2D Raman–THz Spectroscopy of Aqueous Salt Solutions

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The ultrafast time-resolved 2D Raman-THz spectroscopy was applied to study the dynamics of hydrogen bond networks in the aqueous solutions of the chloride salts. We demonstrate that the extent of the echo signal along the correlated $t_1=t_2$ coordinate correlates with the viscosity of the solution.

The change in the viscosity (η) of water upon addition of simple inorganic salt is described fairly well by the semiempirical Jones-Dole equation $\eta/\eta_\circ=1+Ac^{1/2}+Bc$ when $\eta_\circ$ is viscosity of water, c is a concentration and A and B are empirical coefficients. Based on the sign of the B-coefficient the ions are usually classified as "structure maker" (B>0) or "structure breakers" (B<0) based on their ability to increase/decrease viscosity upon solvation [1]. However the consistent molecular level picture beyond this classification, namely how and to what extent ions perturbed the water structure, is still missing. The intensive experimental and computational studies applied for these systems suggesting a very diverse interpretation of the obtained data to the point of mutual exclusivity [2]. Here we apply a recently developed 2D Raman-THz spectroscopy [3] to investigate the effect of ions on the structural and dynamical properties of water. Unlike common two-dimensional spectroscopies in IR regime, this method interrogates the hydrogen-bond stretching and bending modes of liquid water in the low frequency range, thus allowing to observation of the dynamics of the collective intermolecular motion directly. Comparison of the 2D Raman-THz response of neat water (fig 1a) with the series of chloride salts (see for example $MgCl_2$ salt response in fig. 1b) reveal the extended relaxation component along the $t_1=t_2$ diagonal in the 2D plot as the "structure making" ability of the cations are increased. As in case of conceptually similar 2D Raman spectroscopy [4] the signal along $t_1=t_2$ (echo) reflects the degree of the inhomogeneity of the intermolecular motion. The observed trend of the increasing of the relaxation times qualitatively correlates with the empirical Jones-Dole B-coefficients (fig 1c) allowing to connect the macroscopic observable (viscosity) to microscopic hydrogen bond networks dynamics. A detailed understanding of the observed $t_1=t_2$ signal will require requires massive support from theory as well as from molecular dynamics (MD) simulations and first steps in this direction are underway.
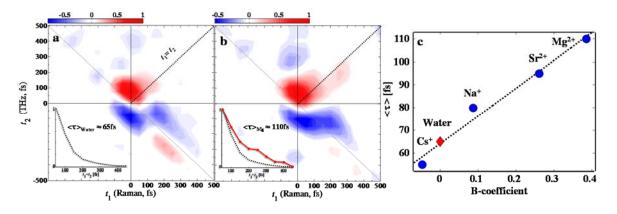

Fig. 1 a) The experimental 2D Raman-THz signal of a) water and b) 2M **Mg**Cl₂. Insets display the cuts along the diagonal $t_1=t_2$. c) Relaxation times for the serious of 2M $\mathbf{X}^{n+}Cl_n$ salts vs. Jones-Dole B-coefficients.

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