**Measurement of Shock Velocity and Temperature in laser-shocked Carbon Disulphide using Time-Resolved Raman Spectroscopy**

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**Abstract**

High-resolution time-resolved Raman spectroscopy of laser-shocked liquid carbon disulfide (CS2) is reported. The symmetric stretching mode (ν1) and first overtone of the bending mode (2 ν2) of CS2 at 656 cm-1 and 802 cm-1 wavenumbers respectively are analyzed to monitor the possible phase transitions occurring in the sample during shock wave propagation in the pressure range 0.4 – 4.4 GPa by varying the laser intensity on target from 0.2 GW/cm2 (40 mJ) to 6.4 GW / cm2 (1300 mJ). A liquid to solid phase transition is observed at 1.5 GPa, as compared to 0.8 GPa in static compression. The difference in these measurements is thought to be due to the high temperatures involved in the dynamic compression experiments described. The shock wave velocities in CS2 at 1.5 GPa and 2.6 GPa are calculated by measuring the intensity ratio of Raman modes emerging from the shocked region to that of the whole sample. 1D radiation-hydrodynamic simulations are performed to corroborate the experimental data. Enhancement of the Raman cross-section of carbon disulfide is observed from 2.5 GPa, which is much lower than the previously reported threshold of 8 GPa as reported by Yoo et al., [24]. This discrepancy in results is thought to be due to the significant contribution of temperature as along with the pressure in laser-driven nanosecond single shock experiment.

**Keywords:** Phase Transitions, Shock compression, Vibrational spectroscopy, Laser matter interaction, Resonance Raman effect;

1. **Introduction:**

Dynamic compression subjects materials to extremely high pressure and high temperatures for a short duration of time leading to a series of physical and chemical changes. Conditions of high-pressure and moderately high temperature can be found in nature in the interiors of the earth and other planetary bodies [1-4]. Shock wave experiments can additionally provide specific insights into the impact processes that can occur during planetary formation and evolution [5]. The application of pressure drives densification via atomic reordering. As pressure is increased, particles forming the crystalline structure are brought into repulsive regions of intermolecular potential, increases the coordination, decreases the length of covalent bonds and size of anions, and eventually promotes more significant structural reorganizations and chemical bonding changes [6]. As the compression energy begins to approach the chemical bond energy, delocalization of electrons can be observed and filled valence shell atoms become chemically reactive. Upon further compression, the electrostatic forces get more significant at extreme conditions [7]. Shock waves provide uniaxial stress to materials and can make significant changes to both structure and properties [8].

The most popular methods used for shock generation are explosion, impact, and irradiation. Laser-driven shock generation has advantages over the conventional methods involving gas guns and explosives particularly the ability to attain ultra-high pressures up to gigabars [9], the ability to synchronize measurement devices with sub-picosecond accuracy [10], repeatability, and the lack of destructive consequences for the driver and diagnostic equipment.

Carbon disulfide (CS2) has been widely studied at extreme pressures and temperatures. Bridgman was the first to discover the formation of a black polymer [11] on subjecting liquid CS2 to high pressures and temperatures in a diamond anvil cell (DAC). Thereafter, over the decades, research has been performed to characterize the CS2 static phase diagram [12, 13] and shock equation of state (EOS) [14-19], as well as the high pressure/temperature (*P/T*) chemistry of CS2 [20-23]. Most of these studies are conventional shock and particle velocity measurements used to determine the EOS of CS2 and provide end state information only. Gustavsen and Gupta studied Electronic and chemical changes in shocked liquid carbon disulfide inferred from time-resolved reflection experiments [20]. Yoo et al., were the first to demonstrate the molecular level effect of the shock wave by measuring the pressure-induced resonance Raman effect in shocked carbon disulfide using a gas gun [24]. Dias studied the phase transitions, metallization, superconductivity and magnetic ordering in dense carbon disulfide and its chemical analogues under static compression [25]. Brown et al. performed ultrafast shock-induced chemistry in carbon disulfide probed with dynamic ellipsometry and transient absorption spectroscopy [26]

