Development of ultrafast spectroscopic techniques to study rapid chemical and physical changes in materials under extreme pressure and temperature conditions

Alexander F. Goncharov,[1] D. Allen Dalton,[1] R. Stewart McWilliams,[1,2] and Mohammad F. Mahmood[1,2]

[1] Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington, DC 20015, U.S.A.
[2] Howard University, Washington, DC, 20059, U.S.A.

ABSTRACT

In the study of materials at extreme pressures and temperatures, there is an enduring need to extend the range of experiments to previously inaccessible regimes. To accomplish this, improvements in diagnostics for *in situ* material characterization at extremes must proceed in parallel with techniques used to generate extreme states. Simultaneously, there is a need to study material phenomena – e.g. phase transformations and chemical reactions triggered by the application of extreme conditions – on their natural timescales. Here we report on recent developments in the application of ultrafast laser spectroscopic techniques to high-pressure high-temperature experiments on materials confined in a diamond-anvil cell. Using a bright broadband source coupled to ultrafast detection to discriminate signal from high thermal and fluorescent backgrounds, we conducted broadband optical spectroscopy up to 60 GPa and 1560 K. By coupling the broadband source to a monochromatic pulse, nonlinear Coherent Anti-Stokes Raman Spectroscopy (CARS) with high signal brightness was achieved. Optical absorption data in hot compressed O_2 and CARS data in N_2 at extreme pressures are reported.

INTRODUCTION

Knowledge of the behavior of materials under extreme pressures and temperatures is fundamental for many fields of science. This information is also important for technology and for national security as it allows predictions of material behavior under relevant conditions. In spite of ongoing technical advances, the development of the required *in situ* measurements of materials properties under extreme conditions remains a challenging problem. For example, classical optical spectroscopy methods such as absorption (e.g. FTIR) or Raman spectroscopy at high temperatures are affected by thermal radiation. Thermal sources provide incoherent radiation, whereas lasers are coherent, making spatial and temporal discrimination feasible for laser-based spectroscopic probes. Thermal radiation may be substantially suppressed through the use of short-pulse, high-brightness sources and time-resolved detectors or through signal modulation and synchronous acquisition [1]. Suppression of background is increasingly important at very high temperatures (approaching 1 eV) and in systems exhibiting strong fluorescence.

In previous technical developments, our research group has coupled pulsed laser heating of the high-pressure diamond-anvil cell (DAC) with time-resolved temperature measurements (using spectroradiometry) [2], spontaneous Raman scattering [3], and x-ray diffraction [4]. The purpose of these studies was many-fold: to achieve higher temperatures than typical (CW) laser-heating experiments; to minimize the time the sample is subjected to extreme temperature and thereby mitigate unwanted chemical reactions, atomic diffusion and sample flow; to enhance

optical stability of the experimental apparatus by preventing heating of optics by high power CW lasers; and to enable synchronization with time-resolved detection and pulsed laser-based probes. Here we discuss further development of time-resolved diagnostics of broadband optical spectroscopy and Coherent Anti-Stokes Raman Spectroscopy. An advantage of the proposed techniques over these previous techniques [2-4] is that the laser sources are very bright, spectrally broad and temporally short, allowing discrimination of signal from thermal and fluorescent backgrounds. These diagnostics can provide further information on optical, electronic and chemical properties of substances confined at extreme pressure and temperature.

EXPERIMENT

Our primary approach in this study is synchronous pulsed laser heating with spectroscopic data collection in the DAC. This technique uses a Nd:YAG, 10 ps mode-locked fiber laser as the fundamental source (Fianium FP1060-2uJ-HE, $\lambda\sim$1064 nm, $\Delta\lambda$=12 nm, rep rate=1 MHz). A supercontinuum broadband source was created by pumping a hermetically sealed, structured photonic crystal fiber [5], or PCF (NKT Photonics, SC-5.0-1040, 5 m in length) with the mode-locked fiber laser. Frequency doubled light (Type I SHG) was generated using a 3 mm long lithium triborate (LBO) crystal (Newlight Photonics). The heating pulse is provided by modulating a CW Ytterbium fiber laser (IPG Photonics) operating with a pulse length of 10-20 microseconds at a repetition rate of 1 to 10 kHz. This pulse was synchronized with a selected pulse from the 1 MHz Fianium. We have found based on our measurements and finite-element models of the pulsed-laser-heated DAC [6] that heating pulses of a few microseconds are sufficient to create a maximum volume of heated sample.

