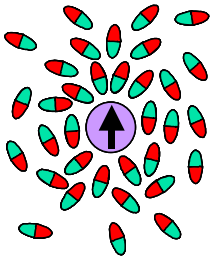
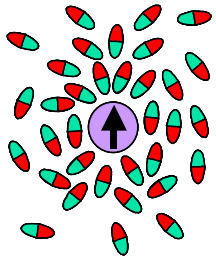




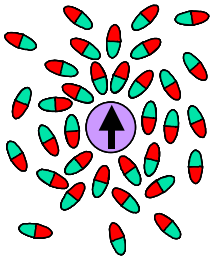
Solvation Dynamics: Fundamentals and A Survey of Results in Simple and Complex Environments

I. Background and Fundamentals

II. Polar Solvation Dynamics

III. Other "Simple" Environments

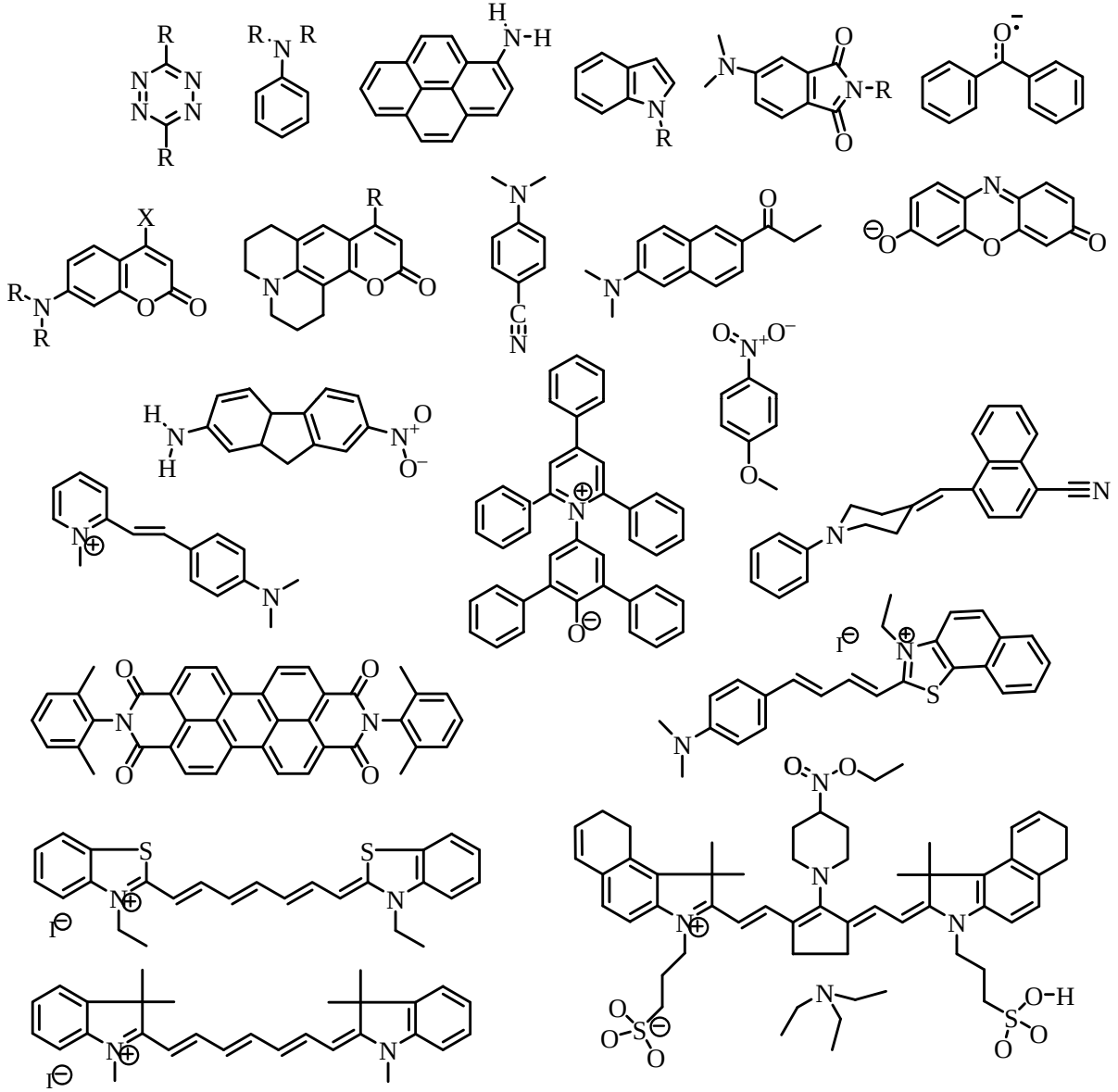
IV. Complex Environments, Biological and Otherwise

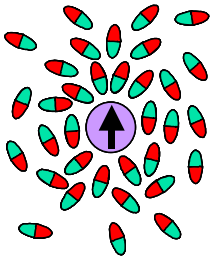


II. Polar Solvation Dynamics

- Experimental Results with C153 Probe
- Dielectric Continuum Models
- Insights from Computer Simulation
- (Molecular Theories)

