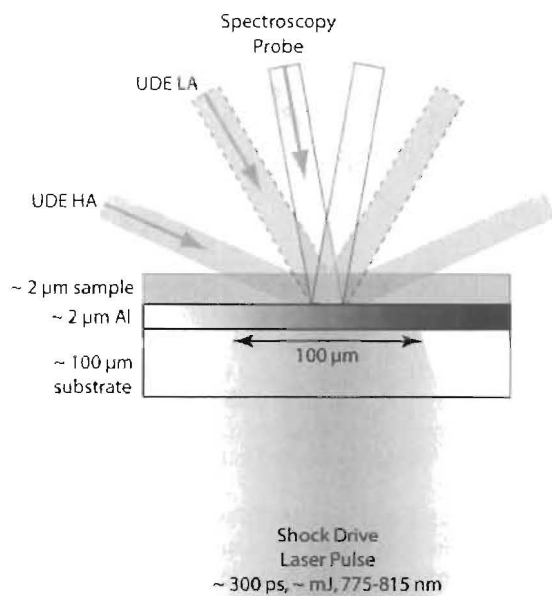
**Figure 3:** Hugoniot measured for liquid cyclohexane using the single shot UDE with the smoothly varying spatial energy distribution of our shock laser providing a range of stresses; compared to LASL Shock Data.

The ease and speed with which this single shot Hugoniot measurements can be performed open up additional possibilities for investigating shocked materials. These include solutions and mixtures as a function of composition, or high value samples.

Finally, we are applying UDE tools to reactive samples, such as nitromethane and carbon disulfide, as well as materials that undergo phase transitions. In these cases, the phase shift and reflectivity versus time plots (like Figure 2) show time-dependent oscillations and intensities, indicative of time dependent changes in the optical properties of the shocked layer. We are using various models of time-dependent chemical and phase transition processes to fit the data.

## ULTRAFAST INFRARED ABSORPTION

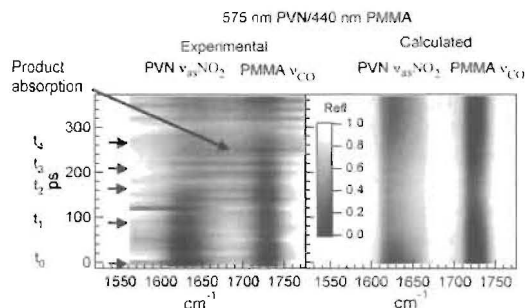
Figure 4 shows our standard laser-shock experiment, including the UDE diagnostics beams and the spectroscopic probe beam. For ultrafast infrared absorption, the spectroscopic probe is a broad band infrared ultrafast laser pulse generated using difference frequency generation between the signal and idler beams from an optical parametric amplifier system. Using  $\sim 100$  fs pulses from our Ti:sapphire laser system resulted in  $\sim 150$   $\text{cm}^{-1}$  frequency bandwidth tunable IR pulses. We have studied shock-induced chemical reactions in several energetic polymers (poly vinyl nitrate – PVN, nitrocellulose – NC, glycidyl azide polymer – GAP) using ultrafast infrared absorption to observe loss of reactant spectral features, as well as to look for growth of product spectral features.



**Figure 4:** Schematic of the ultrafast spectroscopic probe and laser shock experiments, where the spectroscopic probe can be ultrafast infrared absorption, stimulated Raman, or others. UDE HA is ultrafast dynamic ellipsometry high angle; LA is low angle

The ultrafast infrared absorption spectra in shocked thin polymer films are complicated by thin film interference effects, which are due to the same changes in film thickness with time used to measure shock and particle velocities in UDE.

However, the complex refractive index in the infrared for these molecular materials is not a single number, but rather varies considerably with IR wavelength because of characteristic absorption features [9]. The time-dependent spectral changes caused by travel of the compressional shock wave through the thin film samples must be modeled as discussed in Ref. 10 in order to decipher what changes are due to thickness from those due to chemical reaction. We have also performed IR measurements on PVN capped with a PMMA layer, as shown in figure 5 [11]. These data show that the onset of reaction requires an induction time of tens of picoseconds. Such an induction time is expected for reaction mechanisms that involve vibrational energy transfer [12] or electronic excitation relaxing into highly excited vibrational states [13], but distinguishes against prompt mechanisms such as direct high frequency vibrational excitation or direct electronic excitation followed by prompt excited state dissociation.

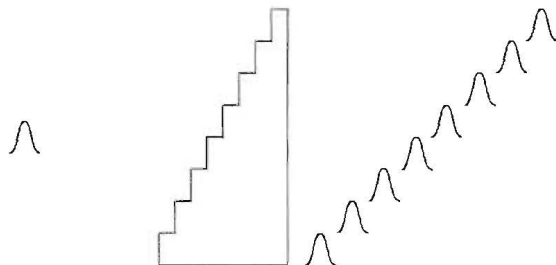


**Figure 5:** Time resolved infrared absorption spectra of 575 nm PVN + 440 nm PMMA stacked films shocked to 18 GPa. The  $1624$   $\text{cm}^{-1}$  peak is PVN  $\nu_{\text{as}}(\text{NO}_2)$  and the  $1728$   $\text{cm}^{-1}$  peak is the PMMA carbonyl stretch. Arrows denote timings:  $t_0$  shock enters PVN;  $t_1$  shock transits PVN/PMMA interface;  $t_2$  shock reaches PMMA/air interface;  $t_3$  rarefaction reaches PMMA/PVN interface;  $t_4$  head of rarefaction fan reaches PVN/Al interface [11].