CS2 is a linear, centrosymmetric molecule with point-symmetry with a similar valence electronic structure as CO2. At atmospheric pressure below 161.7 0K, it forms a solid orthorhombic structure with a space group (Cmca) and two molecules per primitive cell on C2h sites. This crystal structure has been confirmed by Baenziger & Duax, using single-crystal x-ray diffraction and by Powell et al., using neutron diffraction on polycrystalline samples [27, 28]. The CS2 molecule has four normal vibrational modes, out of which only the symmetric stretching mode is Raman active. The asymmetric stretching and bending modes are only infrared active.

Quite a lot of work has been done based upon static pressure based measurements of CS2, [12, 13] and there are also a few works concerning the determination of the Equation of State (EOS) of shocked CS2 using gas guns and energetic material based experiments [14 - 17]. Raman Spectroscopy of shocked CS2 has also been performed in gas-gun experiments. However, high resolution nanosecond-timescale dynamics of shocked CS2 has not yet been reported. In this manuscript, we report high-resolution time-resolved Raman Spectroscopy of laser-shocked carbon disulfide. We have estimated the shock velocities in the sample at various pressures and also determined the shock temperature in the sample by measuring the ratio of stokes and anti-stokes spectrum of CS2 at various pressures. The effect of both the pressure and temperature on the resonance Raman effect in laser-shocked CS2 sample is also discussed.

1. **Experimental Methods**

Nanosecond time-resolved Raman spectroscopy using the pump-probe technique is performed using the experimental facility at HP&SRPD, BARC. The experimental setup consists of an Nd: YAG laser, a confined geometry target, and a Raman detector. The Nd: YAG laser is capable of simultaneously delivering a pump beam of wavelength 1064 nm / 8 ns pulse width as well as a probe beam of 532 nm which is a second harmonic of the same laser. Schematic of the experimental geometry is shown in figure 1. The pump beam is used as a shock wave driver and the probe beam is used for Raman excitation. The spatial profile of the laser is nearly flat (80% flat top profile) which ensures uniform shock pressure in and around the region being probed. An optical delay line is introduced by reflecting the probe beam repeatedly between two parallel plane mirrors to adjust the delay between the pump and probe. The delay time Δt =0 ns denotes the time at which the pump and probe beam arrive simultaneously at the Al-glass interface. The target assembly consists of a 2.5 mm thick, 20 mm diameter quartz glass window onto which a 25 µm thick Aluminum (Al) foil is glued followed by a 200 µm thick Teflon spacer and finally another 2.5 mm quartz glass window (as shown in figure 1). The void between the Teflon spacer, Al foil, and glass rear-window is filled with the liquid CS2 sample. The pump beam is focused to a focal spot of diameter 1.8 mm onto the Al-glass interface thereby generating a laser-heated confined plasma that drives a shock wave through the Aluminium foil and into the liquid sample. The confinement of the ablating plasma by the front window enhances the shock pressure and shock duration. The probe beam is focused from the rear side to a spot size of 500 μm, with the same centring as the pump beam, in order to probe the shocked region that is least perturbed by lateral expansion.

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| **Figure 1.** Schematic of the experimental-setup and confinement geometry (shown in sub-figure) [29]. |

In one set of experiments, which examine the pressure-dependent mode shift, the laser energy of the pump beam is varied from 40 mJ to 1300 mJ with the pump-probe delay kept fixed at 45 ns. In the other, time-resolved, set of experiments, the laser energy is fixed at either 300 or 500 mJ and the delay is varied from 10 ns to 94 ns. The target assembly is mounted on an X-Y-Z stepper motor-controlled translational stage so as to expose a fresh region of the target on each laser shot. The scattered Raman signal is recorded using a 0.5 m Raman spectrometer arranged in a confocal geometry with a charge-coupled device camera fitted with a gated intensifier. Further details of the experimental setup can be found elsewhere [30].

