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FLUIDS: AN OVERVIEW

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COHERENT RAMAN SCATTERING IN HIGH-PRESSURE/ HIGH-TEMPERATURE FLUIDS: AN OVERVIEW*

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Abstract

The present understanding of high-pressure/high-temperature dense-fluid behavior is derived almost exclusively from hydrodynamic and thermodynamic measurements. Such results average over the microscopic aspects of the materials and are, therefore, insufficient for a complete understanding of fluid behavior. At the present, dense-fluid models can be verified only to the extent that they agree with the macroscopic measurements. Recently, using stimulated Raman scattering, Raman induced Kerr effect scattering, and coherent anti-Stokes Raman scattering, we have been able to probe some of the microscopic phenomenology of these dense fluids. In this paper, we discuss primarily the use of CARS in conjunction with a two-stage light-gas gun to obtain vibrational spectra of shock-compressed liquid N₂, O₂, CO, their mixtures, CH₃NO₂, and N₂O. These experimental spectra are compared to synthetic spectra calculated using a semiclassical model for CARS intensities and best fit vibrational frequencies, peak Raman susceptibilities, and Raman linewidths. For O₂, the possibility of resonance enhancement from collision-induced absorption is addressed. Shifts in the vibrational frequencies reflect the influence of increased density and temperature on the intramolecular motion. The derived parameters suggest thermal equilibrium of the vibrational levels is established less than a few nanoseconds after shock passage. Vibrational temperatures are obtained that agree with those derived from equation-of-state calculations. Measured linewidths suggest that vibrational dephasing times have decreased to subpicosecond values at the highest shock pressures.

INTRODUCTION

Presently most models of explosive and shock-induced chemical behavior treat the medium as a continuum^{1,2} that chemically reacts according to either a pressure dependent or Arrhenius kinetics rate law. One or more parameters are used to incorporate the global chemical behavior, hydrodynamic phenomenology and effects of material heterogeneity. In the past few years, several studies³⁻¹⁰ have been started that attempt to improve the methodology by defining the continuum, not as a single

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component, but as one that incorporates ideas such as hot spots, voids or multicomponents. However, in all of these studies essentially no effort is made to incorporate any of the microscopic details of the shock-compression/energy transfer and release phenomenology that constitutes the detonation or reactive process.

The objective of our work has been two fold; (1) to determine the molecular structure and identify chemical species in unreacting and reacting shock-compressed molecular systems and (2) to study the effect of pressure and temperature on condensed phase energy transfer. Also, we would like to identify the unique features of a shock wave that contribute to the energy transfer processes. Achievement of these goals would contribute significantly to understanding the initial mechanisms governing shock-induced chemical reactions and possibly to the steps controlling product formation. Gas guns are being used to dynamically shock compress molecular liquids to pressures where chemical reaction occurs. The high-density/high-temperature fluid is then probed using coherent Raman scattering techniques.

COHERENT RAMAN SCATTERING IN SHOCK-COMPRESSED LIQUIDS

Three coherent Raman scattering techniques have been attempted in shock compressed liquid samples. Advantages of these techniques, primarily because of large scattering intensities and the beam-like nature of the scattered signal, are increased detection sensitivity, temporal resolution limits approaching laser pulse lengths, and possible spatial resolution approaching the diffraction limit of the optical components. As with all optical methods in shock-wave applications, optical accessibility because of material opacity or particulate scattering remains a major difficulty with coherent Raman scattering.

Stimulated Raman scattering (SRS) has been observed in shock-compressed benzene up to pressures of 1.2 GPa.¹¹ Stimulated Raman scattering^{12,13} (Fig. 1) occurs when the incident laser intensity, ω_1 , in a medium exceeds a threshold level and generates a strong, stimulated Stokes beam, ω_3 . The threshold level is determined by the Raman cross-section and linewidth of the transition and by the focusing parameters of the incident beam. Typical threshold intensities are ~ 10 – 100 GW/cm². Figure 2 illustrates the arrangement used for the backward stimulated Raman scattering experiment.

An aluminum projectile of known velocity from a 51-mm-diam, 3.3-m-long gas gun impacted a 6061 aluminum target plate producing a shock wave, which ran forward into ca. 8-mm-thick benzene sample. Standard data reduction techniques¹⁴ using shock velocities determined from time-of-arrival pins and published shock-velocity/particle-velocity data¹⁵ were used to determine the state of the shock-compressed benzene.

A single 6-ns-long frequency-doubled Nd-doped yttrium aluminum garnet (Nd:YAG) laser pulse (Quanta-Ray DCR1A) was focused using a 150-mm focal length lens through the quartz window to a point in the benzene 2–6 mm in front of the rear sample wall. 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. The timing sequence was determined by the incoming projectile. Trigger pins, in conjunction with an appropriate time delay, triggered the laser flash lamp approximately 300 μ s prior to impact. A time-of-arrival pin activated just before impact and the appropriate time delay served to Q-switch the laser just prior to the shock wave striking the quartz window and after it was past the focal point of the incident laser light.

Fig. 1. Coherent Raman scattering techniques.

