

Coherent Dynamics of Phosphate Ions in Bulk H₂O

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We investigate dynamics of phosphate stretching vibrations of the ion H₂PO₄⁻ dissolved in H₂O combining 2D-IR spectroscopy with mixed quantum-classical simulations. Dominantly homogeneously broadened lines are caused by ultrafast librational motions of hydration shell water. Cross peak dynamics reveal vibrational quantum beats with a lifetime of a few hundred femtoseconds.

Charged phosphate groups feature prominently in the energetics of metabolism and are important solvation sites of DNA and phospholipids. While the equilibrium structures of these systems have been well characterized, an understanding of their biological function requires the knowledge of their microscopic interactions with the fluctuating environment through Coulomb interaction and hydrogen bonding, i.e., the ultrafast dynamics on the femto- to picosecond time scale of molecular motions.

As a model system, we study the ultrafast vibrational dynamics of the ion H₂PO₄⁻ in aqueous solution. The model system offers two striking advantages: i) interfacial sensitivity of phosphate stretching vibrations allowing for direct observation of phosphate-water interactions in bulk H₂O, and ii) small molecular structure making them tractable for realistic state-of-the-art simulations [1, 2] allowing to combine the unique information content of two-dimensional infrared (2D-IR) measurements with hybrid quantum-classical molecular dynamics based simulations of the non-linear signal. The characteristic phosphate stretching vibrations are found in the frequency range from 880-1300 cm⁻¹ covering the PO₂⁻ stretching $\nu(\text{PO}_2^-)$, P(OH)₂ stretching $\nu(\text{P}(\text{OH})_2)$ and P(OH)₂ bending $\delta(\text{P}(\text{OH})_2)$ modes. The 2D spectra reveal a coherent beating at frequency positions of cross peaks (Fig. 1) that arise due to a coherent superposition of the coupled $\nu_S(\text{PO}_2^-)$ and $\nu_{AS}(\text{PO}_2^-)$ modes in aqueous solution.

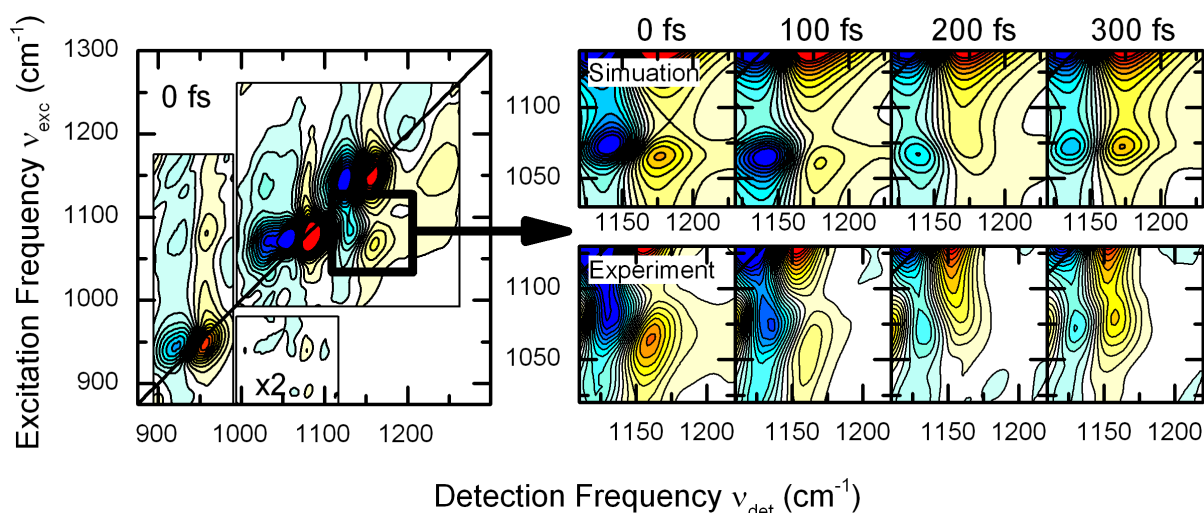


Fig. 1 Left: Experimental 2D spectrum at 0 fs showing predominantly homogeneously broadened peaks of phosphate stretching vibrations due ultrafast fluctuations of the hydration shell. The box indicates the cross peak between the symmetric and asymmetric PO₂⁻ stretching vibrations at 1080 and 1160 cm⁻¹. Right: Comparison of the experimental and simulated time evolution of cross peaks reveals a vibrational quantum beat.

[1] R. Costard, T. Tyborski, B. P. Fingerhut and T. Elsaesser, *J. Chem. Phys.* **142**, 212406 (2015).

[2] R. Costard, T. Tyborski and B. P. Fingerhut, *Phys. Chem. Chem. Phys.* **17**, 29906 (2015).