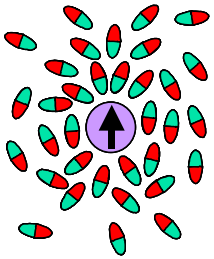
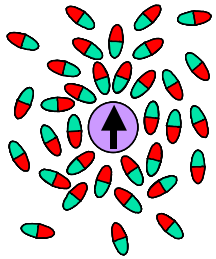




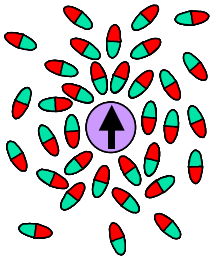
Solvation Dynamics: Fundamentals and A Survey of Results in Simple and Complex Environments

I. Background and Fundamentals

II. Polar Solvation Dynamics

III. Other “Simple” Environments

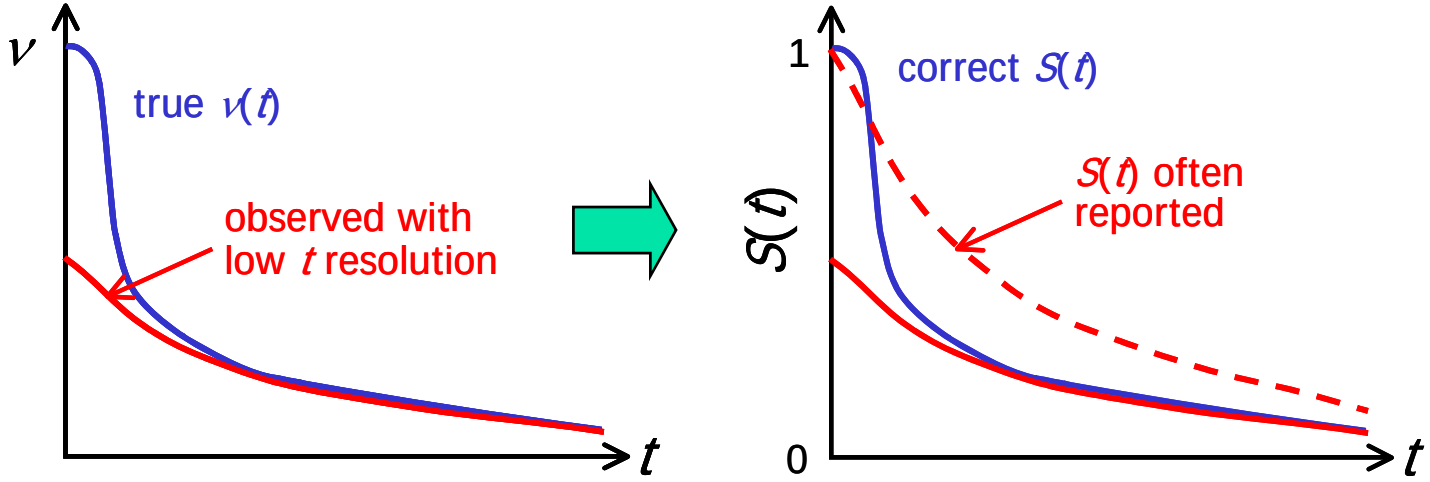
IV. Complex Environments, Biological and Otherwise



