

## X-ray-induced Dissociation of H<sub>2</sub>O and Formation of an O<sub>2</sub>-H<sub>2</sub> Compound at High Pressure

*In this work we used inelastic X-ray scattering to study the high-pressure behavior of H<sub>2</sub>O. At lower pressures and low temperatures, X-ray Raman spectroscopy (XRS) is used for investigating water, ice Ih, ices II and IX. At higher pressures we discovered new radiation chemistry in the H<sub>2</sub>O system. A new compound composed of molecular oxygen and hydrogen was formed after X-ray irradiation of the ice VII sample. This surprising result opens new avenues for radiation chemistry research and studying molecular interactions in the O<sub>2</sub>-H<sub>2</sub> system.*

### Beamline

SP12U1 Inelastic X-ray  
Scattering

### Author

W. Mao  
Stanford University,  
California, USA



**The** high-pressure behavior of H<sub>2</sub>O is a subject of fundamental importance in physics, chemistry, and planetary sciences. H<sub>2</sub>O has a very rich phase diagram—at least ten stable phases of ice and more than five additional metastable forms of crystalline and amorphous ice—and exhibits a wide range of unusual phenomena, such as symmetric hydrogen bonding, multi-site disordering, multiple critical points, etc. These behaviors, however, are all based on the building blocks of H<sub>2</sub>O molecules and OH bonding. Here we extended the investigation to include the molecular species, H<sub>2</sub> and O<sub>2</sub>, by cleaving the H<sub>2</sub>O molecules, breaking OH bonds, and forming O-O and H-H bonds. Although at ambient pressure X-rays are known to produce metastable free radicals in molecular systems or induce stable reactions by overcoming kinetic energy barriers, documented examples of X-ray induced transitions at high pressure are extremely rare.

In the study we observed unexpected radiation chemistry in the 'simple' H<sub>2</sub>O system at high pressure. Beginning with an H<sub>2</sub>O sample contained in a diamond anvil cell at high pressure, we found that exposure to moderately high energy (~10 keV) X-rays resulted in cleaving of the H<sub>2</sub>O molecules, formation of O-O and H-H bonds, and conversion of the O and H framework in ice VII into a new molecular compound of O<sub>2</sub> and H<sub>2</sub>. A suite of in-situ techniques were used to establish that this new crystalline solid differs from previously known phases.

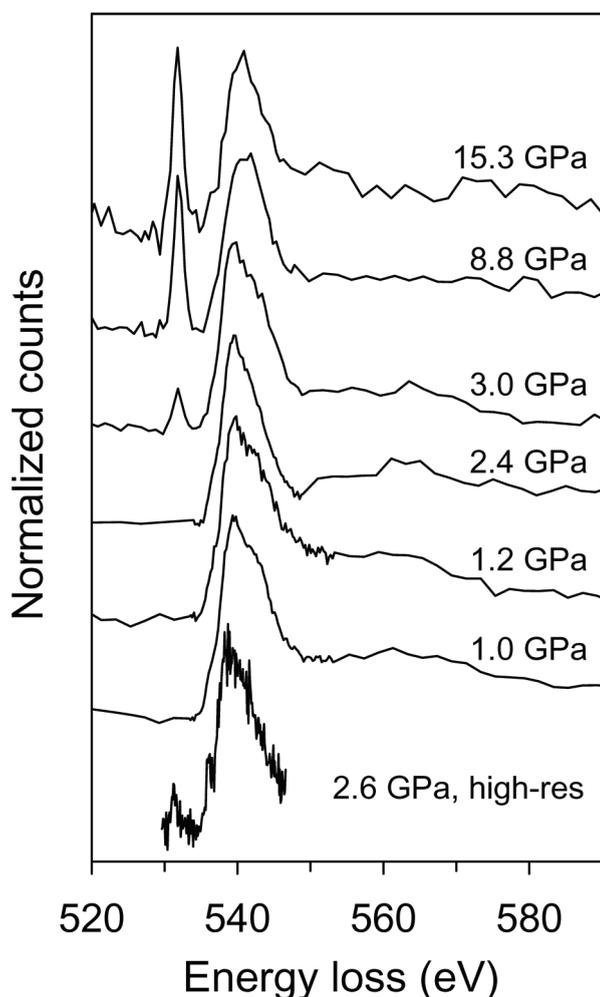
At low and moderate pressures, X-ray Raman spectroscopy (XRS) has been used successfully for investigating water, ice Ih, ices II and IX. XRS was recently developed to study the effect of high pressures on light-element bonding by measuring the near K-edge spectra, particularly for oxygen atoms. We compressed distilled H<sub>2</sub>O in a Be gasket in a diamond anvil cell (DAC) and measured the XRS at high pressure at the Taiwan beamline BL12XU at SPring-8 and beamline 13IDC of the Advanced Photon Source, Argonne National Laboratory (ANL). For oxygen bonded with hydrogen in H<sub>2</sub>O, the oxygen K-edge in XRS spectra is dominated by a cluster of peaks around 540 eV as shown in dense water below 0.9 GPa, ice VI between 1 and 2 GPa, and ice VII just above 2 GPa (Fig. 1). At pressures above 2.5 GPa, however, X-ray

irradiation induces dramatic, irreversible changes in the XRS spectra. A distinctive, sharp peak at 530 eV characteristic of O-O bonding in  $O_2$  grows with time and reaches a plateau after six hours of exposure to the incident X-ray beam (Fig. 1). The plateau intensity increases with increasing pressure, and at 15.3 GPa, the height of the 530 eV peak matches that of the main 540 eV multiplet. Visually, the sample changes from colorless to light brown after the conversion (Fig. 2).

