## Summary:

Understanding the structure and dynamics of water around small solutes is fundamental to problems in physics, chemistry, and biology. Femtosecond “pump-probe” laser spectroscopy provide little or no spatial information. Time-resolved x-ray scatteringm can measure the structure factor of water to sub-angstrom spatial resolution, but can only resolve on the order of 10-100 picoseconds. Currently, there is no technique that provides femtosecond temporal resolution and angstrom spatial resolution simultaneously.

Recently, Abbamonte et al. used inelastic x-ray scattering to image electron density disturbances to attosecond resolution [Abbamonte]. From the measured IXS spectra S(q,ω), the imaginary part of the density propagator X(q,ω) can be recovered using the fluctuation-dissipation theorem:

$$\mathrm{Im}[\mathrm{X}(q,\omega)] = -\pi[S(q,\omega) - S(q,-\omega)]$$

The complex valued density propagator X(q,ω) represents the disturbance caused by a delta function (in time and space) source at t=0. To understand the time and space evolution of the system, the entire propagator is required. Because only the imaginary part can be measured, this is an example of a phase problem. However, the constraint of causality allows the real part of X to be calculated using the second Kramers-Kronig relation [Jackson]. Hence, the entire complex propagator can be recovered from measurement and inverted, via time- and spherical-Fourier transform. The disturbances in water can then be imaged by using superposition to calculate the effect of extended sources on water.

We are attempting to extend this technique to imaging the dynamical behavior of water on molecular lengthscales and timescales (Å spatial resolution, fs temporal resolution). In order to do this, we have measured the dynamical structure factor of water S(q,ω) with the ultra-high meV-resolution IXS instrument at beamline ID-28 at ESRF (see Fig 1) over the necessary range of q and E. We measured from -15meV to 80meV, capturing the important features of the water spectra in this energy range.

## Technical Considerations

From the set of measurements of S(q,ω), we implemented the Kramers-Kronig relation as a continuous, analytic integral to recover the real part of X(q,ω). This required several problems to be addressed. For example:

1) The discrete nature of measurements creates an artificial periodicity when numerically integrating the KK relations. For this reason, we were required to interpolate the data between points to have a “continuous” measurement. To be as transparent as possible, we used linear interpolation to best avoid artificial features in the inversion.
2) The truncation of the integral at finite ω could cause false features to appear in the inversion. For this reason, it was necessary to extrapolate the measured S(q,ω) well beyond the end of the measurement in order to have an effective “infinity”, thereby avoiding the truncation effects. We estimated the ω-value at which to truncate the extrapolation via Lorentzian error-function analysis.

## Progress

At this point, we have used the data set collected during our last experiment at ESRF ID-28 (SC-2147) to show that we can recover the imaginary part of the density propagator X(q,ω) from measurements of S(q,ω), and that we can use the Kramers-Kronig relation to calculate the real part of X. Figure 2 shows frames from a movie of X(r,t), the real-space density propagator from the Fourier transform of the full X(q,ω). The q- and E-parameters of our measurements indicate that we can image X(r,t) to resolutions of ~50fs in time and 0.8Å in space. At present, we are implementing a number of self-consistency checks. Interestingly, we can observe the time evolution of a strong feature at ~3Å which is consistent with the time evolution of the O-O bond length of hydrogen-bonded water molecules. Also, the lifetime of the order in the system (how long the effect of the perturbation is felt by the system) is roughly 1ps, consistent with existing spectroscopic measurements.

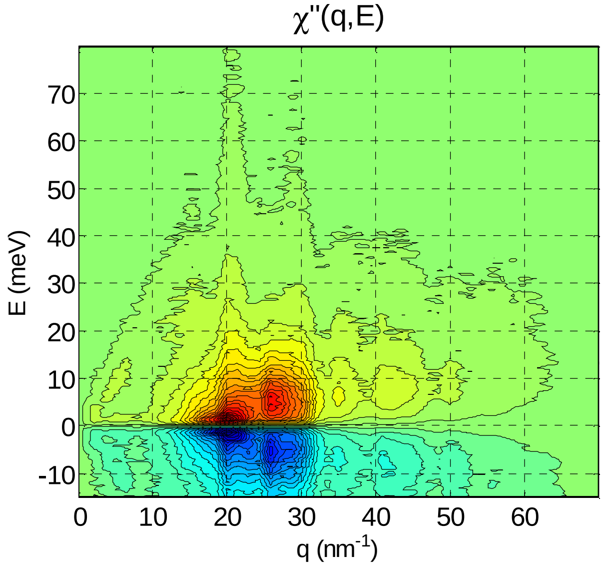

**Figure 1 - Imaginary part of the density propagator X(q,ω) from the measured IXS spectra. Individual measurements of S(q,ω) were made at 50 equally spaced q-positions between 2nm$^{-1}$ and 80nm$^{-1}$.**

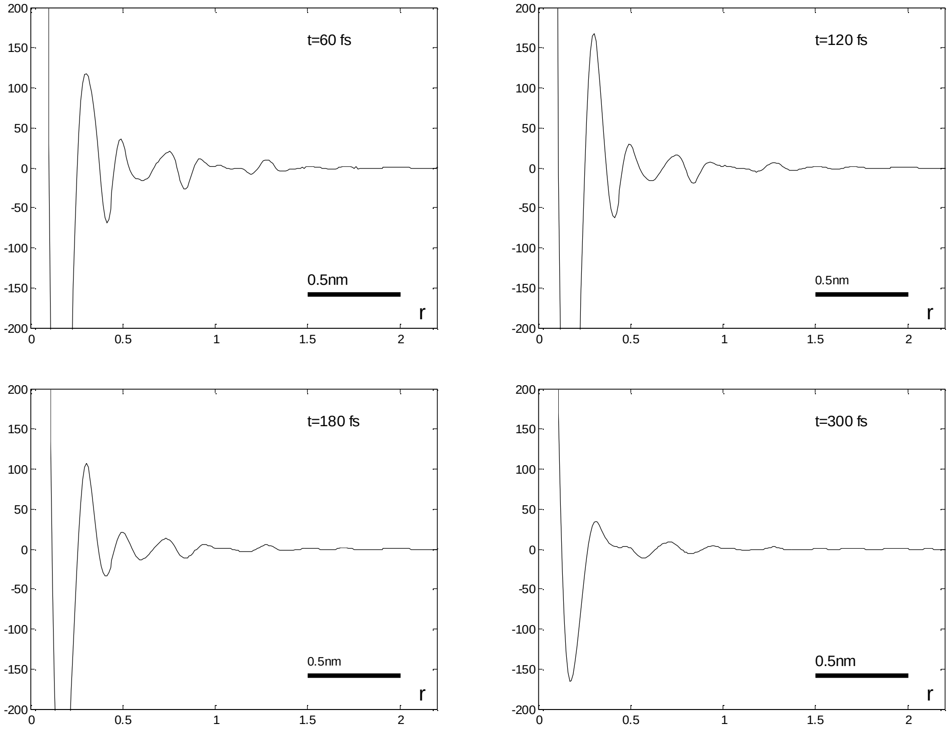

**Figure 2 – 60-fs timesteps of X(r,t).**