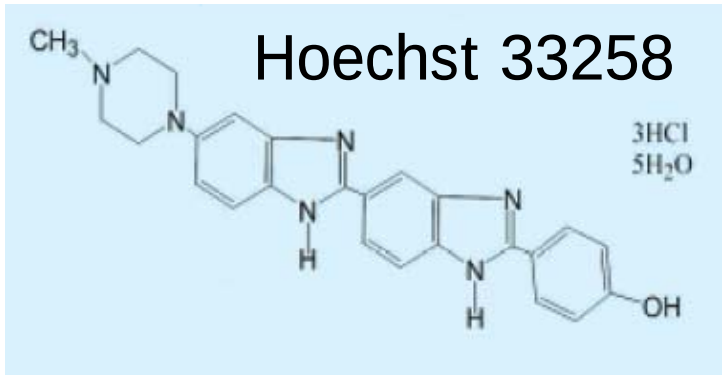
IV. Complex Environments

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

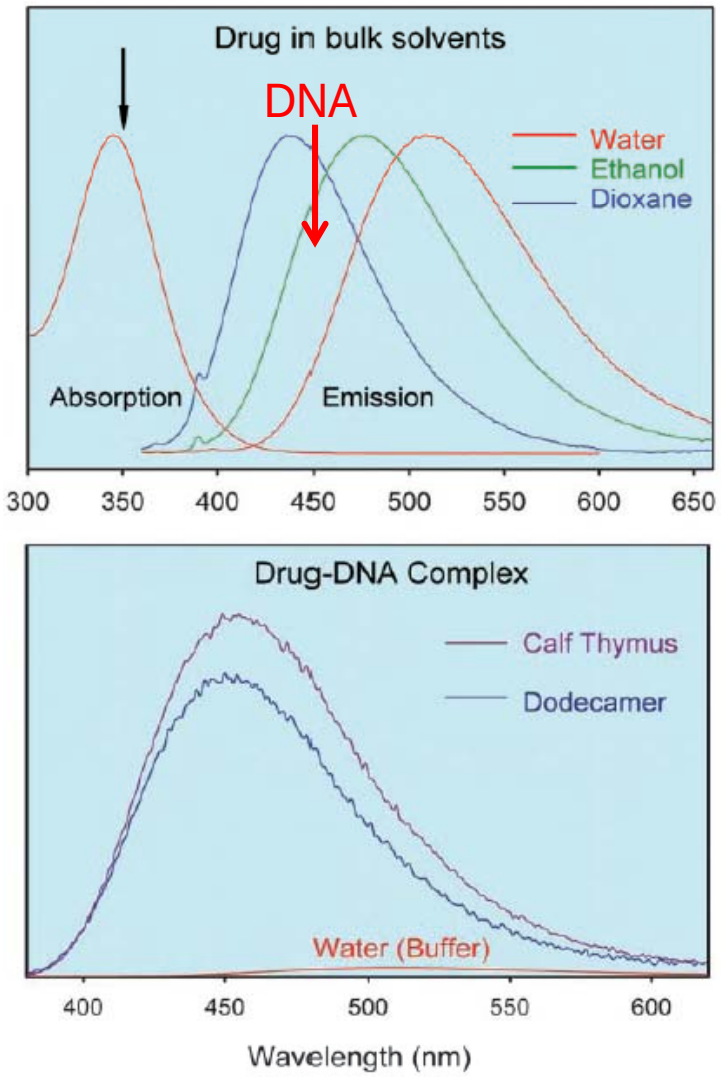
a common problem



$S(t)$ of a DNA-Binding Drug



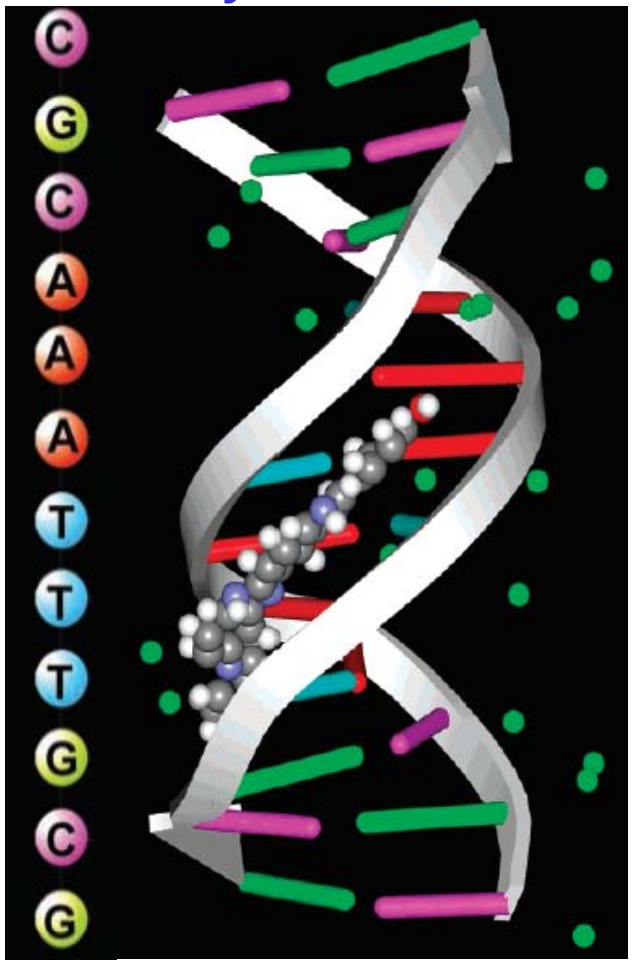
- the minor groove of B-DNA is decorated with an ordered zigzag "spine" of water molecules
- Hoechst 33258 ("H3") is an antimicrobial drug with a high affinity for DNA (K_d~10^{-8} M)
- an X-ray structure of an H3-DNA complex exists
- drug binding to DNA generally displaces some water
- solution-phase spectroscopy of H3 is messy, it is quenched in water...



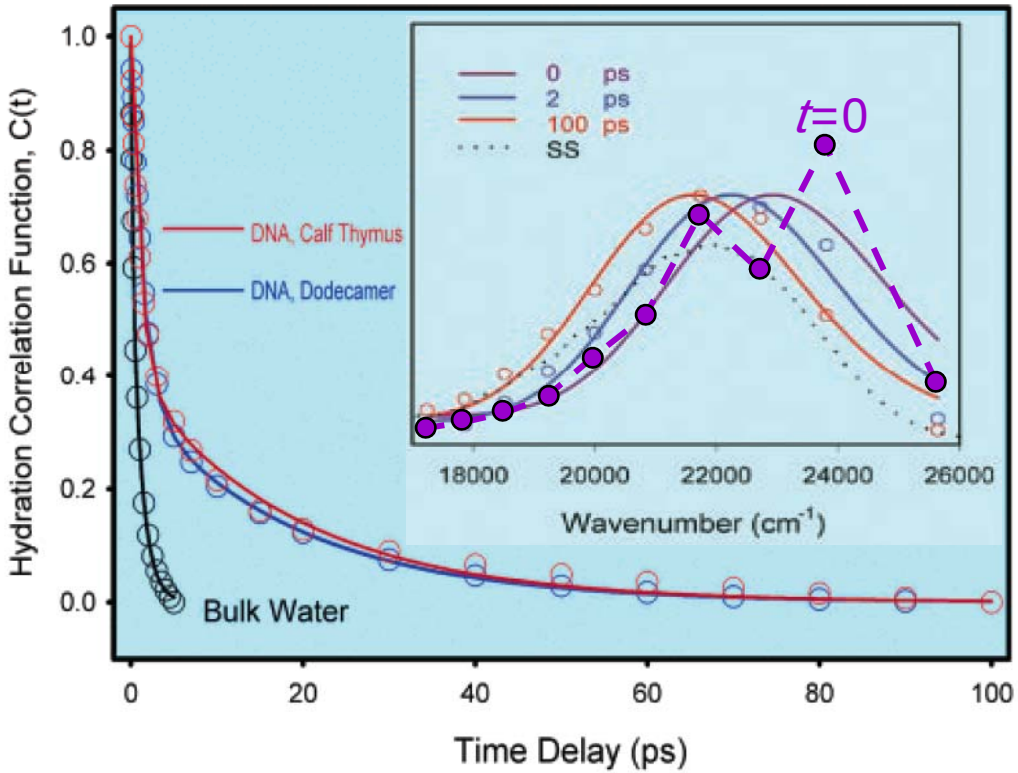
Pal,...Zewail, PNAS 100, 8113 (2003).

DNA-Binding Drug (cont.)

X-Ray Structure



fs upconversion (1λ) to 200 ps



DNA: (64%) 1.4 ps + (36%) 19 ps; $\Delta\nu$=1.3 kK

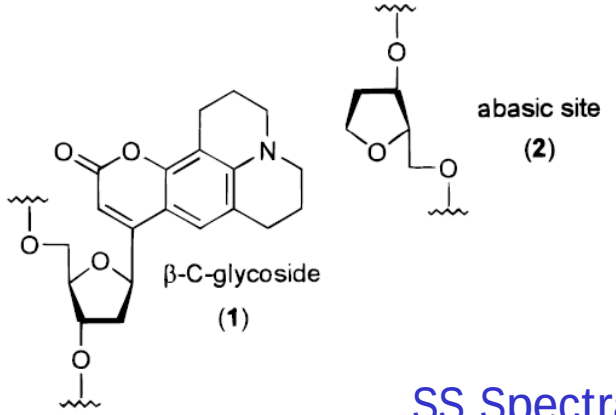
Bulk: (33%) 0.2 ps + (67%) 1.2 ps; $\Delta\nu$=3.2 kK

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

Pal,...Zewail, PNAS 100, 8113 (2003).

