Vibrational Energy Relaxation in Water-Acetonitrile Mixtures

Cringus, Dan; Yeremenko, Sergey; Pshenichnikov, Maxim S.; Wiersma, Douwe A.

Link to publication in University of Groningen/UMCG research database

Vibrational Energy Relaxation in Water-Acetonitrile Mixtures

Dan Cringus, Sergey Yeremenko, Maxim S. Pshenichnikov, and Douwe A. Wiersma

Ultrafast Laser and Spectroscopy Laboratory, Materials Science Centre
Department of Chemical Physics, University of Groningen, Nijenborgh 4, 9747 AG
Groningen, The Netherlands
E-mail: M.S.Pshenichnikov@chem.rug.nl

Abstract. IR pump-probe spectroscopy is used to study the effect of hydrogen bonding on the vibrational energy relaxation pathways. Hydrogen bonding accelerates the population relaxation from 12ps in diluted acetonitrile solution to 700fs in bulk water.

1. Introduction

Water is a unique substance by being the medium in which most chemical reactions that sustain life occur. One of the important issues concerning water dynamics is the question how excess vibrational energy is disposed of. Vibrational energy relaxation (VER) is mainly a radiation-less process, ultimately leading to excitation of the low-frequency thermal motions of molecules. Unveiling the relaxation mechanism implies finding the intermediate steps and routes of the energy transfer process. Water is a very "dynamical" fluid in the sense that the rearrangements of the local structure surrounding a water molecule, occur on a sub-picosecond timescale [1-3]. Vibrational relaxation dynamics in water is also very fast. For instance, the population relaxation lifetime of the OH-stretch mode of HDO molecules in liquid D_2O is about 740 fs [4], while in pure H_2O it reduces to 250 fs [5]. In contrast, the relaxation lifetime is substantially longer (tens of picoseconds) when water molecules are isolated from each other in an inert liquid solvent matrix [6]. Hence, vibrational population (energy) relaxation in water molecules seems to be strongly affected by hydrogen bonding. From another hand, the apparent connection between the VER rate and the presence of the hydrogen bonding in water paves the way for studying the phenomenon of hydrogen bonding itself.

In this contribution we present a study of the effect of hydrogen bonding on VER of the OH-stretch mode of HDO molecules in the liquid phase. To control the extent of the hydrogen bond network, water is dissolved in an inert solvent (acetonitrile) capable of forming water solutions of any concentration. We demonstrate that IR frequency-resolved pump-probe experiments with a 70-fs temporal resolution allow the determination of the solution composition of water and acetonitrile. On the basis of the experimental results, a model is developed that describes the effect of the hydrogen bonding on the process of VER in liquid water.

2. Results and discussion

The result of a combined time-frequency scan for a 50% solution is presented in the Fig.1. It is clear that the signal decay rate is wavelength dependent. Within the induced bleach (induced absorption) band the signal decays slower at the shorter wavelengths than at longer ones (solid curve). Such dependence of the population lifetime on the wavelength is determined by the effect of diverse solvent environments for different OH-bonds. The formation of a hydrogen bond between water molecules leads to a red shift of the absorption band of the OH-stretch vibration. The OH-oscillators that form a hydrogen bond with acetonitrile or are non-hydrogen-bonded, have higher frequencies (~3550 cm^{-1}) and, as Fig.1 shows, longer relaxation times. In contrast, the OH-oscillators that form a hydrogen bond to other water molecules have lower frequencies (~3400 cm^{-1}) and much shorter relaxation times.

Decomposition of the total absorption line into contributions from acetonitrile-bonded and water-bonded water molecules is based on the assumption that there is a clear separation of time scales between the dynamics of water-bonded and non-water-bonded oscillators [7]. At any given wavelength, the pump-probe signal can be represented as a linear combination of these two contributions. We have performed a global fit of the experimental data, i.e. the complete time-frequency scan (like the one depicted in Fig.1) is simulated for each concentration in a single fitting session. The concentration dependencies of the population lifetimes of non-water-bonded and water-bonded OH-oscillators, derived from the global fit to the experimental data, are shown in the Fig.2. Our analysis shows that the main pathway for the vibrational relaxation of the OH-stretching mode in pure water
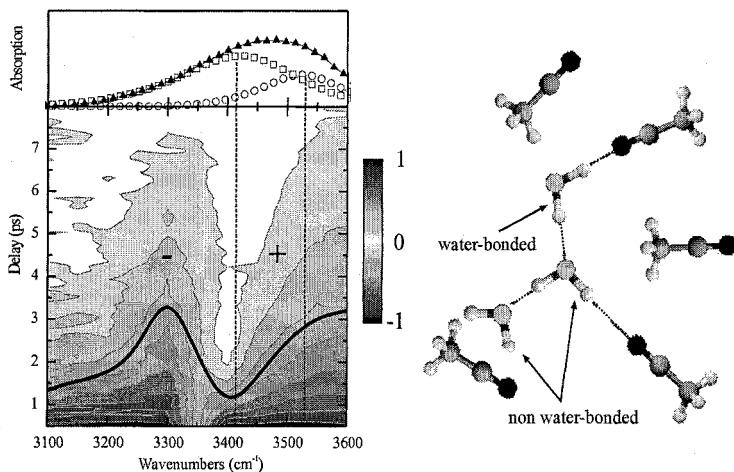