In liquid benzene, the ν_1 symmetric stretching mode¹⁶ 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. As depicted in Fig. 2, the backward stimulated Raman beam was separated from the incident laser by means of a dichroic filter and was then focused onto the $10\text{-}\mu\text{m}$ -wide entrance slit of a 1-m Czerny-Turner spectrograph equipped with a 1200-grooves/mm grating blazed at 500 nm and used in first order. Figure 3 shows the resulting spectrogram for benzene shock-compressed to 0.92 GPa. The reflected incident laser line and the backward stimulated Brillouin-scattering line at 532 nm are observable, as is the backward stimulated Raman-scattering line from ambient benzene. The latter feature resulted as a consequence of the shock wave having passed only about two-thirds of the way through the sample, and hence a stimulated Raman signal was also obtained from the unshocked liquid.

The frequency shift of the Raman line has small contributions of approximately 0.1 cm^{-1} because the light crosses the moving interface between two media of different refractive indices and because of the material motion behind the shock wave.¹⁷ Since these errors are considerably less than the experimental uncertainty of $\pm 0.5\text{ cm}^{-1}$ for the measured frequency shifts and are a small fraction of the shift due to compression, no attempt was made to correct for these effects.

The measured shift of the ν_1 ring-stretching mode vibrational wavenumber versus pressure of the shocked benzene has been published elsewhere.¹¹ Observation of the ring-stretching mode at 1.2 GPa strongly suggests that benzene molecules still exist several millimeters behind the shock wave at this pressure, but does not, however, exclude some decomposition.^{18,19,20}

Beam intensities using SRS are sufficiently large that film can be used as a detector. The large incident intensities required, however, can cause damage to optical components near focal points. Spatial and temporal resolution are determined by the confocal parameter of the focusing lens and the incident laser pulse duration. The SRS technique also suffers because only certain molecules produce stimulated Raman scattering and of those molecules only the lowest threshold transition can be observed. Because of these limitations other coherent Raman scattering processes affording more experimental flexibility were attempted.

Fig. 2. Schematic representation of backward stimulated Raman-scattering experiment. SHG, second harmonic generator; Harm. Sep., harmonic separator. Sample; liquid benzene.

Raman-induced Kerr effect spectroscopy (RIKES)²¹ has been discussed as a diagnostic technique^{22,23,24} for performing measurements in shock-compressed systems which may have a large non-resonant background. RIKES requires a single frequency pump beam, ω_1 , a broad-band probe source, ω_2 , no phase matching and lower incident power levels than stimulated Raman scattering (Fig. 1).

RIKES occurs when a linearly polarized probe laser beam is passed through the rotating electric field of a circularly polarized pump beam. The four-wave parametric process described 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.^{25,26}

Fig. 3. Scattered light spectrogram for shock-compressed benzene.

A schematic of the experimental apparatus used to perform RIKES in shock-compressed benzene is shown in Fig. 4. The shock-compressed benzene sample was obtained using the technique described previously for the SRS experiments. Timing of the 6-ns-long frequency-doubled Nd:YAG laser pulse used for the circularly polarized pump laser beam was also accomplished as described for the SRS experiment. The probe laser beam was obtained by using a portion of the frequency-doubled Nd:YAG laser 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-diam 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 a 304 stainless steel target plate back through the sample and along a path parallel to the incoming beams. Previous experience and a series of reflectivity measurements showed that polished steel would retain c.a. 10 to 40 percent of its original reflectivity under shock compression and release into the lower impedance liquid sample for shock pressures to 1 Mb. A mirror separated the reflected dye laser beam from the other beams and directed 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 a dove prism and focused into the entrance slit of a 1-m spectrometer equipped with a 1200-grooves/mm grating blazed at 500 nm and used in first order. The signals were detected at the exit of the spectrometer using an intensified diode array (Tracor Northern Model TN-6133) coupled to an optical multichannel analyzer (OMA) (Tracor Northern Model TN-1710). The instrument spectral resolution was approximately 4.2 cm^{-1} .

Figure 5 shows RIKES spectra near 992 cm^{-1} of an ambient and two shock-compressed liquid benzene samples. The shock pressure was 1.17 GPa, and the 557.03-nm and 556.22-nm Kr calibration lines are shown. All spectra are obtained at the same power levels. Both traces have spectral features, however, they are not consistent and do not exhibit the pressure-induced frequency shift expected for the benzene ring stretching mode based on previous SRS and coherent anti-Stokes Raman scattering (CARS) experiments. In a polarization sensitive coherent Raman experiment, such as

RIKES, the possibility exists that shock-induced changes in a material could 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 $50\text{-}\mu\text{m}$ slits and $\sim 50\text{-}\mu\text{J}$ dye laser energy. The RIKES signal found for the ring-stretching mode of ambient liquid benzene nearly saturated the detector through $25\text{-}\mu\text{m}$ slits (using $\sim 200\text{-}\mu\text{J}$ 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-band dye laser background passed by the analyzer. The RIKES spectra (Fig. 5) obtained in shocked samples show only broad-band 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 beam (such as SRS and CARS).

Fig. 4. Schematic representation of the RIKES experiment. SHG, second harmonic generator; Harm. Sep., harmonic separator; OMA, optical multi-channel analyzer; sample, benzene.

Fig. 5. RIKES of an ambient and two shock-compressed liquid benzene samples. The shock pressure was 1.17 GPa and the 557.03-nm and 556.22-nm Kr calibration lines are shown. All spectra are obtained at the same power levels.

