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Structural and optical responses of molecular solids to swift heavy ion irradiation under high pressures

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1 Experimental

1.1 Platform for SHI irradiation und high static pressures

This platform is installed at a beamline of the heavy ion synchrotron (SIS18) operated by the GSI Helmholtz Center for Heavy Ion Research (Darmstadt, Germany), enabling the ion irradiation of miniaturized samples in diamond anvil cells (DACs) and provides integrated online diagnostics, including optical microscopy and Raman spectroscopy, for real-time monitoring of structural changes during stepwise fluence accumulation. To protect the diamond anvils from direct exposure, the ion beam passes through a collimation setup consisting of a pair of adjustable slits made from WC cubes with sub-millimeter openings. To achieve accurate targeting, the DAC is mounted on a motorized stage that allows precise alignment of the beam collimator and the DAC position. The DAC is oriented such that the ion beam reaches the sample chamber by passing through the gasket, while optical access through the diamonds remains free for analysis. The technical details of the platform are described elsewhere[1].

1.2 DAC preparation

All experiments were carried out using Boehler–Almax plate DACs[2] equipped with Type Ia diamond anvils having 350 μm culets. To minimize the travel distance of the ions through the gasket, stainless steel gaskets were trimmed, leaving a remaining distance of approximately 2 mm from the edge of the gasket to the center of the gasket hole. The gaskets were first pre-indented to a thickness of about 50 μm, followed by laser drilling of a 100 μm diameter hole at the center to serve as the sample chamber. The precise distance between the gasket edge and the hole was measured using a 3D microscope. This distance is essential for calculating the ion energy loss within the gasket and for determining the initial beam energy required for reaching the sample. A small ruby sphere was placed into the chamber for pressure calibration by monitoring of the R1 fluorescence line[3]. Pressure was applied using a manual gearbox. A gas mixture containing 25 vol% CO in helium was supplied by Air Liquide and loaded into the sample chamber using a custom-built gas-loading system. The presence of helium enabled gas loading in our autoclave-based system, thereby avoiding handling toxic CO directly. Under high-pressure conditions, phase separation occurs between CO and helium[4]. One DAC was compressed to 4.2(2) GPa for irradiation, while another DAC loaded with the same CO-helium mixture was compressed to 8.7(3) GPa as a control experiment. Two additional DACs were loaded with multiple samples each, including urea (Alfa Aesar, 99.3+%) and sulfur (Sigma-Aldrich, 99.9%), using argon as pressure transmitting medium (PTM) to maintain quasi-hydrostatic pressure conditions. The pressures applied to these two DACs were 1.1(2) and 7.1(3) GPa.

1.3 SHI irradiation experiments

The irradiation experiments were carried out at Cave A with ^{238}U beams provided by the synchrotron SIS18 accelerator of GSI. The energy of the ion beam was 258 MeV/u for the DAC filled with CO-helium mixture, 165 MeV/u for the DAC filled with urea and sulfur at

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1.1(2) GPa, and 170 MeV/u for the DAC filled with urea and sulfur at 7.1(3) GPa. No presssure change was observed after irradiation. The ions passed through various in-beam components[1] including, e.g., the beamline exit window and the gasket before reaching the sample chamber. The process for calcualting the required initial beam energy, accounting the energy losses of all component the ions have to traverse before reaching the samples is detailed in the paper[1]. The initial energy of the ions is reduced to around 30 MeV/u upon reaching the sample with a corresponding energy loss in CO of 6.2 keV/nm (assumed density = 0.8 g/cm^3), urea of 10.1 keV/nm (density = 1.3 g/cm^3) and sulfur of 15.6 keV/nm (density = 2.0 g/cm^3).

