

Structural transformations and hydrogen bond reorganization of liquid water under high-pressure conditions.

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We used Non-linear Infrared Spectroscopy (pump-probe and 2D-IR) to study the structural modification and the hydrogen bond reorganization in pure water and in aqueous ionic solution as a function of pressure.

Liquid water has a primary role in many biological, chemical, physical, geological and environmental processes. Despite the enormous amount of experimental and theoretical studies performed in the last century, a full understanding of its dynamical and structural properties is still lacking. By joining anvil cell high-pressure technology, femtosecond two-dimensional infrared spectroscopy and molecular dynamics simulation, we studied the spectral diffusion of the stretching frequency of an HOD impurity in liquid water as a function of pressure and the dynamical exchange process between “differently bounded” water molecules in a solution of ClO_4^- as a function of pressure.

In our previous work we showed that pressure dependence of the anisotropy decay time (τ_R) of an isotopically-diluted mixture HOD/H₂O (7 %) at 298 K and at 363 K has two distinct trends: at 363 K τ_R is constant in the whole inspected pressure range, while at 298 K τ_R initially decreases from 2.5 to 1.4 ps and then (from 0.2 GPa) it has constant trend around a value of 1.3 ps. On the other hand, we observe only a moderate decrease (1.7 to 1.4 ps) of the picosecond component of spectral diffusion (τ_{SD}) at 298 K in the inspected pressure range.

In the second phase of our project we study the dynamical exchange process between “differently bounded” water molecules in a 5M solution of ClO_4^- as a function of pressure.

The solvent is the mixture HOD/H₂O 7 %. The exchange dynamics involves breaking of the hydrogen bonds of water molecules bonded to bulk water molecules and formation of new hydrogen bonds with perchlorate molecules. We measure the exchange constant k_{ex} at room pressure and at 1.3 GPa collecting a series of 2D-IR spectra at different population times (T), extracting the cross-peaks volume as a function of T and performing a non-linear fitting analysis.

We observed a slowdown of the exchange dynamics moving from room pressure ($\tau_{exc}=4.7$ ps) to 1.3 GPa (5.4 ps).