The experimental imaging system (Fig. 1) is confocal, utilizing spatial filtering (not shown) so that a spot 5-10 μm at the target surface (usually a sample in the diamond cell) is imaged to a spectrometer. Similarly, the probe beams are focused at this point. The spectrometer is coupled to either an intensified CCD (Andor IStar) or streak camera (Sydor Instruments ROSS 1000), with relative timings controlled by delay generators (Stanford Research Systems DG535 and DG645).
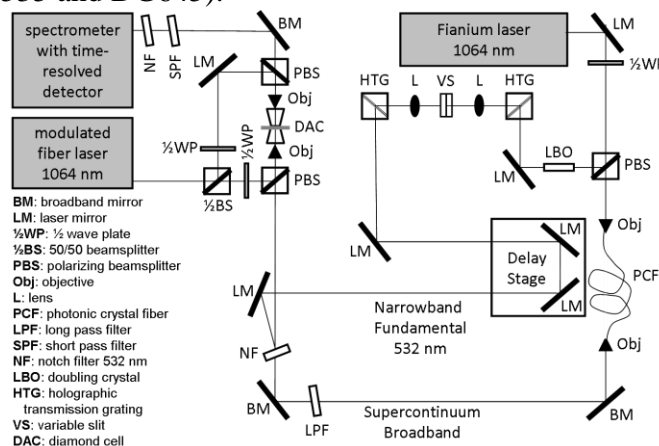

Figure 1. Diagram of experimental setup.

APPLICATIONS AND RESULTS

Transient Absorption Spectroscopy in the diamond anvil cell

The supercontinuum source described above can be used to measure time-resolved broadband optical changes in materials under high P-T conditions. For example, transient absorption spectroscopy can be achieved by synchronizing the broadband pulse, heating pulse, and detection window to effectively discriminate signal from high backgrounds. Figure 2(a) shows multiple single pulses of the supercontinuum source (indicating spectral shot to shot jitter) compared with a calibrated light source at a blackbody temperature of ~3000 K. The supercontinuum source is much brighter than the thermal source and can thus easily overcome thermal background.
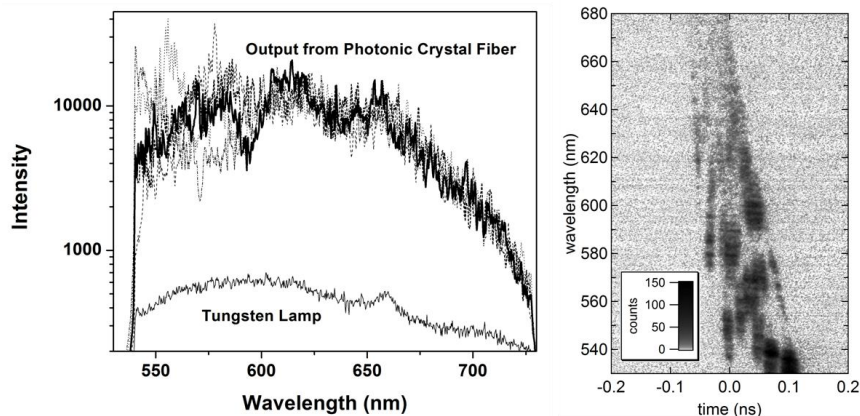

Figure 2. (a) Single pulses from the supercontinuum source (upper curves, signal duration ~100 ps) compared to radiation from a tungsten standard lamp operating at 3000 K (lower curve, signal duration ~100 μs); (b) Spectral and temporal characteristics of a single supercontinuum pulse, collected by a streak camera.