Coherent anti-Stokes Raman scattering (CARS)²⁵⁻³¹ (Fig. 1) occurs as four-wave parametric process in which three waves, two at a pump frequency, ω_p or ω_1 , and one at a Stokes frequency, ω_s or ω_2 , are mixed in a sample to produce a coherent beam at the anti-Stokes frequency, ω_{as} or $\omega_3 = 2\omega_p - \omega_s$. The efficiency of this mixing is greatly enhanced if the frequency difference, $\omega_p - \omega_s$, coincides with the frequency ω_j of a Raman active mode of the sample. An advantage of CARS is that it can be generated at incident power levels considerably below those required for stimulated

Raman scattering. However, since phase matching is required, possible geometrical arrangements are limited.

A schematic of the experimental apparatus used to perform CARS^{32,33,34,35} in shock-compressed benzene, nitromethane, liquid nitrogen, liquid oxygen, liquid carbon monoxide both neat and in mixtures with nitrogen and oxygen, and nitrous oxide, is shown in Fig. 6. For pressures greater than 2 GPa, a two-stage light gas gun was used to accelerate a polycarbonate projectile with 4-mm-thick AZ31B magnesium, 2024 aluminum, or 304 stainless steel impactors to a desired velocity. The target assemblies were of two types, one for ambient liquids (as described previously) and one for cryogenic liquids.^{33,36} The cryogenic target assembly was used to condense and hold the liquid N₂, O₂, CO, their mixtures, and N₂O. It consisted of a toroidal cooling chamber, through which liquid N₂ or cold N₂ gas was passed, surrounding a cylindrical sample chamber. The sample chamber included a highly polished 304 stainless steel target plate at the front and a 6.3-mm-diam quartz or lithium fluoride window at the rear. Lithium fluoride was used at higher pressures because of better optical transmission. Impactor and target plate thicknesses were chosen, and time-of-arrival pin assemblies were installed in the ca. 1.5-mm-long liquid sample, so as to insure that rarefaction waves would not compromise the one-dimensional character of the compression in the region observed optically. Sample gases were condensed into the target from standard stainless steel sample cylinders. High purity gases were used, and the mixtures were homogenized at least 24 hours using convection.

Fig. 6. CARS experiments for shock-compressed materials.

A pair of HeNe laser beams interrupted by the projectile and detected by fast photomultiplier tubes provided redundant trigger signals for the flashlamps of an injection-seeded Nd:YAG laser, after appropriate time delays based on the expected projectile velocity. Time-of-arrival pins located in the target were used to trigger the Q-switch on the Nd:YAG laser after an appropriate time delay, as well as to measure the shock velocity in the liquid. The Q-switch time was usually set so that the laser pulses arrived at the target at the time the shock arrived at the window. Because of imprecision in the actual projectile velocity and projectile tilt, a thin layer of either unshocked (ambient) sample or double-shocked sample was present when the lasers arrived at the sample. These situations will be discussed more completely below.

The pump frequency in the CARS process was obtained by using approximately 40% of the 6-ns-long frequency-doubled output of the Nd:YAG laser (Quanta-Ray DCR-1A or Quanta-Ray DCR-11) to pump a narrow-band dye laser (Quanta-Ray PDL-1) at near 557 nm (Rhodamine 590, Exciton) for the nitrogen data, near 582 nm (Kiton Red), Exciton) for the oxygen data, and near 560 nm (Rhodamine 590, Exciton) for the CO and CO/N₂ mixtures. Two broad ranges of Stokes frequencies were produced using home-built broad-band dye lasers utilizing the laser dye DCM (Exciton, lasing region 630 to 650 nm) in one and Rhodamine 640 (Exciton) in the other, each pumped by half the remaining Nd:YAG output. The second broad-band dye laser was used for measurements of the O₂ vibration in the mixtures. For benzene and nitromethane samples, the frequency-doubled Nd:YAG laser pulse was used directly as the pump beam.³² The CARS signals produced in the sample were reflected by the stainless steel target plate back out the window, collimated by the lens, picked off by a dichroic beam splitter, directed through a 6-nm-band-width filter monochromator and then dispersed by a 1-m spectrometer. Multichannel detection of the CARS signals was done using an intensified photodiode array (Tracor Northern 6132) as 1 analyzer (Tracor Northern 6500). If two spectral regions were being studied, a second dichroic beamsplitter was used along with another 1-m spectrometer and an intensified photodiode array (Princeton Instruments IRY-512G) and analyzer (Princeton Instruments ST-120). In addition, because of significant shot-to-shot variation, the broad-band dye laser spectral profile was measured in each experiment by directing a reflection from the target tank window into a third 1-m spectrometer and a photodiode array (EG&G Reticon 512S) and analyzer (DSP Technologies 2012S/LeCroy CAMAC crate/IBM PC-XT). This measured spectral profile was used, as will be described later, for the analysis of each CARS spectrum.

Phase matching was experimentally optimized in the ambient sample for the focusing conditions used. The dispersion in the sample was assumed to linearly scale with the increase in refractive index due to volume compression.^{33,34,35} Linear scaling of the dispersion results in the same phase-matching angle at all compressions. The focusing was also chosen so that the spatial region producing CARS signals covered the entire thickness of the sample.