1. **Result and Discussion**

In this study, we have used two different gratings for recording the Raman spectra. In the first step, we have used a 600 lpm grating to cover a broad spectral range which includes the symmetric stretching mode ν1 at 656 cm-1 and the first overtone of S=C=S bending 2ν2 at 802 cm-1. However, when the 600 lpm grating is employed, the first overtones of the bending mode, 2ν2, centred at 796 and 802 cm-1 are not resolved, as has been previously reported by others [19] . Shifts in modes at 656 cm-1 and 800 cm-1 are also not clearly resolved. To overcome this problem, we changed the grating to 2400 lpm which provides spectral resolution of 1 cm-1, however, this significantly reduces the spectral range that can be covered and so only one mode at a time could be recorded.

We have also performed one-dimensional (1-D) radiation hydrodynamic simulations to model the experiment using the HYADES code [31]. HYADES is a Lagrangian radiation-hydrodynamics simulation code, which uses a flux-limited diffusion model of electron transport; in these simulations, the flux limit is set at 5% of the free-streaming limit. A multi-group diffusion approximation is employed to mimic thermal radiation transport within the target. The equation of state (EOS) for glass and Aluminium is taken from the SESAME library, while the EOS for CS2 is taken from an in-line Quotidian Equation of State (QEOS) model. This QEOS model takes as an input bulk modulus data from references [16].

* 1. **Shock velocities estimation from time-resolved measurement and its comparison with 1D hydrodynamic simulation**

In the time-resolved measurements performed at pump energies of 300 mJ and 500 mJ, the delay between the pump (1064 nm) and the probe (532 nm) is varied from 10 ns to 94 ns. This enables the complete transit of the shock wave through the sample to be probed as well as states that are induced by the second passage of the shock through the pre-shocked sample after it has partially reflected off the rear window. In this set of experiments, the 2400 lpm grating is used which provides high spectral resolution (1cm-1) within a limited spectral range in which either 656 cm-1 or 800 cm-1 could be recorded at a time. Since, the mode shift for 656 cm-1 is weakly dependent on the pressure, we have concentrated on the first overtones of the bending mode at 802 cm-1 which is more sensitive to the variation in shock pressure. When using the 2400 lpm grating, modes at 796 cm-1 and 806 cm-1 are clearly resolved as shown in figure 2a. Simulated shock wave profiles at different time delays in the carbon disulfide at a laser energy of 500 mJ are shown in figure 2b. The associated Raman spectra are shown next to the simulation data in figure 2a.

As shown in figure 2a, at a 10 ns delay between the pump and the probe, there is no change in the Raman spectra in comparison to the unshocked condition. By considering the simulation data, which shows that the shock wave is only just reaching the Al-sample interface at this time, it is clear that this is because the shock wave has not yet entered the sample. At 24 ns delay, the Raman modes at 796 cm-1 and 806 cm-1 wavenumbers show broadening towards the lower wavenumber (red shifting). The broadening of the Raman peaks is due to the contribution of the signals from shocked and unshocked regions. To separate the contribution of the signal from the shocked and unshocked regions, Lorentzian peak fitting is done for both of the modes. From the peak-fitting shown in the figure 2a, it can be seen that new peaks at 790 cm-1 (green) and 798 cm-1 (cyan) appear due to the shock pressure of ~ 2.6 GPa corresponding to the unshocked modes at 796 cm-1 (blue) and 806 cm-1 (magenta) respectively. With the increased delay between pump and probe, the shock wave has enough time to travel deep into the sample generating a stronger signal from the shocked region due to the larger volume covered. At 52 ns delay, the intensity of the Raman signal coming from the shocked region is more than that from the unshocked region indicating that the shock wave has traveled more than halfway through the sample and consideration of figure 2b provides support for this assessment. At a delay of 73 ns, the signal intensity from the shocked region is now much stronger than from the unshocked region, indicating that the shock wave has almost reached the end of the sample, a conclusion which is also supported by the simulation results which show that the shock wave has reached the rear surface of the sample. It is to be expected that the shock should propagate somewhat faster in a 1-D simulation than in reality due to the absence of two-dimensional (2-D) edge losses. Another interesting observation made using the high resolution (2400 lpm) grating is that the peak at 790 cm-1 shifts with increasing time delay toward its unshocked position. This is due to the expected gradual weakening of the shock wave as it propagates, which can be clearly observed in the simulation output shown in figure 2b. At 80 ns, a new peak at the further red-shifted frequency at 786 cm-1 (red) is observed. This new peak can be explained by consideration of figure 2b, in which it is observed that the shock wave is partially reflected at higher pressure from the sample :rear-window interface due to the glass window having a higher impedance than that of the sample. At 94 ns delay, the new red-shifted peak shifts toward the higher frequency side due to decreasing pressure resulting from the quick decay of the reflected shock wave as it propagates through the rarefaction wave induced by the first passage of the shock wave through the sample

