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## High-Pressure Synchrotron Infrared Spectroscopy: An Integrated and Dedicated Facility at the NSLS

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### Objectives

The goal of the project has been the construction of a versatile facility for measuring far-to near-infrared spectra of natural and synthetic materials from ambient to ultrahigh pressures at variable temperatures using new synchrotron infrared microspectroscopy techniques. The measurements address a broad range of problems in Earth and planetary science.

### Project Description

An integrated synchrotron facility dedicated to high-pressure spectroscopy and microspectroscopy from far-infrared (IR) to visible wavelengths has been constructed at beam line U2A of the National Synchrotron Light Source (NSLS). A high-performance spectrometer was installed, along with new high-pressure (long working-distance) microscopes adapted for diamond-anvil cells, and a commercial, high-magnification infrared microscope for 1-bar and low-pressure experiments. Together with our high-pressure x-ray facilities at the NSLS, the new facility provides the opportunity for users to conduct synchrotron IR, synchrotron x-ray, and other optical experiments on the same samples, representing a unique and unmatched level of integration in high-pressure and synchrotron techniques. The facility is permitting new classes of high-pressure studies of hydrogen and related planetary materials; minerals of the Earth's crust, mantle, and core; geochemical reactions; glasses and melts; surfaces and interfaces; whole-rock samples; and new high-pressure technological materials.

### Description of Facility

The U2A synchrotron facility at the NSLS has been built that includes equipment for measuring optical properties of materials in a wide spectral range (far-IR to visible) integrated with a laser Raman/fluorescence system for sample characterization. The facility is enclosed in a separate hutch placed 10 meters from the bending magnet of the storage ring. The synchrotron radiation is collected with a 40 x 80 mrad aperture and focused by elliptical mirrors on the diamond window, which separates high- and low-

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vacuum compartments. In the mirror box (low vacuum) the radiation is split and collimated separately by two user facilities (U2A and U2B).

The collimated synchrotron beam is brought to the U2A facility through a pipe vacuum system, which encloses adjustable mirrors from outside steering mirrors. This system is a part of the mirror box vacuum system and separated from the down-stream IR facility by two-way changeable-under-vacuum IR filter assembly. The IR facility consists of a Bruker IFS66v vacuum bench equipped with a commercial IRscope II (infrared microscope) and visible to far-IR accessories (50-25000 cm<sup>-1</sup>). The entrance port of the spectrometer has been rebuilt to accommodate the collimated synchrotron beam input. The modulated IR beam of the chosen spectral range, which comes out of the Bruker bench, is directed to the IRscope II or dedicated custom-built high-pressure IR microscopes.

The Bruker microscope features

- changeable magnification (x15 and x32)
- confocal apertures
- absorption-reflectivity measurements
- visible-to-far IR detectors
- mid-IR polarizers
- motorized x-y stage for mapping

The custom microscope is designed specifically for high- and ultrahigh pressure experiments. It features

- changeable refracting visible (Mitutoyo) or pure reflecting IR (Cassegrain) objective lens
- matching of numerical aperture to ultrahigh-pressure diamond anvil cells
- diamond lens for collection of transmitted light through long-piston cylinder diamond cell
- confocal apertures
- absorption-reflectivity measurements
- visible-to-far IR detectors
- mid- or far IR polarizers
- in situ Raman, fluorescence (e.g., for ruby pressure measurements) and visible transmission measurements. This auxiliary facility includes visible-near IR Ar ion / Ti:Sapphire laser, tunable/changeable laser bandpass filter, notch tunable/changeable rejection filters, single stage 0.46 m imaging spectrograph equipped with changeable low- high dispersion gratings and an array CCD detector.
- continuous-flow He/N<sub>2</sub> cryostat with changeable at low T mid IR-to-far IR windows

### Summary of Experiments

This facility has led to a series of studies of materials at ultrahigh pressures, including the discovery of a number of unexpected phenomena in dense hydrogen, such as a striking intensity enhancement of the (formally forbidden) intramolecular stretching mode [1] and new classes of excitations in the solid [2, 3], and accurate bounds on metallization at megabar pressures [4]. The system is rich in physical phenomena and continues to be a

critical testing ground for planetary modeling. Additional discoveries included a series of new excitations and the transition to phase II in pure para-hydrogen [2, 5], and measurements showing stability of the molecule to >250 GPa [6, 7]. Subsequently, we began to explore applications to other simple planetary materials, including water, methane, nitrogen, and oxygen.