1.4 Analysis by Raman spectroscopy

Off-line Raman measurements before and after the irradiation experiments were performed using an Oxford Instruments WITec alpha 300 R Raman microscope equipped with an Olympus SLMPlan N 50× objective lens. A 532 nm excitation laser was used, providing a focused spot of approximately 0.8 μm in diameter and an output power of 1 mW. The Raman spectra were acquired with either a 600 or 1800 g/mm grating mounted in the WITec UHTS 300S (VIS-NIR) spectrograph, which was coupled to an Andor DR316B-LDC-DD CCD detector. Raman measurements at multiple locations across each sample revealed no significant spatial variations.

In situ Raman spectra were collected during short beam stops using Horiba, iHR320 instrument with a 532 nm excitation laser (P=10–20 mW) and a thermoelectrically cooled CCD camera[1].

1.5 UV-Vis absorption spectroscopy

UV-Vis absorption spectra of the samples within the DACs were recorded using a custom-built spectroscopic setup. The system is equipped with a DH-2000 deuterium-halogen light source covering the 190–2500 nm range and an Ocean Optics Maya2000Pro spectrometer for signal acquisition. The beam size was around 10 μm. The data were collected with the OceanView 2.0 spectroscopy software.

2 Figures

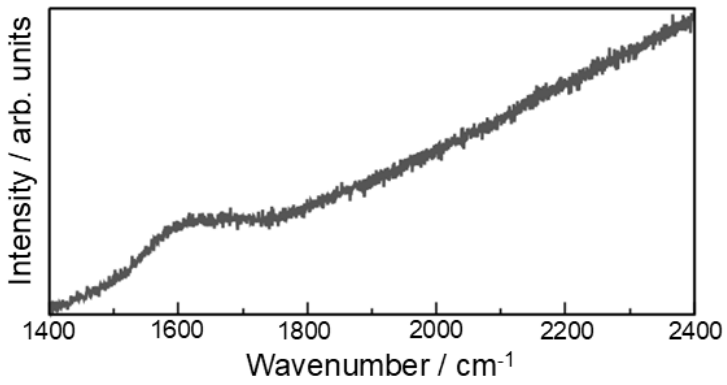

Fig. S1 Off-line Raman spectrum of pressure-induced p-CO at 8.7(3) GPa.

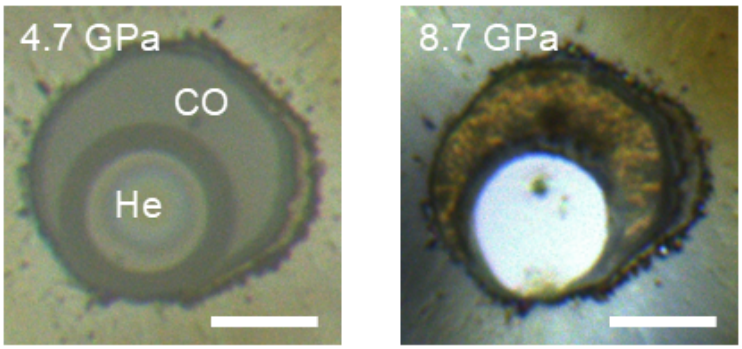

Fig. S2 Optical images of CO at different pressures without SHI irradiation. The scale bar is 50 μm.

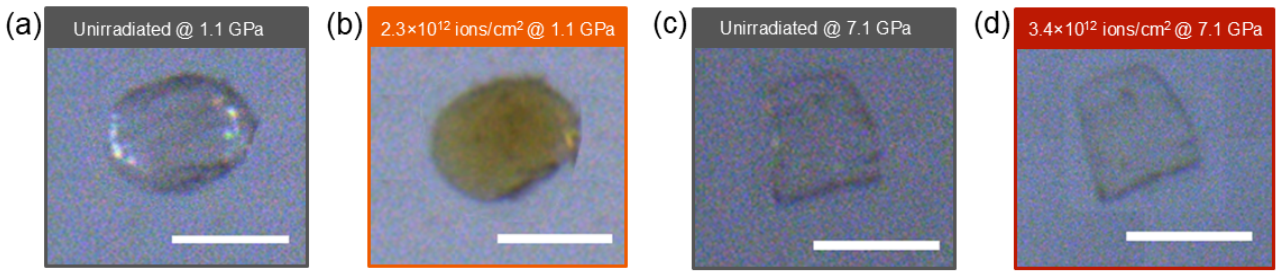

Fig. S3 Off-line optical images of urea at 1.1(2) GPa (a, b) before and after irradiation with fluence up to 2.3×10^{12} ions cm^{-2} and at 7.1(3) GPa (c, d) before and after irradiation with fluence up to 3.4×10^{12} ions cm^{-2}. The scale bar is 50 μm.

