Simultaneous Multimode Pressure-Induced Frequency-Shift Measurements in Shock-Compressed Organic Liquid Mixtures by Use of Reflected Broadband Coherent Anti-Stokes Raman Scattering

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Reflected broadband (multichannel) coherent anti-Stokes Raman scattering was used to measure the ring-breathing-mode vibrational frequencies of neat liquid benzene, neat liquid deuterated benzene (benzene-d_6), and mixtures of these under shock compression to pressures up to 1.53 GPa. The pressure-induced frequency shifts determined for neat benzene agree with those obtained previously by use of backward stimulated Raman scattering. Evidence for nearest-neighbor effects on the vibrational frequency shifts is presented.

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There have been several optical techniques used to probe detonating explosives and shock-compressed materials. Keeler, Bloom, and Mitchell[1] and Bloom and Keeler[2] have observed stimulated Brillouin scattering in shock-compressed acetone and water, and numerous authors[3-10] have reported emission and absorption measurements of shocked materials. Pulsed-laser-induced spontaneous Raman scattering has been used to measure temperature[10] and to identify transient species[11,12] in shocked explosives. Most recently, the fast nonlinear optical technique of backward stimulated Raman scattering (BSRS) was used to measure molecular vibrational frequency shifts in shock-compressed liquid benzene.[13] The signal intensity from BSRS is considerably greater than that obtained using ordinary Raman scattering. However, the technique suffers from a limitation when used as a diagnostic technique for shock-compressed systems. Only that Raman active mode with the largest transition cross section will undergo stimulated scattering. This precludes observation of more than one species or more than one mode of a single species. In addition, for some molecules the incident beam power density required for scattering is large enough to damage optical components located near focal points. We report here the successful use of reflected broadband coherent anti-Stokes Raman scattering (RBBCARS) to detect more than one molecular species and measure their vibrational frequency shifts simultaneously in shock-compressed liquid mixtures.

The experiments were performed in pure liquid benzene, pure liquid deuterated benzene (benzene-d_6), and in mixtures of liquid benzene and benzene-d_6 shock-compressed from ambient pressure and a temperature of 297 K up to pressures of 1.53 ± 0.20 GPa, compressions of (25 ± 5)%, and temperatures of approximately 525 to 600 K. The uncertainties in pressure are dominated by the lack of accurate shock Hugoniot data for benzene below 1.5 GPa. We assumed the shock-velocity, particle-velocity Hugoniot of benzene-d_6 to be the same as that of benzene.

A schematic of the apparatus used for the RBBCARS experiments is shown in Fig. 1. A 51-mm-diam 3.3-m-long gas gun was used to accelerate a magnesium projectile with an 8-mm-thick 304-stainless-steel head to a desired velocity. The projectile struck a 2.1-mm-thick 304-stainless-steel target plate producing a shock wave which ran forward into a 7.5- to 8.0-mm-

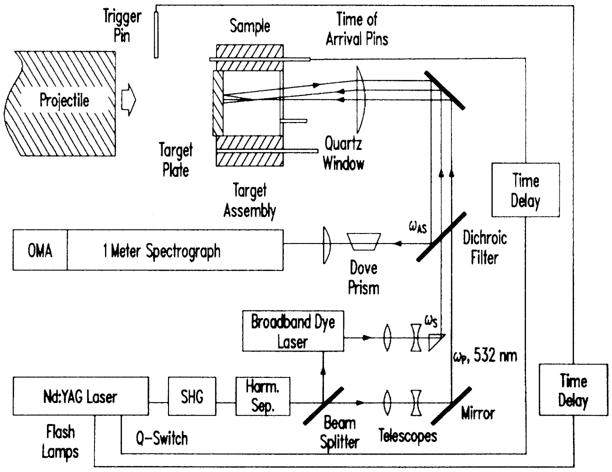

FIG. 1. Schematic representation of the reflected broadband coherent anti-Stokes Raman scattering experiment. SHG—second harmonic generator; Harm. Sep.—harmonic separator; OMA—optical multichannel analyzer; Sample—benzene and mixtures of benzene and benzene-d_6.

