Advanced integrated optical spectroscopy system for diamond anvil cell studies at GSECARS

Nicholas Holtgrewe, Eran Greenberg, Clemens Prescher, Vitali B. Prakapenka & Alexander F. Goncharov

To cite this article: Nicholas Holtgrewe, Eran Greenberg, Clemens Prescher, Vitali B. Prakapenka & Alexander F. Goncharov (2019): Advanced integrated optical spectroscopy system for diamond anvil cell studies at GSECARS, High Pressure Research, DOI: 10.1080/08957959.2019.1647536

To link to this article: https://doi.org/10.1080/08957959.2019.1647536

Published online: 01 Aug 2019.
Advanced integrated optical spectroscopy system for diamond anvil cell studies at GSECARS

Nicholas Holtgrewe, Eran Greenberg, Clemens Prescher, Vitali B. Prakapenka* and Alexander F. Goncharov

aCenter for Advanced Radiation Sources, University of Chicago, Chicago, IL, USA; bPhoton Sciences, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany; cGeophysical Laboratory, Carnegie Institution of Washington, Washington, DC, USA

ABSTRACT
Raman and optical spectroscopy are versatile tools for nondestructive characterization of a wide range of properties of novel materials and minerals in situ at extreme and ambient conditions. These techniques are genuinely complementary to X-ray tools (diffraction and spectroscopy) in the probe energy, momentum transfer, and time scale, making concomitant X-ray and optical probes available for advanced sample analysis. We have built a state-of-the-art, user-friendly integrated Raman and optical spectroscopy system at Sector 13 (GeoSoilEnviroCARS, University of Chicago, IL) of the Advanced Photon Source (APS), Argonne National Laboratory (ANL), where optical probes are available now in combination with high resolution in-situ synchrotron X-ray diffraction and spectroscopy tools (XRD, IXS, XES, NFS, and others) for extensive sample investigation. The integrated optical system enables a variety of techniques including multi-colored (five laser lines: 266, 473, 532, 660, and 946 nm) confocal Raman, fluorescence, and optical spectroscopy from ultraviolet (UV) to near infrared (IR) spectral ranges (266–1600 nm), and Coherent Anti-Stokes Raman spectroscopy (CARS) in combination with near IR double sided laser heating.

ARTICLE HISTORY
Received 21 May 2019
Accepted 21 July 2019

KEYWORDS
Raman spectroscopy; laser heating; diamond anvil cell

Introduction
Optical vibrational and electronic spectroscopy is a useful tool to probe electronic and atomic structure, chemical bonding, and vibrational, elastic, and thermodynamic properties. Such spectroscopic measurements of materials applied under extreme conditions provide unique information about changes in structure, bonding, thermochemical and other properties. These investigations have a broad applicability to several disciplines including studies of the Earth’s and planetary interiors, synthesis of novel materials, nanoscience/nanotechnology, physics and chemistry of materials under extreme conditions, etc. The spectroscopic techniques are uniquely complementary and often indispensable (e.g. in case of light elements) to synchrotron X-ray diffraction (XRD) and
spectroscopy, as well as neutron diffraction methods that are commonly used to determine the structure and a range of material properties. Raman spectroscopy is one of the major analytical tools to probe these material states and has been widely used for the last four decades to study materials under extreme conditions of high pressure and variable temperature (P-T) and to characterize the materials at ambient pressure [1–8]. This technique has important advantages of being noninvasive, nondestructive, fast, easily interpretable, and highly informative about the material’s structural, chemical, and electronic states.