The shock velocity is experimentally calculated by using the equation *Us = r. d* [32], where *d* is the sample thickness which is 200 µm and *r* is the slope of the intensity ratio, *Vs* time delay plot as shown in figure 2c. These intensity ratios are obtained from the curve fitting of the experimental data as shown in figure 2a. The shock velocity is also calculated from the simulation data by plotting the fraction of the volume of the sample traversed by the shock wave vs time delay (see figure 2c), because the intensity of the Raman mode is sample volume dependent. As can be seen from the figure 2c, slope of the experimental data is very similar to that taken from the simulation output.

Analysis of the time-resolved data at 300 mJ energy is done in a similar manner but the details are omitted here for the sake of brevity.

At the laser energies of 300 mJ and 500 mJ, the values of *‘r’* come out to be (0.0115 ± 0.00184) x 109 s-1 and (0.01704 ± 0.00124) x 109 s-1 respectively and the corresponding shock velocities are 2.3 km/s and 3.4 km/s respectively. Shock transit times, i.e. the time taken for the shock wave to traverse the entire length of the sample, are obtained from the time delay analysis by looking for the delays at which the beginning of a new peak starts due to shock wave and the time at which entire contribution to the recorded Raman spectra (this new mode) comes from shocked region only. From these shock transit times and known sample thickness of 200 µm, the shock velocities at 300 mJ and 500 mJ are calculated to be 2.6 km/s and 3 km/s respectively and are shown in figure 2d. The shock velocities calculated from the intensity ratio as well as shock transit time are in excellent agreement with the simulation results of 2.8 km/s and 3.17 km/s respectively at 300 mJ and 500 mJ laser energies. In figure 2d, simulated shock velocities in the range of laser energies 300 mJ to 1350 mJ are plotted, however, time-resolved experiments are performed only at laser energies of 300 and 500 mJ due to the prohibitive expense of making time-resolved measurements at all of the pump energies that were employed. For each data point, we need to take 50 shots.

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| **Figure 2.** (a) Intensity profile of Raman modes at 796 and 806 cm-1 at different time delays between the pump and the probe beams. Both modes are fitted with Lorentzian peak fitting. One is due to the shocked material and the other to the unshocked sample material. (b) Simulated shock wave profiles at different time delays. (c) Intensity ratio of the Raman mode at 796 cm-1 scattered from the shocked sample to that of the total sample (shocked + unshocked) at different time delay and volume coverage ratio (from simulations) at same delay. (d) The calculation of shock velocity from the time delay experiments at 300 mJ ( 0.4 GW/cm2) mJ and 500 mJ (2.46 GW/cm2). The straight line is a linear fit to the simulation results | |

* 1. **Effect of pressure on mode shift and estimation of Gruneisen parameters:**