Vibrational frequencies were all calibrated (± 1 cm⁻¹) using vacuum wave numbers of atomic emission lines obtained from standard calibration lamps. The spectral instrument function of the CARS spectrometer/photodiode array was measured using either an atomic emission line or by extraction from the ambient liquid N₂, O₂, or CO transition. The later method has the advantage of including the spectral profile of the pump laser. This measured instrument function was then convoluted with the synthesized CARS spectra discussed below, to give spectra that could be directly compared with the experimental data.

The intensity of the beam at ω_{as} is given by the semiclassical description:

$$I_{as} \propto \sum_i \frac{\omega_{as}^2 I_p^2 I_s (N_i L_i)^2 |\chi_i^3|^2}{n_p^2 n_s n_{as}} \times \left(\frac{n_{as}^2 + 2}{3} \right) \left(\frac{n_s^2 + 2}{3} \right) \left(\frac{n_p^2 + 2}{3} \right)^4, \quad (1)$$

where I_p and I_s are the incident intensities of the pump and Stokes beams, respectively, and n_{as} , n_s , and n_p are the refractive indices at ω_{as} , ω_s , and ω_p , respectively.^{33,34,35} $N_i L_i$ corresponds to the Lagrangian density of the i th layer and the sum is over non-interfering layers. χ_i^3 , the third order susceptibility of the i th layer is given by

$$|\chi_i^3|^2 \propto \left(\sum_j \frac{\Gamma_j \chi_j^{pk} (\omega_j - \omega_p + \omega_s)}{(\omega_j - \omega_p + \omega_s)^2 + \Gamma_j^2} + \chi^{nr} \right)^2 + \left(\sum_j \frac{\Gamma_j^2 \chi_j^{pk}}{(\omega_j - \omega_p + \omega_s)^2 + \Gamma_j^2} \right)^2, \quad (2)$$

where χ_j^{pk} is the peak third-order susceptibility, χ^{nr} is the nonresonant susceptibility, Γ_j is the HWHM linewidth and the sum on j is over vibrational transitions. This equation only holds in the case of no electronic resonance enhancement.³⁰ The resultant spectra are then convoluted with the ca. 3-cm^{-1} slit function.

Figure 7 shows a series of CARS spectra of shock-compressed liquid N_2 . These spectra are illustrative of the kinds of spectra obtained in these experiments. For experiments where the shock wave had not reached the window, spectra similar to Fig. 7a were obtained. The large peak at 2327 cm^{-1} is the CARS signal from unshocked nitrogen and the remaining progression of lines are the fundamental and hot band transitions from the single-shocked fluid. Because the unshocked liquid has such a narrow linewidth³⁷ compared to the width of several wave numbers for the shock-compressed fluid, two difficulties were found. At the laser intensities used to produce CARS in the shock-compressed fluid, the CARS process could either be easily saturated leading to an increase in the apparent linewidth of the ambient liquid, or could result in large enough signals from the ambient liquid to locally saturate the detector.

If the shock wave reached and reflected from the rear window, both the single and double-shocked regions in the sample were interrogated by the incident laser beams. The resultant spectra, similar to those depicted in Figs. 7b–7d, consisted of two partially overlapped progressions of transitions arising from the two interrogated regions. Figure 7b illustrates the case for which the lines have not broadened sufficiently to obscure the individual peaks of the two progressions. At higher shock pressures and temperatures, the lines broaden considerably (Fig. 7c) and it is difficult to distinguish the two progressions without comparison to computed spectra. Figure 7d is similar to 7c except with much poorer signal-to-noise ratio. Also shown in Fig. 7 as the dashed lines are the computed spectra using Eqs. (1) and (2). The measured broad-band dye laser spectral profiles noted above were used for I_s in these computations. Figure 8 shows for the 0–1 fundamental transition of N_2 the measured frequencies and by a small line segment the frequencies calculated using an empirical fit^{38,39} at the corresponding experimental pressures and temperatures. The values at the lower pressures and temperatures were obtained from spontaneous Raman scattering measurements in a high-pressure diamond anvil cell.⁴⁰ The CARS data in the 10 to 20-GPa pressure range and the 2340 to 2360-cm^{-1} frequency region are from single-shock experiments, while the remaining CARS data were obtained in double-shocked liquid N_2 . In the single-shocked material, there is a monotonic increase of the vibrational frequency with increasing pressure up to a pressure of ca. 17.5 GPa. Above this pressure the frequency

no longer increases, and appears to begin to decrease. The vibrational frequency in the double-shocked material (whose temperature is lower than single-shocked material at the same pressure) shows similar behavior, but the reversal occurs at higher pressures. It is interesting to note the effect of temperature in these data. When the fluid is single or double-shocked to the same density, the difference in measured Raman shift is due to the effects of temperature on the potential and on the portion of the potential sampled on average. Within the precision of the data presented, the anharmonicity of the intramolecular potential appears to be constant for all pressures and is the same as that expected from gas-phase data.³⁴

Fig. 7. Representative CARS spectra of shock-compressed N_2 . (a) is representative of CARS spectra recorded when the shock has not reached the window and contains contributions from ambient (pressure P_1) and single-shocked (pressure P_2) N_2 . (b), (c), and (d) are CARS spectra recorded after the shock has hit the window, and contain contributions from single (pressure P_1) and double-shocked (pressure P_2) N_2 . The solid curves are the experimental data and the dashed curves are computed synthetic spectra.