The advent of synchrotron X-ray sources has made profound advances in understanding properties of geological and planetary materials under variable P–T and compositional environments and in characterization of novel materials of interest to industry and technology [9–11]. Synchrotron XRD facilities across the world have been a staple for sample characterization, however often this data is inconclusive, while complementary spectroscopic techniques are unavailable at the time of X-ray experiments. Thus, most times this spectroscopic analysis is performed separately at a home facility with different samples due to the destructive/hysteretic nature of material compression and decompression at the XRD beamlines. The GeoSoilEnviroCARS (GSECARS, University of Chicago) beamline (Sector 13) at the Advanced Photon Source (APS) in Argonne National Laboratory (ANL) is committed to solving this issue by providing users a variety of advanced analytical techniques to enhance data collection quality and efficiency at the facility. Here we address this problem by building an off-line Raman/optical integrated instrument, where the same samples being investigated by XRD and/or XES can be also probed by optical techniques at identical or very similar P-T conditions. The advanced optical system described in this work was constructed at GSECARS and consists of spectroscopic techniques optimized for (but not limited to) diamond anvil cells (DACs) to fully characterize samples in-situ and in combination with the X-ray data collection. This paper will focus on the detailed descriptions of the optical layout, multi-colored confocal Raman system, Raman mapping features, near IR laser heating, Coherent Anti-Stokes Raman spectroscopy (CARS) system, and additional software tools for data analysis.

Overview

Raman and optical spectroscopy tools in applications to experiments at extreme conditions must have high spatial resolution and be very versatile. This is dictated by a great variability of material properties at a wide range of extreme P-T conditions that include changes in electronic and crystal structure, bonding length and type, amorphization, melting, etc. that all affect substantially the spectral characteristics and the optimal conditions of their collection. Moreover, the optical and vibrational properties of diamond anvils change drastically with pressure and temperature, making it necessary to create appropriate provisions for overcoming the adverse effects (e.g. stress induced fluorescence [12,13]). Many of these problems can be addressed and mitigated by choosing the most appropriate excitation wavelength, objective lens type, spectrometer grating, laser power, etc. [7,14]. For example, to avoid diamond and sample fluorescence caused by defects in electronic levels, which is often within the visible spectrum, one can use either UV or near IR excitations [15,16]. To increase the efficiency of the Raman scattering one should choose as short of an excitation wavelength as possible, as it is proportional to
the fourth power of the excitation frequency, $\nu_{\text{exc}}^4$. On the other hand, high energy photons may destroy sample, while use of longer excitations wavelengths (low energy photons) are less destructive and allows achieving higher spectral resolution routinely. To excite ruby fluorescence at high pressure a variety of different excitation wavelengths may be needed, and additionally time resolved measurements could be advantageous [17,18]. The vibrational excitations often reveal resonance behavior when the laser quantum energy becomes close in energy to the electronic excitation energy or the electronic bandgap [19–21]. This resonance behavior can be utilized to determine changes in the electronic structure of the materials under pressure including metallization via the band gap closure.

In designing our system, we had the above considerations in mind to make a provision for as broad as possible user community and users with different levels of expertise. The system presented here enables Raman studies for a range of excitation wavelengths varying from UV (266 nm) through visible (473, 532 and 660 nm) to near IR (946 nm). These capabilities are supported by the choice of special optics, spectrometer diffraction gratings, and the detectors; all of which provide the Raman coverage up to at least 4500 cm$^{-1}$ for all excitation wavelengths. With the exception of the UV 266 nm excitation, the Raman spectra can be extended down to approximately 10 cm$^{-1}$ due the use of solid state volume Bragg filters [22]. One other extremely important feature of such operation is the ability to perform Raman (and also CARS and optical spectroscopy) measurements from the same sample position. In the system, this is realized via an automatic change of the laser wavelength, which includes change of the interface optics for the laser excitation and signal collection optical paths. All these features enable the most versatile Raman operations. In addition to conventional spontaneous Raman spectroscopy, the new system provides an access to multiplex CARS spectroscopy, which involves a non-linear three-wave stimulated mixing process, thus effectively increasing the efficiency of the scattering process via its coherent nature. This technique (as well as conventional Raman) can be combined with a near IR laser for double-sided sample heating. Moreover, a white pulsed brilliant CARS supercontinuum light source can be used for optical transmission and reflectance spectroscopy to probe the materials electronic properties in situ [23–26].