In the second set of experiments, which examine the pressure-dependent mode shift, we fix the delay between the pump and the probe beams at 52 ns whilst the pump beam energy is varied from 40 mJ to 1300 mJ in steps; as will be shown this corresponds to a change in shock pressure from 0.4 GPa to 4.4 GPa. This delay of 52 ns is sufficient for the shock wave to travel a considerable distance into the sample, such that significant Raman signal is generated from the shocked volume. The pressure corresponding to each laser energy is taken from the simulation after getting a close match in shock velocity between the experimental data and simulation output, as described in the previous section. These experiments are performed using either the 600 lpm grating (figure 3a) which covers the entire spectral range of 100 cm-1 to 1000 cm-1 or the 2400 lpm grating (figure 3b) which can examine only one mode at a time. The first overtone of bending mode (2ν2) is shown in figure 3b recorded with the 2400 lpm grating. The use of this 2400 lpm grating enables us to resolve the two bands at 796 cm-1 and 806 cm-1 in the overtone region which have not been recorded in earlier dynamic compression experiments. This shows that the bending modes are degenerate. Similarly, it is observed that the symmetric mode ν1 (656 cm-1) also has a shoulder peak at 646 cm-1 towards the low-frequency side. This doublet structure in the ν1 region is caused by the isotopomers C32S2 (90%) and C32S34S (10%). To extract the information about the mode shift due to shock pressure, Lorentzian fitting is done for both the modes. Peak fitting of the 796 cm-1 and 806 cm-1 modes is shown in figure 3b. The pressure-dependent Raman frequency changes of carbon disulfide modes are summarized in figure 4. The modes at 646 and 656 cm-1 exhibit slow blue-shifting with pressure (0.5 cm-1/ GPa). Both the modes at 796 and 806 cm-1 exhibit red-shift and follow almost the same scaling law (-1.42 cm-1 / GPa and -1.41 cm-1 / GPa ). Similar observations are reported by Yoo et al [24] in measurements made at 8 GPa using a reverberation shock wave generated by a gas gun (data points shown with star symbols in figure 4). However, in the case of static compression, the mode at 796 cm-1 is more sensitive to pressure (- 4.9 cm-1/ GPa) than the mode at 802 cm-1 (-1.3 cm-1/GPa). Thus, with pressure, symmetric stretching mode ν1 blue shifts whilst the first overtone of the bending mode 2ν2 exhibits red shift thereby decreasing the separation between the two bands. To compare our experimental results, we have also incorporated data from static pressure experiments performed using DACs by Shimizu, [33], Dias et al., [25], Bouldan et al., [34] and Zhou et al., [35] (see figure 4). From figure 4, it can also be seen that our laser-driven shock compression yields relatively lesser (blue/red) shift in all the three studied Raman active modes in comparison to static compression. This is because the laser-driven shock compression typically occurs along the principle Hugoniot and results in the material being strongly heated, whereas static compression is approximately isothermal.

From figure 3a and b, it can also be seen that the shocked Raman signal at 200 mJ pump beam energy (1.12 GPa) is more intense than the shocked signal corresponding to 40 mJ (0.4 GPa) for the same number of accumulated shots (i.e., accumulation taken over 40 shots) and same probe beam energy. This indicates a possible phase transition from the liquid state to the solid state. This possible phase transition is at a higher pressure than that at which it is observed both in static compression experiments [25] (where it occurs at 0.8 GPa) and previously reported multistep shock compression (at 0.62 GPa) [17]. This can be explained based on figure 5a which consists of the pressure vs. specific volume graph derived from multistep (reverberation) shock loading performed by Sheffield et al., [16] double shock loading performed by Dick et al., [17] and our own simulations of the experiments described here. Laser-driven rapid heating on ns timescales raises the temperature significantly and hence lowers the compression value. Same can be seen from figure 7b which will be discussed in detail in section 3.5. It is evident from this figure that at 1.5 GPa pressure, the temperatures estimated from our experimental data are, at equivalent pressures, significantly higher than those reported by Sheffield et al.,[16], Afanasenkov et al., [36] and Granholm, et al., [38] using multistep shock compression; double step shock loading by Dick et al., [17]; and single shock loading (μs) by Dallman [37]. So, in our experiments, to achieve the same compression ratio, a higher pressure is needed.

