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SINGLE-PULSE COHERENT RAMAN SPECTROSCOPY IN SHOCK-COMPRESSED BENZENE

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ABSTRACT

Single-pulse backwards stimulated Raman and reflected broadband coherent anti-Stokes Raman spectroscopy (BSRS and RBBCARS) have been used to measure the vibrational frequency shifts of the 992 cm^{-1} ring-stretching mode of liquid benzene shock-compressed to pressures up to 1.2 GPa. The resulting shifts of $\sim 7.5\text{ cm}^{-1}/\text{GPa}$ in the dynamic experiments are compared to spontaneous Raman-scattering measurements of heated samples compressed in a diamond-anvil cell. RBBCARS was used to simultaneously measure the ring-stretching mode vibrational frequencies of liquid benzene / liquid perdeuterobenzene mixtures shock-compressed to pressures up to .53 GPa. Additional experiments that demonstrate the difficulty of using polarization-sensitive coherent Raman techniques, such as Raman-induced Kerr effect spectroscopy (RIKES), in shock-compressed samples are described.

INTRODUCTION

Material behavior and energy release in shock-induced chemical reactions and explosive detonation have traditionally been studied using bulk property measurements via gauge techniques. Those traditional methods necessitate the inference of microscopic behavior from the macroscopic observables and generally only a global energy release rate is determined. The actual molecular structure of the material, as well as its chemical composition, remains unknown. The use of optical methods to interrogate materials under shock loading would allow direct observation of the microscopic (i.e. molecular) structure. Previous studies of this type using optical techniques include stimulated Brillouin scattering in shock-compressed acetone and water [1,2], emission and absorption spectroscopic measurements of shocked materials [3,4], and spontaneous Raman scattering studies of shocked explosives [5,6]. We have demonstrated the use of two fast, pulsed, coherent Raman techniques - backward stimulated Raman scattering (BSRS) and reflected broadband coherent anti-Stokes Raman scattering (RBBCARS) - for measurements of vibrational frequencies in shock-compressed samples of neat liquid benzene, neat liquid perdeuterobenzene, and mixtures of the two. We have also found severe problems with implementation of a third coherent Raman technique - Raman-induced Kerr effect spectroscopy (RIKES) - because of shock-induced changes in the optical characteristics of shock-compressed samples.

EXPERIMENTAL

The apparatus used in these experiments for studying coherent Raman scattering in shock-compressed condensed phase samples consists of two separable portions: the shock production mechanism and the optical diagnostic. The shock production mechanism consists of a 51 mm diameter, 3.1 m long gas gun that is used to accelerate a magnesium projectile with an 8 mm thick 304 stainless steel warhead to a desired velocity. The projectile impacts a 2.1 mm thick 304 stainless steel target plate, producing a shock wave that runs forward into a 2.5 to 8.0 mm thick condensed phase sample. In the experiments whose results are discussed below, the samples were reagent grade benzene (Mallinckrodt, Inc.), 99.9%

perdeuterobenzene (benzene- d_6 , Wilmad Glass Co., Inc.), or mixtures of benzene and benzene- d_6 . The state of the shock-compressed samples was determined using standard data reduction techniques [7] using published shock-velocity / particle-velocity (u_s/u_p) data [8]. We assumed the u_s/u_p Hugoniot of benzene- d_6 to be the same as that of benzene. Mixture densities were determined by volume fraction.

The timing sequence for the optical experiments is determined by the incoming projectile. A signal from aluminum time-of-arrival pins located in the gun barrel ~ 25 cm up from the target, in conjunction with an appropriate time delay, triggers the laser flash lamps ~ 300 μ s prior to impact. A time-of-arrival pin activated just before impact of the projectile on the target plate, in conjunction with another time delay, serves to trigger the Q-switch on the laser just prior to the time the shock wave would strike the quartz window and after it is well past the point in the sample interrogated by the optical probe.

