

Ultrafast vibrational dynamics of water confined in phospholipid reverse micelles

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Abstract. We study the ultrafast dynamics of OH stretching and bending vibrations of water inside dioleoylphosphatidylcholine (DOPC) reverse micelles in a wide range of hydration. A strong hydration level dependence for the spectral diffusion rates is found and explained by the distinctly different environment for single water molecules bound to the anionic phosphate group. We show that the energy relaxation pathway of the OH stretching vibration at low hydration level involves the OH bending.

Phospholipids, building blocks of biological membranes, typically self-assemble into bilayers in aqueous solution. The amphiphilic nature of phospholipids allows the formation of a variety of other structures, including reverse micelles. We recently introduced reverse micelles composed of dioleoylphosphatidylcholine (DOPC), a phospholipid with hydrophobic tails and a hydrophilic head consisting of a phosphate (PO_4^-) unit and a covalently linked choline group (cf. Figure 1). Such systems form when DOPC is dissolved in nonpolar solvents resulting in hydrophilic head groups pointing to the interior. Addition of water leads to hydration of the head groups as well as the build-up of nanoscopic water pools inside the reverse micelles (the water content is characterized by the parameter $w_0 = [\text{H}_2\text{O}]/[\text{DOPC}]$). Therefore, reverse micelles allow for detailed studies of the fundamental hydration interactions of phospholipids.

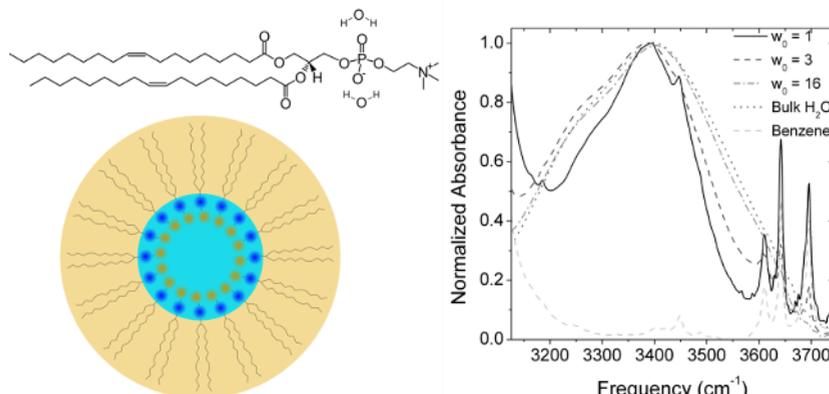


Fig. 1. Structure of DOPC and schematic representation of a DOPC reverse micelle (left); normalized linear absorption spectra of OH stretching vibrations of water inside DOPC reverse micelles for different hydration levels bulk water and benzene absorptions are shown for comparison (right).

Ultrafast mid-infrared spectroscopy makes it possible to follow the dynamics of vibrational marker modes of the phospholipid molecules as well as those of the nanoconfined water. A first series of time-resolved measurements involving the antisymmetric phosphate stretching vibration, a sensitive probe for the hydration of the hydrophilic head groups, identified the confined water pool as an efficient heat sink for excess energy deposited in the phosphate groups [1]. Here we present new results providing specific insight into the spectral diffusion and vibrational relaxation dynamics of the OH stretching and bending vibrations of water inside these reverse micelles [2]. We show that for low hydration samples ($w_0=1$), the water OH stretching excitation redistributes via the bending mode of water.

DOPC reverse micelles were prepared by dissolving DOPC (dried over P_2O_5 in vacuum) into benzene to yield a 0.25M solution. We added appropriate amounts of water to obtain reverse micelles with hydration levels in the range of $w_0=1$ to 16. Time-resolved one- and two-color pump-probe spectra of the OH stretching and OH bending vibrations were acquired with pump and probe pulses centered at 3400 cm^{-1} and between 1600 and 3500 cm^{-1} , (bandwidth $150\text{--}200\text{ cm}^{-1}$).

Figure 2 shows results of pump-probe experiments of the OH stretching mode for $w_0=1, 3$, and 16. Transient spectra (Figure 2a) at early delay times display an enhanced absorption at low frequencies around 3000 cm^{-1} and a broad bleaching around 3400 cm^{-1} . While the enhanced absorption decays due to depopulation of the $v=1$ state, the bleaching undergoes a spectral reshaping and an enhanced absorption builds up at the blue side of the spectrum indicating the formation of a hot ground state. To analyze the spectral reshaping in more detail we calculated the first moment of the bleaching (Figure 2b). For $w_0=16$ this analysis is limited to frequencies below 3520 cm^{-1} to avoid contributions from the pronounced hot ground state absorption. The results of this analysis (Figure 2b) show an increase of the reshaping time scales from 330 fs for $w_0=16$ to 1.4 ps for $w_0=1$. For high hydration we attribute the rapid changes to spectral diffusion. The rate of spectral diffusion is slightly slower than for bulk water, where resonant energy transfer between OH stretching oscillators and fluctuations of the hydrogen bond network play a prominent role [3]. At low