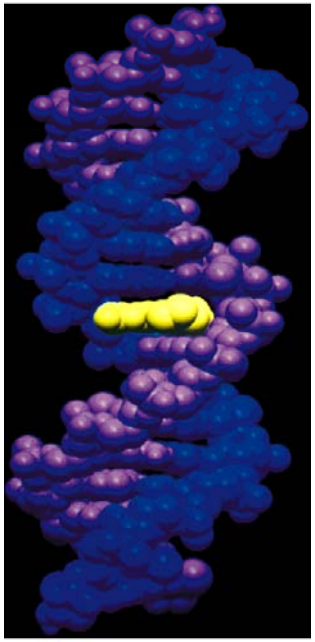
S(t) of DNA Base Replacement

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

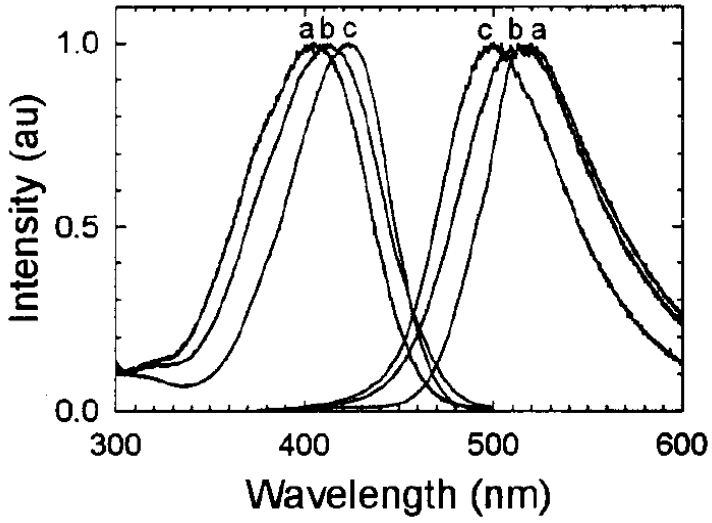


- paired with an abasic site the C102 replaces a pair of bases with little disruption of the B-DNA helix
- in typical 17-mer sequence T_m=46 °C compared to 58 ° C for the native sequence
- using TCSPC (IRF=100 ps) find:

(47%) 300 ps + (53%) 13.4 ns; $\Delta\nu$=312 cm^{-1}



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

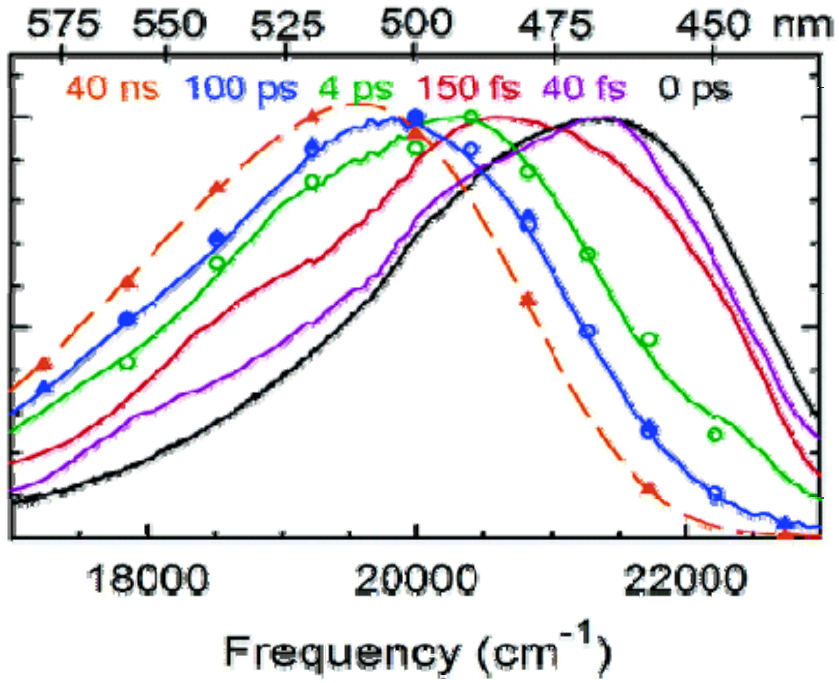


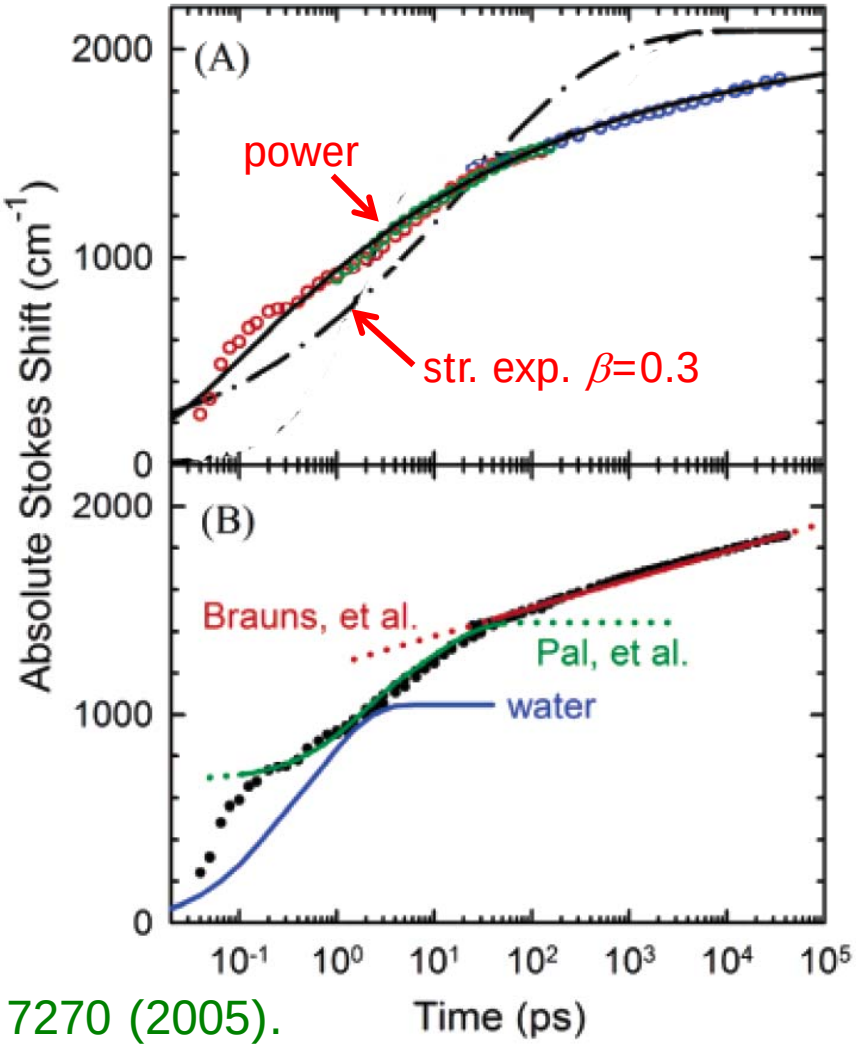
- dynamics "too slow to represent even low-frequency motion of DNA"
- "hydrogen bonds in the base pairs have strong dipole and quadrupole moments"
- "phosphate groups have full charges"
- "counterion atmosphere"
- "water to and next to the grooves in DNA is strongly perturbed"

Berg, Murphy & Co., JACS **121**, 11644 (1999).

