Solvation Dynamics: Fundamentals and A Survey of Results in Simple and Complex Environments

I. Background and Fundamentals
II. Polar Solvation Dynamics
III. Other “Simple” Environments
IV. Complex Environments, Biological and Otherwise
IV. Complex Environments

- Polymers
- Cyclodextrins & Other Inclusion Complexes
- Micelles, Bilayers
- DNA, Proteins

A common problem observed with low \( t \) resolution is that \( S(t) \) is often reported as

\[
S(t) = \frac{1}{\tau_1 + \tau_2}
\]

where

\[
\tau_1 = \tau_c \left( \frac{T_1}{T_1 - T_2} \right)
\]

\[
\tau_2 = \frac{T_1}{T_2 - T_1}
\]
S(t) of a DNA-Binding Drug

- The minor groove of B-DNA is decorated with an ordered zigzag “spine” of water molecules.

- Hoechst 33258 ("H3") is an antimicrobial drug with a high affinity for DNA ($K_d \sim 10^{-8}$ M).

- An X-ray structure of an H3-DNA complex exists.

- Drug binding to DNA generally displaces some water.

- Solution-phase spectroscopy of H3 is messy; it is quenched in water...

DNA-Binding Drug (cont.)

X-Ray Structure

DNA: (64%) 1.4 ps + (36%) 19 ps; $\Delta \nu = 1.3$ kK
Bulk: (33%) 0.2 ps + (67%) 1.2 ps; $\Delta \nu = 3.2$ kK

“a bimodal hydration behavior … reflecting the presence of two types of water, bulk-type, labile water and weakly bound, ordered water”

Berg, Murphy & Co. synthesized a riboside using the probe C102

- paired with an abasic site the C102 replaces a pair of bases with little disruption of the B-DNA helix
- in typical 17-mer sequence $T_m=46$ °C compared to 58 °C for the native sequence
- using TCSPC (IRF=100 ps) find:
  
  $(47\%) \ 300 \text{ ps} + (53\%) \ 13.4 \text{ ns}; \ \Delta \nu=312 \text{ cm}^{-1}$

SS Spectra:
- $a=$ free, $b=$ melted, $c=$ duplex

- dynamics “too slow to represent even low-frequency motion of DNA”
- “hydrogen bonds in the base pairs have strong dipole and quadrupole moments”
- “phosphate groups have full charges”
- “counterion atmosphere”
- “water to and next to the grooves in DNA is strongly perturbed”

Berg, Ernsting & Co. used TCSPC (40 ps-40 ns), upcv (1-150 ps), & transient abs. (40 fs-120 ps) to measure C102 substituted 17-mer.

Andreatta et al. JACS 127, 7270 (2005).

\[ S(t) = S_\infty [1 - (1 + t/t_0)^{-\alpha}] \]

\[ S_\infty = 2086 \text{ cm}^{-1}, \alpha = 0.15 \pm 0.03 \]

\[ t_0 = 19 \text{ fs} \]
3PEPS (Recall)

cavity dumped
Ti:Sa 250 kHz,
<1 nJ, 20 fs

Passino,…Fleming, J. Phys. Chem. A 101, 725 (1997);

11/2/2005  Topic IV - Complex Environments
Fleming & Co. used 3PEPS to measure solvation dynamics of eosin in water and in a protein complex.

- amp. Ti:saph, 4 kHz, 50 fs + OPA to 520 nm 30 fs

Fit with Exptl $\varepsilon(\omega)$ Only

**Eosin / Lysozyme Complex**

- prominent fast portion of dynamics is water
- slower dynamics likely protein motions
- some ns dynamics not observed

Water: (73%) 17 fs+(15%) 330 fs+(12%) 3 ps
Cmplx: (69%) 18 fs+(9%) 310 fs+(8%) 7 ps+(8%) 135 ps

Hochstrasser & Co. measured dynamics of C153/343 in solution and in a peptide-calmodulin complex and examined validity of LR

- 1 kHz amp. Ti:saph
- 400 nm pump, OPA 510-700 nm (1λ) probe
- trans. abs. & pump-dump
- IRF 150-200 fs

**Single λ Idea**


Pump-Dump Idea

Kovaleko JCP 109, 1894 (1998)

wait for equilibration ($S_1$ & $S_0$) then dump

405 nm Linear $\lambda$ for abs.
NLR in Calmodulin Complex


- no spectral dynamics observed with apo complex (too fast in bulk water?)
- in CaM/Ca\(^+\) observe fs-ps dynamics
- different in \(S_0\) and \(S_1\)

\[ C(t) \quad \text{Peptide+CaM} \]

\begin{align*}
S_1: \ (72\%) \ 120 \text{ fs} + (18\%) \ 3 \text{ ps} + (20\%) \ 22 \text{ ps} \\
S_0: \ (93\%) \ 101 \text{ fs} + (7\%) \ 2.4 \text{ ps}
\end{align*}


Parting Shots