

Infrared and Raman Microspectroscopy of Materials Under Pressure

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Understanding the effects of pressure on materials is fundamental to an expanding range of problems in the physical and even biological sciences [1]. Microspectroscopic probes, including those that utilize synchrotron radiation, are among the most important techniques for characterizing materials to very high pressures. The P-T range of these studies extends well into the megabar (>100 GPa) range at variable temperatures from cryogenic conditions to >5000 K. These experiments are carried out using a variety of devices based on the diamond-anvil cell. The high brightness of synchrotron infrared radiation is ideally suited to many of these studies [2]. These spectroscopic investigations complement various microdiffraction and transport measurements, often on the same samples.

The behavior of hydrogen at high pressure and variable temperatures is a critically important problem in physics, planetary science, and astrophysics [1]. Measurements of vibrational spectra of dense hydrogen over an expanded range of pressures and temperatures provide new insight into the behavior of the material under extreme conditions. High P-T Raman measurements have been performed on solid and fluid hydrogen to above 1100 K and to 155 GPa [3]. The data give a direct measure of the melting curve to above 40 GPa. The magnitude of the vibron temperature derivative increases significantly over the measured pressure range, indicating an increase in intrinsic anharmonicity and weakening of the molecular bond. Additional information has been obtained from Brillouin, infrared, and optical spectra of hydrogen over a range of P-T conditions [4].

These results may be compared with studies of other diatomic systems. A new class of molecular phases of solid nitrogen at high pressures and temperatures has been documented [5]. Unlike the diatomic phases reportedly stable over a wide P-T range, one of the new phases is diatomic with only disk-like molecules. A second, higher pressure phase is characterized by strong intermolecular interactions and infrared vibron absorption. Both phases exhibit wide P-T regions of stability and metastability. Raman spectra of oxygen to 134 GPa confirm that the metallic phase that appears near 100 GPa is a molecular solid, though the spectra differ from previous reports [6]. Studies of more complex chemical systems reveal additional phenomena. The properties of the unusual compound nitrosonium nitrate (NO^+NO_3^-) were investigated synchrotron infrared spectroscopy to 32 GPa following synthesis by laser heating of N_2O and N_2O_4 by [7]. At temperatures below 180 K, the NO^+NO_3^- species was found to persist at atmospheric pressure. The results contrast with the behavior of CO_2 , which forms a polymeric phase at comparable P-T conditions.

High-pressure studies of various ices continue, with new phases being uncovered by microspectroscopic methods. Recent work at low temperatures (<150 K) and pressures (<10 GPa) reveal new metastable phases [8]. Raman measurements of methane clathrates under pressure reveal polymorphism and multiple occupancy of the of the guest molecules in the structure [9]. Related observations have been made for the Xe- H_2O system [10], with the observation of a Xe-clathrate stable to ~2 GPa and which appears to form the sH clathrate structure. More remarkable is the behavior of H_2 - H_2O , which forms a dense ice structure at high pressure but on release of pressure at low temperature transforms to the sII clathrate that is stable to ~150 K [11].

These techniques have also been applied to biological molecules under pressure. High-pressure synchrotron far-infrared spectroscopy measurements down to 20 cm^{-1} have been used to characterize the low-frequency dynamics of model heme Fe-CO compounds. The long-sought “doming” mode in which the iron atom moves out of the porphyrin plane was found near 60 cm^{-1} [12]. Calculations of frequencies and absorption intensities, together with the measured pressure dependence of vibrational modes in the model compounds, were used to identify the normal modes.

Historically, these methods have been very useful for probing the behavior of minerals at high pressures. Among the most important developments is the use of Raman methods to study metals such as core-forming alloys at megabar pressures [13]. Another area of application is in the study of the interactions of volatile components with silicates. High P - T investigations of the Xe-SiO₂ system using both laser heating and resistive heating methods show evidence of new chemistry [14]. Raman and x-ray diffraction show that silica can take up Xe to form new phases at $<0.7\text{ GPa}$ and $\sim 1000^\circ\text{C}$. Recent studies of hydrous phases include synchrotron infrared spectroscopy of OH-chondrodite and OH-clinohumite that indicate that the crystal structures of both minerals are preserved up to 38 GPa at room temperature [15]. However, disordering of the silicate framework appears to become more pronounced at high pressure, as found for other hydrous silicates.

These techniques continue to evolve as a result of developments in new instrumentation and radiation sources. Of particular interest is the use of micro inelastic x-ray scattering to study electronic, vibrational, and magnetic excitations of materials under pressure using new third-generation synchrotron radiation methods [16].

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