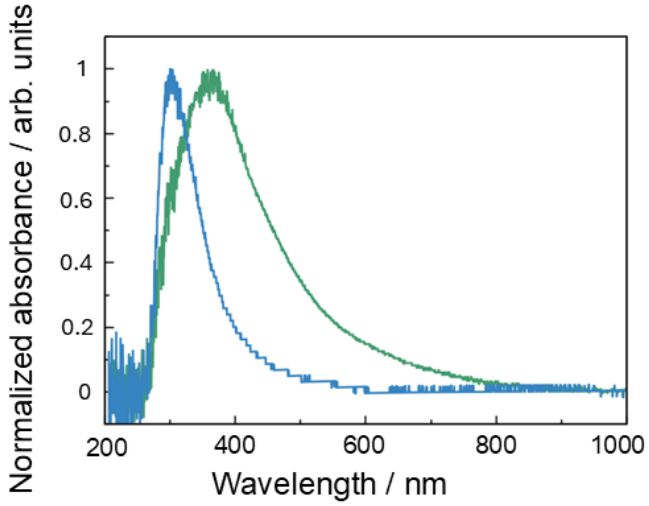

Fig. S4 Absorbance spectra of urea after SHI irradiation at 1.1(2) GPa (green curve) with fluence up to 2.3×10^{12} ions cm^{-2} and 7.1(3) GPa (blue curve) with fluence up to 3.4×10^{12} ions cm^{-2}.

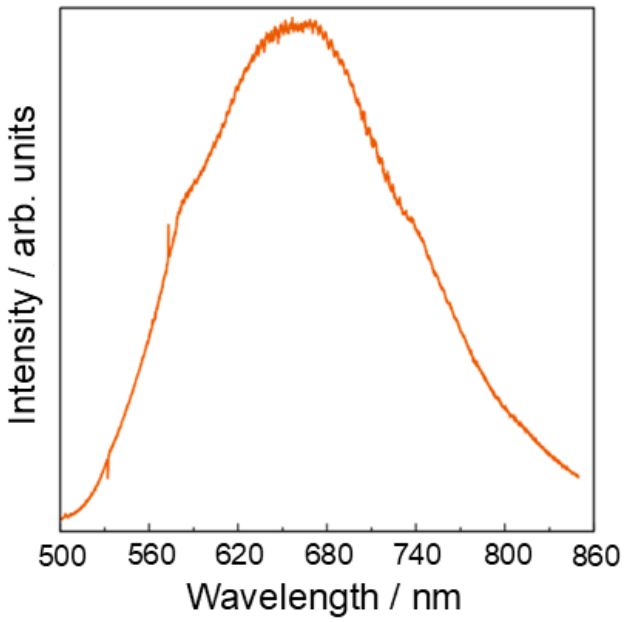

Fig. S5 Fluorescence spectrum of urea after SHI irradiation (2.3×10^{12} ions cm^{-2}) at 1.1(2) GPa excited by a 532 nm laser.

