Electrolytes induce long-range orientational order and free energy changes in the H-bond network of bulk water

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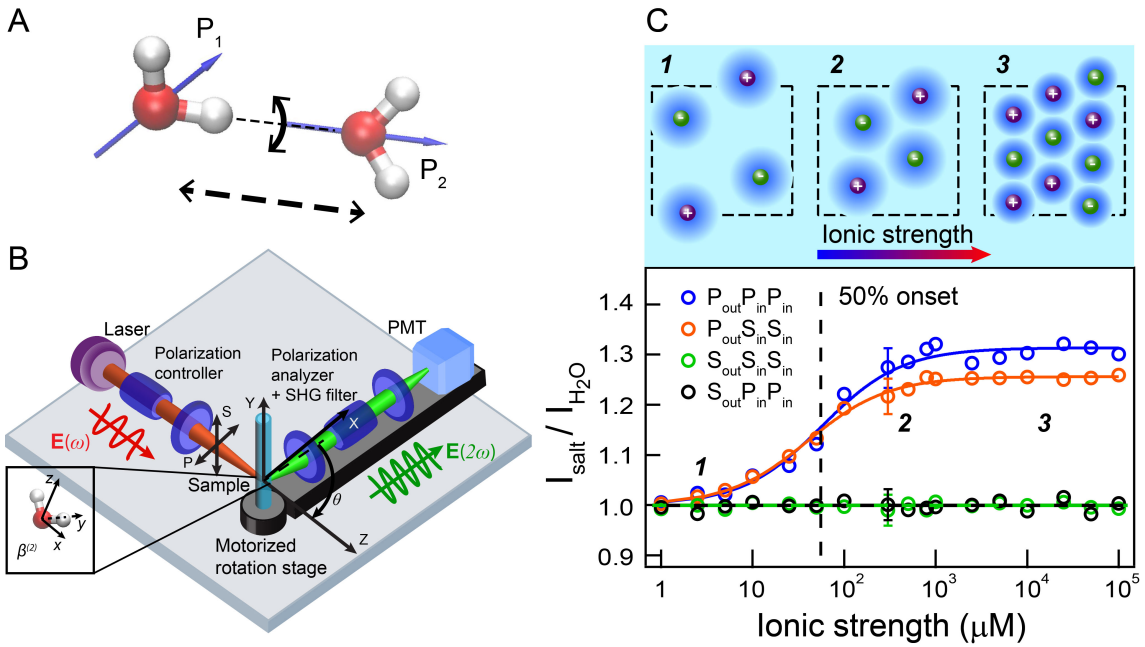
Electrolytes interact with water in many ways: changing dipole orientation, inducing charge transfer, and distorting the hydrogen-bond network in the bulk and at interfaces. Numerous experiments and computations have detected short-range perturbations that extend up to three hydration shells around individual ions. We report a multiscale investigation of the bulk and surface of aqueous electrolyte solutions that extends from the atomic scale (using atomistic modeling) to nanoscopic length scales (using bulk and interfacial femtosecond second harmonic measurements) to the macroscopic scale (using surface tension experiments). Electrolytes induce orientational order at concentrations starting at 10 μM that causes nonspecific changes in the surface tension of dilute electrolyte solutions. Aside from ion-dipole interactions, collective hydrogen-bond interactions are crucial and explain the observed difference of a factor of 6 between light water and heavy water.



[1] Yixing Chen *et al.*, *Science Advances*, **2016**, 2, 4, e1501891.