TITLE Coherent Raman Scattering Measurements of Vibrational
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Abstract

The techniques of backward stimulated Raman scattering (BSRS) and reflected broad-band coherent anti-Stokes Raman scattering (RBBCARS) have been used to measure vibrational frequency shifts in shock-compressed liquid benzene and mixtures of liquid benzene and liquid deuterated benzene. BSRS was used only for measurements in neat liquid benzene as it only allows observation of the highest gain vibrational transition. RBBCARS was used to simultaneously measure multiple vibrational modes of multiple species. Accompanying static high pressure Raman experiments in a heated diamond anvil cell were used to establish the phase of the shocked samples. These experiments demonstrate the capabilities of fast non-linear optical techniques in the study of material structure and chemical reaction induced by shock-compression.

Introduction

Traditional methods used to study material behavior under conditions similar to those encountered in explosive detonation have been bulk property measurements and gauge measurements. In those methods, the microscopic behavior of the material had to be inferred from the macroscopic observables. The actual molecular structure of the material, as well as the chemical composition, was unknown. The use of optical methods to interrogate materials under shock loading would allow direct observation of the microscopic (molecular) structure, and would bypass the inference step. Previous studies of this sort 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 indentification of transient species and temperature measurement in shocked explosives.[5,6] We have demonstrated the use of two coherent Raman techniques -- backward stimulated Raman scattering (BSRS) and reflected broad-band coherent anti-Stokes Raman scattering (RBBCARS) -- in the measurement of vibrational frequencies in shock-compressed liquid benzene and mixtures of liquid benzene and liquid deuterated benzene (benzene-d_6).

Experimental

The coherent Raman apparatus for studying shock-compressed samples consists of two separable portions; the shock production mechanism and the optical diagnostic. The shock production mechanism consists of a 51 mm diameter 3.3 m long gas gun 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 which runs forward into a 7.5 to 8.0 mm thick benzene (or mixture) sample. Reagent grade benzene (Mallinckrodt, Inc.) and 99.5% benzene-d_6 (Wilmad Glass Co., Inc.) were used. Standard data reduction techniques[7] using published shock-velocity / particle-velocity data[8] were used to determine the state of the shock-compressed samples. We assumed the Hugoniot of benzene-d_6 to be the same as that of benzene. Mixture densities were determined according to 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, trigger the laser flash lamps approximately 300 μs prior to impact. A time-of-arrival pin activated just before impact, and another time delay, serves to Q-switch the laser just prior to the shock wave striking the quartz window on the front of the sample and after it is well past the point in the sample interrogated by the optical probe.

The backward stimulated Raman scattering (BSRS) optical diagnostic has been discussed previously.[9] 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 light at the focus and a large cross-section Raman active mode in the sample combine to produce gain in the backwards direction at a frequency that is different from the Nd:YAG laser frequency by the characteristic

frequency of the Raman 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 meter focal length spectrometer, and is recorded on Polaroid film, along with the Nd:YAG laser beam. The frequency shift is obtained by accurately measuring the distance between the Nd:YAG laser frequency and the backwards stimulated Raman frequency, as recorded on the film, under a microscope.

The apparatus used for the RBBCARS experiments has also been extensively discussed previously.[10] Coherent anti-Stokes Raman scattering 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, $\omega_{as} = 2\omega_p - \omega_s$.[11-13] 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 broad-band dye laser, which lases on all frequencies across 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 excite 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 approximately 1 mm length of overlap) 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 and along a path parallel to the two incoming beams by the highly polished front surface of the target plate. After being separated from the pump and Stokes beams using a long-wave-pass dichroic filter, the beam is then passed through a dove prism and focused into the 75 μm wide entrance slit of a 1 m spectrometer equipped with a 1200 l/mm grating blazed at 500 nm and used in first order. The dove prism is used to rotate the image of the CARS signal so that any beam movement resulting from the changing position of the reflecting surface during the shock-compression process would translate to 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 multi-channel analyzer (OMA) (EGG-PAR 1205A).