Experiments using backward stimulated Raman scattering (BSRS) as the optical diagnostic have been discussed previously [9,10]. The experimental arrangement is shown in figure 1. Briefly, the technique consists of focusing a medium energy (1-5 mJ), short duration (5-6 ns) pulse from a frequency-doubled Nd:YAG laser into the sample using a 150 mm focal length lens. The high intensity of the laser at the focus, coupled with the presence of a large cross-section Raman active vibrational mode in the sample, produces gain in the forward and backward directions along the beam at a frequency that is different from the Nd:YAG frequency by the frequency of the active mode. In liquid benzene, the ring-stretching mode at 992 cm^{-1} has the lowest threshold for stimulated Raman scattering induced by 532 nm light, and was the transition observed in these experiments. The backwards directed, frequency shifted beam is routed into a 1 m focal length spectrometer equipped with a 1200 1/mm grating blazed at 500 nm and is recorded on Polaroid film, along with a portion of the diffusely reflected Nd:YAG beam. The frequency shift is obtained by accurately measuring the distance on the film between the Nd:YAG laser frequency and the backwards stimulated Raman frequency.

FIG. 1. Schematic representation of the backward stimulated Raman scattering experiment. SHG - second harmonic generator; Harm. Sep. - harmonic separator.

FIG. 2. Schematic representation of the reflected broadband coherent anti-Stokes Raman scattering experiment. OMA - optical multichannel analyzer.

The apparatus used for reflected broadband coherent anti-Stokes Raman scattering (RBBCARS) experiments has also been described previously [10,11]. A schematic representation of this apparatus is shown in figure 2. Coherent anti-Stokes Raman scattering (CARS) occurs as a four-wave parametric process in which three waves, two at a pump frequency, ω_p , and one at a Stokes frequency, ω_s , are mixed in a sample to produce a coherent beam at the anti-Stokes frequency, $\omega_{as} = 2\omega_p - \omega_s$ [12,13]. The efficiency of this mixing is greatly enhanced if the frequency difference $\omega_p - \omega_s$ coincides with the frequency of a Raman active mode of the sample. Since the Raman frequencies of the shock-compressed materials are not precisely known, and in order to produce CARS signals from more than one species, a broadband dye laser, which has a bandwidth equivalent to the gain profile of the dye, is used as the Stokes beam [14]. A portion of the 6-ns-long frequency-doubled Nd:YAG laser pulse is used to pump the dye laser. The resulting two laser beams (dye and remaining pump) are passed through separate Galilean telescopes and sent along parallel paths towards the sample. The beams are focused and crossed (with about 1 mm length of overlap at the focus) at a point 4 mm in front of the rear sample wall using a previously described technique [15]. The beam crossing angle (phase matching angle) is tuned by adjusting the axial distance between the parallel beams. The CARS beam is reflected back out of the shocked sample by the highly polished front surface of the target plate. The reflection sends the beam along a path parallel to the two incoming beams. After being separated from the pump and Stokes beams using a long-wave-pass dichroic filter, the beam is passed through a dove prism and focused into the 75 μm wide entrance slit of the 1 m focal length spectrometer. The dove prism is used to rotate the image of the RBBCARS signal so that any beam movement resulting from the changing position of the reflecting surface during the shock-compression process would translate into movement along, rather than across, the spectrometer entrance slit. The signals are detected at the exit of the spectrometer using a silicon intensified-target vidicon (EGG-PAR 1205D) coupled to an optical multichannel analyzer (OMA - EGG-PAR 1205A).