DNA Base Replacement fs-ns

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





power law fit over >5 decades in time!

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

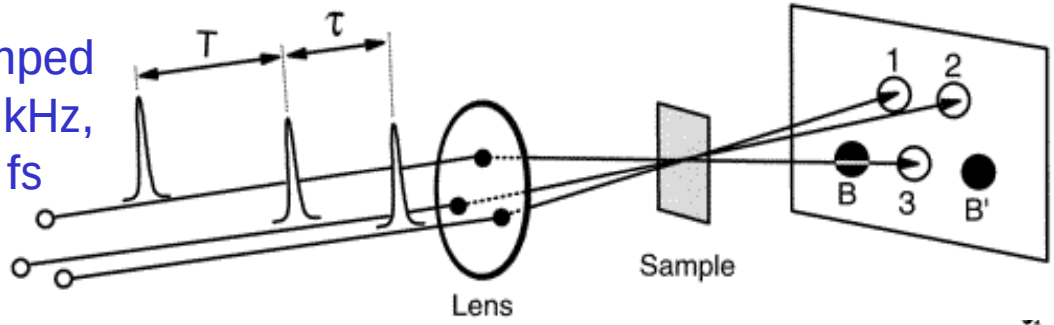
$$S_\infty = 2086 \text{ cm}^{-1}, \alpha = 0.15 \pm 0.03$$

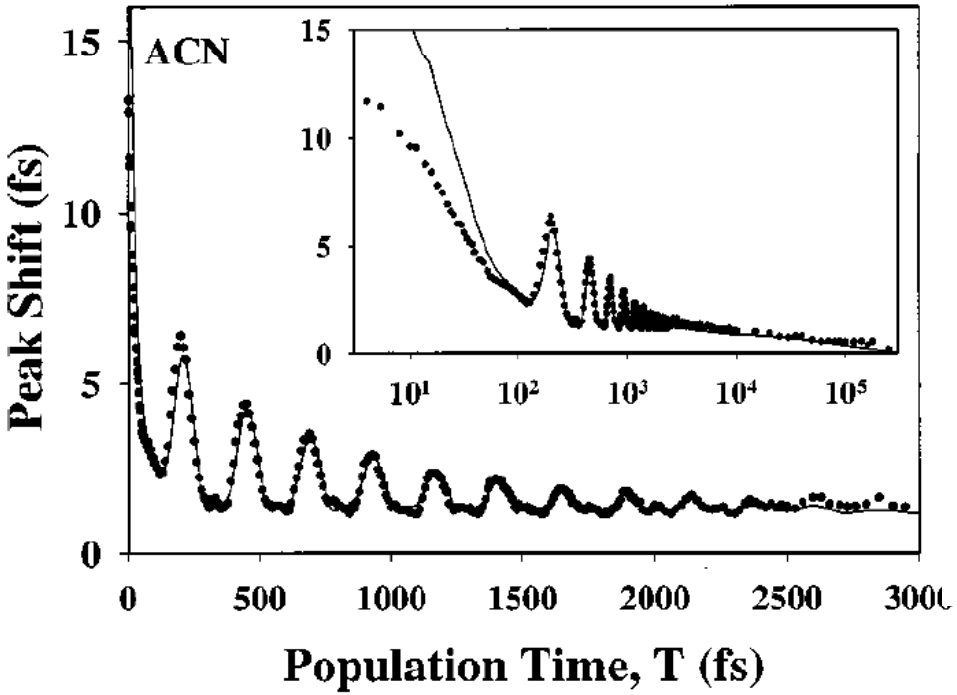
$$t_0 = 19 \text{ fs}$$

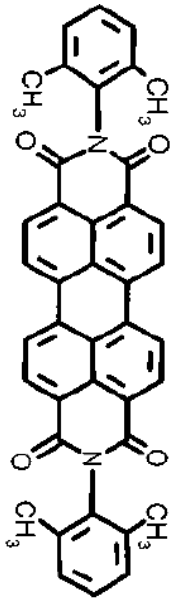
Andreatta *et al.* JACS **127**, 7270 (2005).

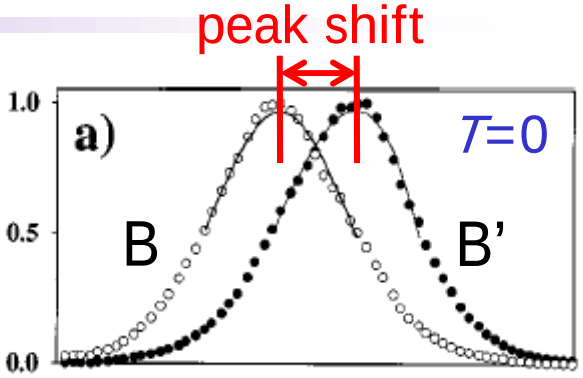
3PEPS (Recall)

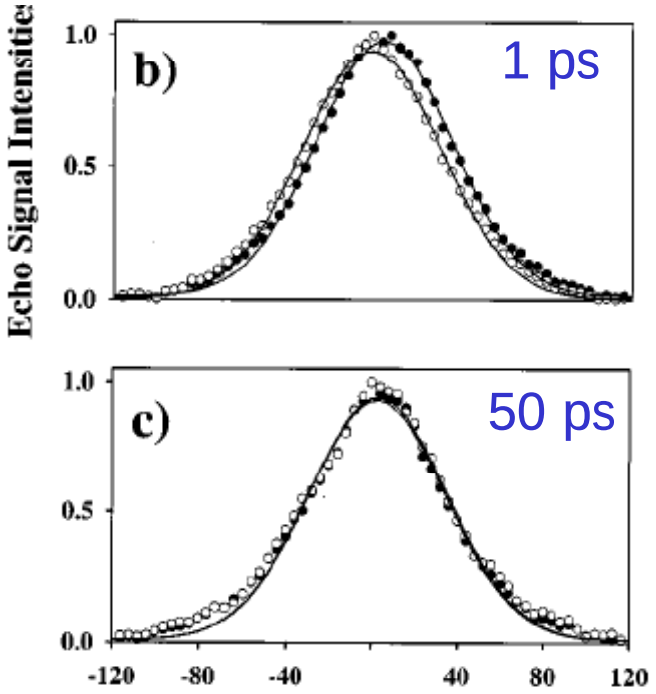
cavity dumped
Ti:Sa 250 kHz,
<1 nJ, 20 fs









