Femtosecond vibrational relaxation dynamics of the
OH-stretching vibration of HOD in liquid-to-supercritical D2O

Jörg Lindner¹, Dirk Schwarzer², and Peter Vöhringer¹

1) Department of Molecular Physical Chemistry, Institute for Physical and Theoretical Chemistry
University of Bonn, Wegelerstraße 12, 53115 Bonn, Germany, email: p.voehringer@uni-bonn.de
2) Max-Planck-Institute for biophysical Chemistry, Am Faßberg 11, 37077 Göttingen, Germany

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) Ultrasfast mid-IR-pump-pulse prepares the first excited state of the OH-stretching mode νOH of HOD

(ii) Ultrasfast mid-IR-probe-pulse detects the ground state recovery through the transient νOH bleach or the excited-state decay through the anharmonically shifted absorption to νOH=2

Experiment

Femtosecond mid-infrared pump-probe spectrometer

| Fs-Front-End modelocked, frequency doubled Erbium fiber & Ti:S:CP-Rep-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,p)-phase diagram of heavy water and density-dependent linear absorption spectrum in the OH-stretching region

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


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

Analysis using isolated binary collision theory for VER

\[ k_B(p,T) = \frac{P(T)}{Z(p,T)} \]

\[ Z(p,T) = 4\pi R^2 g(R) \cdot k_B T/M \]

g(R) from MC simulations using attractive hard sphere (for HOD) in a Lennard-Jones fluid (D2O)

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

‘Dielectric constant is 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 !

Discussion

H2O in MeCN from M.S. Pechinishteinov (private communication)

Literature