Fig.1. A typical time-frequency pump-probe scan (50% of water in acetonitrile). Thick solid line in the 2D plot depicts the level at which the signal decays by a factor of *1/e*. Triangles at the top plot depict the linear absorption spectrum for this concentration, while the open squares and circles show the spectral components corresponding to water-bonded and non water-bonded OH-oscillators, respectively. A schematic illustration of the microscopic structure is depicted at the right side.
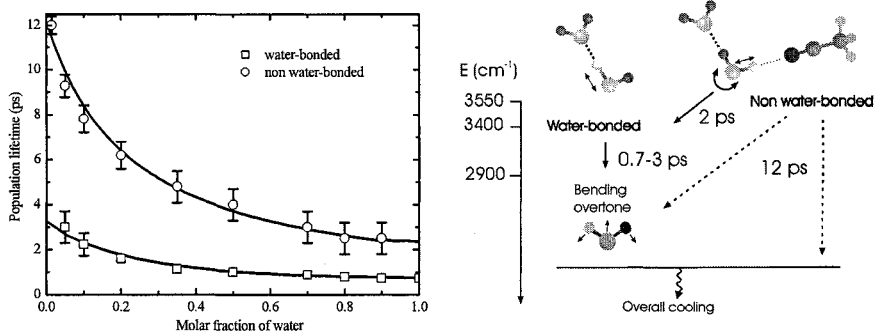
Fig.2. Left: concentration dependence of population lifetimes for non-water-bonded (circles) and water-bonded (squares) OH-oscillators. The solid curves represent the results of simulations. Right: schematic representation of the energy relaxation pathways for the OH-stretch vibrational mode of water molecules in acetonitrile solution.

involves the overtone of the bending mode [8,9]. Hydrogen bonding is found to accelerate the population relaxation from 3 ps in dilute solutions to 700 fs in neat water, since the energy overlap between the donor and acceptor modes increases.

For the OH oscillators that have not initially been water-bonded, there are two relaxation pathways. First, the oscillator can relax directly to the first overtone of the bending mode with a 12-ps lifetime. Second, the water molecule first rotates (~2 ps as derived from rotational anisotropy experiments), then forms a hydrogen bond to a neighboring water molecule, becomes hydrogen-bonded, and finally relaxes via resonance with the bending mode overtone. While the second path is much faster that the first one, it requires another water molecule in close proximity and therefore becomes only efficient at high concentrations. The rate-limiting step in this process is molecular reorientation that occurs at a 2 ps time scale.

References

1   S. Yeremenko, M. S. Pshenichnikov, and D. A. Wiersma, Chem. Phys. Lett. **369**, 107 (2003).
2   J. Stenger, D. Madsen, P. Hamm, E. T. J. Nibbering, and T. Elsaesser, J. Phys. Chem. A**106**, 2341 (2002).
3   C. J. Fecko, J. D. Eaves, J. J. Loparo, A. Tokmakoff, and P. L. Geissler, Science **301**, 1698 (2003).
4   H.-K. Nienhuys, S. Woutersen, R. A. van Santen, and H. J. Bakker, J. Chem. Phys. **111**, 1494 (1999).
5   A. J. Lock and H. J. Bakker, J. Chem. Phys. **117**, 1708 (2002).
6   H. Graener, G. Seifert, and A. Laubereau, Chem. Phys. **175**, 193 (1993).
7   D. Cringus, S. Yeremenko, M.S. Pshenichnikov, and D.A. Wiersma, J. Phys. Chem. **B108**, 10376 (2004).
8   D. D. Dlott, Chem. Phys. **266**, 149 (2001).
9   C. P. Lawrence and J. L. Skinner, J. Chem. Phys. **117**, 5827 (2002).