Results and Discussion

Figure 1 shows typical spectral data obtained using BSRS in a sample of neat liquid benzene shock-compressed to 0.9 GPa. In this particular sample, the shock wave had only traversed ~ 2/3 of the distance to the window, allowing BSRS to occur in both the shocked and ambient benzene.
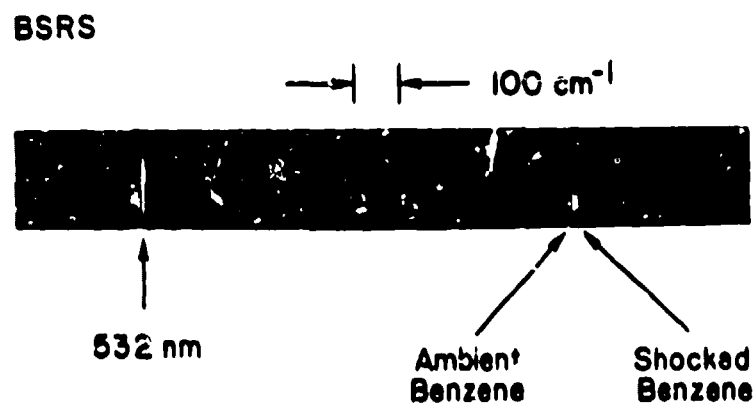
BSRS

Figure 1. Backward stimulated Raman scattered light spectrogram for shock-compressed benzene.

Figure 2 shows the OMA recorded RBBCARS signals for the ring-stretching modes of benzene and benzene-d_6 in a 60% to 40% (by volume) mixture, both at ambient conditions and shock-compressed to 0.91 GPa. Also shown is the 253.652 nm Hg line in second order used as a wavelength reference. The spectral data obtained using RBBCARS show no evidence for the presence behind the shock of decomposition product species (at concentrations above the 10-20% level) having Raman active transitions within the frequency regime covered by the broad-band Stokes laser (i.e. 800 to 1100 cm^{-1}). In addition, the spectra obtained for the

mixtures do not contain any evidence for deuterium exchange reactions between the benzene species during the $\sim$ 1 μs reaction time after passage of the shock If exchange was occuring, new peaks would appear between the benzene and benzene-d$_6$ transitions.

RBBCARS

Shocked
Mixture

Hg calibration line

Ambient
Mixture

Intensity (Arb Units)

1000   950   900   850

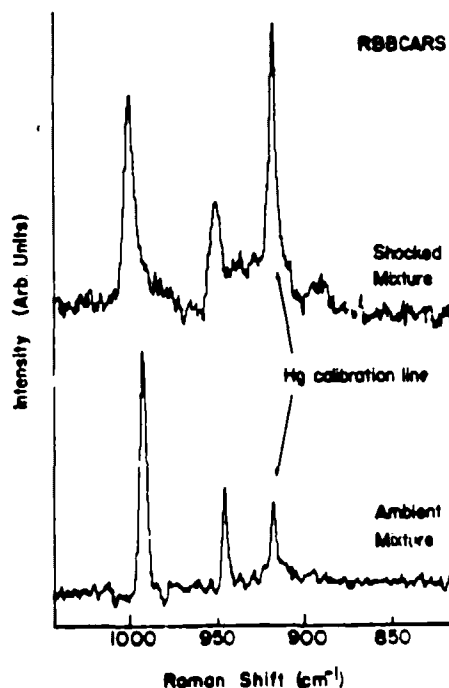Raman Shift (cm⁻¹)

Figure 2. RBBCARS spectra of ambient and shock-
           compressed 60%/40% by volume mixture of
           benzene and benzene-d$_6$. The ambient peak
           positions of the two species are 992 cm⁻¹
           and 945 cm⁻¹, respectively. The shock
           pressure was 0.91 GPa.