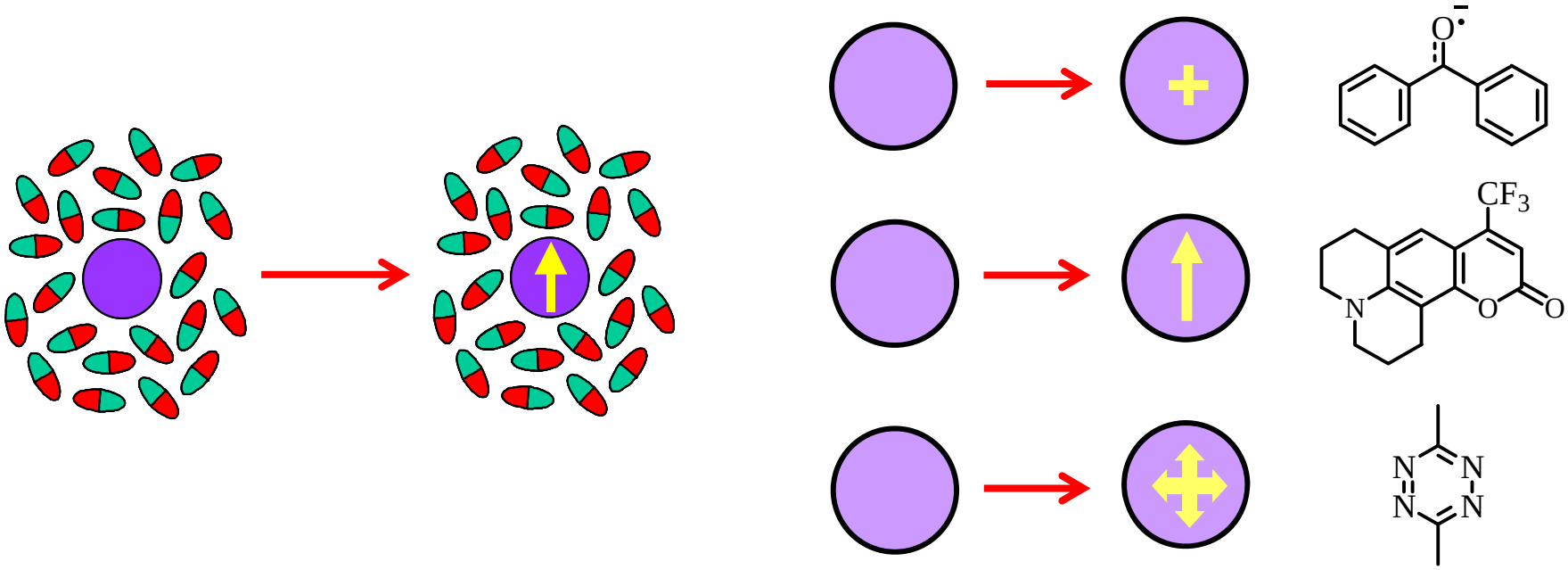
Solvation Dynamics Probes





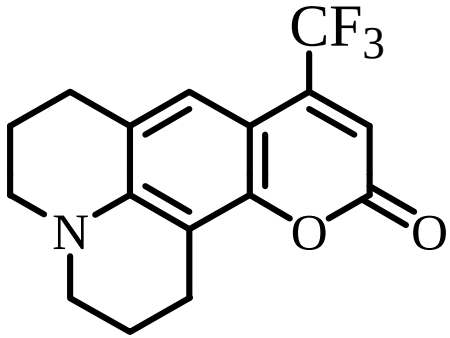
“Polar” Solvation Dynamics

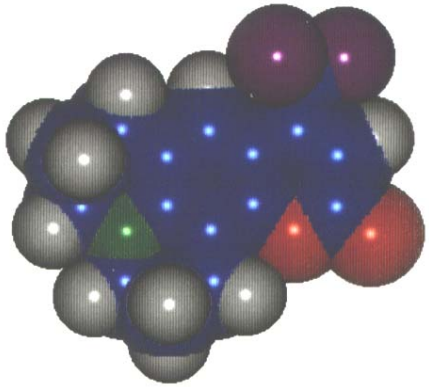
- change in u-v interaction due to change in solute permanent charge distribution interacting with solvent permanent charge distribution
- non-specific part (i.e. not H-bonding dynamics) in dipolar solvents well understood



