Stochastic infrared signatures of protons in HCl

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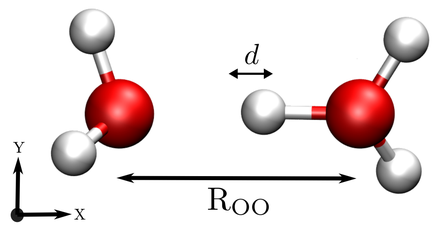
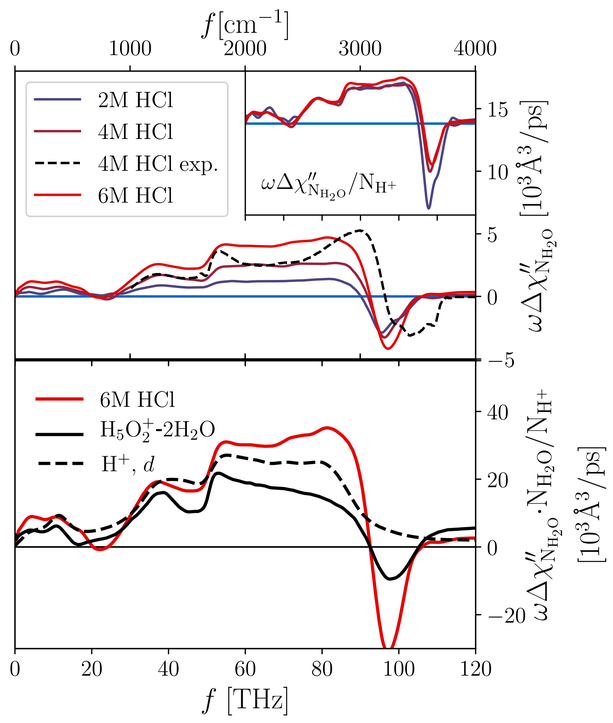
Abstract

The dynamics of excess protons in water or protein environments produce unique spectral signatures as the characteristic IR continuum band [1,2]. The microscopic origin of the IR continuum band as well as spectroscopic models for the proton barrier-crossing dynamics between different meta-stable states are derived and applied to data from DFT-MD simulations. Frequency-dependent friction and anharmonic broadening effects of infrared line shapes are studied in a more fundametal system, the intramolecular vibrations of water in gas and bulk phase.

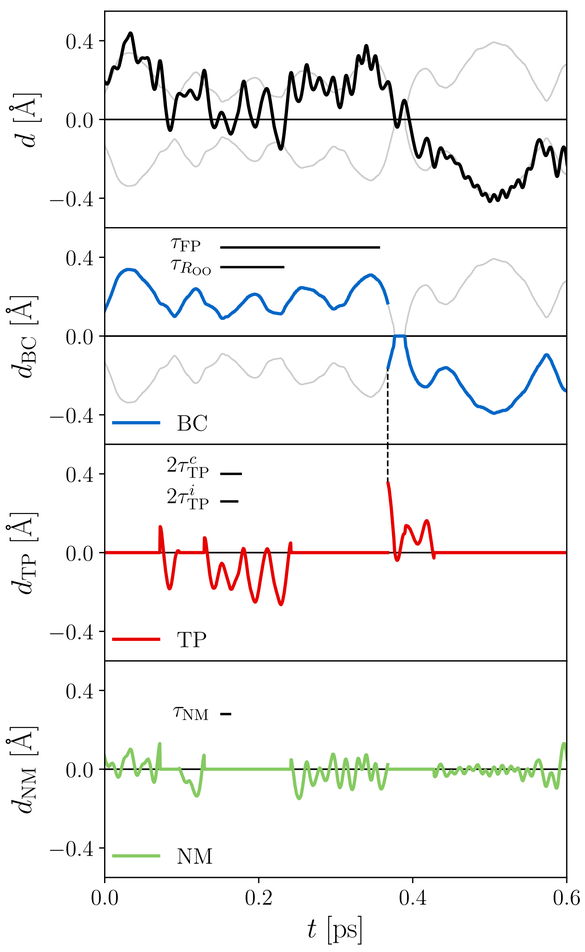
Excess-proton dynamics in HCl revealed by IR spectroscopy

Infrared power spectra $\omega\tilde{\chi}''$ are computed from DFT-MD simulations of HCl and water and compared to experimental difference spectra [3]. The difference spectra can be decomposed to represent the excess-proton dynamics, which are projected onto a two-dimensional coordinate system inspired by the Zundel cation.