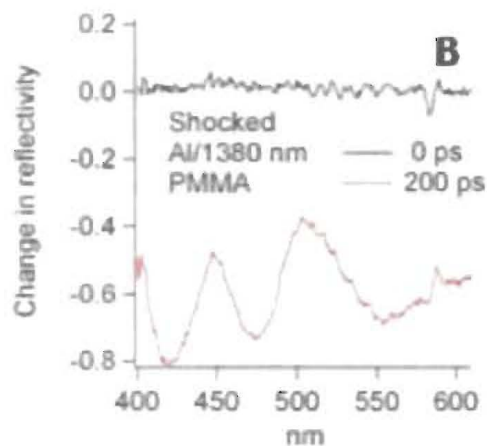
## SINGLE-SHOT UV/VIS ABSORPTION

We are developing time-resolved single shot UV/visible absorption methods to differentiate between the two shock induced reaction mechanisms showing an induction time (see above). The concept of single shot methods is to measure many different shock/probe delay times

on every laser shot. A CCD camera has two dimensions. For spectroscopy one of these is the spectral dimension. The other is a spatial image of the input slit of the spectrometer. If time delay information is spatially encoded onto the probe pulse, the CCD image will measure spectra at a number of different delay times. One method to spatially encode time delays is by passing the probe beam through an echelle or stepped wedge, as illustrated in Fig. 6. We generate a femtosecond broadband supercontinuum in calcium fluoride and use it as our white light spectral source. A preliminary single-shot UV/visible absorption spectrum of PMMA on Al at a single delay time using this methodology is shown in Fig. 7. Further results can be found in McGrane et al. in these proceedings.



**Figure 6:** Spatial encoding of different time delays using a stepped wedge.



**Figure 7:** Preliminary single shot UV/visible absorption spectrum of PMMA/Al at 0 and 200 ps time delays after shock enters the PMMA. The oscillations are due to thin film interference from the shocked PMMA layer.

## COHERENT RAMAN

Raman spectroscopy has been used by numerous authors to measure vibrational spectra, chemical reactions, and temperatures of shocked materials [14-16]. However, common old ordinary Raman spectroscopy (COORS) provides insufficient signal levels to allow interrogation of shocked thin films [17]. Instead, a number of coherent Raman methods are candidates to measure vibrational spectra in thin films under shock loading. Coherent anti-Stokes Raman spectroscopy (CARS) has been used to measure vibrational spectra and extract vibrational temperature in shocked liquid samples [17]. A number of challenges exist to extend that work to thin films and ps time resolution, including the  $N^2$  dependence (where  $N$  is the number of molecules) of CARS intensities, damage thresholds limiting probe pulse(s) intensity, and convolution of distance and time behind the shock, which affects path integrating optical probes.

We are pursuing femtosecond stimulated Raman scattering (FSRS), CARS, and femtosecond Raman induced Kerr effect spectroscopy (FRIKES). FSRS has the advantage of large efficiency ( $\sim 6$  orders larger than COORS) and the ability to measure temperature via Stokes/anti-Stokes intensity ratios. We have demonstrated large Stokes gains in a single laser shot, and are presently adding anti-Stokes as well as scaling to thin films.

FRIKES is background free and has the same line shapes as COORS, but the signal intensity is limited by the intensity of the probe pulse. Also, shock induced birefringence may distort the Raman spectrum [18]. We have demonstrated simultaneous Stokes and anti-Stokes spectral region acquisition, but are still investigating single shot capability and use in thin films.

CARS, when combined with CSRS, can also produce vibrational temperature information. We have simulated and tested the CARS/CSRS ratio method for measuring temperature, using a resistively heated  $\text{SiO}_2$  crystal, as shown below in Figure 8. CARS/CSRS has a possible disadvantage of requiring large bandwidth in the pump (rather than probe) laser to achieve large signal to noise in a single shot, effectively negating use of a white light continuum to obtain Stokes and anti-Stokes spectral regions to high wavenumber.

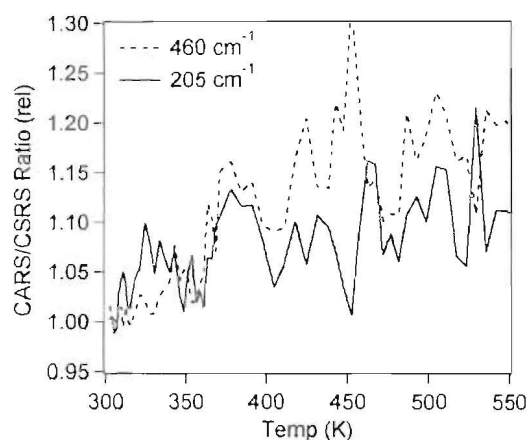


Figure 8: CARS/CSRS peak intensity ratio versus temperature for a resistively SiO<sub>2</sub> crystal at ambient pressure. Ratios for both the 205 and 460 cm<sup>-1</sup> peaks are shown.

## OUTLOOK

We have demonstrated the use of UDE to measure shock and particle velocities, as well as shocked material index of refraction, in thin films of dielectric materials shocked using shaped ultrafast laser pulses. Time synchronicity better than 100 fs is achieved using portions of the same laser pulse to drive shocks and perform UDE. We are extending these measurements to reactive systems, with preliminary results on nitromethane, carbon disulfide, and single crystal Si. We have demonstrated infrared absorption and UV/visible absorption spectroscopic interrogation of the shocked thin film materials, providing experimental evidence to distinguish energy transfer mechanisms for shock-induced reactions. We are pursuing three types of coherent Raman diagnostics, with the ultimate aim to provide concrete chemical reaction rate and mechanism information during shock induced chemistry.

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