The 2D-Raman-THz response of salt solutions reveals an echo, whose decay time correlates with the water structuring capability of the cation. Polarizable force fields of water and ions are developed to simulate the spectroscopic response.

Water is a complex liquid due to the hydrogen-bond network that it forms. The associated low-frequency spectrum of water reports directly on its thermally excited intermolecular degrees of freedom. In this frequency range, the intermolecular spectrum of water consists of broad, almost featureless bands at ~600 cm\(^{-1}\) (hindered rotations), ~200 cm\(^{-1}\) (hydrogen bond stretching) and at ~60 cm\(^{-1}\) (hydrogen bond bending). In order to resolve the lineshape functions of these modes as well as their couplings, a multidimensional spectroscopy directly in this frequency range is needed, which we have introduced recently with the 2D-Raman-THz spectroscopy.

In a previous publication, we have measured the 2D-Raman-THz response of neat water [1], revealing a slightly extended signal in the echo direction along the diagonal \(t_1 = t_2\). In order to introduce additional heterogeneity to the water structure, we continued to study salt solutions, and indeed, the echo feature is getting more pronounced in certain cases (see Fig. 1, most-right panel). Interestingly, the decay time of the echo correlates with the water structuring capability of the cation. We have shown previously that 2D-Raman-THz spectroscopy is a very sensitive probe of the level of accuracy with which the polarizability of water is described [1], and we expect the same to be true for the ions. We currently work on a consistent parametrisation of both ion and water polarizability, which we believe will give unprecedented insights into the effect of salts on the water structure.

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Fig. 1. Experimental 2D-Raman-THz signal of salt solutions with increasing capability to structure water (left to right).