thick benzene (or mixture) sample. Stainless steel was chosen because previous experience has shown it to retain its reflectivity under shock compression. Reagent grade benzene (Mallinckrodt, Inc.) and 99.5% benzene-d_6 (Wilmad Glass Co., Inc.) were used. Standard data reduction techniques[14] using published shock-velocity, particle-velocity data[15] were used to determine the state of the shock-compressed samples. Mixture densities were determined according to volume fraction of benzene and benzene-d_6. The timing sequence for the RBBCARS experiment was determined by the incoming projectile. A signal from aluminum time-of-arrival pins located in the gun barrel 25-cm from the target, in conjunction with an appropriate time delay, triggered the laser flash lamps approximately 300 μs prior to impact. A time-of-arrival pin activated just before impact and another time delay served to Q-switch the laser just prior to the shock wave striking the quartz window and after it was well past the point in the sample interrogated by the optical probe.

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, $\omega_{as} = 2\omega_p - \omega_s$.[16-18] 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 since we wish to produce CARS signals from more than one mode or species, a broadband dye laser, with a bandwidth equivalent to the gain profile of the dye, was used as the Stokes beam.[19] A portion of the 6-ns-long frequency-doubled Nd:YAlG (yttrium aluminum garnet) laser pulse was used to pump the dye laser. The resulting two laser beams (dye and remaining pump) were passed through separate Galilean telescopes and sent along parallel paths towards the sample. The beams were 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.[20] The beam crossing angle (phase-matching angle) was tuned by adjusting the distance between the parallel beams using a precision translation stage on the dye-laser-beam turning prism. The CARS beam was reflected out of the shocked sample by the highly polished front surface of the target plate and along a path parallel to the two incoming beams. After being separated from the pump and Stokes beams using a long-wavelength-pass dichroic filter, the beam was then passed through a dove prism and focused onto 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 was 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 were 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).

Figure 2 shows the OMA recorded RBBCARS signals for the ring-stretching modes of benzene and benzene-d_6 in a 60% benzene, 40% benzene-d_6 (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

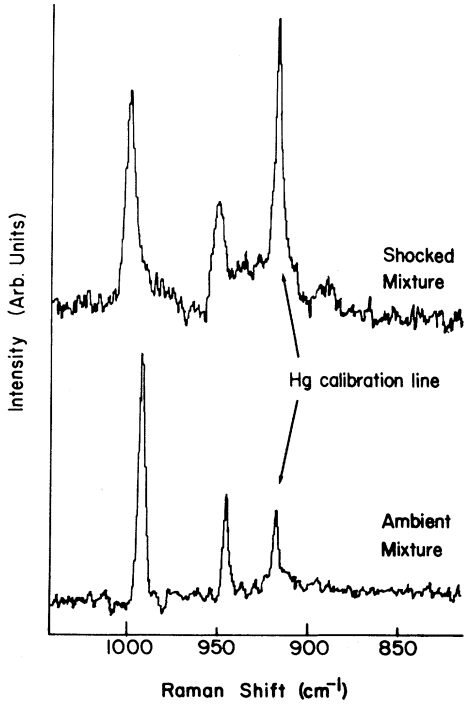

FIG. 2. RBBCARS spectra of ambient and shock-compressed 60%-40% by volume mixture of benzene and benzene-d_6. The ambient peak positions of the two species are 992 cm^{-1} for benzene and 945 cm^{-1} for benzene-d_6. The shock pressure was 0.91 GPa.