Coumarin 153

- well characterized dipolar solvation probe



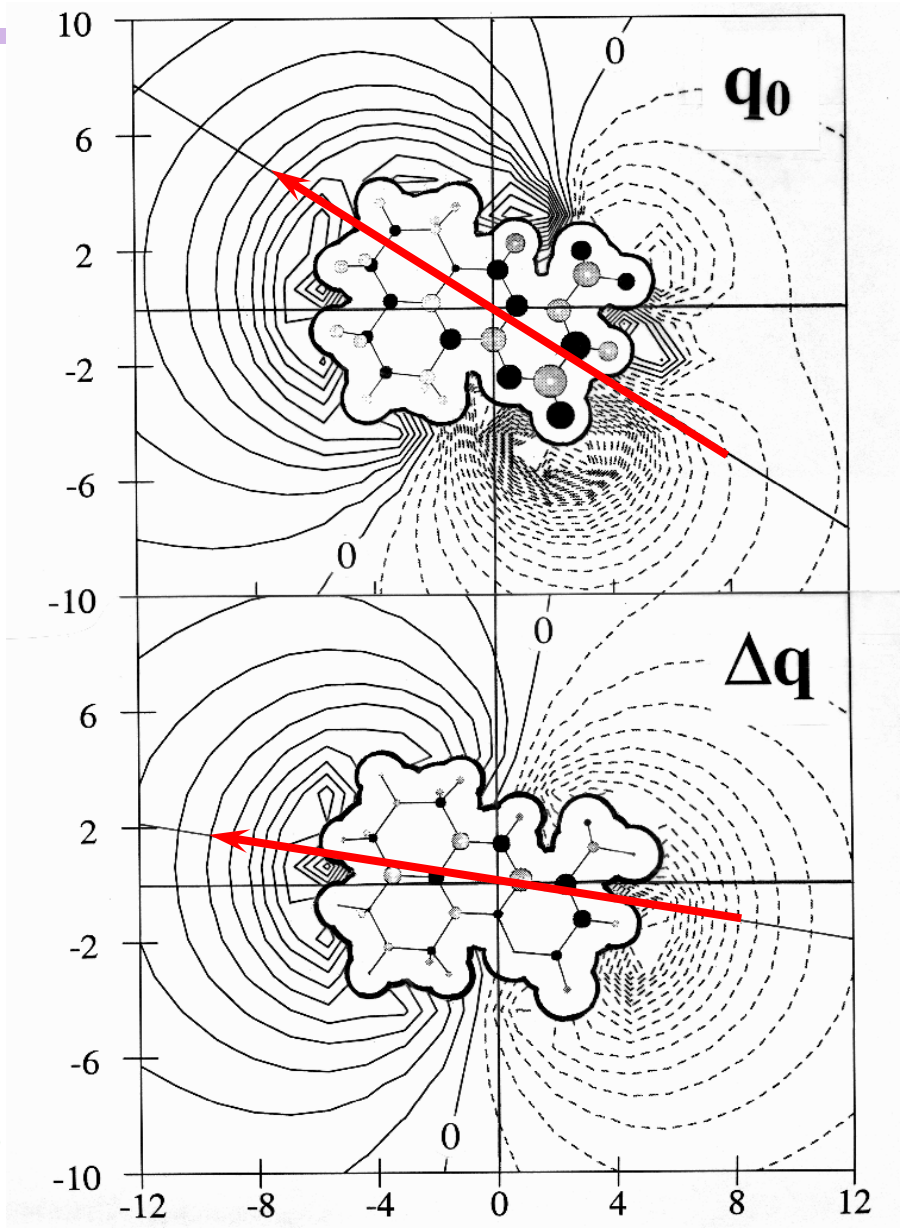


	μ(obs.)	μ(calc.)
S_0	6.5 D	6.8 D
S_1	14-15 D	15 D
$\Delta(S_1\text{-}S_0)$	8-9 D	8.0 D

7.1±.4D*

*Kanya & Oshima, CPL **370**, 211 (2003)

