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Water in confinement: ultrafast dynamics of water in reverse micelles

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Water is the most abundant liquid on our planet and has a ubiquitous presence in our lives. It constitutes the main component of all living organisms, supporting the popular knowledge that water is crucial to the existence of life. When examining the role of water in biological systems, we see many examples of water not being present as a bulk liquid, but hydrating lipid or protein surfaces, often in strongly confined regions. The cell is a crowded environment in which macromolecules occupy a considerable fraction (between 10% and 40%) of the total volume. The conformations of proteins and membrane sheets in cells are often such that their surface encloses small pockets of water, either continuously or during part of their functional cycle. Confinement of water to volumes of only a few nanometre length scale is a regularly encountered motive in biological systems.

Water containing reverse micelles have emerged as a suitable model system for studying confined water. These micelles consist of small aqueous droplets that are coated by a layer of surfactant molecules, and form spontaneously in an apolar solvent. The dimensions of reverse micelles are similar to confined spaces found in cavities in biological systems. The work presented in this thesis aims at studying the properties of water inside reverse micelles and at understanding how the properties of water change as a result of confinement. In bulk water the water molecules are arranged in a dynamical hydrogen bond network, in which each molecule is near tetrahedrally coordinated by four other molecules. By confining water to small volumes this hydrogen bond network gets truncated, which may change both the structural and dynamical properties of the liquid.

Mid-infrared spectroscopy is well suited for studying the hydrogen bonding properties of water. The O–H stretch vibration of a water molecule, which absorbs in the mid-infrared spectral region, is very sensitive to the precise strength of the donated hydrogen bond. To study the dynamics of confined water, we use femtosecond pump-probe spectroscopy. In these experiments we use two short (∼100 fs) infrared light pulses: a pump pulse to excite the O–H stretch vibration of a fraction of the water molecules, and a second probe pulse to monitor the absorption changes in the sample resulting from the vibrational excitation. By probing the sample at various time delays after the pump, we can measure the O–H stretch vibrational relaxation. If we perform the experiment with a combination of different pump and probe polarisations, we can also obtain information on the reorientational motions of the excited water molecules.
Most experiments have been performed on the O–H stretch vibration of isotopic dilutions of HDO in heavy water D$_2$O and not on neat water H$_2$O. In neat water vibrational excitations rapidly hop from one water molecule to another (by Förster energy transfer) and as a result we cannot measure water reorientations.

Experiments on water confined in anionic reverse micelles [using the surfactant AOT (Sodium bis(2-ethylhexyl) sulfosuccinate)] reveal that primarily two types of water molecules can be distinguished in the interior of such a reverse micelle. We find that water molecules hydrogen bonded to the outer micellar wall have a slower vibrational relaxation and a much lower orientational mobility ($\tau_{or}>15$ ps) than water molecules in the core of the reverse micelles, which behave much like bulk water ($\tau_{or}=3$ ps). The micellar confinement only affects the mobility of approximately a single layer of interfacial water molecules, and no long range effect on the orientational mobility is observed. The experiment also illustrates that the strength of its hydrogen bond does not determine the orientational mobility of a water molecule. The interfacial water molecules are more weakly hydrogen bonded than the water molecules in the micelle core, but nevertheless their mobility is lower.

The effect of confinement of water in AOT reverse micelles was also studied for neat water H$_2$O. Förster energy transfer in neat water causes rapid sampling of different water molecules by a single vibrational excitation. The observed dynamics is thereby averaged over the core and interfacial water molecules, and only an averaged single exponential vibrational relaxation is observed. Consistent with the results obtained for isotopically diluted water, the lifetime of the O–H stretch vibration is found to increase upon confinement ($T_1=0.85\pm0.1$ ps), which is more than three times as long as in bulk liquid water ($T_1=0.26\pm0.02$ ps).

Because specific interface-water interactions are important in explaining the different behaviour of interfacial water compared to bulk water, it is interesting to see how other surfactants than AOT affect water dynamics within reverse micelles. We therefore studied water contained in cationic instead of anionic reverse micelles, by preparing micelles with the surfactant salt CTAB (cetyltrimethylammonium bromide). For this system we find an anomalously slow vibrational relaxation rate for water that is hydrogen-bonded to the Br$^-$ counterions of the surfactant. Such slow vibrational relaxation points to a very high local concentrations of Br$^-$ ions (>10M). Most of the Br$^-$ ions are found to be densely packed at the micellar interface. Such a dense layer of counterions is also observed at the interface of normal (not reversed) ionic micelles, and is referred to as the Stern layer. Within our experimental accuracy, bulk-like water in the core of the micelles is found to have an orientational mobility similar to bulk liquid water, as was found previously for anionic AOT micelles. Water bound to Br$^-$, found predominantly at the micellar interface, has a much lower orientational mobility, that further decreases with decreasing micelle size ($\tau_{or}=8\rightarrow55$ ps).

The confinement of liquid water to small volumes can also affect its phase behaviour and transition to solid ice. Preliminary experiments were undertaken
to first measure and understand the femtosecond pump-probe spectra of normal crystalline ice $Ih$, after which we performed experiments on ice confined in reverse micelles.

We find the vibrational lifetime of bulk HDO:D$_2$O ice to be $420\pm30$ fs, and show that the OH-stretch relaxation proceeds via a localised mode which is likely the H–O–D bending vibration. A striking feature of the pure pump-probe spectrum of ice is the strongly broadened $v_{OH} = 1 \to 2$ transition. We modelled the $v_{OH} = 0 \to 1$ and $v_{OH} = 1 \to 2$ line shapes of ice using the Lippincott-Schröder model for the O–H stretch potential. Using this model, we find that the strongly broadened $v_{OH} = 1 \to 2$ line shape cannot be explained from proton delocalization in the $v_{OH} = 2$ vibrational state, as has been reported for liquid water, but that this broadening arises from a very short vibrational lifetime of the $v_{OH} = 2$ state ($20\pm4$ fs). This short vibrational lifetime can be explained from the resonance between the $v_{OH} = 1 \to 2$ transition with the overtone of the H–O–D bending mode (2900 cm$^{-1}$).

We find that HDO:D$_2$O water confined in small AOT reverse micelles can no longer freeze in a crystalline form. Instead a type of amorphous ice is observed in the micelle interior. The vibrational relaxation rate of the micellar amorphous ice is found to increase almost linearly with the O–H stretch absorption frequency, from 0.7 to 4 ps, which is considerably slower than the vibrational relaxation rate of bulk ice.