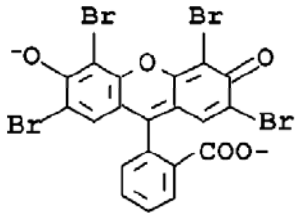


Passino,... Fleming, J. Phys. Chem. A **101**, 725 (1997);
Larsen,...Fleming, J. Chem. Phys. **111**, 8970 (1999).

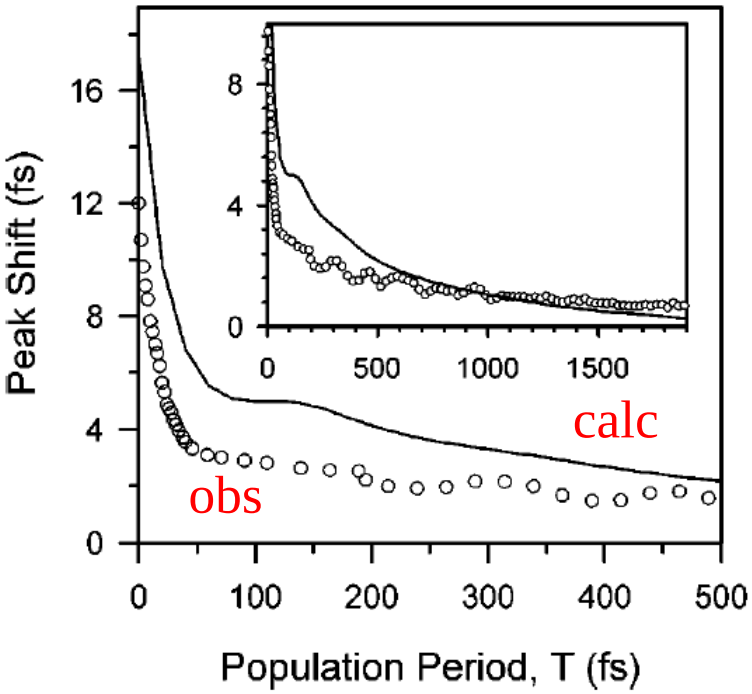
3PEPS of Eosin/water

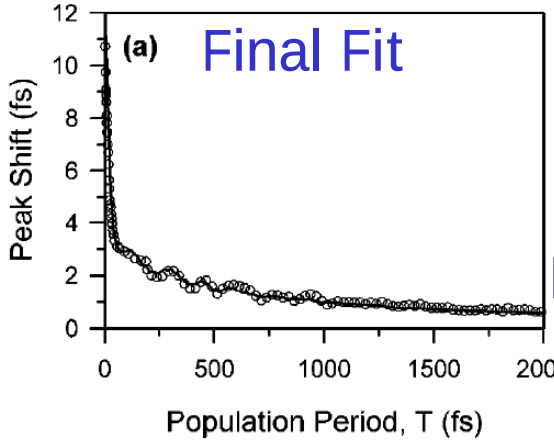
Fleming & Co. used 3PEPS to measure solvation dynamics of eosin in water and in a protein complex

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



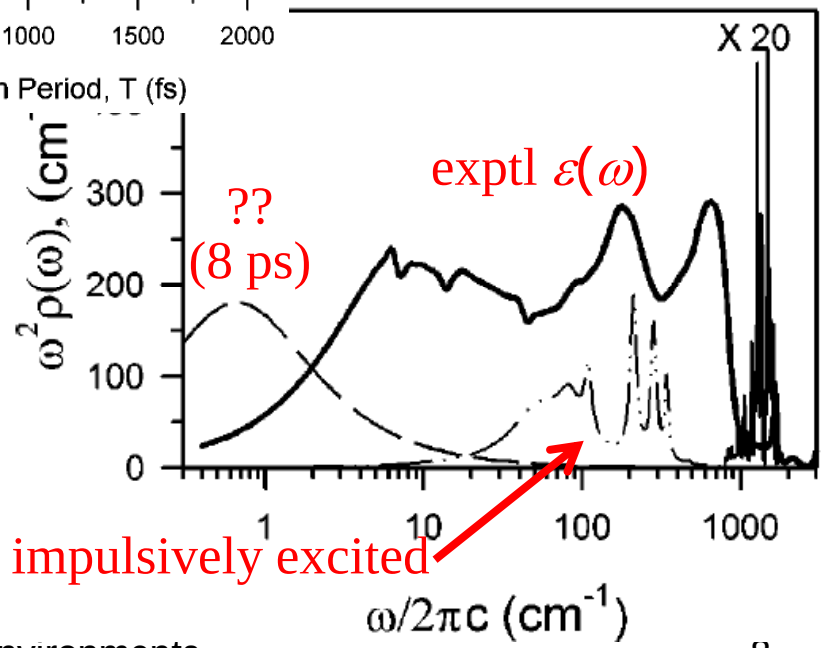
Fit with Exptl $\varepsilon(\omega)$ Only