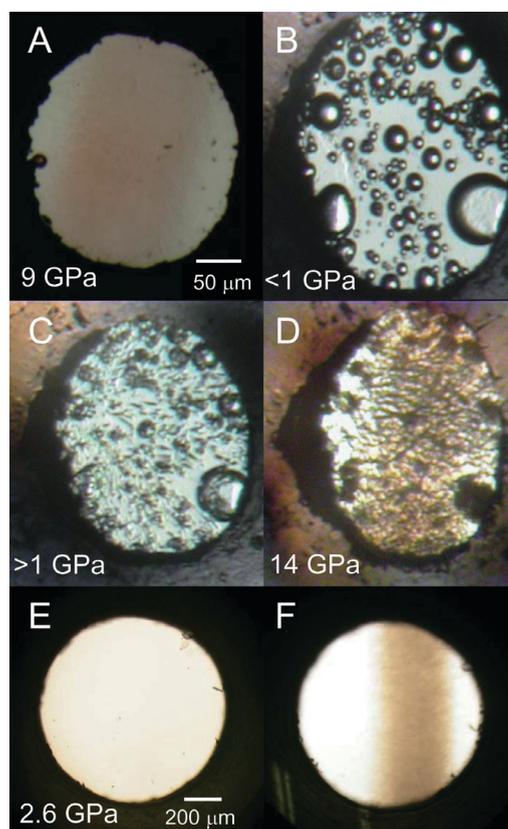
Optical Raman spectroscopy measurements of the  $H_2O$  sample after XRS irradiation show intense, characteristic  $H_2$  and  $O_2$  vibrons and a diminished  $H_2O$  signal, clearly demonstrating the dissociation of  $H_2O$  molecules and the recombination into  $O_2$  and  $H_2$  molecules. The resultant  $O_2$  and  $H_2$  molecules do not exist in the known high pressure phases of hcp- $H_2$  and  $\epsilon$ - $O_2$ , but form a new

compound consisting of both molecular  $O_2$  and  $H_2$ . X-ray diffraction studies of this new  $O_2$ - $H_2$  compound indicate that the new material is a well-crystallized solid. Its diffraction pattern shows some similarity to  $\epsilon$ - $O_2$ , but closer comparison of the two patterns reveals that the diffraction peaks do not exactly fit  $\epsilon$ - $O_2$ , and that the new compound has a number of additional peaks, a more complicated crystal structure, and possibly lower symmetry than  $\epsilon$ - $O_2$ .

Once synthesized and held at high pressure, the new phase is extremely stable with respect to laser exposure, further X-ray irradiation, and long shelf-time up to at least 120 days. Bubbles of  $O_2$ - $H_2$  gaseous mixture (identified by ORS) were released from the solid when the pressure was reduced below 1 GPa. When these bubbles were compressed to high pressures and irradiated with X-rays



**Fig. 1:** XRS patterns of  $H_2O$  sample at high pressure after irradiation. Bottom spectra at 2.6 GPa was measured at beamline BL12XU, SPring-8 using 9.886 keV X-rays with high energy resolution (300 meV). All other spectra were measured with 9.687 keV X-rays at beamline 13-IDC, Advanced Photon Source with 1 eV resolution.



**Fig. 2:** Photomicrographs of two diamond anvil samples. Top four panels were taken at 13-IDC, APS, ANL. (A) After XRS measurement 8.8 GPa. The light brown streak through the middle of sample shows the portion irradiated by the X-ray beam. A small ruby ball on left the edge of gasket was used for pressure calibration. (B) After release of pressure to below 1 GPa, bubbles of  $O_2$  and  $H_2$  formed. (C) Bubbles collapsed upon increase of pressure as the  $H_2$  and  $O_2$  were incorporated into the crystalline sample. (D) Sample after XRS measurement at 15.3 GPa. Bottom two panels were taken at BL12XU, SPring-8. (E) Before and (F) after X-ray exposure at 2.6 GPa.

again, they reformed the new alloy (Fig. 2). Formation of this material has thus been approached from both directions: starting with H<sub>2</sub>O and with an O<sub>2</sub>-H<sub>2</sub> mixture. Heated in a diamond-anvil cell, the new phase is stable up to 700 K at 15 GPa. At higher temperature, this material reverts to ice VII before melting. While the pressure at which this phenomena occurs at ambient temperature is quite high (i.e. 2.6 GPa), it is feasible that low temperature could metastably quench this new compound to more modest pressures. This material opens new possibilities for studying molecular interactions in the O<sub>2</sub>-H<sub>2</sub> system in particular and molecular hydrogen containing systems in general, and may open the door to exciting new directions in radiation chemistry research.

### Experimental Station

IXS Spectrometer

### References

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### Contact E-mail

wmao@stanford.edu