Hydrogen bond dynamics probed with vibrational echo correlation spectroscopy

Abstract:
Hydrogen bond dynamics of H2O and methanol-OD oligomers are elucidated with exceptional detail using Vibrational Echo Correlation Spectroscopy of the hydroxyl stretch. The time evolution of the methanol correlation spectrum demonstrates that the strongest hydrogen bonds break preferentially following vibrational relaxation. Detailed model calcns. corroborate the conclusion. The evolution of the strengths of hydrogen bonds in dil. HOD in H2O is studied by monitoring the spectral diffusion dynamics displayed in the OD hydroxyl stretch. Anal. of the correlation spectra reveal marked deviations of water from std. simulation models, TIP4P and SPC/E. Significant differences as a function of wavelength in the rate of spectral diffusion are obsd. for time scales <400 fs, with dynamics of the red side of the line (strong H-bonds) slower. The wavelength dependent spectral diffusion shows that std. theory based on a single frequency-frequency correlation function cannot be used to describe the broad hydroxyl stretch band. [on SciFinder(R)]