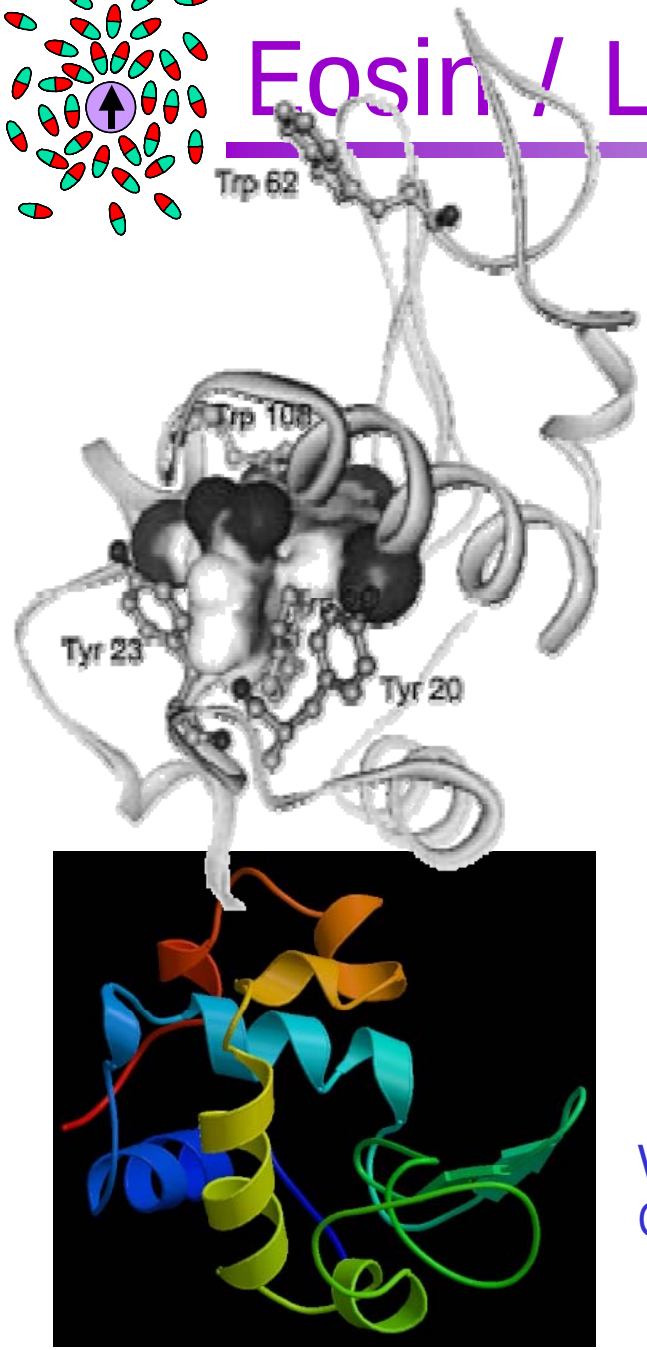
Final $\rho(\omega)$ Inputs

intra vibs.

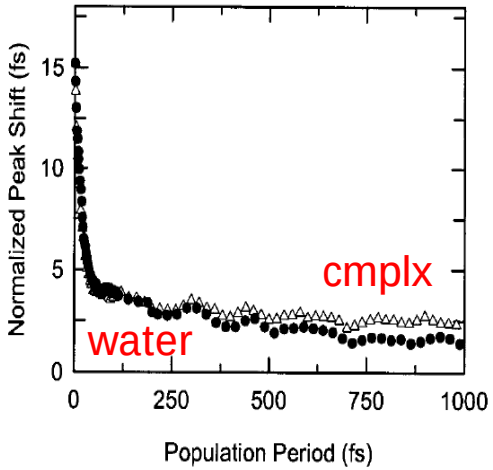


Lang,...Fleming, JCP **110**, 5884 (1999).

Eosin / Lysozyme Complex

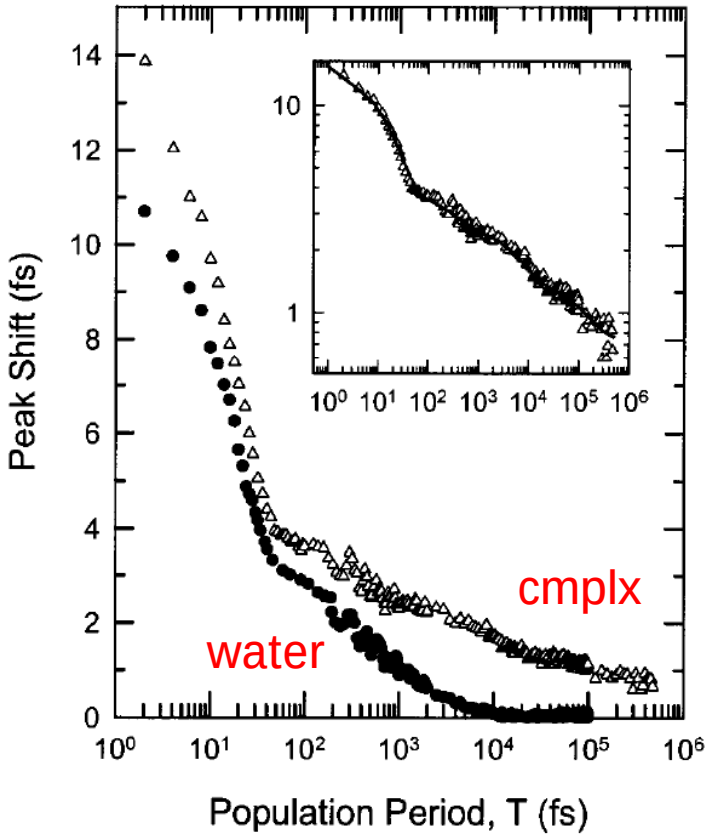


Normalized 3PEPS



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

Complete 3PEPS



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

Jordanides,...Fleming, J. Phys. Chem. B **103**, 7995 (1999).

