

X-RAY-INDUCED DISSOCIATION OF H₂O AND FORMATION OF AN O₂-H₂ COMPOUND AT HIGH PRESSURE

The high-pressure behavior of H₂O is a subject of fundamental importance in physics, chemistry, and planetary sciences. H₂O 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. 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.

We observed unexpected radiation chemistry in the 'simple' H₂O system at high pressure. Beginning with an H₂O 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 H₂O 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 O₂ and H₂. X-ray diffraction, X-ray Raman spectroscopy (XRS), and optical Raman spectroscopy were used to establish that this new crystalline solid differs from previously known phases.

For oxygen bonded with hydrogen in H₂O, the oxygen *K*-edge in XRS spectra were 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-radiation induced dramatic, irreversible changes in the XRS spectra. A distinctive, sharp peak at 530 eV characteristic of O-O bonding in O₂ grew with time and reached a plateau after approximately six hours of exposure to the incident X-ray beam, with the plateau intensity increasing with increasing pressure (Fig. 1). Visually, the sample changed from colorless to light brown after the conversion (Fig. 2).

Optical Raman spectroscopy measurements of the H₂O sample after XRS irradiation showed intense, characteristic H₂ and O₂ vibrons and a diminished H₂O signal, demonstrating the dissociation of H₂O molecules and the recombination into O₂ and H₂ molecules. The resultant O₂ and H₂ molecules do not exist in the known high pressure phases of hexagonal close-packed H₂ and ϵ -O₂, but form a new compound consisting of both molecular O₂ and H₂. X-ray

diffraction studies of this new H₂-O₂ compound indicate that the new material is a well-crystallized solid. Its diffraction pattern shows some similarity to ϵ -O₂, but the new compound has a number of additional peaks, a more complicated crystal structure, and possibly lower symmetry than ϵ -O₂.

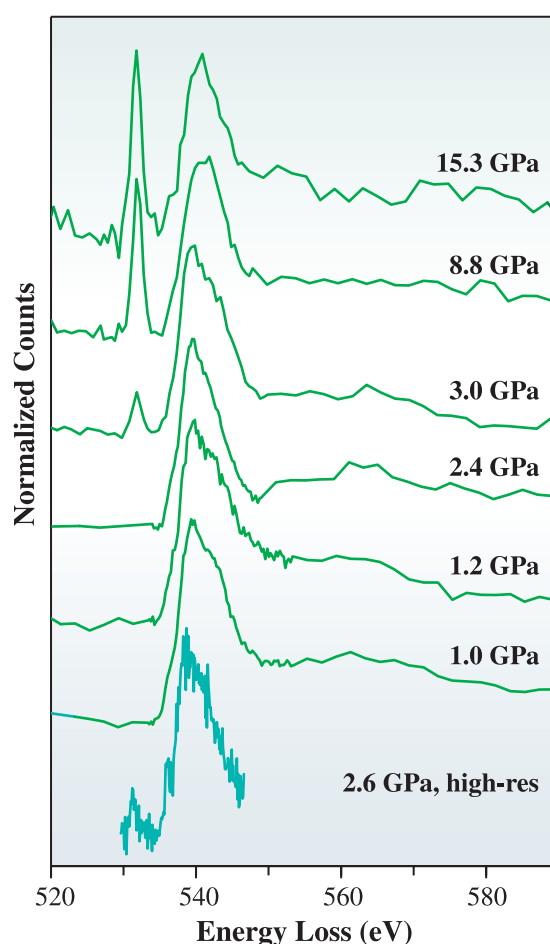


Fig. 1. XRS patterns of H₂O sample at high pressure after irradiation [1]. Bottom spectra at 2.6 GPa was measured at beamline BL12XU, SPRing-8 using 9.886 keV X-radiation with high energy resolution (300 meV). All other spectra were measured with 9.687 keV X-radiation at beamline 13-IDC, Advanced Photon Source with 1 eV resolution.

Once synthesized and kept at high pressure, the new phase is extremely stable with respect to laser exposure, further x-radiation, and long shelf-time up to at least 200 days. Bubbles of a $\text{O}_2\text{-H}_2$ 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 again, they reformed the new compound (Fig. 2). Formation of this material has thus been approached from both directions: starting with H_2O and with an $\text{O}_2\text{-H}_2$ 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 $\text{O}_2\text{-H}_2$ system in particular and molecular hydrogen containing systems in general, and may open the door to exciting new directions in radiation chemistry research.

Wendy Mao [†]

Lujan Neutron Scattering Center,
Los Alamos National Laboratory, USA

E-mail: wmao@pangea.stanford.edu

[†] Present Address:

Geological & Environmental Sciences, Stanford Univ. and
Photon Science, Stanford Linear Accelerator Center

References

[1] W.L. Mao, H-k. Mao, Y. Meng, P.J. Eng, M.Y. Hu, P. Chow, Y.Q. Cai, J. Shu and R. Hemley: *Science* **314** (2006) 636.

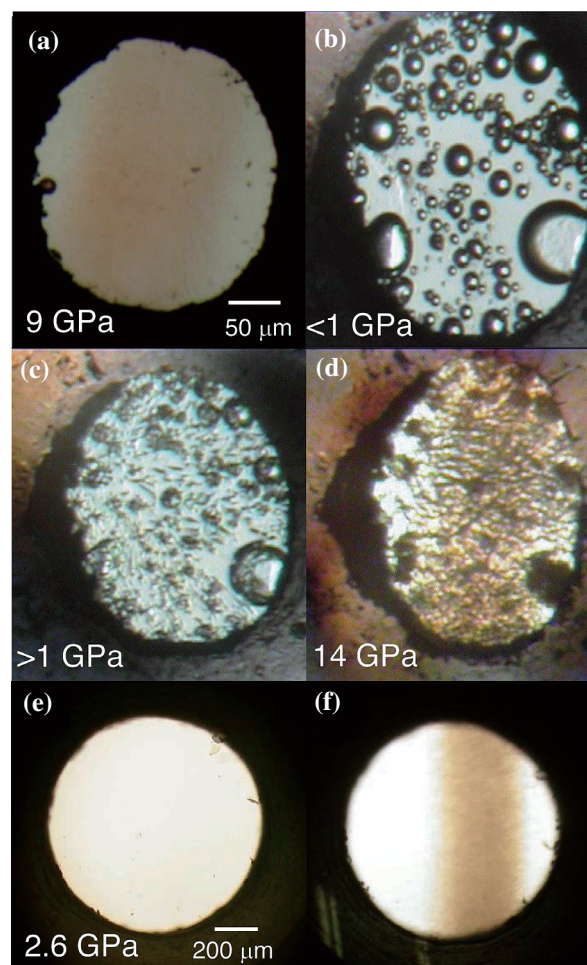


Fig. 2. Photomicrographs of two diamond anvil samples [1]. Top four panels were taken at beamline 13-IDC. (a) After XRS measurement at 8.8 GPa. The light brown streak through the middle of sample shows the portion irradiated by the X-ray beam. A small ruby ball on left edge of gasket was used for pressure 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. (e) Before and (f) after X-ray exposure at 2.6 GPa.