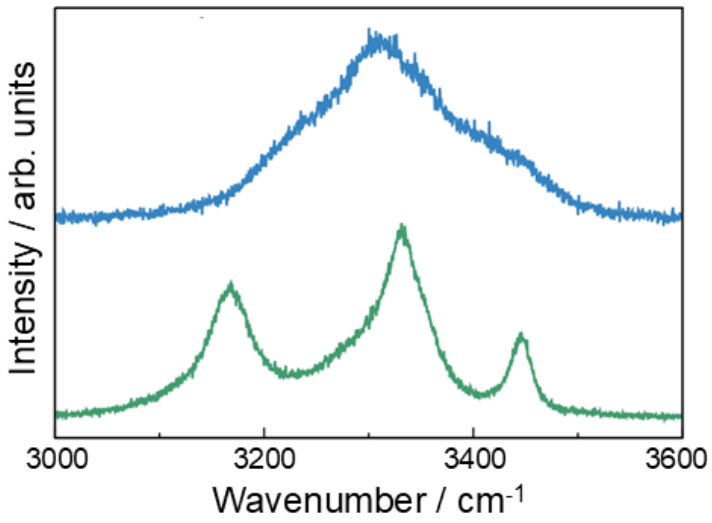

Fig. S6 Off-line Raman spectra of urea at 1.1(2) GPa (green curve) and 7.1(3) GPa (blue curve) before SHI irradiation.

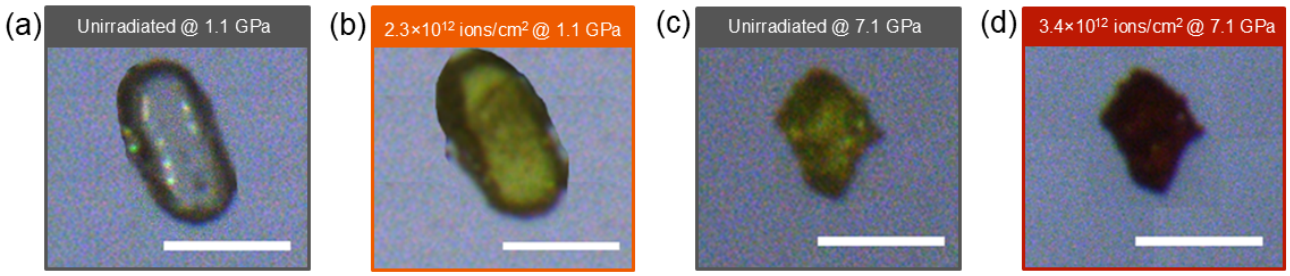

Fig. S7 Off-line optical images of sulfur at 1.1(2) GPa (a, b) before and after irradiation with fluence up to 2.3×10^{12} ions cm^{-2} and at 7.1(3) GPa (c, d) before and after irradiation with fluence up to 3.4×10^{12} ions cm^{-2}. The scale bar is 50 μm.

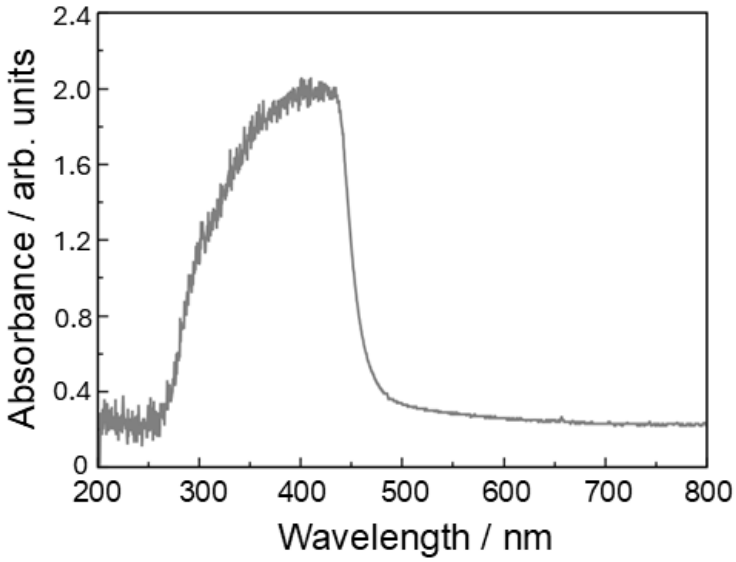

Fig. S8 Absorbance spectrum of sulfur after SHI irradiation (2.3×10^{12} ions cm^{-2}) at 1.1(2) GPa.

Notes and references

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