X-ray Raman Studies of Liquid Water and Ice

T. PYLKKÄNEN[1,2], S. HUOTARI[1], G. MONACO[1], J.A. SOININEN[2], K. HÄMÄLÄINEN[2]

1 European Synchrotron Radiation Facility.
2 University of Helsinki, Finland. tuomas.pylkkanen@esrf.fr

X-ray absorption spectroscopy (XAS) is a well-established tool for element-specific chemical and structural studies in various environments. However, since the absorption edges of light elements fall in the soft x-ray regime, their study is possible only under vacuum conditions and yields intrinsically surface-sensitive information. X-ray Raman Scattering (XRS) allows the use of high-energy x-rays to study low-energy absorption edges [1]. This lifts the constraints of a soft x-ray experiment, allowing bulk measurements on liquids and access to demanding sample environments such as high pressure cells. However, since the scattering cross section for the non-resonant XRS process is very weak, intense x-ray sources and sensitive detection systems are needed.

Recent substantial improvements in synchrotron-radiation based setups are making the XRS technique suitable for an extended range of applications. We have used a new multi-analyser spectrometer installed at beamline ID16 of the European Synchrotron Radiation Facility to measure XRS at the oxygen K-edge in liquid water and in single crystals of hexagonal ice. These experiments provide determinations of both the near-edge (XANES) and the extended x-ray absorption fine structure (EXAFS), and in both cases, marked differences are observed between liquid and crystal. We compare our experimental results with cluster calculations utilizing structures obtained from various water models.

While at low momentum transfer q the XRS spectra are fully equivalent to XAS results, the q-dependence of the XRS spectra can also be utilized to gain extra information on the system. To this end, we have extracted the angular-momentum-projected local density of states (ℓDOS) from our q-dependent near-edge measurements. We thus gain access to the s-type density of states (sDOS) in addition to the XAS-equivalent pDOS. These experimental results are interpreted with the help of recently developed codes which allow the momentum transfer dependence of XRS to be fully utilized within both the multiple-scattering [2] and the density-functional theory [3] based approaches to cluster calculations.

References

[1] - U. Bergmann, P. Glatzel, and S. P. Cramer. Microchem. J. **71**, 221, (2002)
[2] - J. A. Soininen, A. L. Ankudinov, and J. J. Rehr. Phys. Rev. B **72,** 045136, (2005)
[3] - A. Sakko, M. Hakala, J. A. Soininen, and K. Hämäläinen. Phys. Rev. B **76,** 205115, (2007)