Water hydrogen bond dynamics
in aqueous solutions of amphiphiles

Supporting Information

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1 – Infrared spectra for TMAO solutions of increasing concentration

We have computed the OD infrared absorption intensity for TMAO solutions of increasing concentrations. The infrared absorption lineshape is defined as the Fourier transform of the time-dependent transition dipole (see eg ¹). The lineshape clearly shifts to the red for increasing TMAO concentrations.
2 – Frequency distribution for $O_{\text{water}}$ and $O_{\text{solute}}$ acceptors in 8 m TMAO, TMU, TBA

The calculated frequency shifts between the $O_{\text{solute}}$ and $O_{\text{water}}$ distribution peaks are respectively - 30 cm$^{-1}$, +18 cm$^{-1}$ and + 10 cm$^{-1}$ for 8 m TMAO, TMU and TBA solutions.

In the TMAO case, the marked redshift of the OD frequency when donating an H-bond to a TMAO oxygen with respect to a water oxygen shows that the OD···O$_{\text{TMAO}}$ H-bond is stronger than the OD···O$_{\text{water}}$ H-bond. It also explains the redshift of the infrared spectra for increasing TMAO concentration (see Section 1 and Ref. 2).

In the TMU case, the blueshift of the OD frequency when donating an H-bond to a TMU carbonyl oxygen with respect to a water oxygen shows that the OD···O$_{\text{TMU}}$ H-bond is weaker than the OD···O$_{\text{water}}$ H-bond. It also explains the experimentally observed blueshift of the infrared spectrum 3.
3 – Comparison between Center Line Slope and frequency time correlation function for different TMAO concentrations

The frequency time correlation function (ftcf) is compared with the Center Line Slope (CLS) for increasing TMAO concentrations, from 0.1 m to 8 m. This comparison clearly evidences that while in dilute solutions – where the frequency dynamics is very much bulk-like – the CLS captures very well the ftcf dynamics (beyond the short-time non-Gaussian effects\textsuperscript{4,5}), the agreement deteriorates for increasing TMAO concentrations. This originates from the increasing fraction of deuteroxyls donating an H-bond to a TMAO oxygen, which renders the frequency dynamics increasingly less Gaussian, thus violating an assumption in the CLS derivation. At 8 m, the CLS very slow decay essentially reflects the slow chemical exchange between $O_W$ and $O_{TMAO}$ acceptors, whose amplitude is smaller in the ftcf decay (see Section 5)\textsuperscript{6}. 
Analytic expression for the ftcf decay in the presence of chemical exchange

We consider two populations undergoing chemical exchange

\[ A \xrightleftharpoons[k_-]{k_+} B \]

The resulting population dynamics is

\[
\begin{align*}
A(t) &= \frac{1}{K+1} + \left[ A(0) - \frac{1}{K+1} \right] e^{-t/\tau_{ex}} \\
B(t) &= \frac{K}{K+1} - \left[ A(0) - \frac{1}{K+1} \right] e^{-t/\tau_{ex}},
\end{align*}
\]

where \( K = k_+/k_- \) is the equilibrium constant and \( \tau_{ex} = 1/(k_+ + k_-) \) is the exchange timescale.

We assume that the average vibrational frequencies in each state are different \( \langle \omega_A \rangle \neq \langle \omega_B \rangle \), but that in the absence of exchange, the frequency dynamics are identical in both states, i.e.

\[
\left[ \langle \omega(0) - \langle \omega \rangle \rangle \right] \left[ \langle \omega(t) - \langle \omega \rangle \rangle \right] = \langle \delta\omega_i(0)\delta\omega_i(t) \rangle = \sigma^2 C_0(t) \text{ with } i=A,B,
\]

where \( C_0(t) \) is the normalized frequency time-correlation function (ftcf) in state A or B in the absence of exchange and \( \sigma = \langle \delta\omega_i^2 \rangle \). We further assume a) that the frequency has fully dephased before the exchange occurs, i.e. that \( C_0(t) \) relaxes faster than the exchange timescale \( \tau_{ex} \), and b) that no frequency correlation remains after exchange.

The average frequency and frequency difference are respectively \( \langle \omega \rangle = (\langle \omega_A \rangle + K \langle \omega_B \rangle)/(K+1) \) and \( \Delta = \langle \omega_B \rangle - \langle \omega_A \rangle \).

For a system initially in state A, the ftcf is

\[
\langle \delta\omega(0)\delta\omega(t) \rangle = \left[ \langle \delta\omega_A(0) + \langle \omega_A \rangle - \langle \omega \rangle \rangle \right] \left[ \langle \delta\omega_A(t) + \langle \omega_A \rangle - \langle \omega \rangle \rangle \right] + \left[ \langle \delta\omega_B(t) + \langle \omega_B \rangle - \langle \omega \rangle \rangle \right] \left[ \langle \delta\omega_B(0) + \langle \omega_B \rangle - \langle \omega \rangle \rangle \right],
\]

which leads to

\[
\langle \delta\omega(0)\delta\omega(t) \rangle = \sigma^2 C_0(t) + \frac{\Delta K}{K+1} e^{-t/\tau_{ex}},
\]

and the normalized ftcf is
\[ \frac{\langle \delta \omega(0) \delta \omega(t) \rangle}{\langle \delta \omega^2 \rangle} = \frac{1}{1 + \left( \frac{\Delta}{K} \right)^2} C_0(t) + \frac{\left( \frac{\Delta}{\sigma K + 1} \right)^2}{1 + \left( \frac{\Delta}{\sigma K + 1} \right)^2} e^{-t/\tau_{ex}}. \]