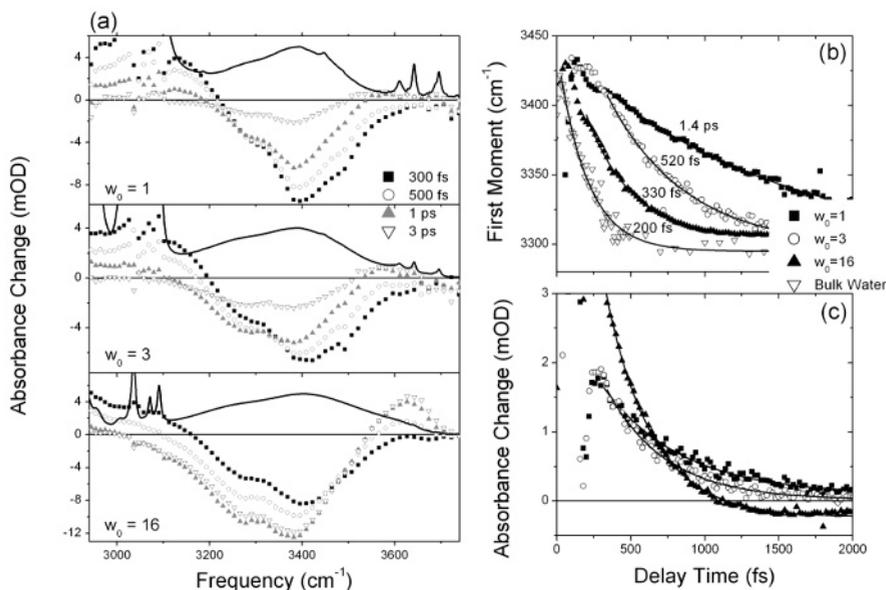


Fig. 2. (a) Transient OH stretching spectra after excitation with pump pulses centered at 3400 cm^{-1} for three different hydration levels, solid lines correspond to linear absorption spectra; (b) time-dependent shift of the first moment of the transient spectra with the indicated exponential decay times, values for bulk water [3] are shown for comparison; (c) decay of the excited state absorption at 3004 cm^{-1} indicating lifetimes of 530 fs ($w_0=1$), 400 fs ($w_0=3$) and 310 fs ($w_0=16$).

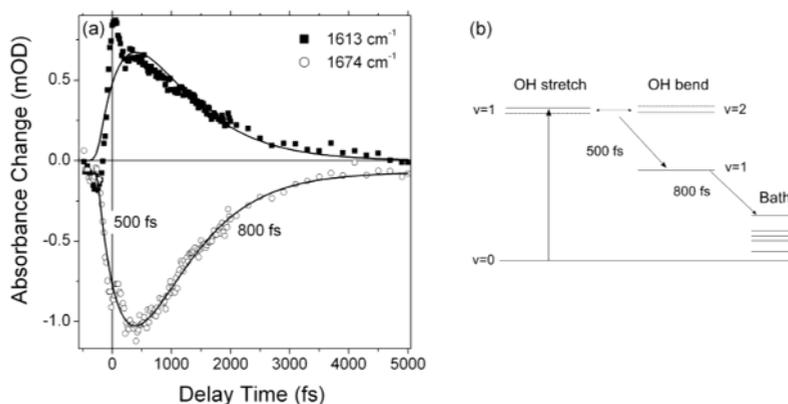


Fig. 3. (a) Transient response of the OH bending mode after OH stretching excitation; (b) level scheme with the indicated lifetimes for OH stretching and bending modes for $w_0=1$.

water content ($w_0=1$) a contribution of the developing hot ground state cannot be excluded. Nevertheless, the 1.4 ps timescale sets a lower limit for the spectral diffusion of single water molecules bound to the phosphate groups as a result of the absence of a fluctuating hydrogen bond network that is present in bulk water.

Figure 2c displays time-resolved pump-probe transients recorded at 3000 cm^{-1} , illustrating the depopulation of the excited $v=1$ state. It is evident that the lifetime of the OH stretching mode increases from ~ 300 fs to ~ 500 fs when decreasing the hydration level from $w_0=16$ to $w_0=1$. To understand the increased lifetime, we investigated the energy relaxation pathway with two-color pump-probe measurements monitoring the OH bending response after OH stretching excitation. Figure 3(a) shows data for $w_0=1$ along with fits that correspond to a rise time of 500 fs and a decay time of 800 fs, corresponding to the 500 fs lifetime of the OH stretching and an 800 fs lifetime of the OH bending vibration at this hydration level. Our results clearly demonstrate that the OH bending is involved in the energy relaxation pathway of the OH stretching mode. This is similar to the case of bulk water – however with different lifetimes [3]. In this scenario, a coupling between the $v=1$ of the OH stretching and the $v=2$ of the OH bending leads to an efficient energy transfer from the former to the latter vibrational mode.

The different OH stretching lifetimes at different hydration levels (w_0) can be rationalized by considering the slowing down of spectral diffusion with decreasing water content. Because the overtone of the OH bending mode is located at 3200 cm^{-1} , OH stretching oscillators at the red part of the spectrum can directly relax via the OH bending mode. Oscillators in the blue part of the spectrum undergo spectral diffusion to bridge the energy gap to the $v=2$ OH bending state. In contrast to bulk water, spectral diffusion occurs on a picosecond timescale for reverse micelles with $w_0=1$ resulting in the longer OH stretch lifetimes. In this way, the absence of the manifold of intermolecular vibrational modes of water at $w_0=1$ can explain the energy relaxation of intramolecular vibrational modes. Similarly, the longer OH bending lifetimes can be explained by the absence of low-frequency librational modes so that the OH bending mode has to relax via low-frequency modes of the DOPC.

References

1. N. E. Levinger, R. Costard, E. T. J. Nibbering, T. Elsaesser, *J. Phys. Chem. A* **115**, 11952 (2011)
2. R. Costard, N. E. Levinger, E. T. J. Nibbering, T. Elsaesser, *J. Phys. Chem. B* **116**, 5752 (2012)
3. D. Kraemer, M. L. Cowan, A. Paarmann, N. Huse, E. T. J. Nibbering, T. Elsaesser, R. J. D. Miller, *Proc. Natl. Acad. Sci. USA* **105**, 437 (2008)