Also shown for comparison in Fig. 8 are the Raman frequency shifts along a 2000-K isotherm from an empirical approximation to Monte Carlo calculations by Belak et al.⁴¹ As pointed out by the authors, the Monte Carlo calculations give frequencies that are slightly larger than experimental results, with the discrepancy becoming greater for increasing pressure.

The experimentally determined linewidths and peak Raman susceptibilities of the fundamental and hot band transitions were used to estimate the vibrational relaxation time and to determine a vibrational temperature. The relationship between CARS

intensities and the spontaneous Raman cross section and vibrational-level populations can be approximated by³⁰

$$\Gamma_j X_j^{pk} \frac{h}{2\pi c^4} \omega_p \omega_s^3 = \left(\frac{d\sigma}{d\Omega} \right)_j (\rho_j - \rho_k) \quad , \quad (3)$$

Fig. 8. Raman shift vs pressure for 0-1 transition. o-spontaneous Raman scattering in diamond-anvil cell. •-CARS with shock compression. Solid lines are isotherms obtained using an empirical fit to the data.^{38,39} Dotted line is the 2000-K isotherm from Belak et al.⁴¹

where h is Planck's constant, c is the speed of light, $(d\sigma/d\Omega)_j$ is the spontaneous Raman cross section of the j to k vibrational transition, and ρ_j and ρ_k are the number densities in vibrational levels j and k , respectively. Ratios of Eq. (3) for the excited-state transitions to the fundamental transition were used to explore the possibility of a non-Boltzmann population distribution and a decreased vibrational relaxation time at the pressures and temperatures shown in Fig. 8. The right-hand side ratios were calculated using the harmonic oscillator approximation for the dependence of the Raman cross section on vibrational level, $(d\sigma/d\Omega)_j \propto (j+1)$, and assuming Boltzmann population distributions, with vibrational temperature T_{vib} , for ρ_j and ρ_k . In Fig. 9, these results are presented vs E/kT_{vib} for several transitions. The energy, E , of the vibrational transition is slowly varying, hence the abscissa depends primarily on the temperature of the shocked fluid. Similar ratios of the left-hand side of Eq. 3 using the

susceptibilities and linewidths used to generate the synthetic spectra³⁴ are also depicted in Fig. 9. Within the previously stated errors it is evident that the experimental parameters, and consequently the spectra, are adequately represented by a simple model based on Boltzmann equilibrium of the vibrational levels. This result implies that energy has been transferred from the bulk translational motion into the vibrational energy levels in a time less than or comparable to the characteristic time of the shock-compression experiment. For the highest pressure experiments, this time is 10 ns or less, a change of ten orders of magnitude from the ambient vibrational relaxation time of ca. 60 s.⁴² Because the vibrational populations appear to be in equilibrium, they can be used as a measure of the vibrational temperature. Figure 10 shows the equation-of-state temperature and vibrational temperature vs shock pressure for both single and double-shocked N₂. The good agreement between the measured and calculated temperatures lends strong support to the model used to obtain the equation-of-state temperatures.⁴³

Fig. 9. The ratios of the left-hand side of Eq. (3) for the observed hot band transitions to that of the fundamental transition (plotted as the symbols) vs E/kT_{eos} , where E is the energy of the transition. Also shown as the lines in the figure are the expected ratios assuming Boltzmann population distributions (using T_{vib}) and the harmonic-oscillator-approximation dependence of Raman cross section on vibrational level.

Fig. 10. Equation-of-state temperatures and vibrational temperatures (extracted from the computed synthetic spectra) vs shock pressure. The lowest pressure single and double shock points have no T_{vib} because that data has insufficient signal/noise to observe excited state transitions.

In Fig. 11, the Raman linewidths³⁴ used to obtain the spectral fits of the shock-compressed fluid nitrogen spectra are presented vs temperature. Note that Eqs. (1) and (2) used to calculate the CARS spectra uses Lorentzian profiles to represent the spectral lines shapes. While this choice provides an adequate representation of our measured CARS spectra, it does not preclude the possibility of inhomogeneous broadening (i.e., Gaussian contribution to the line shapes). This effect would appear predominately in the line wings where the accuracy of our data is insufficient to distinguish between shapes. In addition, the limited signal/noise does not permit the observation of line shape differences between the fundamental transition and the observed hot bands. Lorentzian profiles were chosen because they are generally a good first approximation far from the critical region.^{44,45}

Two statements can be made about the spectral linewidth data. First, the vibrational dephasing time T_2 (where $T_2^{-1} = 2\pi c\Gamma_j$) has decreased from tens of ps at liquid and near-critical densities^{45,46} to about 0.3 ps near 40 GPa and 5000 K. Collapse of the Q branch from motional narrowing^{47,48} is probably complete at the pressures and temperatures investigated here, and the line broadening probably results only from pure dephasing. (However, it must be noted that this notion may not be entirely correct because other lower density studies⁴⁹ have shown that vibrational dephasing may not be separable from energy relaxation processes.)

Fig. 11. Raman linewidths extracted from the synthetic spectral fits to the fluid N₂ CARS spectra plotted against shock temperature. The solid and open circles represent single and double-shock data, respectively. The dephasing times noted on the ordinate assume homogeneous broadening.

