Coherent Raman studies of shocked liquids

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Abstract. Coherent anti-Stokes Raman spectroscopy (CARS) is reported following shock loading for the liquids phenylacetylene (18 and 13 GPa), cyclohexane (17 GPa), and acrylonitrile (17 GPa). The evolution of the spectra over the first 300 ps was recorded in each case. All spectra show monotonic decay of all peaks with increasing time after shock. No new peaks due to either chemical reaction or pressure shifting of the vibrational frequencies were observable. This loss of signal after shock is attributed to the decreased coherence time in the shock heated liquids, which leads to rapid signal loss in the nonresonant background free version of CARS used in the measurements. These results suggest that more complex methods may be required to measure picosecond shock induced chemistry with coherent Raman techniques that are free of nonresonant background interference.

1. Introduction
Shock induced chemical dynamics are essential to the processes of initiation and detonation in high explosives [1-8], but are difficult to measure in situ. Numerous nonexplosive organic materials are also known to react under shock loading [9-16], but details of what chemical reactions occur, the rates of those reactions, and how those reactions and rates are affected by shock conditions are almost completely unknown. Transient vibrational spectroscopy offers the time resolution and chemical specificity necessary to begin to address the details of shock induced chemical dynamics [17-25].

The experiments reported in this paper represent an attempt to measure shock induced chemical dynamics of organic liquids using the technique of broadband multiplexed CARS [26]. Shocked CARS has been performed with nanosecond [27, 28] and <100 ps laser pulses [17, 29, 30] previously, and we pursued broadband multiplex CARS method both to enhance the time resolution and remove the interference between the nonresonant background and the vibrationally resonant signals of interest.

2. Experimental
A tabletop ultrafast laser shock drive source was used in the experiments [31]. The sample geometry is illustrated in figure 1. The CARS probe required three pulses, as shown in figure 2. The spectrally narrow pump and probe pulses are formed by passing ~700 µJ of 200 cm⁻¹ full width half maximum (FWHM), ~100 fs pulses through two narrow band filters (Omega optical, 800 nm center, 2 nm FWHM) to achieve 31 cm⁻¹ spectral resolution at a pulse width of ~500 fs. A beam splitter separates this light into pump and probe pulses, which were attenuated to 2 µJ to avoid burning the sample. The Stokes pulse is generated by focusing ~30 µJ of 800 nm, 100 fs light into a 4 mm thick CaF₂ plate with a 6” focal length lens and collimating with a 2” focal length achromat. The Stokes pulse then traverses
an 800 nm wavelength long-pass filter to remove the residual pump pulse and short wavelengths that would overlap the CARS at 630-800 nm.

All three pulses are aligned in BOXCARS geometry, i.e., parallel to each other at three corners of a box with ~15 mm sides before focusing onto the sample with a 5” focal length lens. The CARS is collected with a 6” focal length lens and the signal is spatially isolated with a ~3 mm iris. The CARS pulses were timed to the shock using frequency mixing in BBO to synchronize to an ultrafast dynamic ellipsometry [32] pulse that measured the shock onset interferometrically. All data is presented where \( t = 0 \) is the time where the shock enters the liquid layer. Some fraction of the liquid film remains unshocked in all the data shown.

There is an inherent tradeoff between spectral and time resolution [33]. The pump and probe temporal pulsewidth limits the spectral resolution, consistent with the uncertainty principle, but also determines the delay required between the pump and the probe. Increasing the delay between the pump and the probe until they do not overlap removes the electronic (nonresonant) contribution to the CARS signal, since this electronic coherence decays in femtoseconds. The pump and Stokes pulses also excite Raman active vibrational coherences that undergo a free induction decay with time constants typically in the range of a few picoseconds at room temperature. The coherences that remain at the time the probe pulse arrives are responsible for the CARS signal observed. The decay of coherence between the pump and the probe is essential in understanding the results below. While it is well understood that the coherences decay faster at higher temperature, vibrational coherence decay times are not known under shock conditions.

Figure 1. The thin films are impinged with a laser shock drive pulse through the tamper. The aluminum (Al) absorbs the energy, creating a plasma that drives a mechanical shock into the sample. The response of the sample is probed through the window, double passing the sample and the window after reflection off the Al. The Al reflectivity change by <35% for all times reported here.

