Femtosecond vibrational relaxation dynamics of the OH-stretching vibration of HOD in liquid-to-supercritical D_2O

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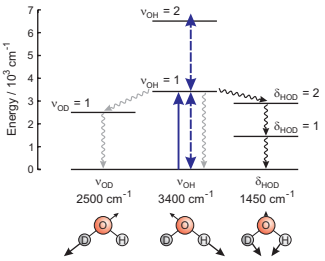
Introduction

The famous anomalies found in the thermodynamic quantities of liquid water can be connected to the formation of an extended network of hydrogen-bonds (H-bonds), which is structurally and dynamically highly random in nature. Exploring the geometric distribution of H-bonds and determining the time scales and mechanisms of their structural relaxations is therefore of key importance to a comprehensive understanding of the physico-chemical properties of this highly peculiar solvent of life.
To understand the time scales and molecular mechanisms responsible for vibrational energy relaxation (VER) in the H-bonded network of bulk water, we performed femtosecond mid-IR pump-probe spectroscopy on the OH-stretching vibration of HOD in heavy water over wide ranges of pressure and temperature corresponding to the liquid and the supercritical phase of the mixture.



(i) Ultrashort mid-IR-pump-pulse prepares the first excited state of the OH-stretching mode ν_{OH} of HOD

(ii) Ultrashort mid-IR-probe-pulse detects the ground state recovery through the transient ν_{OH} bleach or the excited-state decay through the anharmonically shifted absorption to ν_{OH}=2

Experiment

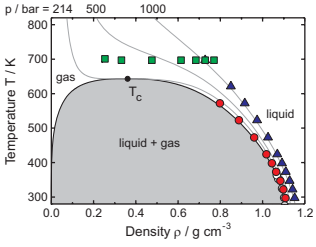
Femtosecond mid-infrared pump-probe spectrometer

Fs-Front-End modelocked, frequency doubled Erbium fiber & Ti:S-CP-Regen-Amplifier

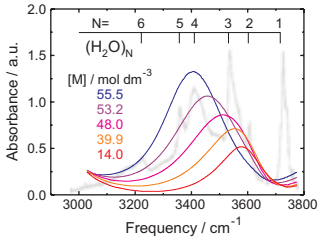
Two synchronously pumped TOPAs w/ DFG of signal/idler in AgGaSe

Pump-probe setup w/ wavelength-resolved detection using 2x32-MCT-array detector

(T,ρ)-phase diagram of heavy water and density-dependent linear absorption spectrum in the OH-streching region



thermodynamic data from PROPATH, a program package for thermophysical properties, version 12.1, June 2001



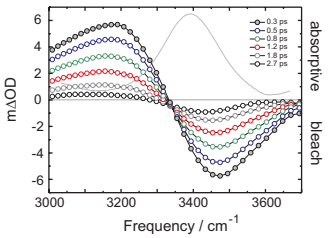
cluster spectra from IR cavity ring-down laser spectroscopy by Saykally & coworkers, J. Phys. Chem. A 101, 5211 (1997)

Literature

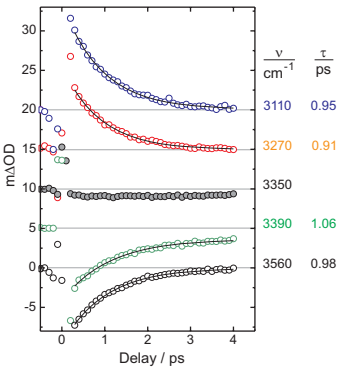
D. Schwarzer, J. Lindner, P. Vöhringer; Energy relaxation versus spectral diffusion of the OH-stretching vibration of HOD in liquid-to-supercritical deuterated water; J. Chem. Phys. 123, 161105 (2005)
D. Schwarzer, J. Lindner, P. Vöhringer; OH-stretch vibrational relaxation of HOD in liquid-to-supercritical D2O; J. Phys. Chem. A. 110, 2858 (2006)

Results

Transient differential transmission spectra



Probe-frequency dependent kinetic traces

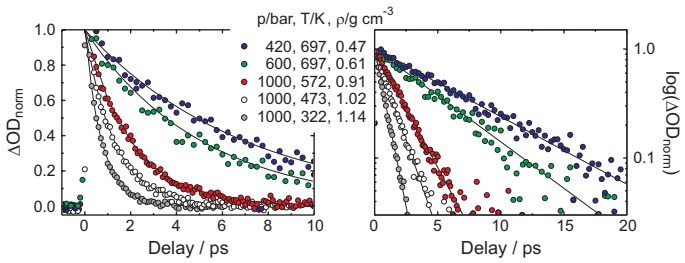


1.) spectra exhibit isosbestic point
2.) kinetics are single exponential
3.) bleach and absorption decay with identical time-constants

Ground-state repopulation and excited-state depopulation occur on identical time scales !

No intermediate states are significantly populated during relaxation of OH stretching vibrational energy !

Temperature and density dependent energy relaxation



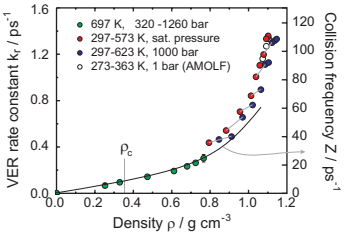
Discussion

Analysis using isolated binary collision theory for VER

$$k_{if}(\rho,T) = P(T)\cdot Z(\rho,T)$$

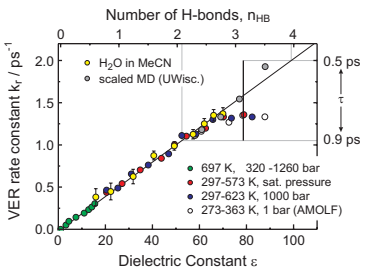
$$Z(\rho,T) = 4\pi R^2 \cdot g(R) \cdot \sqrt{k_B T/\pi M}$$

g(R) from MC simulations using attractive hard sphere (for HOD) in a Lennard-Jones fluid (D_2O)



Number of H-bonds as a measure for local solvent density

MD simulations by Okazaki & coworkers, Chem.Phys. Lett. 345, 195 (2001):
"Dielectric constant ε proportional to average coordination number !"



In the thermodynamic stability range of the liquid under ambient pressure:
Vibrational spectral diffusion due to H-bond breakage and formation occurs on times scales similar to vibrational energy relaxation !!

Nonexponential kinetics !

MD from Skinner & coworkers, J. Chem. Phys. 119, 3840 (2003)
H_2O in MeCN from M.S. Pchenitchnikov (private communication)
1 bar, T-dependent data from Bakker & coworkers, Phys. Rev. Lett., 81, 1106 (1998)