Measured vibrational ring-stretching frequency shifts for benzene obtained using RBBCARS and previously published data[9]   on the shifts measured using BSRS as a function of shock pressure are shown in figure 3. Also shown in the figure are the ring-stretching mode vibrational frequency shifts measured by spontaneous Raman (induced by the 568.2 nm line of a krypton ion laser) for benzene isothermally compressed at temperatures between 299 and 482 K using a diamond-anvil cell and techniques previously described.[16] Measurements of the phonon spectrum in the 40-200 cm⁻¹ region were used to distinguish between the various phases. At fixed pressure, no temperature shift was observed in these static measurements. The frequency shifts for the dynamic experiments agree well with the static data of both liquid benzene and benzene II, but differ substantially from the data of benzene I. At pressures below the I-II-liquid triple point of benzene, which occurs near 1.2 GPa, the shocked benzene is therefore probably at temperatures high enough for it to be in the liquid state. The temperature achieved in dynamic experiments is difficult to estimate better than ± 40 K at 1.2 GPa. 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, an the Hugoniot appears to lie close to the phase boundary. The data also indicates that the BSRS and RBBCARS techniques measure equivalent frequency shifts at equivalent shock pressures. There was some uncertainty about the reliability of frequency shifts measured using BSRS because of the slim possibility that the high laser power involved induced a phase transition from the shock-induced phase into the liquid phase. Since the RBBCARS measurements only require a small fraction of the incident power necessary to produce BSRS signals, the equivalence o the frequency shifts measured by the two techniques indicates that power induced phase transitions are probably not occuring.

<u>Summary</u>

In summary, we have demonstrated the use of two fast ($\sim$ 6 ns) non-linear optical techniques in the study of the microscopic nature of materials shock-compressed to high
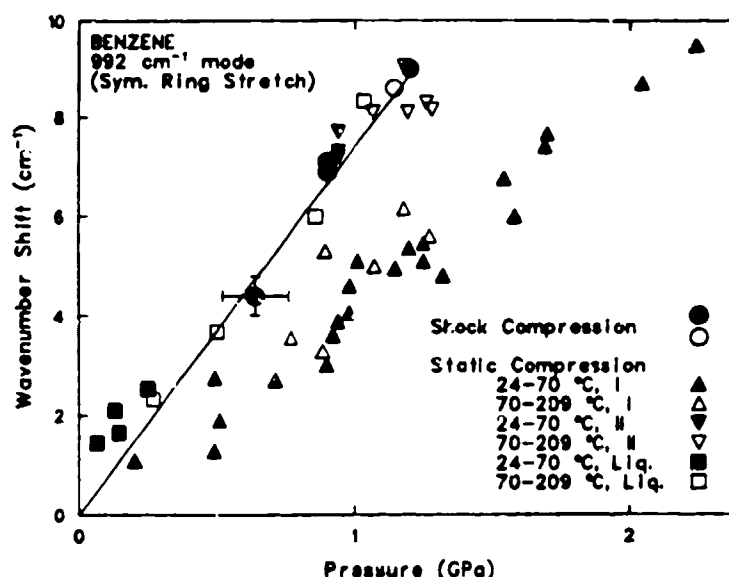
Figure 3. Benzene ring-stretching mode vibrational
frequency shifts (with respect to 992 cm⁻¹)
vs. pressure. Data recorded using BSRS and
RBBCARS are denoted by closed and open circles
respectively. The single open circle for
RBBCARS represents two data points. Uncer-
tainties in the shock data are given on one
data point. In the static measurements, at
299 K benzene I was observed as a metastable
phase above 1.2 GPa and benzene II was metastable
below this pressure. Both spectrometers were
calibrated using the ambient liquid benzene
Raman transition at room temperature. The
straight line is a fit of the shock-compression
data.

pressures and temperatures. The ease with which the BSRS signals could be generated and detected (in materials with large Raman cross-sections) was found to be a great advantage of the technique. The RBBCARS technique overcomes two disadvantages of BSRS; namely its inability to detect more than one mode in a sample, and its requirement of large laser powers to overcome the threshold condition. We have also demonstrated the ability of RBBCARS to simultaneously detect multiple vibrational modes of multiple species in a shock-compressed sample. This result shows the potential of RBBCARS for the detection of product and intermediate species in shock-induced chemical reactions. We are using these techniques for the study of molecular structure of materials shock-compressed to states similar to those that occur in explosive detonation.

Acknowledgments

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