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TITLE: VIBRATIONAL SPECTROSCOPY IN HIGH TEMPERATURE DENSE FLUIDS

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Vibrational spectroscopy in high temperature dense fluids

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ABSTRACT

Coherent anti-Stokes Raman spectroscopy (CARS) in conjunction with a two-stage light-gas gun has been used to obtain vibrational spectra of shock-compressed liquid N₂, O₂, CO, and their mixtures, as well as liquid N₂O. The experimental spectra are compared to spectra calculated using a semiclassical model for CARS intensities to obtain vibrational frequencies, peak Raman susceptibilities, and linewidths. The derived spectroscopic parameters suggest thermal equilibrium of the vibrational populations is established in less than a few nanoseconds after shock passage. Vibrational temperatures obtained are compared to those derived from equation-of-state calculations. The variation of the vibrational frequency shift at pressure with species concentration in mixtures is investigated.

1. INTRODUCTION

The behavior of simple molecular fluids at high pressure and temperature is of considerable interest because of the importance of these fluids in the planetary sciences, in chemical explosives technology, and for the fundamental understanding of inter- and intramolecular forces and energy transfer mechanisms. Our present understanding of high temperature dense fluid behavior is derived almost exclusively from hydrodynamic and thermodynamic measurements. Such measurements average over the microscopic aspects of the materials and are therefore insufficient for a complete understanding of fluid behavior. Presently, dense fluid models can be verified only to the extent that they agree with macroscopic measurements. However, recently, we have begun to probe some of the microscopic phenomenology of these dense fluids using CARS.¹⁻⁵ The spectroscopic parameters derived from the vibrational spectra reflect the influence of increased density and temperature on the intramolecular potentials. In addition, the determination of vibrational temperatures provides an important benchmark for equation-of-state calculations, especially with regard to molecular mixtures.

2. EXPERIMENTAL

The high pressure/high temperature states of the liquids investigated in this study were achieved by dynamic compression techniques. The apparatus used has been described in detail previously.^{1,2} A projectile launched by a two-stage light-gas gun dynamically compressed a sample contained in a target designed to reflect the CARS signal back out an optical aperture. The target assemblies were of two types, one for ambient liquids and one for cryogenic liquids.⁶ The cryogenic target assembly was used to condense and hold the liquid N₂, O₂, CO, and their mixtures, as well as liquid 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-diameter quartz or lithium fluoride window at the rear. We have also used an ambient liquid target of similar design but without the toroidal cooling chamber for studies of CH₃NO₂ and C₆H₆.^{1,7,8} Impactor and target plate thicknesses were chosen, and electrical 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.

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. Electrical 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 doubly-shocked sample was present when the lasers arrived at the sample. These situations will be discussed more completely below.

CARS⁹⁻¹¹ is a parametric process in which three waves, two at a pump frequency and one at a Stokes frequency are mixed in a sample to produce a coherent beam at the anti-Stokes frequency. The efficiency of this mixing is greatly enhanced if the frequency difference coincides with the frequency of a Raman active mode of the sample. By providing a broad band of Stokes frequencies using a broad-band dye laser, a portion of the full CARS spectrum can be obtained in a single laser shot if a multichannel detection system is used. The pump frequency in our CARS experiment was obtained by using approximately 40% of the 6 ns-long frequency-doubled output of the Nd:YAG laser (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 O₂ data, and near 560 nm (Rhodamine 590, Exciton) for the CO and CO/N₂ mixtures. Two broad ranges of Stokes frequencies (in order to allow production of CARS spectra in two separate regions of vibrational frequency) were produced using home-built broad-band dye lasers utilizing the laser dye DCM (Exciton, lasing region 625 to 645 nm) in one and Rhodamine 640 (Exciton) in the other, each pumped by half the remaining Nd:YAG output. 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) and 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, 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). This measured spectral profile was used in the analysis of each CARS spectrum, which was performed as has been previously described²⁻⁵ using a semiclassical model for the CARS intensities.

