

Femtosecond mid-infrared spectroscopy of vibrational energy transfer in liquid-to-supercritical ammonia

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Abstract. Femtosecond pump-probe spectroscopy in the ND-stretching spectral region was used to determine the dynamics of vibrational energy relaxation of NH_2D in fluid NH_3 . The density and temperature dependence of the ND-stretching lifetime suggests that hydrogen bonding is unimportant for vibrational energy transfer. Instead, the energy transfer can be understood in terms of a simple Landau-Teller description for a vibrationally excited solute in a weakly interacting Lennard-Jones solvent.

Because of their lone electron pair in combination with their three hydrogen-atoms, ammonia (NH_3) molecules are often believed to form associated liquids with extended networks of hydrogen bonds (H-bond) similar to water (H_2O). Yet, in contrast to the crystalline phase, unambiguous experimental verification for the existence of H-bonds in liquid ammonia is very difficult to obtain. Therefore, we have carried out the first ever femtosecond (fs) mid-infrared (MIR) spectroscopic study aimed at unraveling the vibrational dynamics in this system.¹ To obtain detailed information regarding the possible influence of H-bonding on such processes, we have performed these fs-MIR experiments under as wide a range of thermodynamic conditions as possible, covering both the normal liquid and the supercritical fluid of NH_3 . Since the NH-stretching region of NH_3 is heavily perturbed by Fermi coupling between the stretching fundamental, ν_1 , and the first overtone of the anti-symmetrical bending mode, $2\nu_4$, we focused on the vibrational dynamics of the ND-stretching mode of NH_2D (the solute) in liquid-to-supercritical NH_3 (the solvent).

A semi-logarithmic plot of the transient absorption decay (see Fig. 1) of the ND-stretching mode of the solute demonstrates that the excited state depopulates in a simple mono-exponential fashion, which implies a strict temporal separation of the VER dynamics from spectral diffusion. The same figure also highlights the temperature dependence of the relaxation kinetics. Obviously, since the two transients were recorded at roughly the same solvent densities, the VER dynamics become faster with increasing T . This finding is in stark contrast to the isobaric and isochoric T -dependence we recently reported for VER of HOD in liquid-to-supercritical D_2O . In the case of water, VER slows down upon heating.² This is because for a given bulk density, ρ , the average number of H-bonds per H_2O molecule decreases with increasing T . The surprising temperature dependence observed here for the relaxation kinetics of NH_2D in NH_3 is much more reminiscent of a solute that vibrationally relaxes in a non-associating solvent.

To further substantiate this interpretation, the ρ and T -dependence of the VER rate was interpreted in terms of simple “breathing-sphere” Landau-Teller simulation, in which the spectral density of the fluctuating solvent forces exerted onto the solute vibration was calculated from classical molecular dynamics (MD) simulations employing binary LJ-interactions only. The qualitative agreement between theory and experiment fully confirms the initial interpretation that the influence of H-bonding on the dynamics of VER in fluid NH_3 is minor. However, the simulations fail to reproduce the ρ -dependence for a given temperature. We believe that this is brought about by resonance detuning effects. We will follow up on this explanation in the near future through MD-simulations involving more realistic and flexible models for fluid NH_3 .

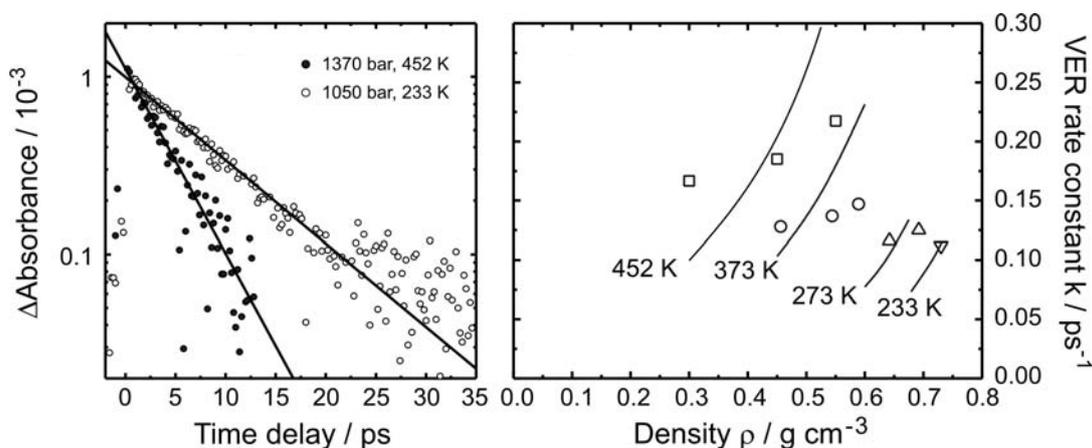


Fig. 1. Left panel: semilogarithmic plot of the temporal transient absorption decay associated with the first excited state of the ND-stretching vibration of mono-deuterated ammonia dissolved in fluid ammonia under two representative thermodynamic conditions. Right panel: Experimentally determined density dependence of the energy transfer rate constant along different isotherms (symbol) in comparison to Landau-Teller simulations using a Lennard-Jones solvent.¹

References

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- ² D. Schwarzer, J. Lindner, and P. Vöhringer, *J. Phys. Chem.* **110**, 2858 (2006).