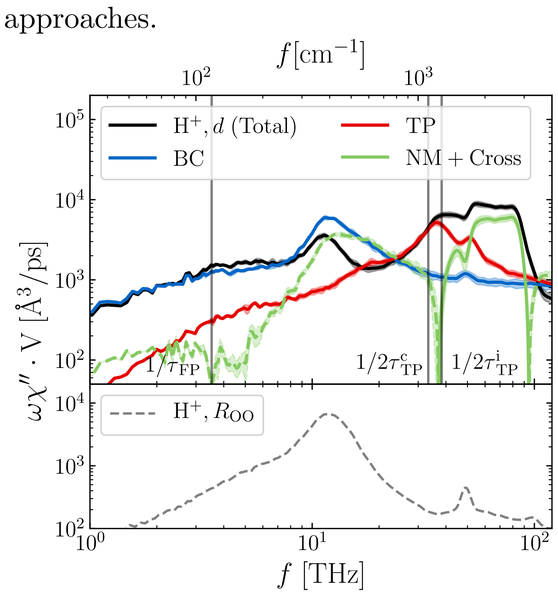




Stochastic infrared signatures of proton dynamics in HCl

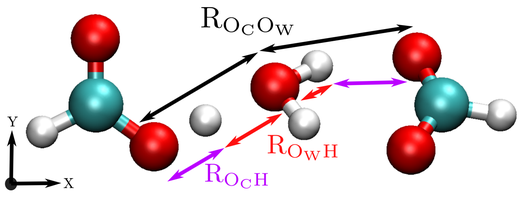


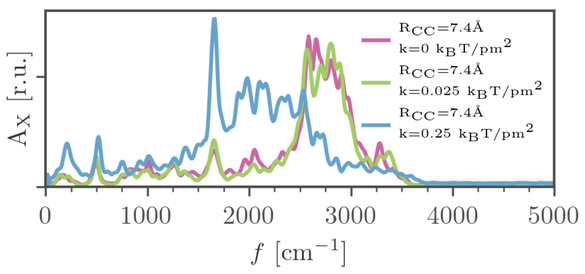
The characterstic time scale distributions of a stochastic barrier-crossing process [4], the transition-path time distribution $p_{TP}(t)$ and the barrier-crossing waiting time distribution $p_{FP}(t)$, are obtained from a decomposition of the protjected excess-proton dynamics and can be related to distinct spectral signatures, that cannot be captured by normal-mode approaches.



Proton dynamics between carboxyl groups

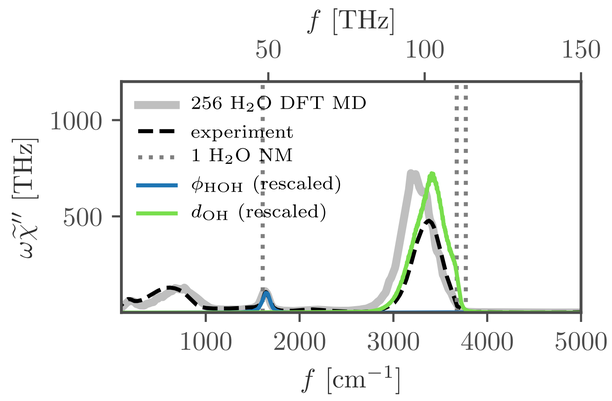
In order to analyse the excess-proton barrier-crossing dynamics and spectral signatures in protein-like environments, simulations with protonated water clusters confined between protein headgroups are performed.



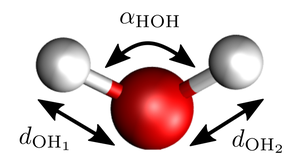


- Equilibrium proton distributions between headgroup and water can be bistable at room temperature [5]
- Several confined protonated systems show IR continuum band

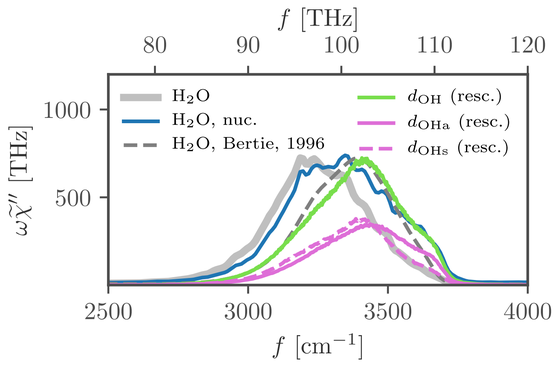
Infrared line shapes of water



The generalized Langevin model is used to decompose infrared line shapes of vibrational coordinates in potential U and frequency-dependent friction $\tilde{\Gamma}(\omega)^+$ effects [6].