Similarly, for a system initially in B, the normalized ftcf is

\[ \frac{\langle \delta \omega(0) \delta \omega(t) \rangle}{\langle \delta \omega^2 \rangle} = \frac{1}{1 + \left( \frac{\Delta}{K} \right)^2} C_0(t) + \frac{\left( \frac{\Delta}{\sigma K + 1} \right)^2}{1 + \left( \frac{\Delta}{\sigma K + 1} \right)^2} e^{-t/\tau_{ex}}. \]

This evidences that exchange is necessary to reach a full decorrelation of the vibrational frequency, and that the long timescale of the ftcf decay is the exchange timescale \( \tau_{ex} \). The amplitude of this slow decay depends both on the frequency difference between the two states \( \Delta \), and on the equilibrium constant.
5 – Analytic expression for the CLS decay in the presence of chemical exchange

We consider the same $A$ and $B$ exchanging populations as in Section 4, and still assume that chemical exchange is slow with respect to frequency dephasing within each state. For the 2D IR spectra, this implies that before any significant population exchange occurs, the diagonal peaks have decayed to a symmetric, round shape.

In order to keep the derivation tractable analytically, we further assume a) that the equilibrium constant $K$ is 1; b) that the transition dipoles are the same in the two states, i.e. $\mu_A = \mu_B$; c) that both states have the same vibrational lifetime; d) that any orientational effect can be neglected; e) that for times longer than frequency dephasing within each state, the 2 diagonal peaks and the 2 off-diagonal peaks in the 2D IR spectra can be modelled by Gaussians with the same width.

These assumptions imply that the amplitudes of the 4 peaks (AA and BB along the diagonal, AB and BA off the diagonal) are proportional to the populations:

\[
\begin{align*}
N_{AA}(t) &= \frac{1}{4} \left( 1 + e^{-t/\tau_{ex}} \right), \\
N_{BB}(t) &= \frac{1}{4} \left( 1 + e^{-t/\tau_{ex}} \right), \\
N_{AB}(t) &= \frac{1}{4} \left( 1 - e^{-t/\tau_{ex}} \right), \\
N_{BA}(t) &= \frac{1}{4} \left( 1 - e^{-t/\tau_{ex}} \right)
\end{align*}
\]

with $\tau_{ex}$ the exchange timescale defined in Section 4, and the 2D IR spectrum is the sum (neglecting the 1-2 vibrational transitions)

\[
S(\omega_{exc}, \omega_{det}, t) = N_{AA}(t) \exp \left[ -\frac{(\omega_{exc} - \omega_A)^2}{2\sigma^2} - \frac{(\omega_{det} - \omega_A)^2}{2\sigma^2} \right] + N_{BB}(t) \exp \left[ -\frac{(\omega_{exc} - \omega_B)^2}{2\sigma^2} - \frac{(\omega_{det} - \omega_B)^2}{2\sigma^2} \right] + N_{AB}(t) \exp \left[ -\frac{(\omega_{exc} - \omega_A)^2}{2\sigma^2} - \frac{(\omega_{det} - \omega_B)^2}{2\sigma^2} \right] + N_{BA}(t) \exp \left[ -\frac{(\omega_{exc} - \omega_B)^2}{2\sigma^2} - \frac{(\omega_{det} - \omega_A)^2}{2\sigma^2} \right]
\]

For a given excitation frequency $\omega_{exc}$, the detection frequency $\omega_{det}^{max}$ where the spectrum amplitude is maximum is defined by $\frac{\partial S}{\partial \omega_{det}^{max}} = 0$. The Center Line Slope is then defined by $CLS = \frac{\partial \omega_{det}^{max}}{\partial \omega_{exc}}$, taken...
at the global spectrum maximum. This global peak is located at \((\omega_{\text{exc}}=\omega_0, \ \omega_{\text{det}}=\omega_0)\), where 
\(\omega_0=(\omega_A+\omega_B)/2\), when \(\Delta^2/\sigma^2<2\), where \(\Delta = \omega_B - \omega_A\), i.e. when the two diagonal peaks overlap sufficiently.

Within the approximations detailed above, this leads to the expression of the time-dependent CLS

\[
CLS(t) = \frac{(\Delta/2\sigma)^2}{1-(\Delta/2\sigma)^2} e^{-t/\tau_{\text{ex}}} \quad \text{(for } \Delta^2/\sigma^2<2).\]

Although this calculation is done in a very simplified case, this evidences that the long timescale of the CLS decay is equal to the exchange timescale \(\tau_{\text{ex}}\), the same as in the ftcf (see Section 4). For the actual systems we considered, the two diagonal peaks do not have the same height and this may affect the CLS relaxation time. In the simplified case, the amplitude of this decay is \((\Delta/2\sigma)^2 / [1 - (\Delta/2\sigma)^2]\), which increases with increasing frequency difference \(\Delta\) between the two diagonal peaks. In addition, this amplitude is always larger than the amplitude of the same decay in the normalized ftcf, which is \((\Delta/2\sigma)^2 / [1 + (\Delta/2\sigma)^2]\) (see Section 4); this explains why the CLS tends to enhance the long-time exchange component with respect to the ftcf, as observed in our calculations (see Figs. 2 and 3.A and section 3).
References


(6) Fitting the long-time decays of the CLS and ftcf in the 8 m TMAO solution leads to similar decay times. However, this decay is very slow and its value suffers from a large uncertainty due to the limited 0-10 ps fitting range. Obtaining reliable results for the CLS at longer delays is difficult because of the fast vibrational relaxation.
