2D Infrared Spectroscopy of High Pressure Phases of Ice

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The OH-stretch vibration of ice is complex and the assignment of distinct peaks of the OH-band remains controversial. We present 2D IR spectra of hydrogen ordered phases of ice. They exhibit distinct features that can aid the understanding of the coupling processes that underlie the OH-stretch mode.

Interpreting the complex lineshape of the OH-stretch band of ice is challenging. In part this can be attributed to the strong 3-dimensional hydrogen-bonded network of ice, but also because of the orientational disorder of the water molecules in hexagonal ice (ice I*h*). 2D IR spectroscopy is a good tool to disentangle the underlying structure of bands. 2D spectra of ice I*h* have been measured previously [1] and a very recent publication uses this data to shed light on the excitonic nature of crosspeaks in the isotropic spectra [2]. The absence of these crosspeaks in the anisotropic signal is believed to be due to the hydrogen disorder of ice I*h*.

To test this hypothesis we study hydrogen ordered phases of ice such as ice II [Fig. 1] and XIII. Measuring solid samples and especially powders is challenging in 2D spectroscopy due to the sensitivity of this technique to unwanted scattering. A new preparation method for high pressure phases of ice was developed by us in order to obtain samples that scatter significantly less than established methods. The resulting 2D spectra are compared to quantum-classical simulations.

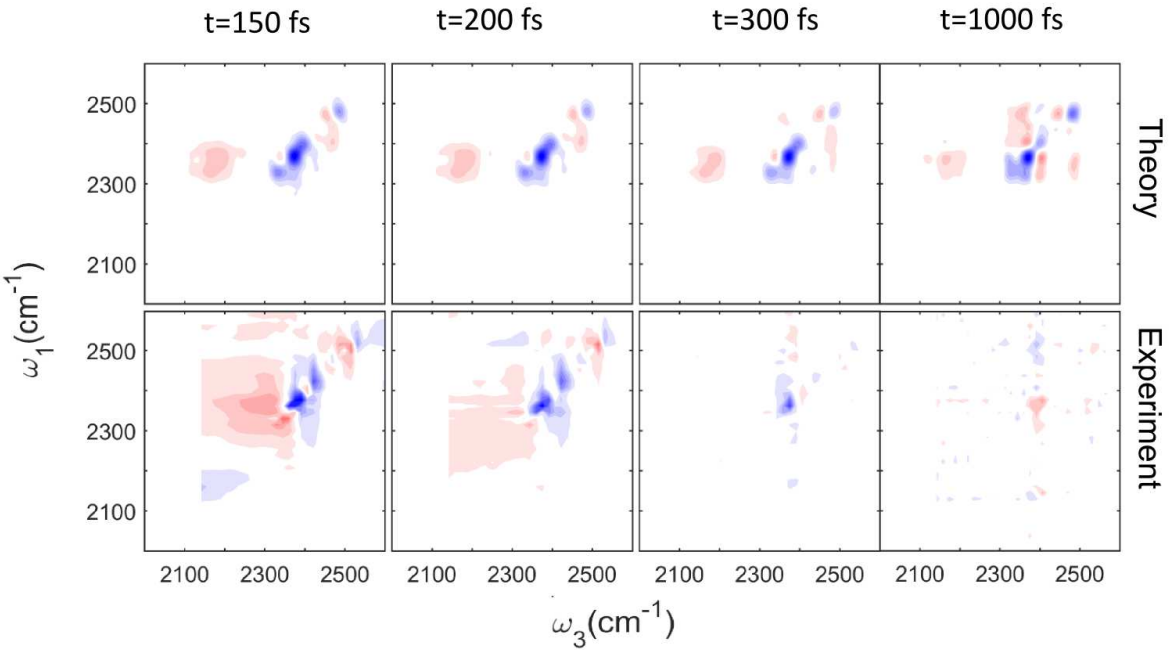

Fig. 1: 2D IR anisotropic response of the OD stretch mode of D_2O ice II. Vertical axis: pump frequency, Horizontal axis: probe frequency. Top row: Quantum-classical simulations. Bottom row: Experimental spectra.

[1] F. Perakis *et al.*, Phys Chem Chem Phys **14**, 6250 (2012).
[2] L. Shi *et al.*, Phys Chem Chem Phys **18**, 3772 (2016).