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.²⁻⁴ Linear scaling of the dispersion results in the same phase-matching angle at all compressions. The scaled refractive indices were also used in the local field correction terms of the equation for CARS intensities. 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 ($\pm 0.5 \text{ cm}^{-1}$) using vacuum wavenumbers 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 to give spectra that could be directly compared with the experimental data.

3. RESULTS

Figure 1 shows CARS spectra for singly-shocked nitrogen and a 50%/50% nitrogen/carbon monoxide mixture. The shock has not quite reached the back window of the target, so that a small amount of

ambient material was also interrogated by the CARS beams, producing the starred features in each spectrum. In each spectrum the fundamental vibrational band shifted to higher frequency is visible, as is a series of hot bands. Previous publications²⁻⁵ have shown that these hot bands are adequately

Fig. 1. Sample CARS spectra of a) nitrogen and b) 50% nitrogen - 50% carbon monoxide mixture.

represented by a Boltzmann distribution of vibrational populations, implying that the vibrational relaxation time has decreased to <10 ns in the shock compressed material. For nitrogen this represents a ten order of magnitude change from the ambient liquid value. Because the vibrational populations appear to be in thermal equilibrium, they can be used as a measure of the vibrational temperature. We have also previously shown the good agreement between these measured vibrational temperatures of the shocked material and the temperatures calculated from a theoretical equation of state.²⁻⁵

Figure 2 shows the change in Raman shift with shock pressure for the fundamental transitions of nitrogen and carbon monoxide. Delta Raman shifts have been used so that the results for the different molecules can be readily compared. Also shown in fig. 2 are nitrogen Raman scattering data obtained using static high-pressure methods^{12,13}. For both molecules, the vibrational frequencies show a monotonic increase with increasing shock pressure. When the fluid is singly or doubly shocked to the same pressure, the difference in the measured delta Raman shift shown in Fig. 2 is related to the difference in temperatures of the shocked materials. This difference is also observed for Raman scattering measurements of nitrogen made in the diamond anvil cell at equivalent pressures, but lower temperatures. These differences in the vibrational frequencies are a clear manifestation of the effect of temperature on the potential functions and the portion of the potential sampled on average.

The measured Raman frequency shifts depicted in Fig. 2 have been numerically fit to empirical relations of pressure and temperature^{4,5,13}. The cross near each data point in the figure gives the calculated frequency value predicted by the appropriate relation at the measured pressure and temperature and the long curves show the positions of selected isotherms, also obtained using the relevant empirical relation. Each isotherm is drawn over the approximate range of validity of the empirical fit. Also shown for comparison in Fig. 2 is a 2000 K isotherm from an empirical approximation to Monte Carlo calculations of Belak, Etters, and LeSar.¹⁴ 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. Possible reasons for this difference as discussed previously³ include dissociation and/or ionization. This discrepancy is presently being explored by LeSar.¹⁵

Fig. 2. The change in vibrational frequency from the ambient pressure liquid value versus shock pressure for N₂ and CO. The symbols are used as follows: ● N₂ CARS single shock; ○ N₂ CARS double shock; □ spontaneous Raman scattering, diamond anvil cell; ▲ CO CARS single shock; △ CO CARS double shock; x calculated from empirical fit at shock pressure and temperature; - calculated isotherms.

Comparison of isotherms in Fig. 2 shows that the vibrational frequency of shock-compressed CO has a much smaller shift with pressure than does N₂. This difference occurs despite the similarities in the two materials, including density, boiling point, critical temperature and pressure, number of electrons, and shock Hugoniot (locus of shock states) up to 10 GPa. This observation suggests a fundamental difference in the intermolecular interactions in CO versus N₂. One possibility is dipolar interaction, which has been used to explain the larger Raman linewidth of pure liquid CO.¹⁶