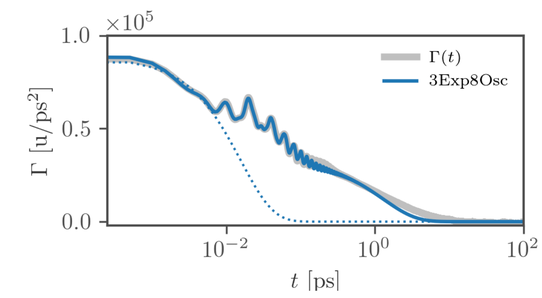


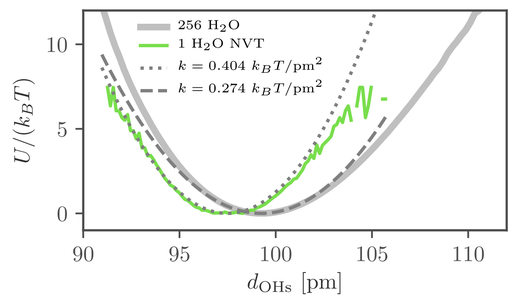
- OH-mode in bulk water is shifted and amplified compare to gas phase, which hints to strong collective effects and softening of the bond potential
- HOH-mode on the contrary shows a small blue-shift; is it stiffer?

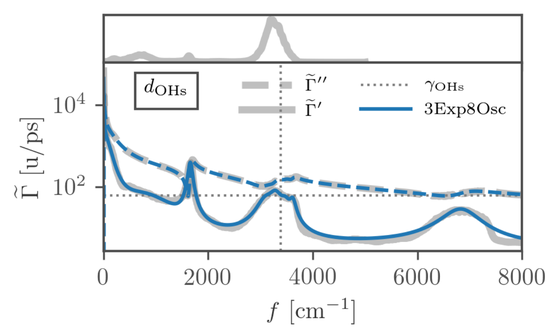


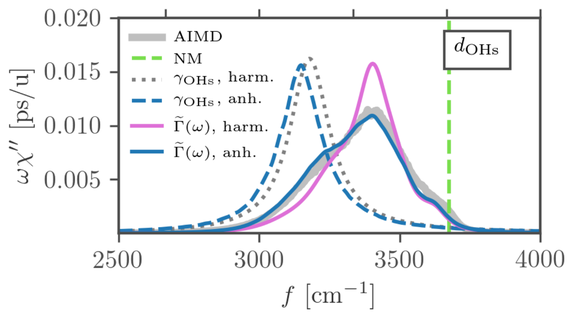
OH stretching mode shows strong inhomogenous broadening

For the OH stretching vibration we find that homogeneous (due to Markovian friction) and inhomogeneous line-broadening (due to non-Markovian friction) contribute equally.



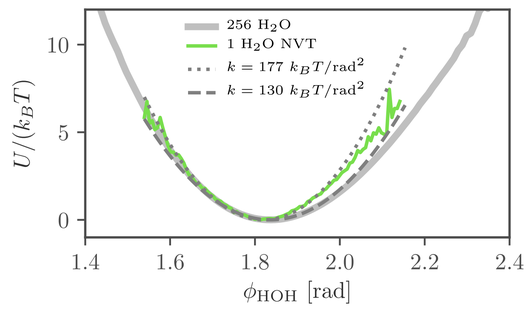


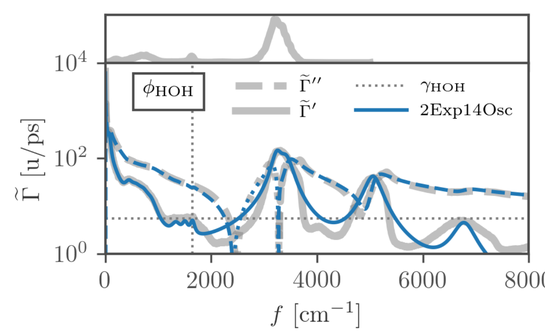


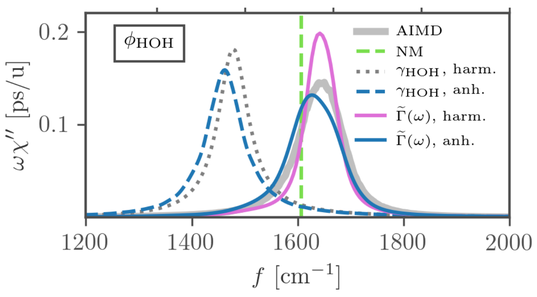


HOH bending mode shows strong frictional blue-shift

For the HOH bending vibration we find a softening of the potential in the liquid phase. The red shift due to this softening is over-compensated by a blue shift due to non-Markovian friction, which is in contrast to the OH stretching vibration.







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[2] Daldrop, J. O., Saita, M., Heyden, M., Lorenz-Fonfria, V. A., Heberle, J., & Netz, R. R. (2018). Nature Communications, 9(1), 311.

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[6] Daldrop, J. O., Kappler, J., Brünig, F. N., & Netz, R. R. (2018). PNAS , 115(20), 5169–5174.