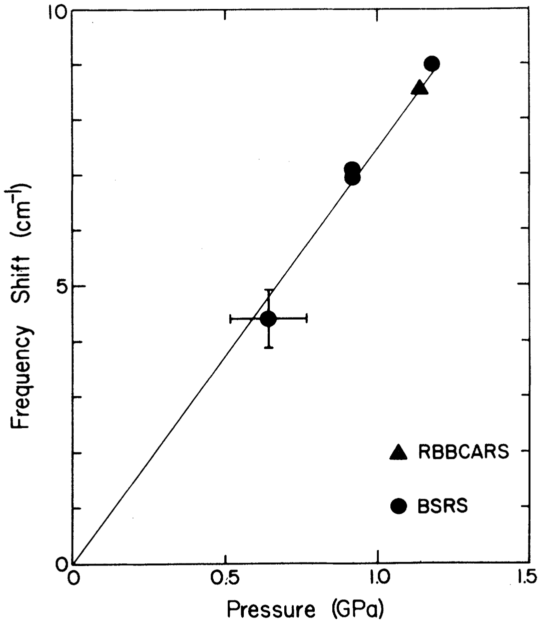

FIG. 3. Benzene ring-stretching-mode vibrational frequency shifts (with respect to 992 cm^{-1}) vs pressure. Data recorded using BSRS and RBBCARS are denoted by circles and triangles, respectively. The single triangle for RBBCARS represents two data points. Uncertainties in the data are given on one data point.

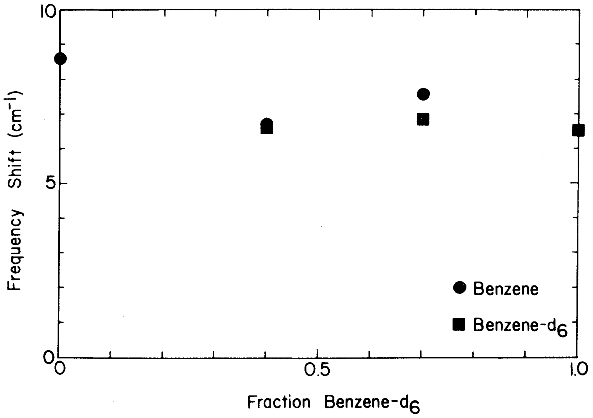

FIG. 4. RBBCARS measured ring-stretching-mode vibrational frequency shifts for both benzene and benzene-d_6 as a function of mixture composition.

data obtained using RBBCARS show no evidence for the presence behind the shock of decomposition product species[21] (at concentrations above the 10–20% level) having Raman-active transitions within the vibrational frequency region spanned by the gain profile of the dye (i.e., between 800 and 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 1-μs time scale after passage of the shock. If exchange was occurring, new peaks would appear between the benzene and benzene-d_6 transitions. Measured vibrational ring-stretching frequency shifts for benzene obtained using RBBCARS and previously published data on the shifts measured using BSRS as a function of shock pressure are shown in Fig. 3. The data indicate that the two techniques measure equivalent frequency shifts at equivalent shock pressures.

Vibrational frequency shifts as a function of composition in mixtures of benzene and benzene-d_6 shock-compressed to 1.17 GPa are shown in Fig. 4. The data indicate a small decrease in frequency shift with benzene-d_6 concentration. This decrease suggests an intramolecular potential that is sensitive to the identity of the neighboring species.

In summary, we have demonstrated the practicality and have illustrated several important advantages of RBBCARS as a diagnostic probe for shock-compressed materials. Most important, the technique is capable of simultaneously detecting and measuring vibrational frequency shifts for more than one species and more than one normal mode so long as the Raman shifts are within the broad bandwidth of the dye laser. By changing the laser dye to shift the bandwidth, most Raman-active modes can be studied in a series of experiments. The time resolution achieved, based on a shock velocity of 2 mm/μs and an active scattering length of 1 mm, was 500 ns. By these measurements we have shown the potential of coherent Raman scattering techniques to determine changes in molecular structure and constituent species identities in chemically reacting shock-compressed materials.

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