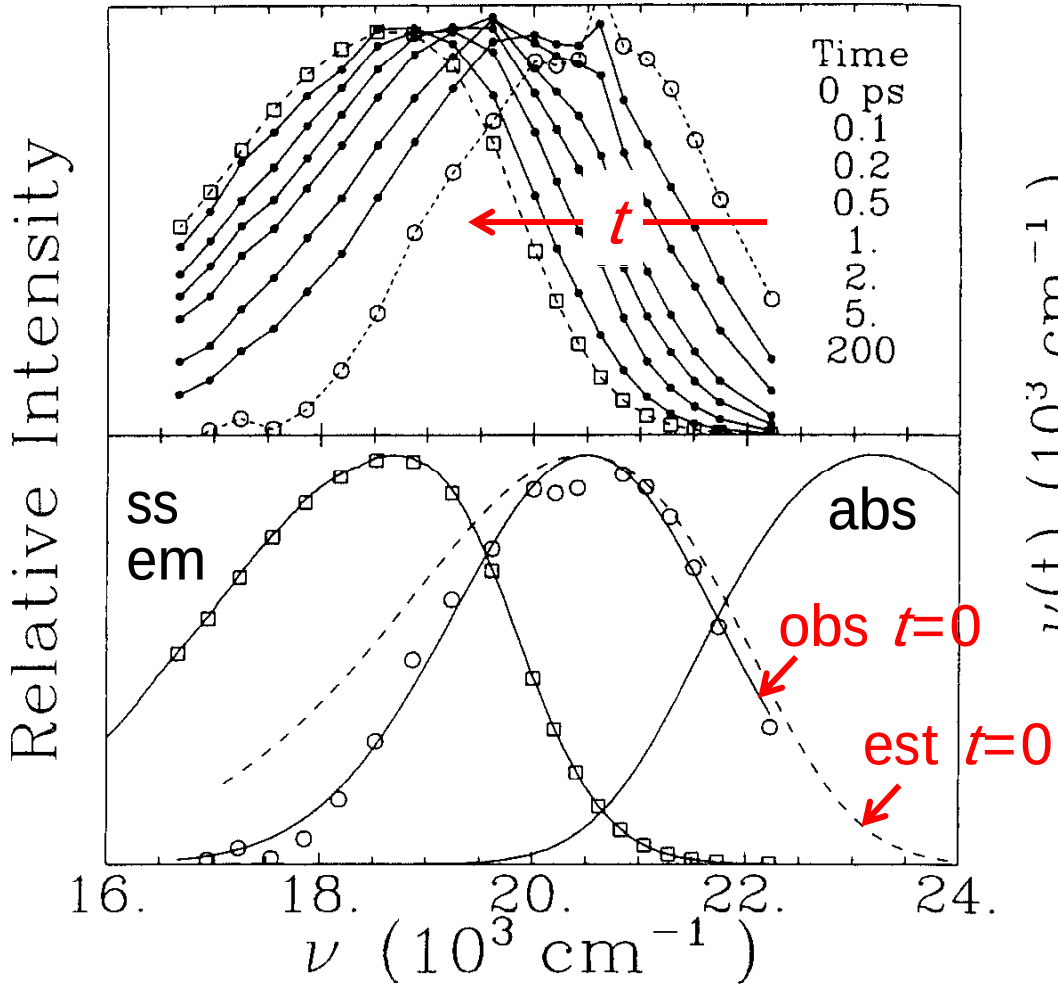
Electrical Potentials from Ψ

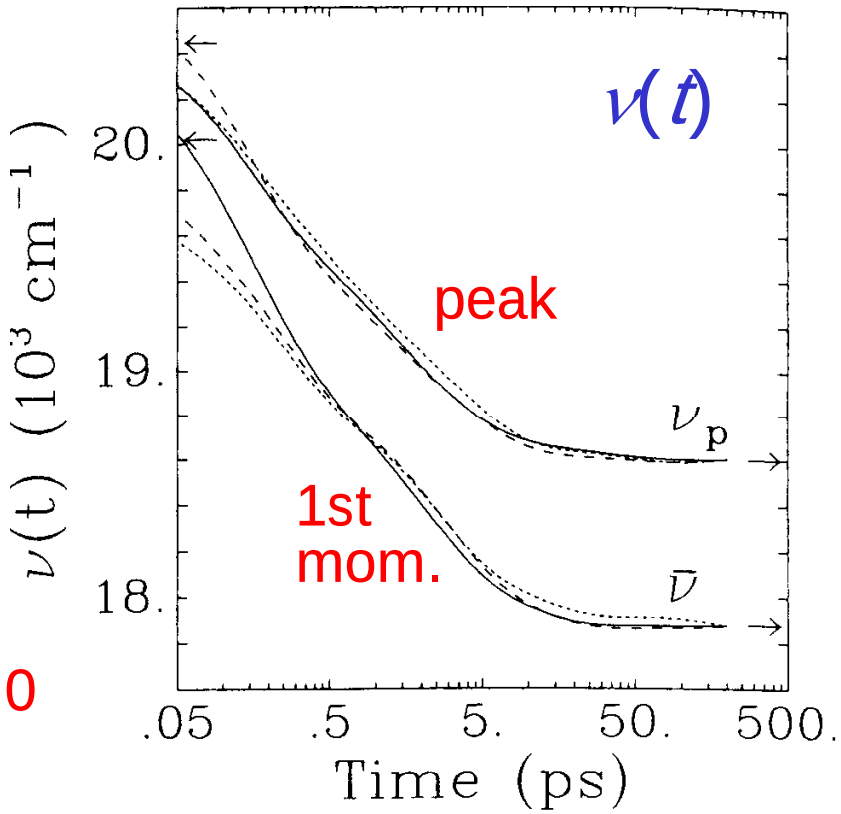


C153 Spectral Dynamics

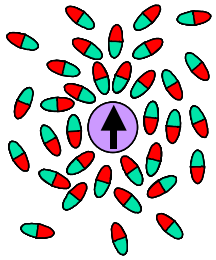
- 1λ upconversion
- 120 fs IRF

C153/DMSO Spectra





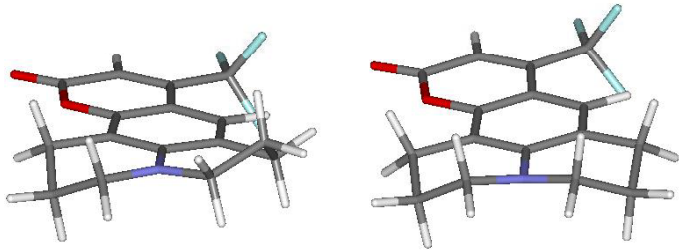
Horng,...Maroncelli, J. Phys. Chem. **99**, 17311 (1995)



Is It Just Solvation?

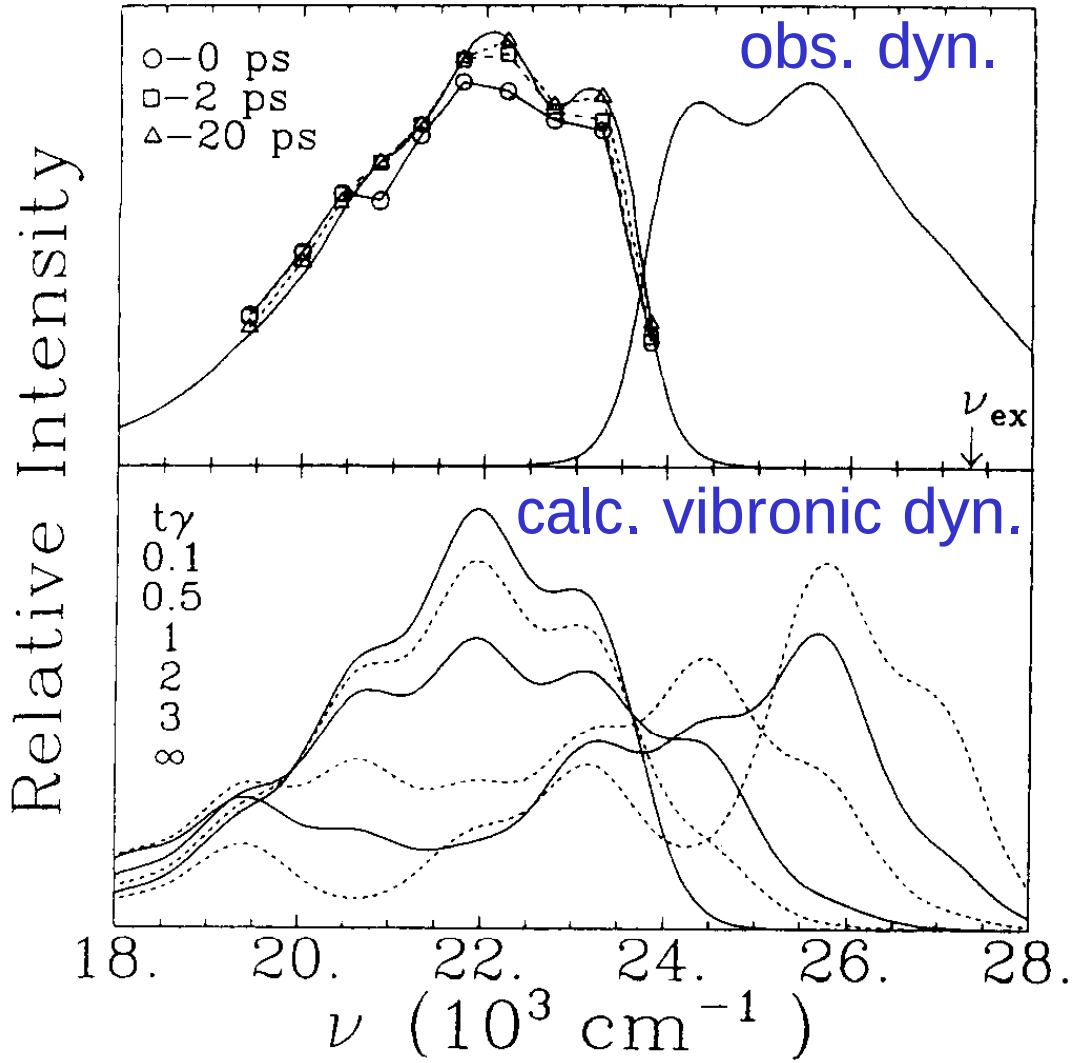
Potential Complications:

- multiple electronic states?
- vibronic effects?
- joulolidine ring conformations?