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| Figure 3. (a). Raman Spectra of CS2 in unshocked and shocked conditions at various laser energies ranging from 200 mJ to 1250 mJ recorded using a 600 lpm grating. (b) High-resolution Raman spectra of 796 and 806 cm-1 modes in unshocked and shocked conditions for various laser energies ranging from 40 mJ to 1350 mJ recorded using a 2400 lpm grating. | |

* 1. **Gruneisen parameters:**

Both internal and external modes of molecular vibration are quite sensitive to small changes in the equilibrium values of the internuclear distances which change with both pressure and temperature. The dimensionless Gruneisen parameter γ is generally used as a thermomechanical property characterizing solids at high pressure. It is used to explain the anharmonic properties of solids in condensed matter physics. In terms of the lattice vibration spectrum of solids, individual mode Gruneisen parameters are deﬁned as

(1)

On integration we get

(2)

Where, is the Gruneisen parameter of the *ith* mode having frequency when the unit mass of the crystal occupies a volume *V* and is the density of the sample. ‘0’ and ‘P’ represent the state of sample at ambient pressure and at pressure *P* respectively.

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| Figure 4. Scaling of mode shift with pressure in static compression experiments, performed by others, shock compression using gas gun experiments performed by Yoo and our own experimental data shown as the light green squares (shock 656 I), dark green solid circles (shock 656 II), inverted magenta triangles (shock 800 I) and inverted red triangles (shock 800 II). |

To determine the individual mode Gruneisen parameters, the compression of material as a function of pressure must be known. However, it is not possible to measure the compression factor purely using Raman spectra of dynamically shocked CS2. It would require either *in situ* X-ray diffraction measurements of CS2 in shocked conditions or another method of measuring the EOS of CS2 [17]. The pressure vs. specific volume relationship deduced by Dick et al, and Sheffield et al., are shown in figure 5a. In our case, we have taken the fractional compressibility in CS2 as a function of the pressure in shocked condition from our 1-D numerical simulation, which seems a reasonable course of action given the good agreement between our experimental and simulation results. These data are shown by the black filled squares in figure 5a. Here, it can be seen that in our case the compression ratio is, as anticipated, smaller than that produced by the slow compression techniques. To calculate the mode Gruneisen parameters, was obtained from the scaling of mode shift with pressure (figure 4) while was obtained from the simulations. A plot of relative frequency change *vs.* relative density change under shock compression for all the modes has been shown in figure 5b. The Gruneisen parameters corresponding to the 646 cm-1, 656 cm-1, 796 cm-1 and 806 cm-1 modes are *γi* = 0.01885 ± 0.00604, 0.00555 ± 0.00122, -0.01577 ± 0.00261, and -0.01341 ± 0.00223 respectively

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| Figure 5(a). Pressure-specific volume plot showing a comparison of our simulation data with the data available from Sheffield et al., [16] and Dick et al., [17]. (b) A log-log plot of the νi (P) / νi (0) versus ρ (P) / ρ(0) for all analysed Raman peaks of CS2. The graph shows the tendency of the vibrational modes to be individual volume independent Gruneisen parameters. The dotted lines are linear fits performed in order to extract the Gruneisen parameters. | |

* 1. **Resonance Raman effect**

The Raman spectrum from liquid CS2 is substantially altered under shock compression, as illustrated in figure 2a. With the increase of the pressure above 2.5 GPa, the intensity of the signal from the shocked sample is significantly higher than that from the unshocked sample. Figure 6 shows the peak intensity ratio of shocked and unshocked Raman modes at 656 cm-1 and 802 cm-1 with shock pressure. At 4.3 GPa pressure, the intensities of the shocked signals for the Raman modes at 802 and 656 cm-1 are is approximately 4.3 and 3.0 times higher than the intensity of unshocked Raman modes. A similar effect but at higher pressure is reported by Yoo et al., [24] in which they reported 5.0 times enhancement in the intensity of the 656 cm-1 mode at 8 GPa pressure and 260 K temperature (also shown in figure 6). This discrepancy is possibly due to the greater initial temperature (will be discussed in the next section) of the single shock in this study versus those reported by Yoo et al. This enhancement of the Raman cross-section of carbon disulfide can be understood in terms of a pressure-induced resonance Raman effect which occurs due to an increase of the red edge of the absorption band (279 nm – 365 nm) [37] toward higher wavelength with increased pressure and/or temperature. To validate our hypothesis, the effects of temperature and pressure on the absorption edge, are summarised in the next paragraph.