To account for the effects of broadband pulse jitter (Fig. 2), a normalization spectrum was collected for each spectrum taken on a sample to monitor and correct for jitter effects (Fig. 3a). In this study, the sample was a uniform layer of molecular oxygen, with lateral dimensions much larger than the probed spot (Fig. 3b). A reference spectrum was collected from an identical diamond cell containing a transparent layer of NaCl. The reference was used to determine the absolute absorbance of the sample (Fig. 4).

We measured thermally-induced optical absorption changes in oxygen to pressures of 60 GPa and temperatures of 1560 K (Fig. 4), conditions where strong background fluorescence is known to complicate spectroscopic studies [7]. The sample consisted of an oxygen layer (gas-loaded in a pressure vessel) separated from the diamonds using 2-3 μm layers of Al_2O_3 formed by sputtering (Fig. 3b). The oxygen sample directly absorbed the heating laser radiation under pressure due to its high absorptivity [8]. During initial heating, recrystallization of the dark oxygen formed ring structures of enhanced transmission around the laser-heated spot (Fig. 3c); however, subsequent heating was highly stable (as evidenced by the stability of emission), permitting integration over many pulses and allowing direct comparisons between measurements at different times during the heating pulse and between separate measurements of transmission and emission (Fig. 4).
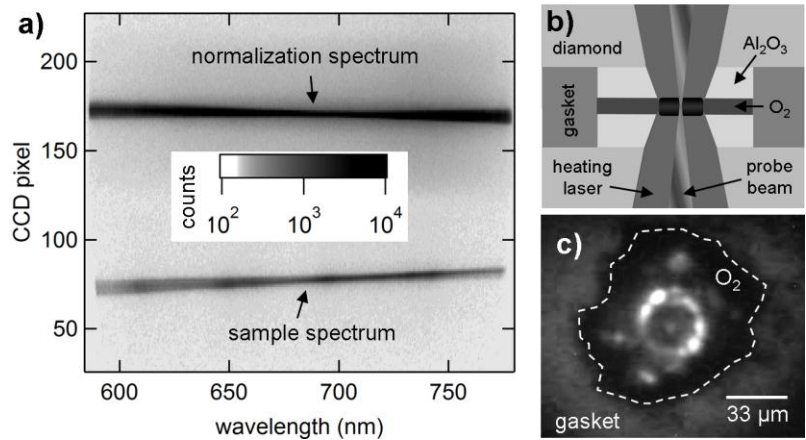
Figure 3. (a) CCD image showing pulse transmitted through sample (lower) and a normalization spectrum for the same pulse (upper) used to monitor pulse jitter; the minimum CCD gating window of 5 ns was used, and 1000 pulses were integrated on the chip at 1 kHz repetition rate. (b) Schematic of diamond cell sample showing configuration of oxygen layer, which was directly heated, and the transparent alumina insulating layers. (c) Photograph of oxygen sample after laser heating in transmitted light at 25 GPa; differences in transmission are attributed to preferred orientation of oxygen crystals [8]; the ring formed around the laser heated spot as a result of recrystallization.
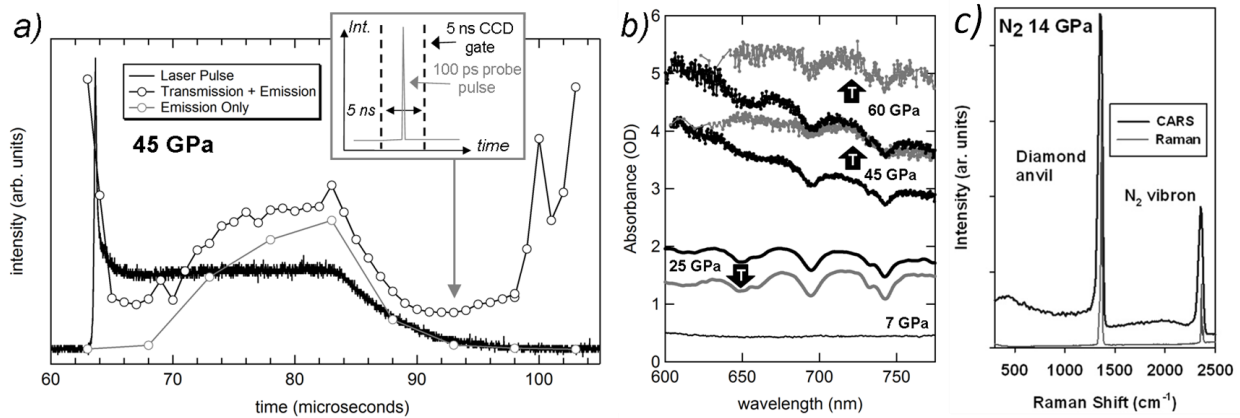