The Raman-induced Kerr effect can be described in terms similar to the above description of CARS. A well polarized probe laser beam is passed through the rotating electric field of a circularly polarized pump beam. The four-wave parametric process described above induces an ellipticity on the probe beam whenever the frequency difference between the two lasers equals that of a Raman active transition in the sample [16,17]. Since both techniques involve use of a single frequency pump laser and a broadband Stokes laser, RIKES can be performed with an apparatus very similar to the above described RBBCARS apparatus. The modifications necessary are shown in figure 3 and are described below. The portion of the frequency-doubled Nd:YAG laser beam that does not pump the dye laser is passed through a Fresnel rhomb to produce a beam of $> 99\%$ circular polarization. The dye laser beam (Stokes frequencies) is passed through a high quality Glan-Taylor (air-gap) prism to produce a beam of ~ 1 part in 10^6 linear polarization. The two beams are focused and crossed in the sample using a 150 mm focal length, 50 mm diameter lens. The crossing angle is near 6 degrees, giving an overlap length of $\sim 150 \mu\text{m}$ at the focus. The Stokes beam is then reflected by the highly polished front surface of the target plate back through the sample and along a path parallel to the incoming beams. A mirror separates the reflected dye laser beam from the other beams and directs it first through a Babinet-Soliel polarization compensator and then through a Glan-Taylor polarization analyzer. The compensator was found to be necessary to remove the ellipticity introduced into the linearly polarized Stokes laser beam by the birefringence inherent in the optical components located between the polarizers, including the ambient sample. When the two Glan-Taylor prisms are crossed, the dye laser beam is blocked except at frequencies corresponding to Raman resonances, where the RIKES signals are passed. These signals are directed through the dove

prism, focused into the entrance slits of the 1 m spectrometer and detected by the OMA system.

FIG. 3. Schematic representation of the Raman-induced Kerr effect spectroscopy experiment.

RESULTS AND DISCUSSION

Figure 4 shows typical spectral data obtained using BSRS in a sample of neat liquid benzene shock-compressed to 0.92 GPa [9,10]. In this particular experiment, the shock wave had traversed $\sim 2/3$ of the distance to the window, allowing BSRS to occur in both the shocked and ambient benzene simultaneously.

FIG. 4. Backwards stimulated Raman scattering (BSRS) spectrogram for shock-compressed liquid benzene. The shock pressure was 0.92 GPa.

Figure 5 shows the RBBCARS spectra obtained in liquid perdeuterobenzene both ambient and shock-compressed to 1.17 GPa. The 253.652 nm line from a Hg lamp was used to calibrate the spectrometer during data accumulation, and is also shown in the figure. The vibrational frequency shifts in shock-compressed neat liquid benzene measured using BSRS and RBBCARS are plotted in figure 6 versus shock pressure [10]. Also plotted in the figure are the ring-stretching mode vibrational frequency shifts measured by spontaneous Raman scattering (induced by the 568.2 nm line of a

FIG. 5. Reflected broadband coherent anti-Stokes Raman spectra (RBCARS) of ambient and shock-compressed perdeuterobenzene. The ambient peak position is 945 cm⁻¹. The shock pressure was 1.17 GPa.

FIG. 6. Benzene ring-stretching mode vibrational frequency shifts (with respect to 992 cm⁻¹) vs. pressure. Data recorded using BSRS and RBCARS are denoted by closed and open circles, respectively. The single open circle represents two data points. Uncertainties in the shock data are given on one point. In the static measurements, benzene I was observed as a metastable phase above 1.2 GPa and benzene II was metastable below 1.2 GPa. Both spectrometers were calibrated using the ambient liquid benzene Raman transition. The straight line is a fit of the shock-compression data.

krypton ion laser) for benzene isothermally compressed at temperatures between 299 and 482 K using a diamond-anvil cell and techniques previously described [18]. Measurements of the phonon spectrum in the 40-200 cm⁻¹

region were used to distinguish between the various benzene phases. At fixed pressure, no temperature-induced frequency shift was observed in these static measurements. The frequency shifts for the dynamic experiments agree well with the static data of liquid benzene, but differ substantially from those for benzene I. At pressures below the I-II-liquid triple point of benzene, which occurs near 1.2 GPa [19], the shocked benzene is therefore probably in the liquid state. The shocked material could be either liquid or benzene II at pressures above 1.2 GPa since both phases exhibit similar frequency shifts of the ring-stretching mode, and the Hugoniot appears to lie close to the phase boundary. The data also indicate that the BSRS and RBBCARS techniques measure equivalent frequency shifts under equivalent shock conditions.

FIG. 7. RBBCARS spectra of ambient and shock-compressed 60%/40% (by volume) mixtures of benzene and benzene- d_6 . The shock pressure was 0.91 GPa.