Several studies on the chemical changes in carbon disulfide (CS2) at elevated pressure and temperature have been conducted under static high pressure [l2], step shock-wave loading [14-16], and single shock wave loading [19, 37] to explain red shifting of absorption edge . Granholm has measured the absorption edge redshift from 355 nm to 530 nm at 8.1 GPa pressure and 700 K temperature during stepwise shock loading using a gas-gun [38]. Ogilvie and Duvall et al., have demonstrated the effects of temperature and pressure on the UV-visible spectrum of dynamically compressed CS2. They observed that at 5.5 GPa and 458 K, or at 3.3 GPa and 523 K, the absorption edge shifted to 410 nm from 365 nm and furthermore that at above 12 GPa it extends through the visible region as well. They observed that the absorption edge red-shifts with temperature and pressure as follows [39]

(3)

(4)

Later, Dallman measured the absorption spectra of shocked liquid CS2 using a high explosive driven flyer plate scheme [37]. Their results show several significant differences from the work of Ogilvie and Duvall. The absorption edge shifted to 450 nm at 2.7 GPa and 635 K temperature, while, for somewhat greater shock pressures (5.8 GPa) Ogilvie and Duvall observed redshifts to 410 nm in a reverberating experiment (at a lower temperature). He explained that this is possibly due to the greater initial temperature of the single shock in his experiment versus a reverberation experiment. This observation of Dallman is in agreement with our measurement in which the resonance Raman effect is observed above 2.6 GPa as in that case the temperature is also significantly higher than in the case of step shock loading. As can be seen in figure 7b, the shock temperature in our laser-driven shock experiments is approx. 670 K even at 1.5 GPa as inferred from measurements of stokes and anti-stokes lines. Thereafter, Stephen et al., [12] also measured the dependence of the red shift of the absorption edge with the temperature at 2.4 GPa static pressure. They measured the absorption edge at 301 K, 371 K, and 380 K as 366.1, 371.6, and 380 nm respectively. From these observations, they also predicted that the shock-loaded CS2 temperature would be 491 K rather than the 626 K which is overestimated from the Sheffield and Duvall EOS. So, from the above discussion it is clear that for higher temperature, the resonance Raman effect may occur even at lower pressure. The static pressure observations at elevated temperatures also seem to be in agreement with our results. So, it can be concluded that the resonance Raman effect observed above 2.6 GPa in our experiment compared to 8 GPa in the study by Yoo et al., is due to the considerably higher shock temperature > 700 K compared to the lower temperatures (~ 260 K) present in the multistep (reverberation) shock-loading experiments performed by Yoo et al.,[24]. Details of the temperature estimation are described in the next section.

* 1. **Temperature measurement**

Temperature measurements are a critical ingredient in understanding and modelling the equation of state (EOS) of shocked materials. The temperatures of shocked metal samples are typically determined using optical pyrometry with accompanying reflectivity measurements to identify the emissivity at similar shock stresses [16, 17, 36, and 38]. When pyrometry is used with an opaque sample, the temperature is determined at its surface. It is, however, the bulk temperature that is required for EOS calculation. Time-resolved Raman spectroscopy is one of the diagnostics that can be used as a temperature measurement tool in shocked materials [40-42]. The measurement of the intensity ratios of anti-stokes to stokes-shifted lines in Raman scattered line pairs of the various vibrational modes can be used to determine the temperature as follows:

(5)