**Optical layout**

The full layout of the instrument on a 5’ $\times$ 7’ optical table (Newport Integrity 2) is shown in Figure 1, a top-view of a 3D model of the table [27] (a) and an image of the table with the enclosure doors open (b). Note that all lasers are located along the far wall and are well blocked by individual enclosures with interlocked shutters in addition to the enclosure doors and ceiling. Each enclosure door is linked to an interlock system that blocks the exposed beam by disabling the laser shutters if the user attempts to open the enclosure while a beam is exposed. A description of each laser line path will follow in the next subsections, but the general sample area is broken into three sample stations: General Raman, Ultra-Violet (UV) Raman, and Advanced (Laser Heating/CARS). The user has the option to choose between any of these three sample positions by using the horizontal movement of the sample stage (S1). The sample mounts are identical to DAC holder mounts used at the Sector 13 and other APS beamlines (BKL-4 kinematic base with DAC holders positioning...
sample at 3.5 in. from base plate surface), allowing for easy transfer of the sample between APS X-ray beamlines and the Raman spectrometer. Additionally, there are custom mounts for any type of free-standing samples. Visualization of the sample is accomplished by semi-transparent pellicle mirrors (Figure 1(a), P) that guide the lights toward the sample and the collected image toward a camera. The pellicle mirrors near the objective lenses are mounted on motorized flip mounts to avoid the signal path during collection. Alignment of the
pellicle mirrors was done visually with a standard sample (e.g. silicon) to make the sample image and laser spot confocal with the spatial filter (i.e. projection of pinhole onto the sample). Only minor adjustments of the spatial filter and sample imaging were optimized for maximum signal. A comprehensive list of the spatial filter sizes is shown in Table 1 for each excitation wavelength and objective lenses. Detection of signals is accomplished using the Princeton Instruments Acton Series 2500 (focal length = 500 mm) spectrograph in combination with three gratings: 1800 (UV enhanced), 1200, and 300 grooves/mm and two detectors: UV-enhanced PIXIS100 (200–1000 nm) and NIRvana (850–1600 nm). A comprehensive chart showing the grating efficiencies, detector ranges, and Raman collection ranges (0–4500 cm$^{-1}$ for each excitation laser) is shown in Figure 2. Additionally, the maximum powers for each excitation laser and percent attenuation due to optics in the system is shown in Table 2.

**General Raman**

The general Raman sample station is meant for users to take routine Raman measurements that do not require any advanced techniques (e.g. laser heating) but still provide the same high-quality data collection as the Advanced station. This is the most versatile position as the user has the option for four different excitation lasers (single frequency narrow band 946, 660, 532, and 473 nm with the bandwidth <0.03 nm) as well as four different long working distance objective lenses (5x, 10x, 20x, and 50x). The objective lenses are mounted onto a kinematic Mitutoyo manual turret for convenient usage. The optical path of each excitation laser is shown in Figure 1(a) and is indicated by its assigned color: gray, red, green, and blue for 946, 660, 532, 473 nm laser wavelengths, respectively. Each line follows the same design where the excitation beam is guided toward a 300 mm translation stage holding an optical breadboard containing specific optical components for individual laser frequencies. In Figure 1(a), only the 660 nm line is shown to be complete, however moving the translation stage in 3′′ steps to the left selects other laser excitations. Changing between excitation lasers is limited by warming up the laser and repositioning of this translation stage, typically a few minutes or faster. Following the 660 nm line, the laser beam is expanded by two lenses to a 6 mm diameter and guided toward the translation stage with protected silver mirrors (Note: all mirrors are protected silver mirrors unless indicated otherwise). On the translation stage, the beam is reflected off a notch filter (NF) (OptiGrate) and guided off the translation stage and toward the sample. The beam is then focused down onto the sample with the user selected objective lens and the backscattered light is collected, following the same path as before back to the notch filter. The notch filter is angled to where it blocks the excitation frequency optimally.