To further investigate this phenomenon, CARS spectra of mixtures of CO and N₂ shocked to near 7 GPa were obtained with varying fractions of each species. The vibrational frequency shift with pressure from the ambient value for each species in these mixtures is plotted in Figure 3 versus fraction CO. Previous work at ambient density shows only a linear dependence of the vibrational frequency shift with concentration for mixtures of the same materials.^{16,17} Fig. 3 shows obvious departure from a linear dependence. As the fraction of CO is decreased, the measured vibrational frequency increases more rapidly near 100% CO and less rapidly near 100% N₂. Similarly, the N₂ frequency decreases more rapidly near 100% N₂, and less rapidly near 100% CO. This is a new observation; no other studies of this phenomenology have been performed in this density and temperature range. Clearly, this behavior of the

vibrational frequencies is a manifestation of the influence different molecular neighbors have on the intramolecular potentials. Also shown on Fig. 3 is an empirical fit of each frequency shift to a cubic dependence on concentration. All of the above observations indicate that, in order for intermolecular potential functions to completely describe these high-density fluids, they must consider the quantum level details of the interactions, especially the shape of the repulsive wall, as well as many-body effects. An attempt to theoretically describe these observations is in progress.¹⁵

Fig. 3. Delta Raman shifts of CO and N₂ compared to the ambient values versus fraction of CO in mixtures of N₂ and CO at approximately 7 GPa and 1420 K. The CO and N₂ data at 0.65 are near 6 GPa and are consequently slightly low.

Fig. 4. CARS spectra of the ν_1 mode of (a) ambient liquid N₂O and (b) liquid N₂O shocked to approximately 4.3 GPa and 735 K (solid curves). A preliminary fit to the data is shown by the dashed curves.

The logical extension of these spectroscopic studies to more complicated molecules has begun. We have obtained CARS spectra of the ν_1 mode of nitrous oxide (N₂O) at several shock pressures and temperatures. A representative spectrum is shown in figure 4b, along with the CARS spectrum of the same vibrational mode in the ambient liquid (Fig. 4a). Fig. 4b is of singly shocked material at approximately 4.3 GPa and 735 K, with a small amount of ambient liquid remaining between the shock and the window. The dashed curve is a preliminary fit of the spectrum, and includes contributions from the fundamental and first excited state transitions of the ν_1 mode, and transitions originating from the

excited states of the ν_2 bending mode. The energy level separations and anharmonic coupling coefficients used in this initial fit were the gas phase values given by Herzberg.¹⁸ The spectral structure resulting from this scheme is readily visible in Fig 4b. The shoulder to the left of the highest peak is thought to be the shock shifted fundamental transition of the ν_1 mode [(100) $\leftarrow$ (000)]. The large peak results from the overlap of the first hot band transition of the ν_1 mode [(200) $\leftarrow$ (100)] and the hot band originating from the first excited state of the ν_2 mode [(110) $\leftarrow$ (010)]. This fit assumes that the values for the anharmonic coupling coefficients do not change with pressure. While the on-diagonal elements of the anharmonic coupling coefficient matrix appear not to change appreciably with pressure (at least for the diatomic molecules studied),²⁻⁵ the behavior of the off-diagonal elements is an important goal of this research.^{19,20} This behavior is of particular importance for the understanding of the intramolecular potentials in high-temperature dense fluids, as well as for the possibility of measuring vibrational temperatures in shock-compressed polyatomic materials. Complete analysis of this and other high pressure/high temperature liquid N_2O spectra are in progress and will be reported in future publications.

4. SUMMARY

We are seeking a fundamental understanding of the detailed microscopic phenomenology of shock-induced chemical reaction and detonation waves by the use of 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 shown that the dynamic shock-compression technique can be used to produce a high temperature dense fluid that can then be interrogated at the molecular level using single-pulse coherent Raman scattering techniques. 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 time scale 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 ten nanoseconds in the shock-compressed state. For nitrogen, this is a rate increase of about ten orders of magnitude from the ambient value. For N_2 and CO the vibrational population distribution appears to be Boltzmann and gives vibrational temperatures that agree satisfactorily with those obtained from equation-of-state calculations. We have experimentally shown the effect of the intermolecular potential, which reflects 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 observed by shock Hugoniot data.

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