The second statement to be made about Fig. 11 is that as the shock pressure increases along the Hugoniot, the spectral linewidth appears to almost linearly increase with temperature.³⁴ A dependence (within experimental error) on density is not readily apparent. For example, the single and double-shock data appear to fall on the same line. At the shock densities investigated here, the steep repulsive core of the intermolecular potential is being sampled. Consequently, the change in density with increasing shock pressure is much less than the change in temperature. This fact, coupled with the observed weak density dependence of the linewidth, produces the result observed in Fig. 11.

Visible absorption bands have been observed in both gaseous and liquid oxygen by several investigators.^{35,50-58} The presence of these proximity (collision) induced absorption bands in the spectral region where CARS experiments were performed for liquid oxygen leads to the possibility of electronic resonantly enhanced CARS,⁵⁹ as well as absorption of the pump, Stokes, and anti-Stokes beams. These possibilities were investigated by incorporating them into the CARS calculations of synthetic spectra using Eq. (1) and an empirical model for the absorption. The empirical model included the following simultaneous transitions: (a) $2^3 \Sigma_g^-(\nu'' = 0) \rightarrow 2^1 \Delta_g(\nu' = 0)$; (b) $2^3 \Sigma_g^-(\nu'' = 0) \rightarrow ^1 \Delta_g(\nu' = 1) + ^1 \Delta_g(\nu' = 0)$; and

(c) ${}^3\sum_g^-(\nu'' = 1) + {}^3\sum_g^-(\nu'' = 0) \rightarrow 2\,{}^1\Delta_g(\nu' = 0)$ as well as the contribution from the high pressure UV bands: (d) ${}^3\sum_g^- \rightarrow {}^3\Delta_u$.

For electronic resonantly enhanced CARS, the third-order susceptibility for a single-vibrational transition ω_{ba} of the i th layer can be written^{30,59-61}

$$\chi_i^3 \propto \chi^{pk} \sum_{a,b,n,n'} (A - B_1 + B_2 - B_3) + \chi^{nr}$$

with

$$\begin{aligned} A &= \rho_{aa}^{(0)} [(\omega_{ba} - \omega_1 + \omega_2 - i\Gamma_{ba})(\omega_{na} - \omega_1 - i\Gamma_{na})(\omega_{n'a} - \omega_4 - i\Gamma_{n'a})]^{-1} \\ B_1 &= \rho_{bb}^{(0)} [(\omega_{ba} - \omega_1 + \omega_2 - i\Gamma_{ba})(\omega_{nb} - \omega_2 + i\Gamma_{nb})(\omega_{n'a} - \omega_4 - i\Gamma_{n'a})]^{-1} \\ B_2 &= \rho_{bb}^{(0)} [(\omega_{n'n} - \omega_3 + \omega_2 - i\Gamma_{n'n})(\omega_{n'b} - \omega_3 - i\Gamma_{n'b})(\omega_{n'a} - \omega_4 - i\Gamma_{n'a})]^{-1} \\ B_3 &= \rho_{bb}^{(0)} [(\omega_{n'n} - \omega_3 + \omega_2 - i\Gamma_{n'n})(\omega_{nb} - \omega_2 + i\Gamma_{nb})(\omega_{n'a} - \omega_4 - i\Gamma_{n'a})]^{-1} \end{aligned} \quad (3)$$

where χ^{pk} is the peak susceptibility, and $\rho_{aa}^{(0)}$ and $\rho_{bb}^{(0)}$ are the initial number densities in the states a and b , respectively. The transition frequencies are as shown in Fig. 12, Γ_{ba} and $\Gamma_{n'n}$ are the vibrational half-width, at half-maximum (HWHM) linewidths, and the remaining Γ 's are the electronic transition linewidths. Druet et al.⁵⁹ have suggested that for a broad absorption continuum such as described above, the resonantly enhanced third-order susceptibility can be described by Eq. (3) using a broad Lorentzian for the excited electronic state. For our experiment $\omega_1 = \omega_3 = \omega_p$, $\omega_2 = \omega_s$, $\omega_4 = \omega_{as}$. Synthetic spectra were calculated using Eqs. (1) and (3) in conjunction with a broad 1400-cm^{-1} wide absorption band centered at $17,700\text{ cm}^{-1}$ to simulate the proximity induced absorption, taking into account absorption of ω_p , ω_s , and ω_{as} for a range of values for χ^{pk}/χ^{nr} , transition frequencies, and linewidths.³⁵ Attempts to favorably compare these results with experimental spectra were unsuccessful. The calculated spectra were always distorted giving too large a scattering intensity at Raman shifts greater than the vibrational transition frequency and insufficient intensity at lower energies. A qualitative examination of the intensities expected based on the relative locations of the absorption bands and the laser frequencies indicates the correct intensity distribution was calculated if resonances were occurring. From this lack of agreement, we concluded that even though ω_p , ω_s , and ω_{as} are being attenuated by proximity induced dipole transitions, an electronic resonance enhancement of the CARS signal is not occurring.³⁵ Based on this finding, we calculated synthetic CARS spectra for O_2 as was done previously for N_2 using Eqs. (1) and (2). A sample spectrum and fit³⁵ are shown in Fig. 13a. The prominent peak results from the 0-1 transition of the shock-compressed oxygen and the smaller feature to the right is the 0-1 transition from a thin layer of unshocked material. Because the temperatures obtained in these experiments were too low to produce hot-band transitions of sufficient intensity to be readily visible, estimates of vibrational temperatures were not possible. Future work using CARS data from shock-compressed mixtures of O_2 with N_2 and CO will, because of increased temperatures, allow estimates of vibrational temperatures. Also shown in Fig. 13b is a spectrum calculated using the same parameters as for the synthetic spectrum depicted by Fig. 13a, but leaving out the effects of absorption. The large change in the ratio of peak intensities demonstrates the importance of including absorption for good simulation of the experimental data.