<table>
<thead>
<tr>
<th>Objective Lens Magnification</th>
<th>946 nm</th>
<th>660 nm</th>
<th>532 nm</th>
<th>473 nm</th>
<th>266 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5x</td>
<td>75 µm pinhole</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>10x</td>
<td>50 µm pinhole</td>
<td>75</td>
<td>16</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>20x</td>
<td>20x (LH)</td>
<td>8</td>
<td>8</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>50x</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>20x (LH)</td>
<td>8</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Note: LH = laser heating objective lens.
but allows the Raman signal to pass. This signal is then sent through a spatial filter, composed of two achromatic convex lenses (L) and a pinhole (PH) optimized for the spectral range of the signal of interest, and two additional notch filters before being focused into the spectrograph with a 75 mm achromatic convex lens for detection. An example of all four excitations being used is shown in Figure 3, where elemental sulfur is analyzed. This shows the low Raman frequencies, for both Stokes and Anti-Stokes frequencies, the system is capable of detecting (estimated to be less than 10 cm$^{-1}$ for all the excitation wavelengths) and spectral resolution of the instrument. An example of ultra-high pressure application of the system is shown in Figure 4, where the diamond edge is located around 1686 cm$^{-1}$ corresponding to a pressure of 197 GPa and a few sample peaks are clearly visible. In addition to Raman measurements, the system is also capable of detecting ruby fluorescence for pressure measurements with a <1 mW supplementary class-II broadband 532 nm laser that can enter the green beam path using pneumatic switches.

**Polarized Raman**

As of the time of this publication, the 660 nm laser line is the only line that has been adapted for polarized Raman spectroscopy. The addition of a rotatable half-wave plate

<table>
<thead>
<tr>
<th>Excitation line (nm)</th>
<th>Maximum power (mW)</th>
<th>Attenuation due to optics (not including objective lens)</th>
</tr>
</thead>
<tbody>
<tr>
<td>660</td>
<td>500</td>
<td>~20%</td>
</tr>
<tr>
<td>532</td>
<td>2000</td>
<td>~20%</td>
</tr>
<tr>
<td>473</td>
<td>350</td>
<td>~40%</td>
</tr>
<tr>
<td>946</td>
<td>200</td>
<td>~50%</td>
</tr>
<tr>
<td>266</td>
<td>200</td>
<td>~30%</td>
</tr>
</tbody>
</table>
near the output of the laser and a rotatable linear polarizer before the spectrograph allows for all four parallel/cross laser polarization orientations, using Porto’s notation [28]: X(YY)X, X(YZ)X, X(ZZ)X, and X(ZY)X. An example of LiNbO₃ Raman signal using all these orientations is shown in Figure 5, which can be compared to previous observations [29]. This feature is a vital tool for characterization of single crystals and liquids as it provides an assignment of various vibration modes due to their selectivity to polarization selection rules (e.g. Ref. [30,31]).

**UV Raman**

The UV Raman path is separate from the other laser excitation paths due to the use of special UV optics (i.e. all mirrors are aluminum enhanced mirrors and lenses are made

![Figure 3](image)

**Figure 3.** Raman spectra of elemental sulfur (S) taken using different excitation wavelengths $\lambda_{ex} = 946$, 660, 532, and 473 nm.

![Figure 4](image)

**Figure 4.** Raman spectrum of a metal hydride at 197 GPa. Collection details: 20 s exposure time, 300 grooves/mm grating, 20x objective lens, $\lambda_{ex} = 660$ nm, 50 mW, PIXIS detector.
of quartz). The 266 nm beam is produced by frequency doubling (Coherent MBD200) the output of a 532 nm laser (Coherent VERDI V2) and is expanded and guided toward a broadband polarized cube beamsplitter, where the power is selected by rotating a half-waveplate prior to the cube. The beam is sent toward the quartz objective lens (Mitutoyo Plan UV Infinity Corrected 10x) where it is focused down onto the sample and the backscattered Raman signal is collected following the same path back to the polarized cube beamsplitter. The signal is then sent through a spatial filter, similar to the general Raman lines, and razor edge filter to reject the excitation line prior to entering the spectrograph in a different entrance port than the other Raman lines. The Raman spectra can be measured down to 230 cm\(^{-1}\) for the UV Raman part of the system that is limited by available UV laser line filters. An example of UV Raman spectra are diamond and sapphire shown in Figure 6. In the case for diamond, the background fluorescence is substantially reduced resulting in clear detection of the first and second ordered signals for diamonds, which are highly fluorescent in the visible spectral range. In addition to fluorescence avoidance, other benefits to UV Raman include increased scattering efficiency and resonance Raman spectroscopy as mentioned above. It is worth noting that in case of high pressure studies with DACs the upstream diamond anvil must be of the Type II variety, as to allow low absorbance of the 266 nm excitation beam/collected signal. There are no specific limits for free standing samples except special attention should be taken for laser power control with available range of 1–200 mW as high energy UV photons may destroy samples.