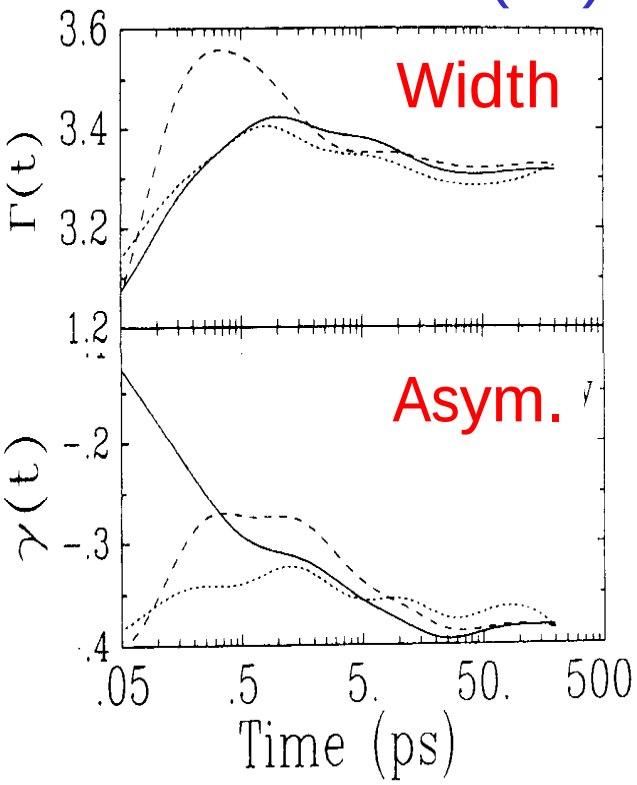
- vibronic relax. <20fs
- conf. not important
- (S_1 well isolated)

C153/cyclohexane



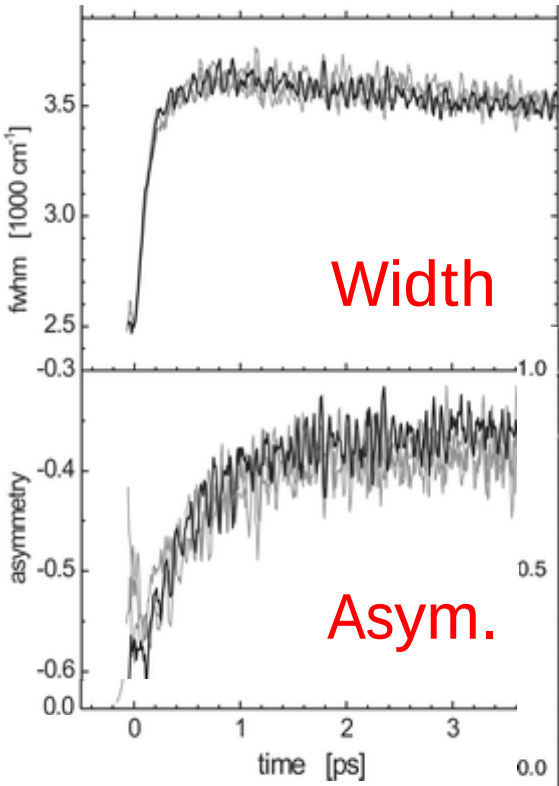
Subtle Aspects of Spectra

C153/DMSO (1λ)

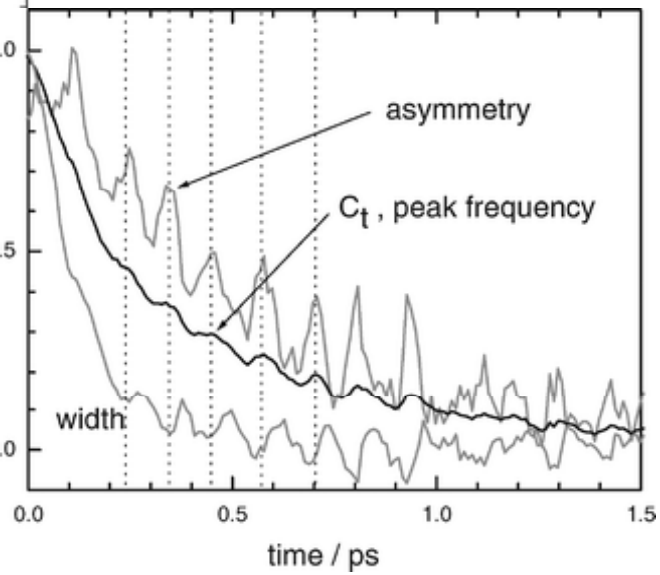


Horng,...Maroncelli, J. Phys. Chem. **99**, 17311 (1995)

C153/CH_3CN (FLUPS)