Fig. 12. Electronic, vibrational, and laser translation frequencies.

Figure 14 shows the measured Raman shifts versus pressure for shock states of liquid O_2 . There is a monotonic increase of the vibrational frequency with increasing pressure. This is in contrast to the behavior observed in nitrogen,^{34,38,39} where the frequency first increases with pressure, then reverses and begins to decrease with further increases in pressure. However, the maximum pressure of these experiments is considerably less than the pressure, ~ 17.5 GPa, where the frequency reversal occurred for nitrogen. When the fluid is single or double-shocked to the same pressure, the difference in the measured Raman shift results from the effects of temperature on the potential and on the portion of the potential sampled on average.^{34,35} An empirical fit was obtained using the measured Raman frequency shifts for ambient, single-shocked and double-shocked oxygen.³⁵ The short segment near each data point in Fig. 14 gives the calculated frequency value from the empirical fit at the measured pressure and temperature and the long curves show the positions of the 300, 500, and 1000-K isotherms. Again it should be noted that Eq. (2) used to calculate the CARS spectra utilizes Lorentzian profiles to represent the spectral line shapes. While this choice provides an adequate representation of our measured CARS spectra, it does not preclude the possibility of inhomogeneous broadening (i.e., Gaussian contribution to the line shapes). This effect would appear predominately in the line wings where the accuracy of our data is insufficient to distinguish between shapes. At lower pressures the liquid oxygen line shape may be influenced by motional narrowing and fluctuations near the critical point.^{62,63} Assuming that the broadening results from pure dephasing, the vibrational dephasing time $T_2/2$ (where $T_2^{-1} = 2\pi c\Gamma_j$) decreased from a few tens of ps at ambient conditions to about 1 ps at the highest pressure shock conditions.

CARS spectra obtained from shock-compressed liquid CO appear to show a small vibrational frequency increase with pressure compared with N_2 , which is iso-electronic with CO. N_2 has very similar density (0.793 vs 0.808) and essentially the same Hugoniot (locus of shock states) up to 10 GPa. Yet, the vibrational frequency shift with shock pressure along the Hugoniot in the two materials appears to be quite different. We have also obtained CARS spectra of mixtures of CO in N_2 and CO in O_2 . Figure 15 shows CARS spectra of unshocked CO, neat CO single-shocked to about 7 GPa, and a 20% mixture of CO in N_2 shock compressed to a similar pressure. There is a clear difference in vibrational frequency shift of the CO in the shocked mixture versus that

in the shocked neat material. Similar measurements with N_2 show that its vibrational frequency appears to show no such variation from the neat material to the mixture.

Fig. 13. Representative CARS spectrum: (a) — experimental data at 7.8 GPa and 782 K, --- synthetic spectrum including effects of absorption, (b) synthetic spectrum neglecting effects of absorption.

These observations suggest a fundamental difference in the intermolecular interactions in CO versus N_2 . One possibility is dipolar interaction, which has been used to explain the larger Raman linewidth of pure liquid CO.⁶⁴ Differences in the CO vibrational frequency shift in neat CO versus CO/ O_2 mixtures were also observed. However, the temperature is also substantially different in these mixtures. Double-shock experiments, not shown here, in neat CO imply that there is a temperature dependence of the CO vibrational frequency similar to what was found in N_2 . Complete analyses

of the CARS spectra of the mixtures will be used to help elucidate this phenomenology, estimate relaxation times, and extract vibrational temperatures for comparison to equation-of-state calculations. The vibrational frequency information, along with the vibrational temperatures, will be used to help refine mixture equation-of-state theory, particularly by providing molecular-level details of the effects of the cross-potentials.

Fig. 14. Raman shift vs pressure. • O₂, single shock; ○ O₂, double shock; — isotherms.

For a polyatomic molecule such as nitromethane, the vibrational spectroscopy is considerably more complicated than that discussed above for diatomic molecules. At low temperatures, only the vibrational fundamentals need be considered, leading to much simplification in the spectra. In the case of nitromethane, there are 15 possible vibrational normal modes,^{65,66} one of which is the nearly free rotation of the methyl group around the CN bond. As the temperature is increased, even just to room temperature, the low frequency modes start to become thermally populated to a measurable extent. The measured band contour is not just a collisionally-broadened single vibrational frequency, but contains contributions from hot bands due to thermal excitation of the level being probed, as well as thermal excitation of all other modes. This situation would still be completely tractable if all the anharmonicity constants were known. In the case of nitromethane, however, we could find only one reliable anharmonicity constant involving the vibration of interest in this work, namely the CN stretching mode, ν_4 .⁶⁵

In order to interpret the CARS spectra of shock-compressed nitromethane correctly, a model^{67,68} of the vibrational band contour was developed that includes the contributions of the hot bands. The model was used to calculate the positions and intensities of the hot bands of the CN stretching mode for ambient nitromethane and sev-

eral shock-compressed pressure and temperature states of nitromethane using Eqs. (1) and (2). Figure 16 shows the improved fit of the synthetic CARS spectrum when including the hot bands for ambient pressure and temperature nitromethane. The low frequency side of the peak is not satisfactorily fit without inclusion of the available hot bands.