### Raman mapping

In combination with all the spectroscopic techniques, there is the ability to perform a Raman map for a user-defined region. The motorized sample mount is computer controlled with all three XYZ axes and can thus move the sample incrementally in a grid-like pattern (rectangular or square). An example of one XY Raman map taken at 532 nm excitation is given in Figure 5.
Figure 6. UV ($\lambda_{ex} = 266$ nm) Raman spectra for diamond (left) and sapphire (right). For diamond, the UV Raman (purple) is compared with 473 nm excitation (blue), which contains the Raman signal with an undesirable fluorescence background.
Figure 7. The map is a grid (Figure 7, inset) where each square represents an integrated intensity distribution that is a user-defined Raman shift frequency range (Figure 7, red box), typically the full-width half maximum of an identifying feature (vibron, roton, etc.) of the sample. In Figure 7, the sample was an iron oxide at high pressure that was analyzed post laser heating with the map representing the intensity of the Raman feature at \( \sim 150 \text{ cm}^{-1} \). The map clearly indicates regions that were heated (purple spectrum) and unheated (blue spectrum), allowing the user to visualize the laser-heated area. The spatial resolution of the Raman mapping is dependent on the choice of both laser excitation wavelength and objective lens magnification, with the lower excitation wavelengths and higher magnifications giving the highest resolution.

**Advanced (laser heating/CARS)**

The third sample position (Figure 1(a)) is reserved for more advanced techniques, such as IR laser heating [32,33] and CARS [23,34]. It is composed of two objective lenses (Mitutoyo near IR 20x) allowing for both double-sided laser heating and CARS which relies on transmission geometry. All excitation lasers listed in the general Raman path can be used in the Laser Heating/CARS path by use of one flip mirror (Figure 1(a), FM1) that picks off the input laser. The laser heating is accomplished by a linear polarized 100W near IR (1064 nm) laser (IPG Photonics 1YLR-100-1064-LP) that is shaped into a flat-top profile by a Pi-shaper (AdlOptica) and divided into two beams by a polarized cube beamsplitter. The power ratio between both sides of the sample can be adjusted by a single half-waveplate prior to the beamsplitter. These two beams are guided into the sample by a pair of 1064 nm dichroic mirrors (Semrock). Temperature detection is accomplished by using the corresponding Raman optical path, moving grating positions and motorized mirror

![Figure 7](image.png)

**Figure 7.** Example of a Raman map generated in the updated T-Rax software of laser-heated LiFe₅O₈ ordered spinel at 15 GPa (heated to 1600 K, quenched to 300 K). The 7×7 grid (inset) represents the user-defined map (2 \( \mu \)m step size) for a total of 49 Raman spectra (two spectra shown on the plot). The normalized intensity of each square (scale-bar left inset) is directly related to the Raman frequency at \( \sim 150 \text{ cm}^{-1} \) (red box), showing the location of unheated (blue square) and heated regions of sample (purple square). Collection details: 10 s exposure time, 1200 grooves/mm grating, \( \lambda_{\text{ex}} = 660 \text{ nm} \), 100 mW, PIXIS detector.
flipping. For example, in Figure 1(a), if the temperature from the down-stream side of the sample is desired, the pellicle mirrors would flip out and mirror FM2 would flip into the optical path. The collected thermal radiation signal would then be sent to the spectrograph through the user defined laser line path.

