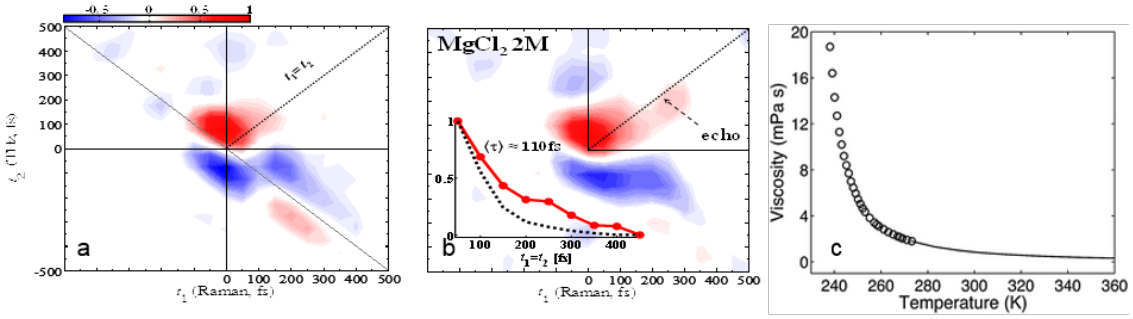
Towards 2D Raman-THz spectroscopy of supercooled water

G. Ciardi[1], A. Berger[1], A. Shalit[1], P. Hamm[1]*

[1]University of Zurich

Two dimensional Raman-THz spectroscopy, as a new multidimensional spectroscopic technique directly in the THz regime [1], was proposed and used in our group to explore the low-frequency intermolecular modes dynamics in liquid water and aqueous salt solution [1][2]. This new approach has given new insights to the relaxation dynamic of complex collective hydrogen bond networks; the amount of inhomogeneity in the system is quantified by the time persistence of the "echo" signal along the diagonal $t_1=t_2$ [1] (Fig.1 (a)). The series of measurement of aqueous salt solution has revealed that the extent of the diagonal feature is directly related to the increase or decrease of viscosity driven by different kind of dissolved ions in water; in particular, as salts "structure" water (i.e. viscosity increases), the echo feature becomes more pronounced [2] (Fig. 1 (b)). To have a more complete picture regarding the appearance of this extended diagonal component and its connection to viscosity, next step is to measure the response of supercooled water. Cooling water below its freezing point leads essentially to the same viscosity change [3] of "structure making" salts but it comes without the addition of any external compound. For this reason and for the purpose of directly relating the appearence of the "echo" with viscosity effects , supercooled water is even a more reliable and direct probe of the structure of intermolecular hydrogen bond network.



[1] Savolainen, J., Ahmed, S. & Hamm, P. *Proc. Natl Acad. Sci.* USA 110, 20402–20407 **(2013)**.
[2] Shalit A., Ahmed S., Savolainen J. and Hamm P., *Nat. Chem*. **(2016)**.
[3] Y. A. Osipov, et al *Russ. J. Phys. Chem.* **51**, 748–749 **(1977)**.