Hydrogen Bond Dynamics in Alcohols
Studied by 2D IR Spectroscopy

Keisuke Shinokita, Ana V. Cunha, Thomas L. C. Jansen, and Maxim S. Pshenichnikov

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
email:K.Shinokita@RuG.nl

Abstract: Ultrafast hydrogen-bond dynamics in alcohols are studied with 2D IR spectroscopy and combined molecular dynamics – quantum mechanical simulations on the OH stretching mode. Timescales of ~200 fs and 1 ps are attributed to hydrogen-bond fluctuations and hydrogen-bond exchange dynamics, respectively.

OCIS codes: (300.6530) Spectroscopy, ultrafast, (260.7120) Ultrafast phenomena

1. Introduction

Hydrogen bond (HB) dynamics in liquids plays a significant role in chemical and biological reactions. In the past decade, tremendous advances in 2D IR spectroscopy and combined molecular dynamics (MD) - quantum chemistry calculations have put water dynamics in the research spotlight due to its fundamental role in nature. In particular, the important process of HB dynamics has been studied and fascinating spectroscopic aspects of inter- and intramolecular vibrational couplings and vibrational exciton formation have been addressed.

Alcohols present another example of hydrogen-bonded liquids that differ from water in many important aspects. First, in alcohols the number of donated HB per molecule is different from the number of accepting HBs. This disrupts the 3D HB network so characteristic for water. Second, alcohol molecules being amphiphilic contain both hydrophobic and hydrophilic parts, which add complexity to the HB dynamics. Third, the size of alcohol molecules can be easily varied, e.g. by going from primary to secondary or tertiary alcohols. Finally, alcohols can be mixed with a wide variety of solvents. Some of these properties of alcohols have been explored spectroscopically by studying the HB dynamics in solution, mainly dissolved in CCl_4 [1-3].

Here we use ultrafast 2D IR spectroscopy to reveal HB dynamics in liquid alcohols taking the OH stretching mode in methanol as the simplest example. Experimental results are supported by combined MD - quantum mechanics calculations to elucidate the molecular picture of HB dynamics.

2. Experimental

We used a pump-probe geometry setup for the 2D measurements with two collinear pump pulses and one probe pulse, all centered at 3400 cm^{-1} and of ~75 fs duration. A 2% solution of MeOH in MeOD was placed in a 200 μm-thickness free-standing jet and maintained at OD~0.5 at the maximum of OH-stretch absorption. The circulatory pump system was purged with nitrogen to minimize water adsorption from the air. All experiments were performed at room temperature.

3. Theory

We performed MD simulations using the OPLS/AA force field [4] for methanol. After initial equilibration a 1 ns trajectory with snapshots stored at 10 fs intervals was obtained. From this, a single methanol molecule was selected for the generation of the vibrational hamiltonian for the spectral simulations. The OH vibration frequency and transition dipole were determined using an electrostatic mapping for the OH stretch [5]. The anharmonicity was
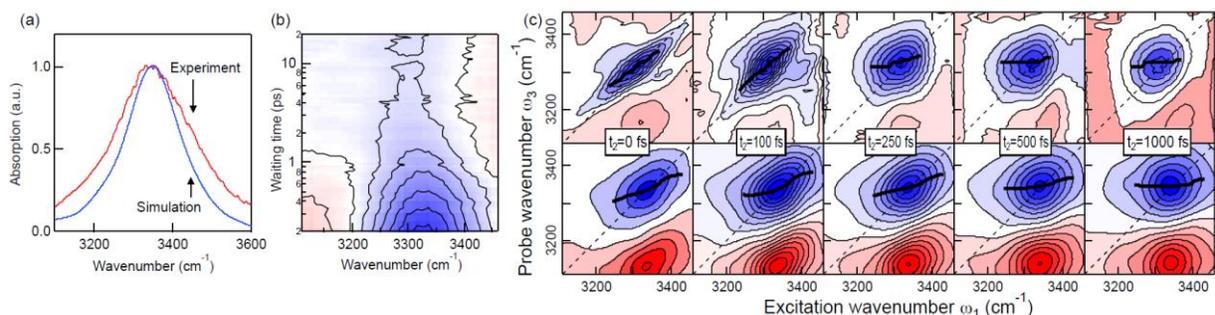

Fig.1. (a) The experimental (red) and simulated (blue) linear absorption spectra of hydroxyl stretch in MeOH:MeOD. (b) Frequency-resolved pump-probe signal. (c) Normalized experimental (top panel) and simulated (bottom panel) absorptive 2D spectra at different waiting times t_2. The blue and red colors show bleaching and induced absorption, respectively. Thick black lines show the results of the CLS analysis. All simulated spectra were red-shifted by 130 cm^{-1}.

fixed at 200 cm^{-1} and the harmonic rule was applied for the $|1>\rightarrow|2>$ transition dipoles. The linear absorption and two-dimensional infrared spectra were obtained using the NISE simulation code [6] with coherence times of 320 fs.

