University of Groningen

Ultrafast IR Spectroscopy on Aqueous Reverse-Micellar Nano-Droplets

Cringus, Dan; Milder, Maaike T.W.; Pshenitchnikov, Maxim; Wiersma, Douwe A.; Lindner, Jörg; Vöhringer, Peter

Published in:
Ultrafast Phenomena XIV. Proceedings of the 14th International Conference

Publication date:
2005

Citation for published version (APA):
Cringus, D., Milder, M. T. W., Pshenichnikov, M. S., Wiersma, D. A., Lindner, J., & Vöhringer, P. (2005). Ultrafast IR Spectroscopy on Aqueous Reverse-Micellar Nano-Droplets. In T. Kobayashi, T. Kobayashi, K. A. Nelson, T. Okada, & S. D. Silvestri (Eds.), Ultrafast Phenomena XIV. Proceedings of the 14th International Conference (79 ed., pp. 431-433). Niigata, Japan: University of Groningen, The Zernike Institute for Advanced Materials.

Ultrafast IR Spectroscopy on Aqueous Reverse-Micellar Nano-Droplets

Dan Cringus[1], Maaike T.W. Milder[1], Maxim S. Pshenichnikov[1], Douwe A. Wiersma[1], Jörg Lindner[2], and Peter Vöhringer[2]

Department of Physical Chemistry, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands
E-mail: M.S.Pshenichnikov@chem.rug.nl
Université Louis Pasteur, Faculté de Chimie, 4 Rue Blaise Pascal, 67000 Strasbourg, France
E-mail: Lindner@chimie.u-strasbg.fr

Abstract. The ultrafast dynamics of water nano-droplets (1-10 nm size) of the L_2-phase of the ternary mixture H_2O-AOT-CCl_4 have been studied using frequency-resolved mid-infrared pump-probe spectroscopy in the spectral region of the OH-stretching vibration.

1. Introduction

The geometric confinement of liquid water is a central issue for a wide variety of research areas ranging from materials to life sciences (for example, see [1] and references therein). Aqueous droplets embedded in nano-porous hosts serve as perfectly size-adapted reaction media for the heterogeneous synthesis of novel semi-conducting colloidal materials with promising applications in optoelectronics. Nanometer-dimensioned water inclusions such as water wires and pockets are key ingredients that determine the tertiary structure and, consequently, the function of proteins.

In the past, the direct observation of molecular dynamics in aqueous bulk phases has been under extensive experimental scrutiny through a variety of femtosecond time-resolved spectroscopies. Despite its tremendous relevance, experimental information regarding dynamical properties of water under geometrically confined conditions is still rather sparse. Therefore, aqueous nano-droplets confined to reverse micelles of the type oil-surfactant-water have recently raised considerable interest. Studies on molecular dynamical processes in aqueous reverse-micellar nano-droplets included solvation dynamics of water-soluble chromophores [2], and vibrational energy relaxation of small inorganic anions [3]. Furthermore, the dynamics of thermal cooling of reverse micellar nano-droplets has been measured, following an initial deposition of vibrational energy by pumping the intramolecular OH-stretching vibration of water [4]. Here, we report on time and frequency-resolved femtosecond experiments on vibrational energy relaxation of aqueous reverse micellar nanodroplets following the intramolecular OH-stretching excitation of the liquid ternary mixture CCl_4:Aerosol OT:H_2O. The experiments are performed with either 150-fs tunable or 70-fs IR pulses on a sample contained in a rotating sample-cell or a 100-μm thick freestanding jet.
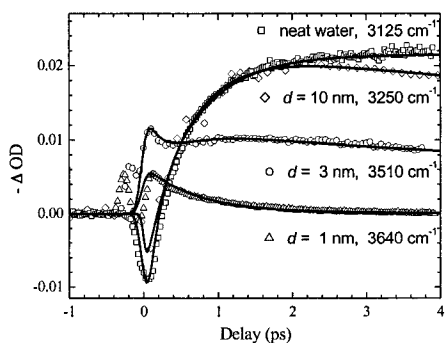
Fig.1. Transients for three types of water nano-droplets and bulk water. The solid curves represent the results of simulations.
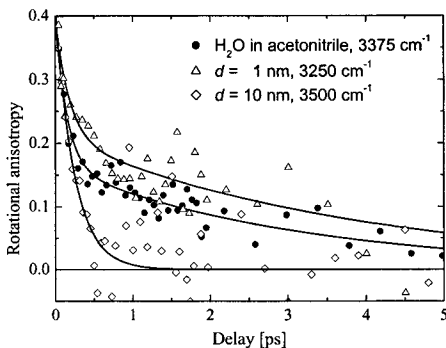
Fig.2. Rotational anisotropies for H_2O in small (d = 1 nm), large (d = 10 nm) micelles, and acetonitrile matrix.