Figure 7 shows the OMA recorded RBBCARS signals for the ring-stretching modes of benzene and perdeuterobenzene in a 60%/40% (by volume) mixture, both at ambient conditions and shock-compressed to 0.91 GPa [10,11]. Also shown is the 253.652 nm Hg line in second order used as a wavelength reference. The spectral data obtained using RBBCARS in this and other mixtures at shock pressures up to 1.53 GPa show no evidence for the presence behind the shock of decomposition product species (at concentrations above the 10% level) having Raman active transitions within the frequency regime covered by the broadband Stokes laser (800 to 1100 cm^{-1}). In addition, the spectra obtained do not contain any evidence for deuterium exchange reactions between the benzene species during the $\sim 1 \mu\text{s}$ time available for reaction after passage of the shock and before the laser is fired. New peaks would be expected to appear between the benzene and benzene- d_6 transitions if reaction were occurring.

In a polarization sensitive coherent Raman experiment, such as RIKES, the possibility exists that shock-induced changes in a material would perturb the probe laser polarization sufficiently to obscure the desired signals. Therefore, the sensitivity of the RIKES apparatus to minor

rotations of the dye laser polarization was investigated. The figure of merit used was the polarization analyzer rotation angle necessary to saturate the detector with unblocked dye laser. It was found that the detector could be driven from zero signal to saturation with a polarization rotation angle of ~ 20 arc minutes ($20'$) (using $50 \mu\text{m}$ slits and $\sim 50 \mu\text{J}$ dye laser energy). The RIKES signal found for the ring-stretching mode of ambient liquid benzene nearly saturated the detector through $25 \mu\text{m}$ slits (using $\sim 200 \mu\text{J}$ pump laser energy and 6° beam crossing angle). These data suggest that, if the shock-compressed sample induced a rotation of the probe laser polarization $\geq 20'$, the signal would be masked by the broad dye laser background passed by the analyzer.

The above arguments were tested by attempting to measure the Raman-induced Kerr effect spectra of neat liquid benzene shock-compressed to 1.17 GPa, where earlier BSRs and RBBCARS data suggest the material is still in the liquid phase (see above). Two of the RIKES spectra obtained are shown in figure 8, along with the RIKES spectrum of ambient neat liquid benzene obtained under the same laser power levels and the 557.03 nm and 556.22 nm calibration lines from a Kr lamp.

FIG. 8. Raman-induced Kerr effect spectra (RIKES) of ambient and shock-compressed liquid benzene. The shock pressure was 1.17 GPa. No RIKES signals can be distinguished in the data from the shock-compressed samples.

All of the RIKES spectra obtained in shocked samples show only broadband dye laser which has been passed by the polarization analyzer. These results indicate that the shock-compressed sample induces a rotation of at least $20'$ on the dye laser polarization. They also lead to the conclusion that, while it may be possible to perform RIKES experiments in shock-compressed materials in spite of our failure, the experiment is considerably more difficult than techniques not sensitive to the absolute polarization of the laser beams (such as BSRs and RBBCARS).

SUMMARY

We have demonstrated the use of fast (~ 6 ns) non-linear optical techniques in the study of the microscopic nature of materials shock-compressed to high pressures and temperatures. The ease with which the BSRS signals could be generated and detected (in materials with large Raman cross-sections) was a great advantage of the technique. The RBBCARS technique surmounts two disadvantages of BSRS, specifically its inability to detect more than one vibrational mode in a sample, and its requirement of potentially damaging laser powers to overcome the threshold condition. We have demonstrated the ability of RBBCARS to simultaneously detect multiple vibrational modes of multiple species in a shock-compressed sample. These results show the potential of RBBCARS for the detection of product and intermediate species in shock-induced chemical reactions. We have discussed and demonstrated the difficulty of using polarization sensitive coherent Raman techniques, specifically RIKES, as optical diagnostics in shock-compressed materials. We are using BSRS and RBBCARS for the study of molecular structure of materials shock-compressed to states similar to those that occur in explosive detonation.

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