4. Results

Figure 1a shows the linear absorption spectrum of the OH hydroxyl stretching mode of methanol (peak at 3350 cm^{-1} with FWHM of ~210 cm^{-1}). The population lifetime deduced from the frequency-resolved pump-probe spectrum (Fig.1b) amounts to ~600 fs which is consistent with Ref.[2] (albeit slightly faster). Development of the thermal response due to local heating of the solvent is also apparent at long (>1 ps) times. The lifetime of the OH stretch of MeOH:MeOD is even shorter than that for HDO:D$_2$O (~700 fs) which hints to CH stretching modes as possible acceptors. However, pump-probe data on MeOH diluted in acetonitrile, showed a ~5 ps lifetime demonstrating that the intermolecular degrees of freedom are necessary for OH-stretch energy dissipation.

Figure 1c presents 2D IR spectra of MeOH:MeOD at different waiting times. At short times, the spectrum is elongated along the diagonal, which indicates a highly correlated response. With time, the memory for initial excitation frequency vanishes, making the 2D signal almost circular, already at ~1 ps. To quantify the phase memory, the center line slope (CLS) analysis was applied (Fig. 1c, black lines), with results summarized in Fig.2a (red dots). The retrieved correlation function initially decays at a time scale of ~200 fs followed by a longer tail which is comparable to the HDO:D$_2$O case (Fig.2a, green stars).

The calculated 1D and 2D spectra (Fig.1a,c) present a reasonable agreement with the experimental results. The simulated spectra were red-shifted by 130 cm^{-1} to match the experimental peak position. The predicted line width is somewhat too narrow. At the same time, the CLS (Fig.2a) determined from the simulated spectra in Fig.1c exhibits a too fast memory loss at short times. Altogether this suggests that the used force field and mapping overestimate initial frequency fluctuations (see the CF in Fig.2a). These fluctuations are determined by the hydrogen bond stretching motion and librations.

On the other hand, the longer time dynamics (>200 fs) reflecting the HB exchange processes are well captured by the simulations. Figure 2b illustrates the low- and high-frequency HB configurations (typically denoted δ and ε, respectively [3]) which can be observed at ~3350 and 3475 cm^{-1} in the experimental absorption spectrum, but not in the calculated one. This suggests that the non-Condon effects are also overestimated in the simulation, and a better electrostatic mapping would be beneficial. From the histograms in Fig 2c an approximate frequency difference of 100 cm^{-1} between these two hydrogen bond configurations is determined. From the simulated frequency correlation function, the exchange time between the two configurations is inferred to be ~1.5 ps.
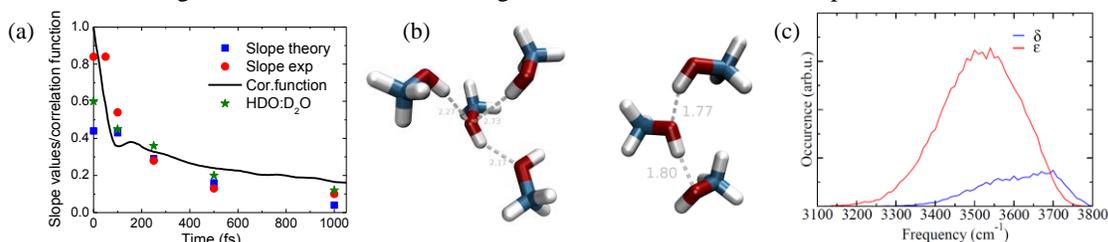

Fig.2. (a) Slope values and frequency correlation function obtained from simulations. SLC value for HDO:D$_2$O are also shown for comparison. (b) Snapshots from MD simulations that show two different HB configurations. Left: The low frequency configuration where the central methanol donates one hydrogen bond and accepts two (ε). Right: The high frequency configuration where the central methanol donates one hydrogen bond and accepts one (δ). (c) The frequency distribution for the two hydrogen bond configurations.

In conclusion, we find that the excited-state lifetime in deuterated methanol is shorter than for deuterated water while the characteristic HB lifetime is slightly longer. In pure methanol, we confirm the previous findings [3] that the δ and ε hydrogen bond configurations are dominating. Experimental and theoretical investigations on alcohols with longer hydrophobic tails are underway.

[1] J.B. Asbury *et al*., "Ultrafast heterodyne detected infrared multidimensional vibrational stimulated echo studies of hydrogen bond dynamics", Chem. Phys. Lett. **374,** 362–371 (2003).
[2] S.Yamaguchi *et al*., "Vibrational Dynamics of Hydrogen-Bonded Complexes Studied by Infrared Pump-Probe Spectroscopy", Rev. Laser Eng. **36,** 1024–1027 (2008).
[3] K. Kwac and E. Geva, "A Mixed Quantum-Classical Molecular Dynamics Study of the Hydroxyl Stretch in Methanol/Carbon Tetrachloride Mixtures III: Nonequilibrium Hydrogen-Bond Dynamics and Infrared Pump–Probe Spectra", J. Phys. Chem. B. **117,** 7737–7749 (2013).
[4] W.L Jorgensen *et al.*, "Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids". J. Am. Chem. Soc. 118 (45): 11225–11236 (1996).
[5] B.Auer *et al*., "Hydrogen bonding and Raman, IR, and 2D-IR spectroscopy of dilute HOD in liquid D$_2$O", P. Nat. Acad. Sci, **104,** 14215–14220 (2007).
[6] C. Liang, T.L.C. Jansen, "An Efficient N^3-Scaling Propagation Scheme for Simulating Two-Dimensional Infrared and Visible Spectra", J. Chem. Theory Comput. **8,** 1706–1713 (2012).