Infrared reflectivity spectra of H<sub>2</sub>O to above two megabars (210 GPa) showed that the transition of ice to the long-sought, non-molecular, symmetric hydrogen bonded structure occurs at 60 GPa [8, 9]. In this work, extremely weak vibrational reflectance spectra were measured on a 20  $\mu$ m sample within a metallic (reflecting) gasket, thereby demonstrating the power of the synchrotron technique. Multiple Fermi resonances (mode couplings) of the soft mode with other excitations before and after the transition to the non-molecular (ionic) phase were uncovered, and the isotope effect on the symmetrization transition was determined (*i.e.*, for D<sub>2</sub>O) [10]. Infrared measurements of H<sub>2</sub>O in clathrates have been used to determine the stability field and physical properties of these potential fuel sources [11]. The technique also has been instrumental in the discovery of new, dense H<sub>2</sub>-bearing molecular compounds, including dense H<sub>2</sub>O-H<sub>2</sub> clathrates [12], a plethora of new CH<sub>4</sub>-H<sub>2</sub> phases [10, 13, 14], and the novel Ar(H<sub>2</sub>)<sub>2</sub> phase (shown to be stable to record pressures of 240 GPa) [1, 15].

A growing number of studies of minerals under pressure have been performed. Cumingtonite exhibits a pressure-induced structural phase transition that results in symmetry changes at the OH sites [16]. Synchrotron IR absorption spectra of brucite single crystals reveal a phase transition involving displacements of hydrogen atoms from their original axial sites, as proposed on the basis of Raman and neutron diffraction measurements; the results are largely consistent with previous IR and Raman measurements. In other studies, synchrotron measurements of a natural grossular were used to identify the hydrogen-bonding environments [12]. The observation of structural and electronic transitions in glasses show the promise of the technique for application to melts [12].

Just as the techniques developed for high-pressure Raman spectroscopy helped lead the way for general micro-Raman spectroscopy, these efforts have spurred the development of general synchrotron IR microspectroscopy (*i.e.*, at ambient pressure). Synchrotron IR measurements of pressure-quenched high-pressure phases and of natural samples at 1 bar have been obtained with a commercial IR microscope. In early experiments carried out at U2B, the uptake of hydrogen in magnesium silicate perovskite, the most abundant mineral in the planet, was examined. Although nominally anhydrous, the synchrotron IR measurements revealed that the material can take up a surprising amount of hydrogen such that a significant fraction of the water in the current oceans could be stored in the deep mantle. Synchrotron IR spectra were used to identify the phases in quenched multiphase sample charges containing  $\alpha$ -,  $\beta$ -, and  $\gamma$ -(Mg,Fe)<sub>2</sub>SiO<sub>4</sub> synthesized at high *P-T* conditions in the presence of water. IR reflectance spectra were collected from sample areas as small as 6  $\mu$ m (with the synchrotron beam) to identify the phases and to study structural variations and zoning within a capsule [17-19]. Systematic study of phase relations as a function of pressure and temperature demonstrated that the stability field of

the  $\beta$ -phase expanded into both  $\alpha$ - and  $\gamma$ - fields when  $H_2O$  and Fe are present (*i.e.*, San Carlos olivine, which contains 11% Fe). The  $\beta$ - and  $\gamma$ - phases were unambiguously identified because of their different symmetries and distribution of IR bands. By contrast, there is only a 1-2% difference in Fe content between  $\beta$ - and  $\gamma$ - phases according to phase equilibrium experiments, thereby making phase identification difficult by conventional electron probe techniques. In related experiments on pressure-quenched hydrous phases, coesite was also found to be capable of taking up a significant amount of hydrogen [20].

Measurements of the OH content in a suite of silicate inclusions in diamond were not possible with conventional IR methods but were readily obtained with the new technique [21]. In contrast to studies on typical mantle minerals, OH was not detected in either olivines or orthopyroxene inclusions in diamonds, while its presence was clearly demonstrated in kyanite inclusions, with IR spectra similar to kyanites from mantle eclogite xenoliths. These results have important implications for the hydration history of the mantle and place constraints on processes of diamond formation. Reflectivity spectra of a  $\sim 6$  micron grain in the eclogite matrix clearly reveal vibrational characteristics of the silicate garnets (within one minute of accumulation time) that are not resolvable with the global source [17]. Measurements on cuboid diamonds showed that they can contain high-pressure  $H_2O$  ices (at room temperature) and indicating confining pressures of at least 2 GPa [22]. Additional measurements of IR spectra of interplanetary dust particles have been performed to provide bases for their possible identification in space. These spectroscopic methods have also been useful for accurate characterization of new synthetic materials, including providing information about the bonding state (*e.g.*,  $sp^2$  versus  $sp^3$  of carbon [23]). In these and other studies, the IR technique does not have interference from fluorescence, which often plagues Raman spectroscopic measurements of pressure-quenched (and other) samples. These studies, which were performed with a commercial infrared microscope, have demonstrated the importance and complementary nature of high-quality "1-bar" infrared microspectroscopy in this effort.

### Keywords

Synchrotron radiation, infrared spectroscopy, earth and planetary science, high-pressure, diamond anvil cells.

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