Figure 4. (a) Time history of transmission and emission at 45 GPa in O_2; inset shows timing configuration for a single data point. (b) Transient absorption spectra at room temperature (black) and at peak absorption (gray) obtained by removal of emission contributions; black arrows indicate the direction of change induced by temperature. (c) CARS spectra of N_2 under pressure compared to spontaneous Raman spectra (Stokes).

Our results show that at 25 GPa, heating increases the transparency of oxygen, consistent with the onset of melting to a fluid state with enhanced transparency at these pressures [9]. At 45 GPa and above, heating increased the opacity of oxygen. At 60 GPa, emission spectra appeared to be dominantly thermal, indicating a maximum temperature of 1560 ± 105 K in that experiment, conditions of melting for oxygen [10]. This suggests that a high pressure fluid may exhibit enhanced absorptivity, consistent with increased fluid conductivity observed in shock

wave experiments [11], or that heating excites electrons into the conduction band in the solid. Recrystallization at high temperature could also contribute to the transparency changes, given the optical anisotropy of oxygen [8] and the predictions of scattering theory [12], though the relevant changes in grain size and distribution would have to be reversible. At 45 GPa, emission is highly nonthermal [7], with an intensity even higher than thermal radiation, yet absorption studies remain possible via subtraction of background signal.

CARS spectroscopy under high pressure

Coherent Anti-Stokes Raman Spectroscopy (CARS) spectra within the DAC have been demonstrated before for both N_2 [13-14] and D_2 [15] using a broadband dye laser, requiring measurement integration times of 30-90 minutes. CARS is a nonlinear optical technique in which a pump beam ω_p, probe beam ω_{pr} (in our case $\omega_p = \omega_{pr}$) and a Stokes beam ω_s are mixed via third-order nonlinear susceptibility to generate a resonantly enhanced, phase-matched anti-Stokes Raman emission ($\omega_{as}=2\omega_p-\omega_s$). The corresponding molecular vibration has a frequency of $\omega_{mol}=\omega_p-\omega_s$. CARS has the advantage of reduced fluorescence, large signal and the potential for spatial and temporal discrimination of signal from background.

The multiplex CARS setup uses the supercontinuum from the PCF [16] along with frequency doubled light (Fig. 1). Spectral pump filtering of the frequency doubled beam is performed by spectrally dispersing light into the spatial domain via a holographic transmission grating. A 1:1 telescope collects and images the beam from one holographic transmission grating to another. The spectrum of the pump can be controlled at the Fourier plane between the lenses within the telescope, where a variable slit is used to pass a narrow portion of the spectrum corresponding to the brightest band of the doubled light. The second harmonic is made collinear with the supercontinuum using a notch filter for recombination (Semrock NF03-532E-25).

These pulses are imaged to the sample with a fast objective and a tight focusing, transmission geometry is employed. The average powers into the focusing objective are 5 mW for the green and 3.5 mW for the supercontinuum respectively. Due to the extensive spectral-temporal structure of the Stokes beam (Fig. 2b), the intensity of the various spectral modes of a sample is enhanced by controlling the delay between the pump beam and the Stokes beam. A longpass filter for the output of the PCF passes wavelengths above 532 nm (Semrock LP03-532RS-25), spectrally isolating the supercontinuum from the generated CARS signal. A notch filter (Semrock NF03-532E-25) and short pass filter (Semrock SP01-532RU-25) further isolate the CARS signal. Figure 4c shows CARS signal of solid molecular N_2 in a DAC.

