2D IR Spectroscopy on OH Stretch in Diluted Alcohols

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Hydrogen bond (HB) dynamics of strongly diluted alcohols were studied with 2D IR spectroscopy and combined molecular dynamics – spectral simulations on the OH stretching mode. For eight studied alcohols, the HB dynamics have similar behavior with fast (~200 fs) initial relaxation and long (3 ps) tail.

Alcohols are the hydrogen-bonded[1] liquids which are perfectly miscible with a wide variety of polar and nonpolar[2] solvents. Recently, Shinokita *et al.*[3] showed that HB dynamics of bulk alcohols are strongly dependent on the size of the molecule. To assess the significance of intermolecular interaction in the bulk alcohols, HB dynamics of isolated (strongly diluted) alcohol molecules would form a convenient starting point. Here we study a series of primary alcohol molecules (methanol, ethanol, two isomers of propanol, and four isomers of butanol) diluted in acetonitrile, with 2D IR spectroscopy and combined molecular dynamics - spectral simulations using the OH-stretching mode as a reporter.

Central frequencies of the OH-stretch absorption spectra do not show any dependence on the size of the alkyl chain length, nor do the spectral widths. The OH stretch lifetime of ~4.5±0.5 ps does not possess any significant alkyl group dependence. Results of the center line slope (CLS) analysis on 2D IR spectra (Fig.1b) are similar for all alcohols, too: fast (200-300 fs) initial relaxation due to OH librations is followed by a long, ~3 ps tail (Fig.1c). Combined MD – spectral simulations reveal both components, but underestimate the amplitude of the short one. Overall, OH-stretch lifetimes and dynamics of the diluted alcohols do not depend on the size of the alcohol molecule which implies the dominance of intermolecular interactions in the bulk alcohols.
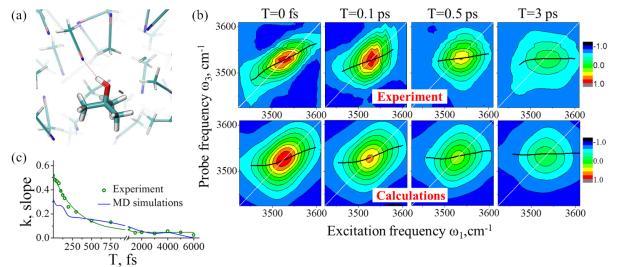

Fig. 1 (a) A snapshot from MD simulations; (b) Experimental and simulated 2D IR spectra of methanol at different waiting times *T*; (c) CLS values for methanol. A bi-exponential fit to the experimental data is shown as the olive line. Note change in the time scale after 1 ps.

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[2] I. Piletic *et al*., JCP **119**, 423 (2003); S. Woutersen *et al*., JCP **107**, 1483 (1997);
[3] K. Shinokita *et al*., JCP **142**, 212450 (2015); K. Mazur *et al*., JPC B **119**, 1558 (2015).