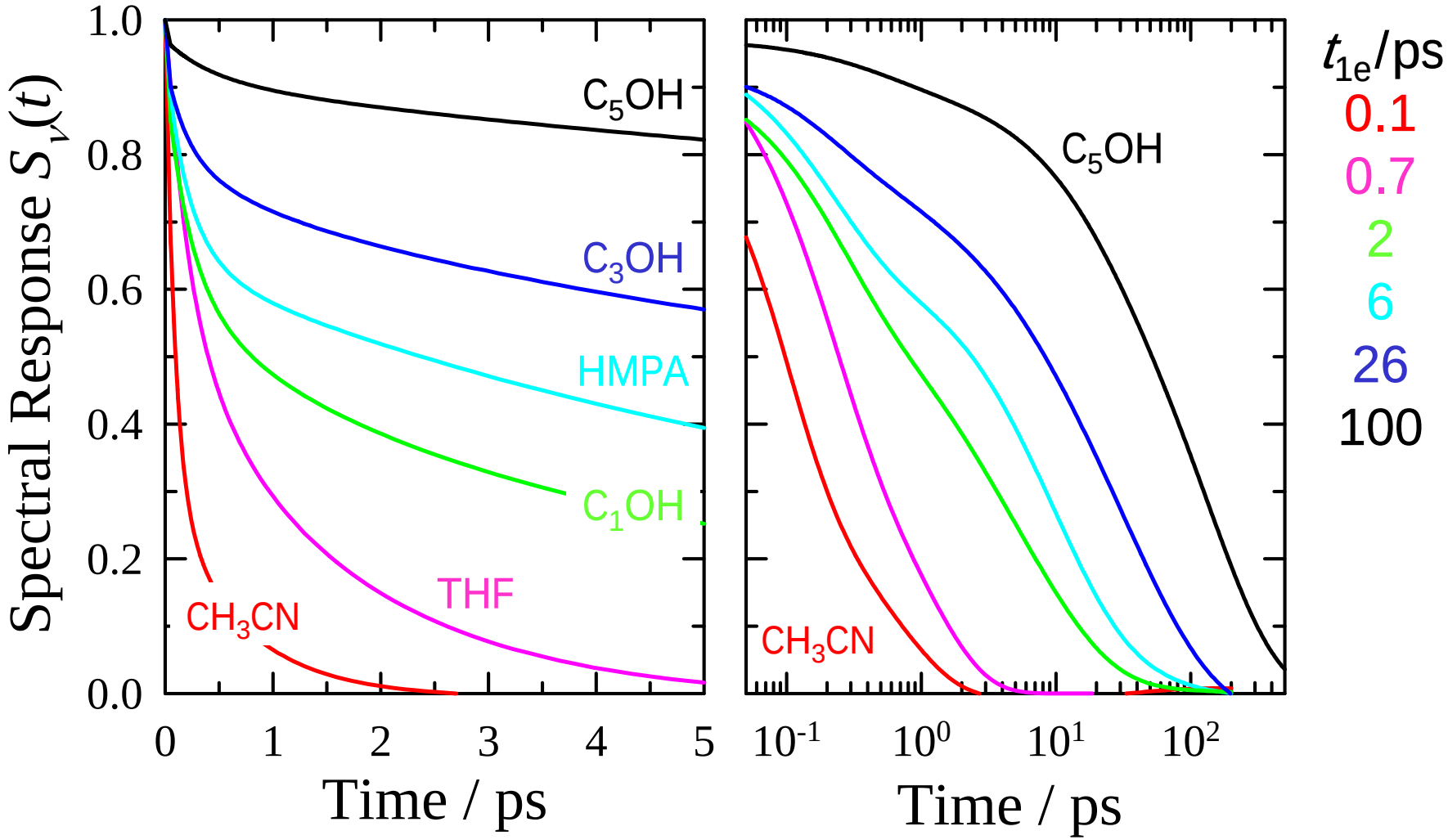
(norm. & expanded)

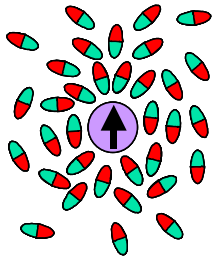


Zhao, ...Ernsting, Phys. Chem. Chem. Phys. **7**, 1716 (2005)

The Spectral/Solvation Response

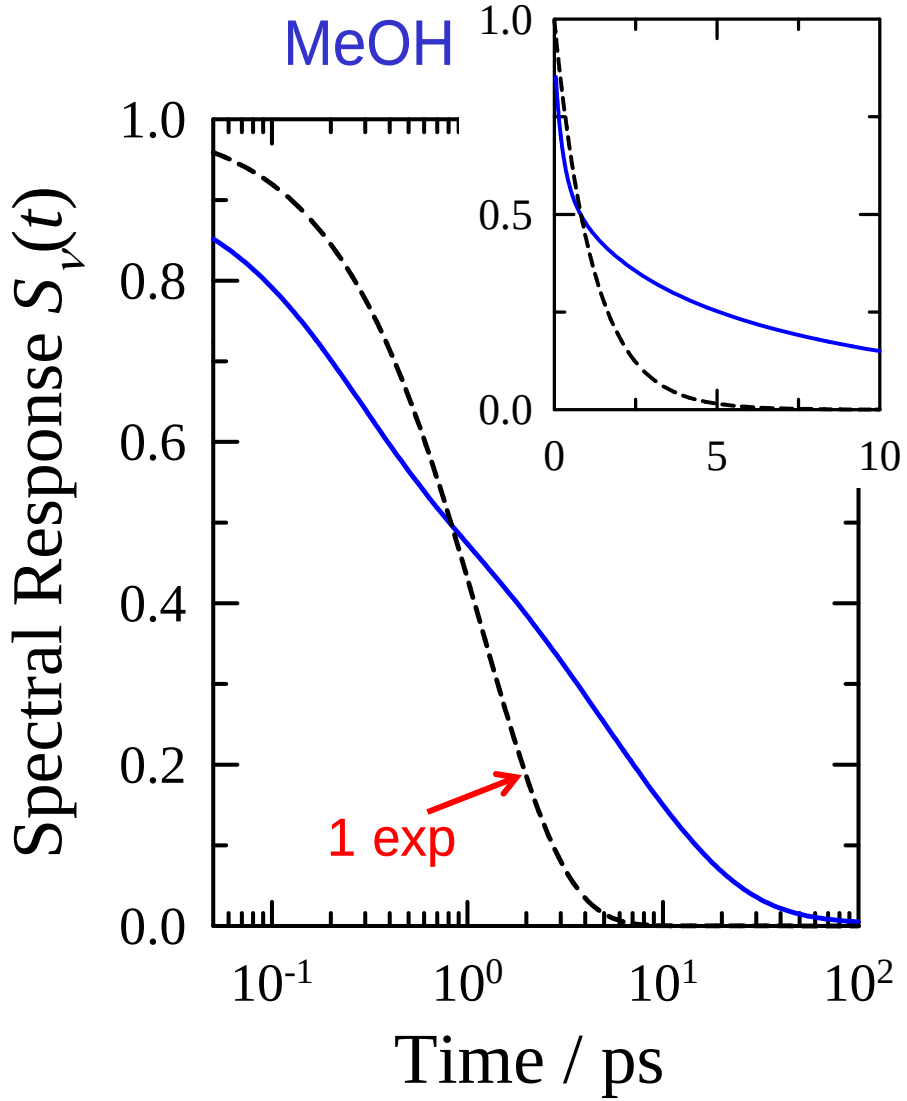
$$S_\nu(t) \equiv \{\nu(t) - \nu_\infty\}/\{\nu_0 - \nu_\infty\}$$