Coherent Anti-Stokes Raman spectroscopy (CARS) is a technique of choice when stronger signals selective for the materials of interest are needed. This method can also be combined with laser heating to provide information that can be difficult to obtain with standard Raman plus laser heating in a diamond anvil cell. The CARS signal is generated through a three-wave mixing process between the $w_{\text{pump}}$, $w_{\text{probe}}$, and $w_{\text{stokes}}$ frequencies [34]. In this system we utilize a pulsed supercontinuum light source with a 532 nm output (LEUKOS, 1 ns, 33 kHz), where the supercontinuum ($w_{\text{stokes}}$) and 532 nm ($w_{\text{pump}}$ and $w_{\text{probe}}$) beams are overlapped spatially and temporally to achieve maximum intensity of the CARS signal. As the name implies, CARS probes the enhanced Anti-Stokes vibrational signal, which is always higher in energy than the excitation laser frequency and hence avoids background contamination from fluorescence and/or certain high temperature conditions. An example of CARS signal taken in the optical system is high pressure nitrogen (N$_2$, 22 GPa) at room temperature, shown in Figure 8, with the N$_2$ vibrons in agreement with previous reported data [35].

Software

The entire system is computer controlled using the Experimental Physics and Industrial Control System (EPICS), which integrates with the data collection software LightField (Princeton Instruments).

Preliminary data analysis is performed using the T-Rax software (http://www.clemensprescher.com/programs/t-rax). T-Rax is a Python based software which provides the capability to:

1. Obtain temperatures during laser heating by fitting a Planck curve to the spectro-radiometric measurement signal for both sides and as a temperature series when multi-frame
data has been recorded. In order to estimate temperatures, the measured signal has to be corrected for the optical system response. In T-Rax, two procedures are implemented. The calibration of the system can be achieved by measuring either a spectrum of a source with a known intensity at each wavelength (etalon) or a source with black body radiation at a known temperature. Different calibrations for e.g. multiple setups or different calibration sources can be saved and restored on the fly for fast comparison.

2. Obtain pressure in the sample chamber by fitting the position of ruby fluorescence peaks or the position of the diamond edge, whereby the several different available pressure calibrations can be selected.

3. Compare Raman spectra using overlays or combined with the above-mentioned mapping feature.

In all the different modes of T-Rax the region of interest of the detected image in the spectrometer can be selected graphically. T-Rax makes heavy use of the existent scientific open source Python infrastructure. The graphical user interface (GUI) is written using the PyQt5 library (www.riverbankcomputing.com/software/pyqt), which provides Python bindings for the Qt5 library (www.qt.io). We chose to use PyQt-Graph (http://www.pyqtgraph.org) for plotting images and spectra.

**Conclusion**

We have designed and built the integrated optical system combining in one instrument Raman spectroscopy with five excitation wavelengths (266, 473, 532, 660, 946 nm), double sided IR laser heating, coherent anti-Stokes Raman scattering, and broadband (200–1600 nm) high-efficiency optical laser spectroscopy (with a supercontinuum laser source above 400 nm). The system is optimized for sample characterization in situ at extreme conditions in the diamond anvil cell (DAC) but could be also used for free-standing samples as well. Utilizing a compact custom-designed cryogenic high pressure system, that is currently under development at GSECARS, we will be able to study optical properties of materials at temperatures down to 10 K.

The advanced optical system for materials and minerals research under extreme pressure and temperature is fully operational and located at the GSECARS, Sector 13, APS, ANL. It is available for users through the APS GUP proposal system if it is a part of beamline proposal or upon submitting a request at the GSECARS website (https://gsecars.uchicago.edu). It is expected that the additional spectroscopic data acquired with this system will complement X-ray synchrotron data collected at various beamlines at APS as well as enhance the user’s individual projects.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by NSF MRI proposal (EAR-1531583). The system is located at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation – Earth Sciences (EAR –
and Department of Energy-GeoSciences (DE-FG02-94ER14466). The Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This work was also supported by DOE – Geosciences and DOE Office of Science by ANL.

References


