

2D-IR spectroscopy of water molecules in a hydrated lithium nitrate crystal

Wilbert J. Smit*, Huib J. Bakker

FOM Institute AMOLF, Science Park 104, 1098AR Amsterdam,
The Netherlands, *smit@amolf.nl

Water molecules in lithium nitrate trihydrate have a well-defined geometrical arrangement and contain three distinct hydrogen-bond strengths: strong, bifurcated, and weak. The vibrational relaxation dynamics of the three distinct OD stretch vibrations of dilute HDO molecules is studied using 2D IR pump—probe spectroscopy in the temperature range 22—295 K.

Water molecules in lithium nitrate trihydrate have two well-defined geometrical arrangements, leading to three distinctly different types of hydrogen bonds and three well-separated absorption peaks of the hydroxyl stretch vibrations (Fig.1a). As a result, hydrated lithium nitrate trihydrate forms an excellent model system for studying the effects of the hydrogen-bond environment on the vibrational energy relaxation.[1]

In the temperature range from 22 K to 295 K we observe a decrease in vibrational lifetime from 3.8 ± 0.2 to 2.8 ± 0.1 ps for the strongly hydrogen-bonded species, from 5.4 ± 0.1 to 4.1 ± 0.1 ps for the bifurcated hydrogen-bonded species, and from 10.4 ± 0.2 to 8.8 ± 0.4 ps for the weakly hydrogen-bonded species (Fig. 1b). This temperature dependence is opposite to that of the OD stretch vibration of dilute HDO:H₂O ice, for which the vibrational lifetime increases from 480 ± 40 fs at 25 K to 850 ± 60 fs at 265 K.[2] We discuss the origin of this difference in temperature dependence.

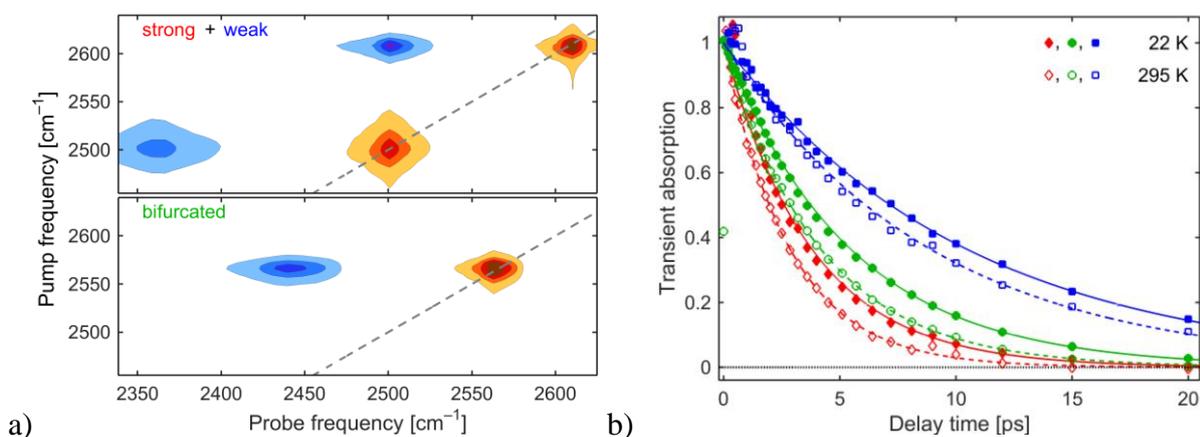


Fig.1 (a) 2D transient absorption spectra at 295 K of the OD groups with strong and weak hydrogen-bonds (top) and bifurcated hydrogen-bonds at a pump—probe delay of 0.5 ps. The positive absorption changes are shown in red and the negative absorption changes in blue. (b) Fitted normalized absorption changes as a function of delay for the OD groups with strong (red), bifurcated (green) and weak (blue) hydrogen bonds, at 22 K (solid line and filled points) and at 295 K (dashed line and open points).

[1] Werhahn, J. C.; Pandelov, S.; Xantheas, S. S.; Iglev, H. *J. Phys. Chem. Lett.* **2011**, 2, 1633–1638

[2] Smit, W. J.; Bakker, H. J. *J. Chem. Phys.* **2013**, 139, 204504