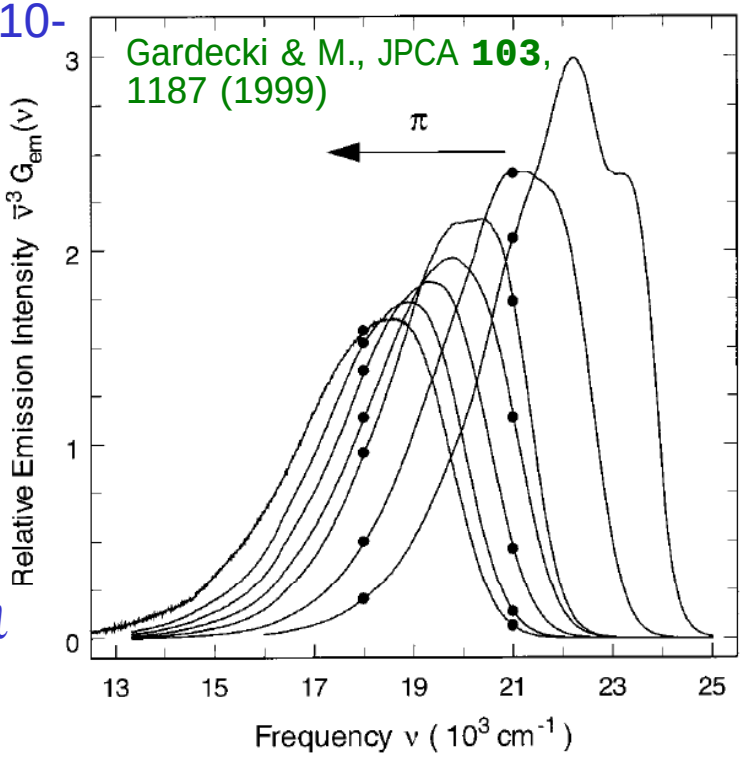
J. Phys. Chem. A 1999, 103, 1187−1

Linear Response & Biology

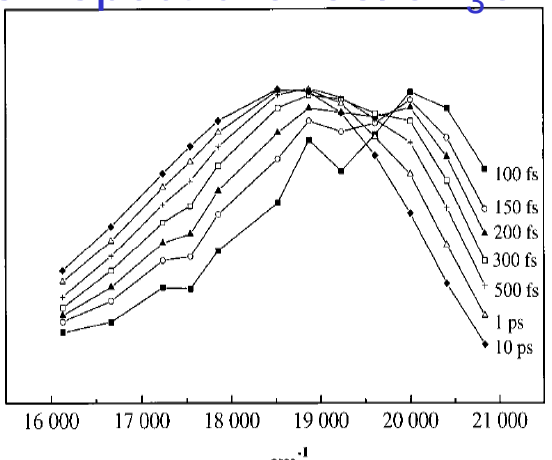
Hochstrasser & Co. measured dynamics of C153/343 in solution and in a peptide - calmodulin complex & examined validity of LR

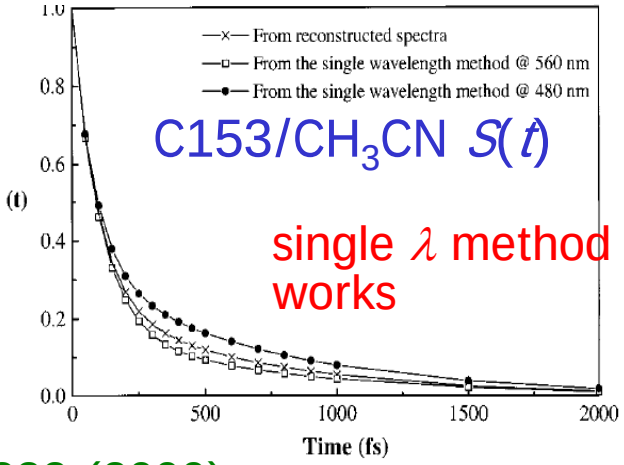
- 1 kHz amp. Ti:saph
- 400 nm pump, OPA 510-700 nm (1λ) probe
- trans. abs. & pump-dump
- IRF 150-200 fs

Single λ Idea



SE Spectra C153/CH_3CN



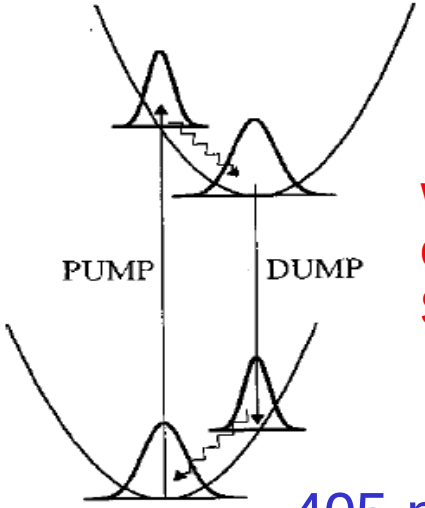


Single λ method: replace tedious spectral reconstruction with measurement at only 1λ
Barbara & Co. Chem. Phys. **152**, 57 (1991)

Changenet-Barret,...Hochstrasser, J. Phys. Chem B **104**, 9322 (2000)