Figure 2. The pump, Stokes, and probe pulses are focused from three corners of a square, with the CARS emission isolated at the 4th corner after the sample. Pump and Stokes are time coincident, while the probe is delayed by 1.2 ps to make the nonresonant contribution negligible. The intensity falloff of the Stokes is largely due to decreased long wavelength sensitivity of the Si detector.
The CARS spectra of phenylacetylene shocked to 18 GPa at times up to 300 ps after shock loading are shown in figure 3. Phenylacetylene has been observed to chemically react under these conditions, as observed by volume reduction through Hugoniot measurements and by large increases in transient absorption across the visible to near infrared range [34]. The loss of reactants as the shock runs through increasing amounts of the sample is apparent in figure 3, but there are no new peaks attributed to product formation, or even due to pressure shifting of the vibrational frequencies. Note that CARS signals are proportional to the number of molecules squared, so shocking half the thickness of the sample leads to a 25% CARS signal of the unshocked material. Despite the high signal to noise, even close examination of the data in figure 3 shows no indication of significant new peaks. This lack of shocked CARS peaks could originate in the shortened coherence time ($<<1.2$ ps) under the high temperature/high pressure reactive shock conditions. Transient absorption of the CARS excitation could also diminish the CARS intensity.

Phenylacetylene was shocked to 13 GPa to test whether lower temperature would allow new peaks to be observed, while remaining under conditions that allow significant chemical reaction on the time scale of our experiments. The results shown in figure 4 exhibit decreased CARS signals, but still no new peaks. The larger remaining unshocked CARS signal is partially due to lower shock velocity, but is also affected by initial sample thickness. The initial thickness can increase by several micrometers if the 6 µm thick gasket is not flat or if a dust particle settles between the window and the drive layer.

Cyclohexane does not chemically react at 17 GPa under the conditions of our experiments, and has no increase in transient absorption that could interfere with the CARS excitation. Figure 5 shows that the CARS signals monotonically decrease with time after shock, but still no new peaks are identifiable. These data support the interpretation that lowered coherence time due to increased temperature is a larger factor in limiting CARS signals than the effects of increased transient absorption or chemical reaction.

The CARS of acrylonitrile shocked to 17 GPa was measured as a second material known to be chemically reactive under our shock conditions [34]. Figure 6 shows monotonic loss of CARS superposed on a broad incoherent emission that leaked through our spatial filter. The incoherent emission is not time resolved, and may be occurring long after the CARS measurement is over. The incoherent emission was only seen in reactive materials.
Figure 5. CARS spectra of cyclohexane liquid shocked to 17 GPa. Cyclohexane is not chemically reactive under these conditions. The shock just enters the liquid at $t = 0$ ps.

Figure 6. CARS spectra of acrylonitrile liquid shocked to 17 GPa. Acrylonitrile is chemically reactive under these conditions. The shock just enters the liquid at $t = 0$ ps.

Finally, we tested the hypothesis that the CARS signals from the shocked material were unobservable due to the coherence time being much less than our 1.2 ps probe delay. By setting the probe delay to zero, we remove the sensitivity to coherence time, but we also gain nonresonant interference. Phenylacetylene shocked to 6 and 18 GPa at 0 and 500 ps time delays are shown in figure 7. The initial lineshapes are dispersive, but can be easily identified in the unshocked material. If the shocked material, there are significant increases in signals between 2100 and 2900 cm$^{-1}$, but it is difficult to say if this is due to pressure shifting of the strong 2110 cm$^{-1}$ mode or due to changes in the nonresonant component. Fortunately, the unshocked signal has no intensity at frequencies higher than the C-H stretch at 3025 cm$^{-1}$, but the shocked signals show a broad band at $\sim 3150$ cm$^{-1}$ that is most easily assigned as the pressure shifted C-H stretch. This shift and broadening of the C-H stretch is reasonable in comparison to C-H shifts $> 80$ cm$^{-1}$ observed in nitromethane shocked to 14 GPa [36]. Removing the probe delay allowed observation of the hot, reacting shocked material. However, the nonresonant background still interferes with the analysis over most of the spectrum. Note that materials with longer coherence times at high temperature may remain measurable under shock using background free CARS [35].

Figure 7. CARS spectra of shocked phenylacetylene with zero time delay between the three excitation pulses. The $\sim 2000$ cm$^{-1}$ FWHM feature is the nonresonant electronic component. The resonant vibrational peaks interfere constructively on the low Raman shift frequency side and destructively on the high frequency side, producing dispersive line shapes. Note that new signals appear at frequencies $> 3025$ cm$^{-1}$ upon shock loading that are attributed to pressure shifted carbon-hydrogen stretching peaks. Times of 0 and 500 ps are relative to shock entry into the liquid film.
4. Conclusions
CARS measurements were performed in shocked thin organic liquid films, but the 1.2 ps probe delay time necessary to remove the nonresonant background eliminated our ability to measure CARS in the high temperature and pressure shocked materials. Apparently, the temperature and pressure increase was sufficient to limit vibrational coherence times to much less than 1.2 ps. Achieving separation of resonant and nonresonant CARS with zero probe time delay will be necessary for measurements of shock induced chemical dynamics. Such separation has been performed using polarization based methods [7], however input polarization may not be maintained under shock loading. Separation of resonant and nonresonant components has also been achieved with interferometric methods [38, 39]. Application of interferometric CARS to shock studies is the subject of ongoing investigations.

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