Fig. 15. CARS spectra of CO in neat CO (dotted line) and in a 1/4:CO/N₂ mixture (dashed line), shocked to near 7 GPa. The feature in the mixture at ca. 2137 cm⁻¹ is from a small amount of unshocked material. The features between 2110 and 2120 cm⁻¹ result from the first hot-band transition. The unshocked CO spectrum (solid line) is shown for reference.

CARS spectra of the ν_4 mode at several pressures in shock-compressed nitromethane have been previously reported,⁶⁹⁻⁷¹ as has a preliminary estimate of the ν_4 vibrational frequency versus shock pressure.⁷¹ The spectral fit of the shock-compressed nitromethane CARS spectrum in Fig. 17a is that given by the model with the assumption that the anharmonic coefficients do not change with pressure. The linewidth of the transition was the only variable adjusted for the fit shown. There is something obviously wrong with this model when it is applied to the shock-compressed material, even at modest pressures and temperatures.

The discrepancy probably arises because of changes in the anharmonicity coefficients with pressure, contrary to assumption. Also, because the ν_4 vibrational frequency increases with pressure, indicating a stiffening of the potential for that motion, it might become more resilient to the presence of other thermally populated vibrational motions. The consequence of this picture would be that the off-diagonal anharmonic coefficients would be comparatively smaller. Figure 17b shows a synthetic CARS spectrum assuming the off-diagonal anharmonicity coefficients are zero and only the

diagonal terms and Γ are varied for the best fit. The quality of the fit in Fig. 17b is clearly better than that of 17a. There is obviously more work to do to understand these spectra.

Fig. 16. CARS experimental spectrum of ambient nitromethane CN-stretching mode. a) synthetic spectrum (dashed) includes no hot bands; b) synthetic spectrum (dashed) includes contribution from hot bands.

Figure 18 shows spectra of the ν_1 mode of unshocked (0.0003 GPa and 191 K) N_2O and N_2O shocked to approximately 4.3-GPa pressure and 735-K temperature. Because the temperature of the unshocked liquid is low, the data can be fit with a synthetic spectrum comprised of only the fundamental transition. Inclusion of hot bands as was done for the ν_4 mode of CH_3NO_2 is not necessary. However, a preliminary fit of the spectra for shock-compressed N_2O suggests inclusion of both the first excited state transition of the ν_1 mode and also transitions originating from the excited states of the ν_2 bending mode. The energy level separations used in this initial fit were the gas phase values given by Herzberg.⁷² The spectral structure resulting from this scheme is

readily visible in Fig. 18b. The shoulder to the left of the highest peak is thought to be the shock shifted 0-1 transition. The large peak is the result of the fundamental 1-2 transition and the hot band originating from the first excited state of the ν_2 bending mode. Analyses of this and other high-pressure/high-temperature liquid N_2O spectra are in progress and will be reported in the near future.

Fig. 17. CARS experimental spectrum of the CN-stretching mode of liquid nitromethane shock compressed to ca. 33 GPa. a) Synthetic spectrum (dashed) with all hot bands and using model; b) synthetic spectrum (dashed) with combination hot bands set to zero.

Fig. 18. CARS spectra of a) unshocked N_2O and b) shocked N_2O . The solid lines are experimental data and the dashed lines are spectral simulations.

SUMMARY

Fundamental understanding of the detailed microscopic phenomenology of shock-induced chemical reaction and detonation waves is being sought by using pulsed coherent optical scattering experiments to determine the molecular structure, constituents, and energy transfer mechanisms in shock-compressed, high-pressure/high-temperature fluids. To date we have confirmed that N_2 , O_2 , CO , N_2O , CH_3NO_2 , and C_6H_6 still exist as molecules on the nanosecond timescale behind the shock front, but that energy transfer is occurring from the translational degrees of freedom into the vibrational modes. For N_2 , O_2 , and CO , the vibrational relaxation times have decreased to less than a few nanoseconds in the shock-compressed state. For nitrogen, this is about a ten order of magnitude rate increase from ambient conditions. For N_2 (work is in progress with O_2 and CO), the vibrational population distribution appears Boltzmann-like and

gives temperatures that agree satisfactorily with those obtained from equation-of-state calculations. We have experimentally shown the effect of the intermolecular potential (reflecting the thermodynamic environment of the shock-compressed state) on the intramolecular potential through frequency shift measurements. These results show differences for N_2 and CO behavior previously not elucidated by shock Hugoniot data. Linewidth data have been used, assuming homogeneous line broadening, to provide an estimate of dephasing times. For N_2 and O_2 these have decreased to less than one picosecond at the highest pressures.

Also we have shown that the dynamic shock-compression technique can be used to produce a high-pressure/high-temperature dense fluid, which can then be interrogated at the molecular level using short pulsed coherent Raman scattering techniques.

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