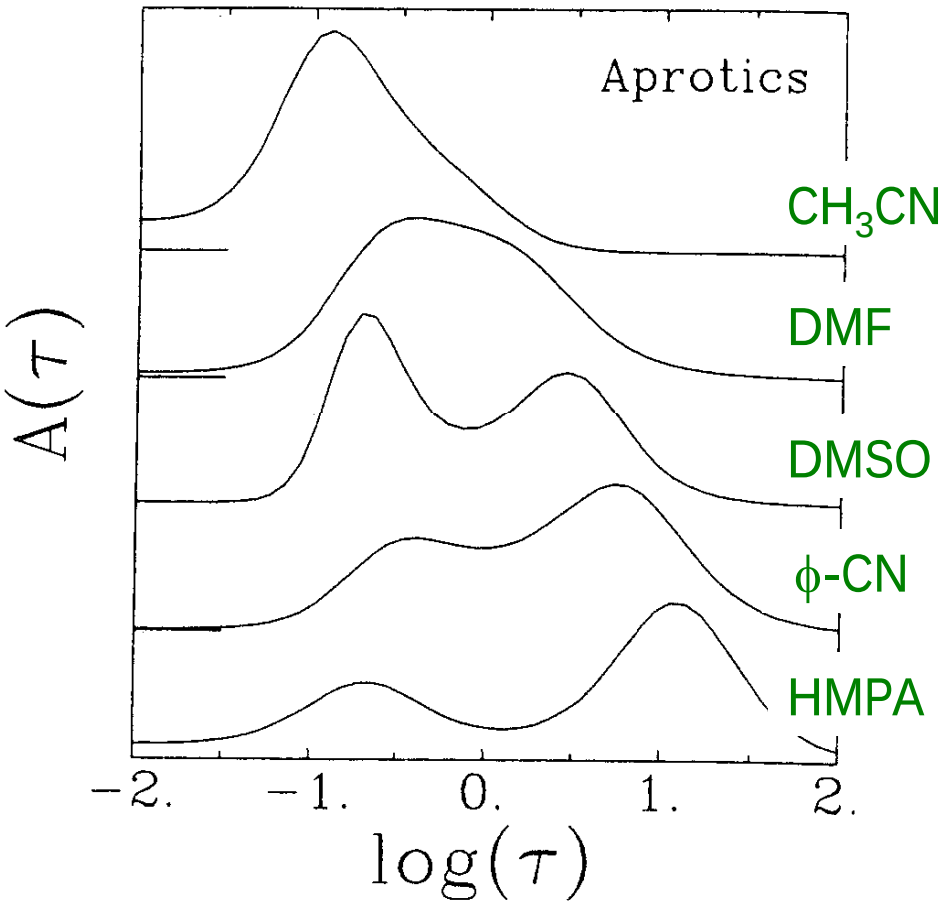
$S_\nu(t)$ Characteristics

MeOH

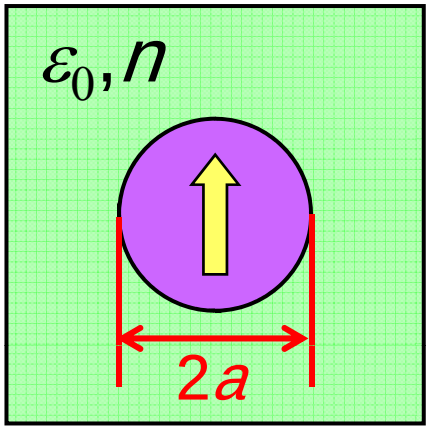


Decay Time Distributions

$$S_\nu(t) = \int_0^\infty A(\tau)\exp(-t/\tau)d\tau$$



Dielectric Continuum Models

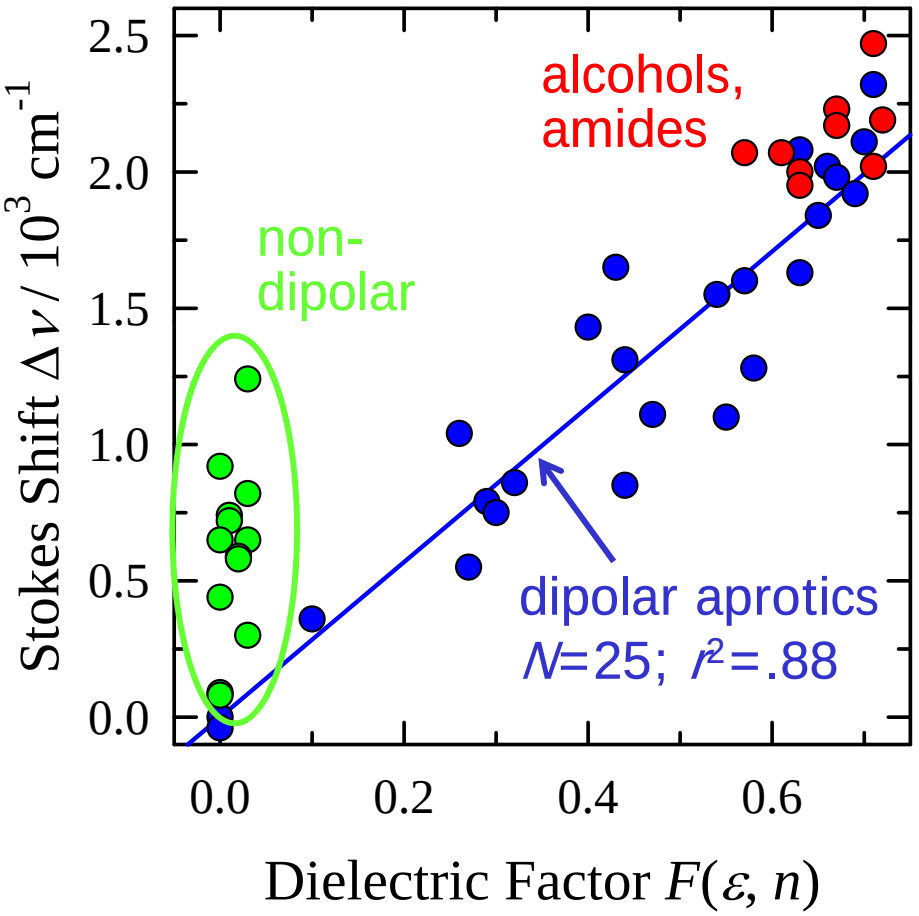


Predicted Stokes Shift:

$$\Delta\nu = \frac{2(\Delta\mu)^2}{a^3} F(\varepsilon_0, n)$$

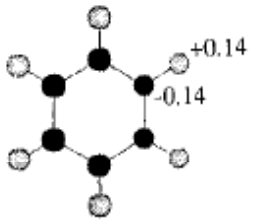
$$F(\varepsilon_0, n) = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2}$$