Here, and are the anti-stokes- and stokes-shifted line intensities, and are the probe-laser and Raman-shift frequencies, and h and k are the Planck and Boltzmann constants, respectively. Stokes and anti-stokes Raman scattering of the symmetric stretching mode at 646 and 656 cm-1 in ambient (unshocked) and shocked conditions with100 mJ laser energy (0.7 GPa) are shown in figure 7a. The delay between the pump and the probe was kept in such a way that the shock wave reached at the end of the sample leading to whole sample under compression. This will reduce the error in measurement of temperature due to contribution of signal from unshocked regions. The intensity of the modes were taken using the area under the individual curve. The temperature estimated at 100 mJ (0.7 GPa) using 646 and 656 cm-1 peaks are 410 K and 420 K respectively. This temperature estimation is slightly higher than the temperature measured by Afanasenkov et al., [36], and is similar to that inferred by Sheffield et al., [16], Granholm et al., [38] and Dallman [37]. Similarly, the temperature estimated at 300 mJ (1.5 GPa), from 646 and 656 cm-1 peaks is 658 K and 688 K. The higher temperature in this study is due to the single shock compression employed, as compared to the multistep (reverberation) shock compression by the other authors. At 500 mJ (2.6 GPa) laser energy, a sudden drop in the temperature to 355 K is observed. The reason for this drop in the temperature estimate is apparent from figure 6. At this laser energy, there is a sudden enhancement in the shocked stokes signal compared to the unshocked signal due to the resonance Raman effect. So, this lower temperature is due to enhanced stokes’s signal and this technique cannot be used above this pressure. At lower pressures and temperatures, the UV absorption band red-edge (365 nm) is far away from the laser probe beam wavelength of 532 nm, so the resonance Raman process cannot affect the measurement.

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| Figure 6. Intensity ratio of shocked and unshocked Raman modes at 656 cm-1 (red filled circle) and 802 cm-1 (black filled square) with laser energy (Shock pressure). For comparison, data from Yoo et al [24] shown in blue triangles is included. |

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| Figure 7. (a) Experimental data (black) and fits the 656 cm-1 mode (red and green) in the spectrum at a peak pressure of 0.7 GPa, (above), and (b) at ambient pressure (unshocked conditions) (below graph of figure a). The solid deep blue line, representing the sum of the Lorentzian fits. (b) The scaling of shock temperature with shock pressure along with the data published by the stated authors [ref 16, 36, 37 and 38] | |

1. **Conclusion**

Time resolved Raman spectroscopy of dynamically compressed CS2 has been performed using a 1.6 J / 8 ns Nd: YAG laser. The laser intensity (energy) on target was varied from 0.2 GW/cm2 (40 mJ) to 6.4 GW / cm2 (1300 mJ) which generates a pressure in the range of 0.4 to 4.4 GPa. A liquid to solid phase transition is observed at 1.5 GPa. Pressure dependent blue shifts of the symmetric stretching mode (ν1), and red shifts of the first overtone of the bending mode, (2ν2), have been measured, and the separation between the two bands is observed to decrease with pressure. These results are in agreement with static high-pressure measurements and also with the results of explosive and gas gun experiments. The Raman modes scale with pressure as 656 + 0.5 cm-1/P(GPa) and 802 – 1.42 cm-1 /P(GPa). Based on the Raman mode frequency shift, the Gruneisen parameters for 646, 656, 796 and 802 cm-1 mode have been calculated to be *γi* = 0.01885 ± 0.00604, 0.00555 ± 0.00122, -0.01577 ± 0.00261, and -0.01341 ± 0.00223 respectively. The resonance Raman effect is observed above 2.6 GPa at 700 K temperature which is considerably lesser than in the case of the reverberating shock experiments conducted at a pressure of 8 GPa and at a temperature of 260 K by Yoo et al. This demonstrates that, as expected, the resonance Raman effect is not only pressure dependent rather it depends on both pressure and temperature. These measurements are in agreement with the static compression data at elevated temperature and high explosive driven flyer plate data where the temperatures are also comparable. The intensity ratio of anti-stokes to stokes signals in Raman scattered line pairs at 646 and 656 cm-1 were used to determine the temperature at lower pressures and are in good agreement with previously measured temperatures found using pyrometric detectors.

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