# Are Hydrogen Bond Dynamics in Alcohols Different from Water?

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

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, *M.S.Pchenitchnikov@RuG.nl

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. **Max 50 words**

In the past decade, water dynamics have been put in the research spotlight thanks to tremendous advances in 2D IR spectroscopy and combined molecular dynamics (MD) - quantum chemistry calculations. In particular, the important in chemistry and biology process of hydrogen-bond (HB) dynamics has been studied, and fascinating spectroscopic aspects of inter- vs intramolecular vibrational couplings and vibrational exciton formation have been identified. Alcohols present another example of HB liquids that differ from water in many important aspects. In alcohols the number of donated HB per molecule is different from the number of accepting HBs which disrupts the 3D HB network so characteristic for water. Alcohol molecules contain both hydrophobic and hydrophilic parts, which add complexity to the HB dynamics. [1-3].

Here we use ultrafast 2D IR spectroscopy to reveal HB dynamics in liquid alcohols taking the OH stretching mode as a reporter. Experimental results are supported by combined MD - quantum mechanics calculations to elucidate the molecular picture of HB dynamics (Fig.1).
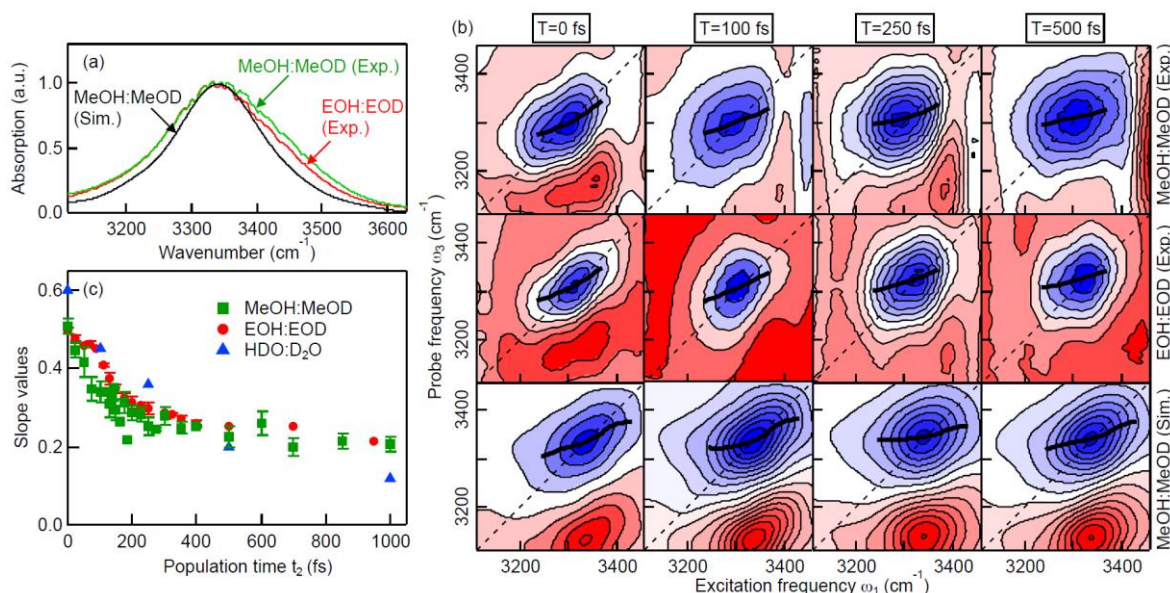


Fig.1 (a) The experimental linear absorption spectra of MeOH:MeOD and EtOH:EtOD at room temperature, and simulated spectra of MeOH:MeOD. Similarity between the experimental spectra suggests minor difference of HB strength. (b) Normalized experimental and simulated absorptive 2D spectra at different waiting times. Thick black curves connect the maxima of the $\omega_1$ cuts to calculate the slope values. The simulations reproduced the experimental results reasonably well. All simulated spectra were red-shifted by 130 cm$^{-1}$ to match the experimental peak position. (c) Slope values of absorptive 2D spectra. Slope values for HDO:D$_2$O are also shown for comparison. Note the minor difference between the three curves.

[1] J.B. Asbury *et al.*, CPL**374,** 362 (2003).
[2] S.Yamaguchi *et al.*, Rev.Laser Eng. **36,** 1024 (2008).
[3] K. Kwac and E. Geva, JPCB **115**, 9184 (2011)