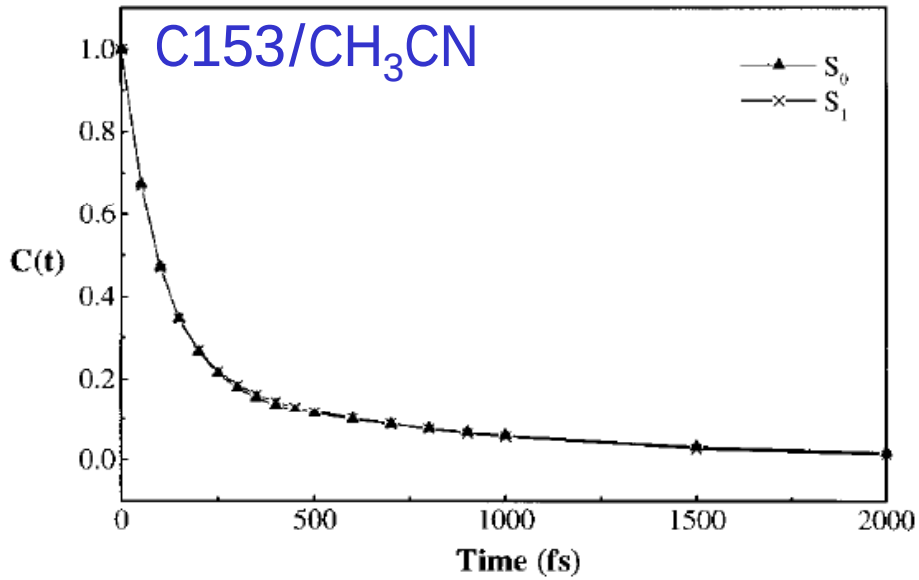
Linear Response in Solution

Pump-Dump Idea

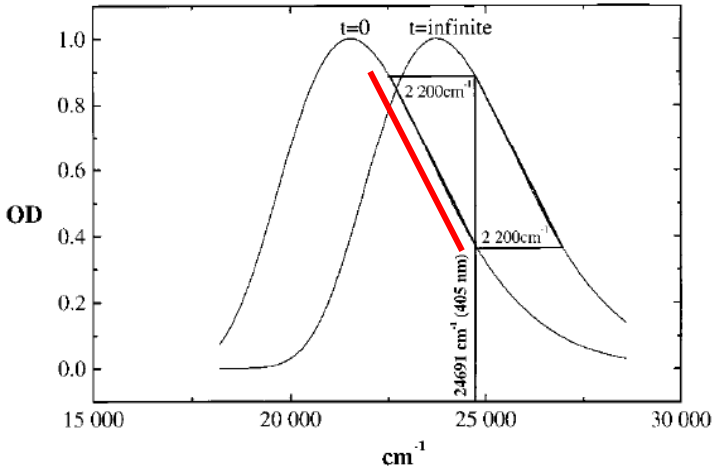


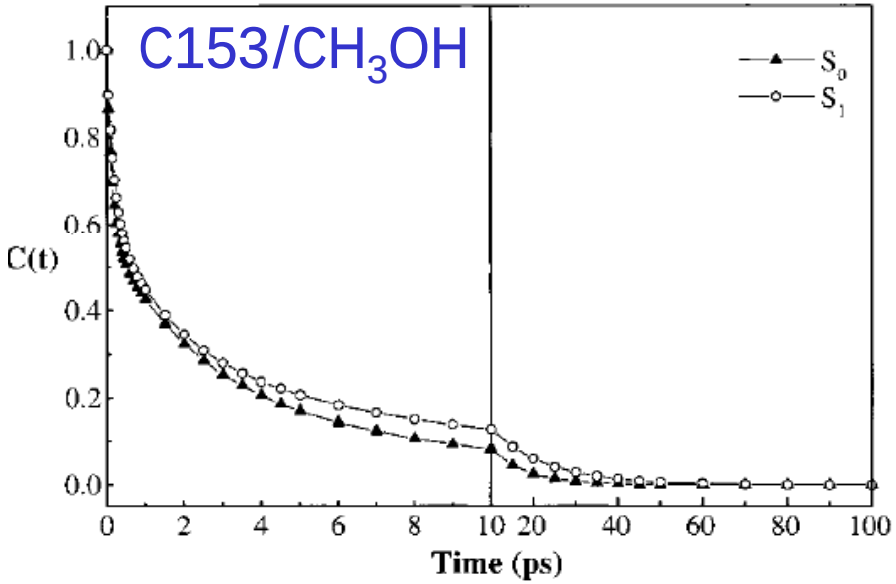
Kovaleko JCP **109**, 1894 (1998)

wait for equilibration (S_1 & S_0) then dump



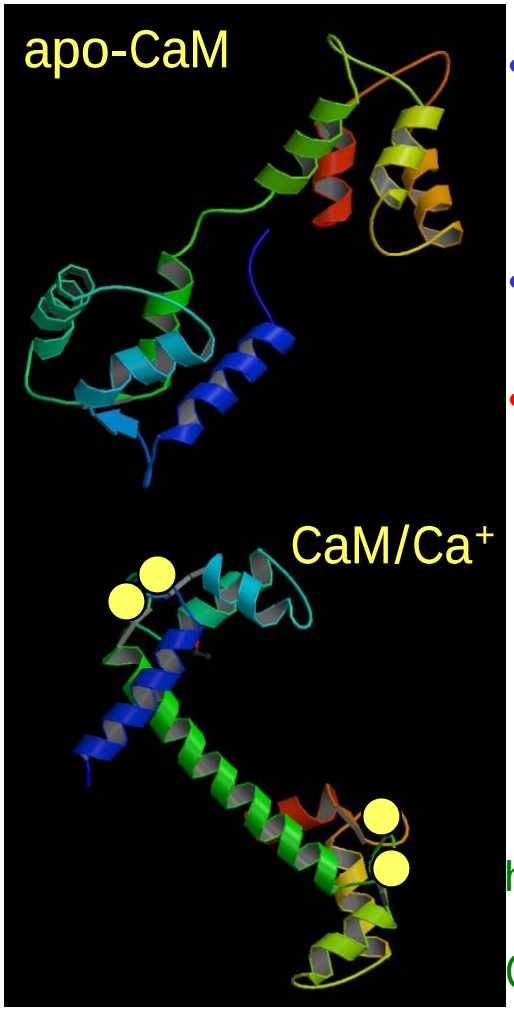
405 nm Linear λ for abs.





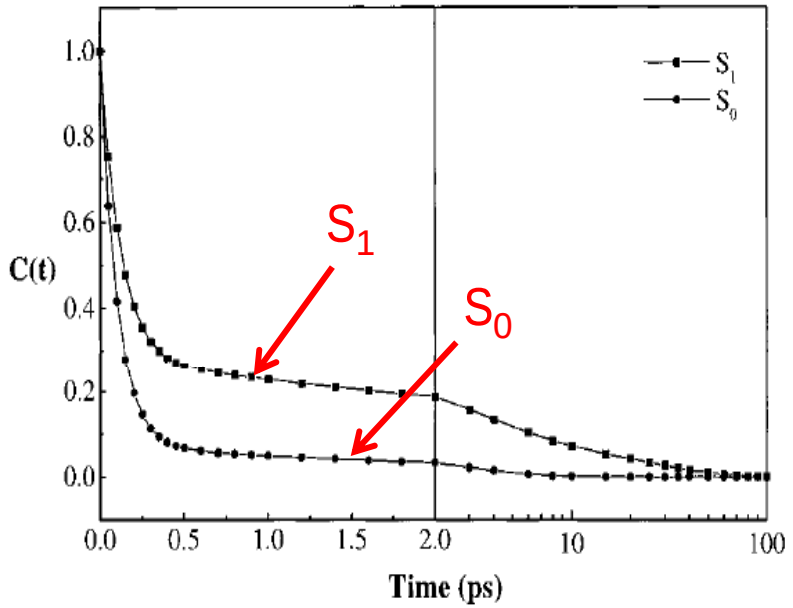
NLR in Calmodulin Complex

- CaM from bovine brain complexed with a labeled tight binding peptide: Lys-Lys-Leu-Leu-Lys-Leu-Leu-Lys-Lys-Leu-Leu-Lys-Leu-amide-C343



- 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

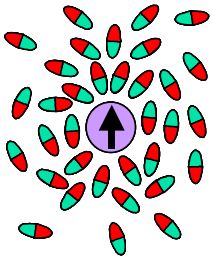
$S(t)$ Peptide+CaM



S1: (72%) 120 fs+(18%) 3 ps+(20%) 22 ps
S0: (93%) 101 fs+(7%) 2.4ps

http://www.chemsoc.org/exemplarchem/entries/2004/warwick_robinson/

Changenet-Barret *et al.*, J. Phys. Chem B **104**, 9322 (2000)



Useful Reviews

K. Bhattacharyya, "Solvation Dynamics and Proton Transfer in Supramolecular Assemblies," Acc. Chem. Res. 36, 95-101 (2003).

B. Bagchi, "Water Dynamics in the Hydration Layer around Proteins and Micelles," Chem. Rev. 105, 3197-3219 (2005).

S. K. Pal and A. H. Zewail, "Dynamics of Water and Biological Recognition," Chem. Rev. 104, 2099-2123 (2004).

L. Nilsson and B. Halle, "Molecular origin of time-dependent fluorescence shifts in proteins," Proc. Natl. Acad. Sci. 102, 13867-13872 (2005).

Parting Shots