As opposed to using a dye laser source for Stokes photons, our solid state infrastructure with a fiber laser and PCF offers greater potential for portability with less hazards. Our setup is also able to produce high quality spectra within ~1 minute. It is noteworthy that this technique shows no indication of nonlinear or thermally induced optical damage in either the diamonds or the samples that we tested.

CONCLUSIONS

Our results have demonstrated the potential for using ultrafast spectroscopic diagnostics incorporating nonlinear optics along with gated detectors in high-temperature, high-pressure experiments in the diamond cell. Measurement of optical and chemical properties of materials at high P-T conditions are achievable using the techniques presented here.

Our transient absorption spectroscopy technique can operate both at high temperature and under conditions of high background fluorescence (emerging either from the sample or from the stressed anvils). Our technique is novel in that it operates on very small volumes of sample required for diamond cell experiments (~5 μm diameter) and has the potential for application at ultrahigh temperatures (approaching 1 eV). Very large sample optical densities (up to optical depth of ~ 5.5) can be studied.

Currently we see two different applications for CARS within the diamond anvil cell: (1) for imaging spatially complex samples under static pressure where the enhancement of signal over spontaneous Raman could significantly reduce collection time for spatially mapping vibrational characteristics and (2) for time-resolved applications in samples under extreme pressure and temperature.

ACKNOWLEDGMENTS

REFERENCES

1. A.F. Goncharov and J.C. Crowhurst, *J. Low Temp. Phys.*, **139**, 727 (2005).
2. P. Beck, A.F. Goncharov, V.V. Struzhkin, B. Militzer, H.-k. Mao, and R.J. Hemley, *Appl. Phys. Lett.*, **91**, 181914 (2007).
3. A.F. Goncharov, V.B. Prakapenka, V.V. Struzhkin, I. Kantor, M.L. Rivers, and D.A. Dalton, *Rev. Sci. Instrum.*, **81**, 113902 (2010).
4. A.F. Goncharov, J.C. Crowhurst, V.V. Struzhkin, and R.J. Hemley, *Phys. Rev. Lett.*, **101**, 095502 (2008).
5. J.M. Dudley, G. Genty, and S. Coen, *Rev. Mod. Phys.*, **78**, 1135 (2006).
6. J.A. Montoya and A.F. Goncharov, "*Finite element calculations of the time dependent thermal fluxes in the laser-heated diamond anvil cell". submitted to J. Appl. Phys.*, (2011).
7. M. Santoro, E. Gregoryanz, H.-k. Mao, and R.J. Hemley, *Solid State Commun.*, **144**, 225 (2007).
8. S. Desgreniers, Y.K. Vohra, and A.L. Ruoff, *J. Phys. Chem.*, **94**, 1117 (1990).
9. G. Weck, P. Loubeyre, J.H. Eggert, M. Mezouar, and M. Hanfland, *Phys. Rev. B*, **76**, 054121 (2007).
10. A.F. Goncharov, N. Subramanian, T.R. Ravindran, M. Somayazulu, V.B. Prakapenka, and R.J. Hemley, *J. Chem. Phys.*, **135**, 084512 (2011).
11. M. Bastea, A.C. Mitchell, and W.J. Nellis, *Phys. Rev. Lett.*, **86**, 3108 (2001).
12. R. Apetz and M.P.B. van Bruggen, *J. Am. Ceram. Soc.*, **86**, 480 (2003).
13. H. Hellwig, W.B. Daniels, R.J. Hemley, H.-k. Mao, E. Gregoryanz, and Z. Yu, *J. Chem. Phys.*, **115**, 10876 (2001).
14. B.J. Baer and C.-S. Yoo, *Rev. Sci. Instr.*, **76**, 013907 (2005).
15. B.J. Baer, W.J. Evans, and C.-S. Yoo, *Phys. Rev. Lett.*, **98**, 235503 (2007).
16. H. Kano and H.-o. Hamaguchi, *Appl. Phys. Lett.*, **85**, 4298 (2004).