2. Results and discussion

Typical pump-probe transients for three representative micro-emulsions are compared in Fig.1 to equivalent data on bulk water. For micelles with diameter of d=1 nm, the amount of free "bulk-like" water is vanishing, for d=3 nm an approximately equal number of bound and free water is present into the nano-droplet while for d=10 nm most of the water molecules belong to the aqueous core. In the case of bulk water the signal remains nearly constant [5] for pump-probe time delays of up to 100 ps. Contrary to the bulk phase, for the water nanodroplets entrapped in reverse micelles, the transient bleach partially recovers within our observation window (Fig.1).

Figure 2 presents the measured rotational anisotropy for two types of micelles. For the large micelles, where the bulk water properties are dominant, the anisotropy decays with a time constant of 200±50 fs, which is in line with previous measurements on bulk water [6]. In the smallest micelles (d=1 nm), most of the water molecules are embedded in the membrane and are isolated from each other. The anisotropy displays a bi-exponential behavior, with fast component of 200±50 fs and slow one of 3±1 ps. The latter value is similar to the orientational diffusion time found for HOD [7]. For comparison, we measured the anisotropy decay of a water molecule isolated in an acetonitrile matrix (Fig. 2, filled circles), which turns out to be similar to the case of the smallest micelles. This strongly suggests that the 200-fs anisotropy decay is mainly due to an (anharmonic) coupling between symmetric and antisymmetric modes of the H_2O molecule.

The analysis of the data of aqueous nano-droplets is built on the generalized kinetic model depicted schematically in Fig.3. The model combines the previously reported mechanism for energy equilibration in the aqueous bulk [4], with a heat conduction description for subsequent cooling of the droplets. (i) At time t = 0, the pump-pulse (dashed arrow) excites a fraction of the entrapped water molecules from the ground state to the first excited state of the OH stretching
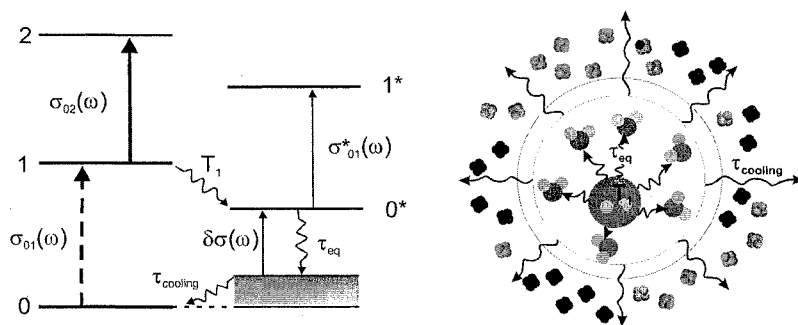
Fig.3. Energy level diagram for the kinetic model and the relaxation schematics.

vibration. (ii) The absorbed photon energy is then transferred with a time constant T_1, into vibrational states of the same molecule and/or to vibrational quanta of neighboring particles. (iii) The excited vibrational states of these accepting molecules are depopulated with a rate constant, $1/\tau_{eq}$, resulting in a complete and statistical redistribution of the pump energy such that the droplet temperature is raised. (iv) Finally, thermal relaxation due to heat diffusion from the entrapped water pools through the surfactant layer into the surrounding oil phase results in a decay of the local temperature. The proposed model therefore describes a light-triggered temperature jump experiment, which takes into account a delayed perturbation resulting from the intermediate energy transfer (ii) and redistribution (iii) events.

Representative fits with this model are depicted in Figs.1,2 as solid curves. It can be concluded that by ~1-ps time delay, the interior micelles volume is canonically heated such that a temperature can be assigned. The times T_1 and τ_{eq} for the microemulsions obtained from the transients are for d=1 nm (10 nm) τeq = 3 ps (~0.5 ps) with T_1 decreasing from 800 fs for d=1 nm to 250 fs for d=10 nm. The latter value is consistent with the population lifetime for bulk water [8]. The longer time of ~8 ps (d=4 nm) and 30 ps (d=10 nm) (Fig.1) is assigned to heat diffusion out of the micelles [4].

References

1 G.-G. Chang, T.-M. Huang, and H.-C. Hung, Proc. Natl. Sci. Counc. ROC(B) **24**, 89 (2000).
2 D. M. Willard, R. E. Riter, and N. E. Levinger, J. Am. Chem. Soc. **120**, 4151 (1998).
3 Q. Zhong, P. Baronavski, and J. C. Owrustsky, J. Chem. Phys. **118**, 7074 (2003).
4 G. Seifet, T. Patzlaff, and H. Graener, Phys. Rev. Lett. **88**, 147402-1 (2002).
5 A. J. Lock, S. Woutersen, and H. J. Bakker, J. Phys. Chem. **A105**, 1238 (2001).
6 S. Woutersen and H. J. Bakker, Nature **402**, 507 (1999).
7 H. J. Bakker, S. Woutersen, and H.-K. Nienhuys, Chem. Phys. **258**, 233 (2000).
8 A. J. Lock and H. J. Bakker, J. Chem. Phys. **117**, 1708 (2002).
9 A. Pakoulev, Z. Wang, and D. D. Dlott, Chem. Phys. Lett. **371**, 594 (2003).