C153 Stokes Shifts

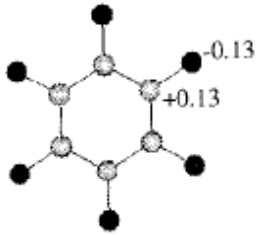


Reynolds,...Maroncelli, J. Phys. Chem. **100**, 10337 (1996)

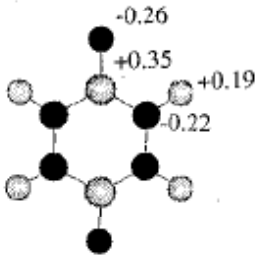
Benzene is a Polar Solvent



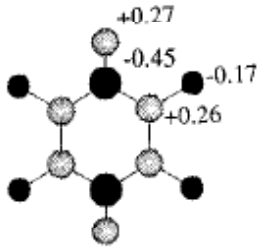
Benzene



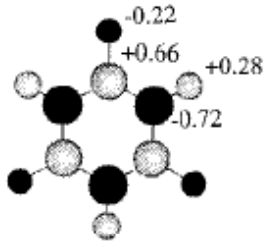
Hexafluorobenzene



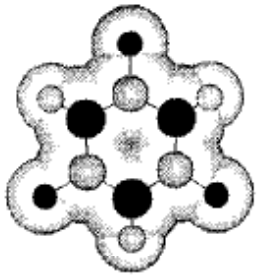
1,4-Difluorobenzene



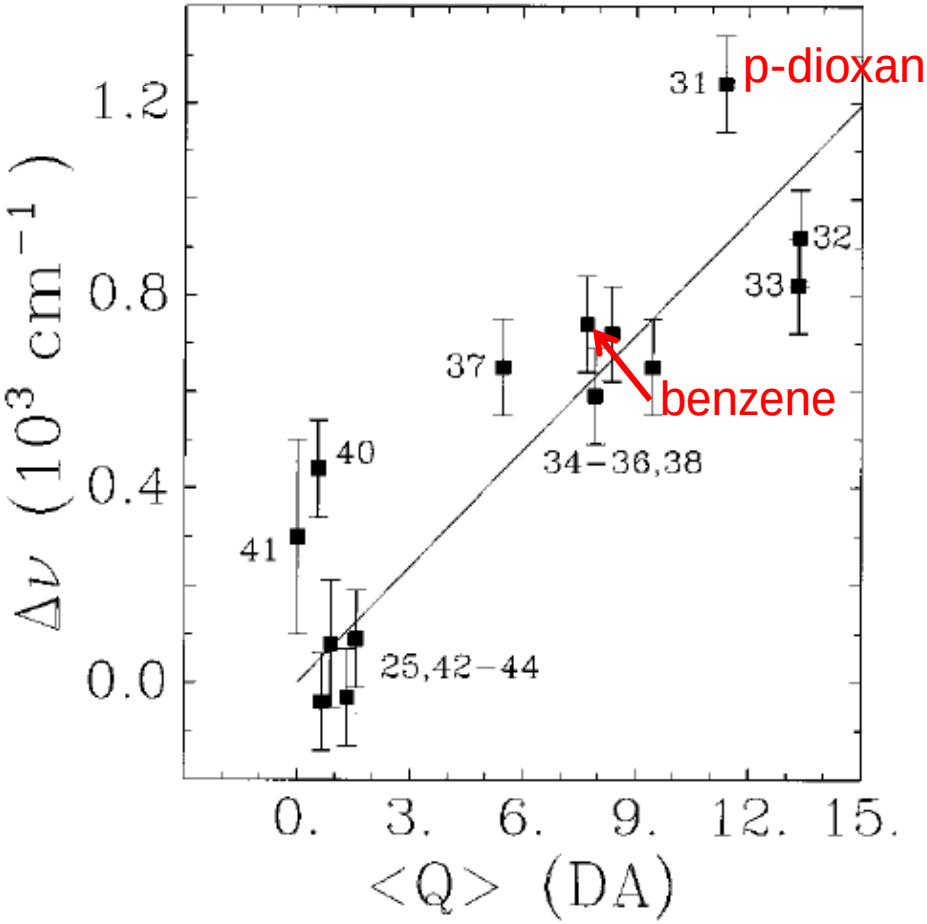
1,2,4,5-Tetrafluorobenzene



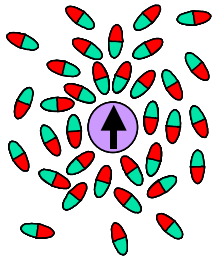
1,3,5-Trifluorobenzene



C153 Stokes Shifts in Non-Dipolar Solvents



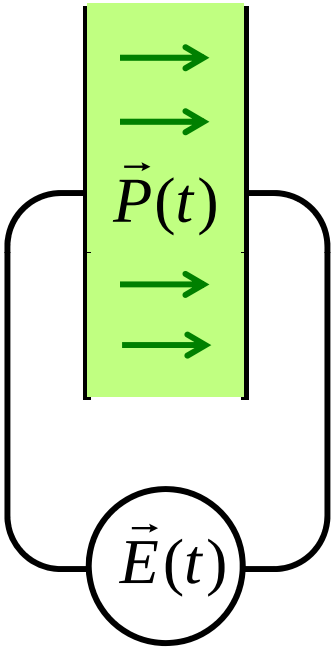
Reynolds,...Maroncelli, J. Phys. Chem. **100**, 10337 (1996).

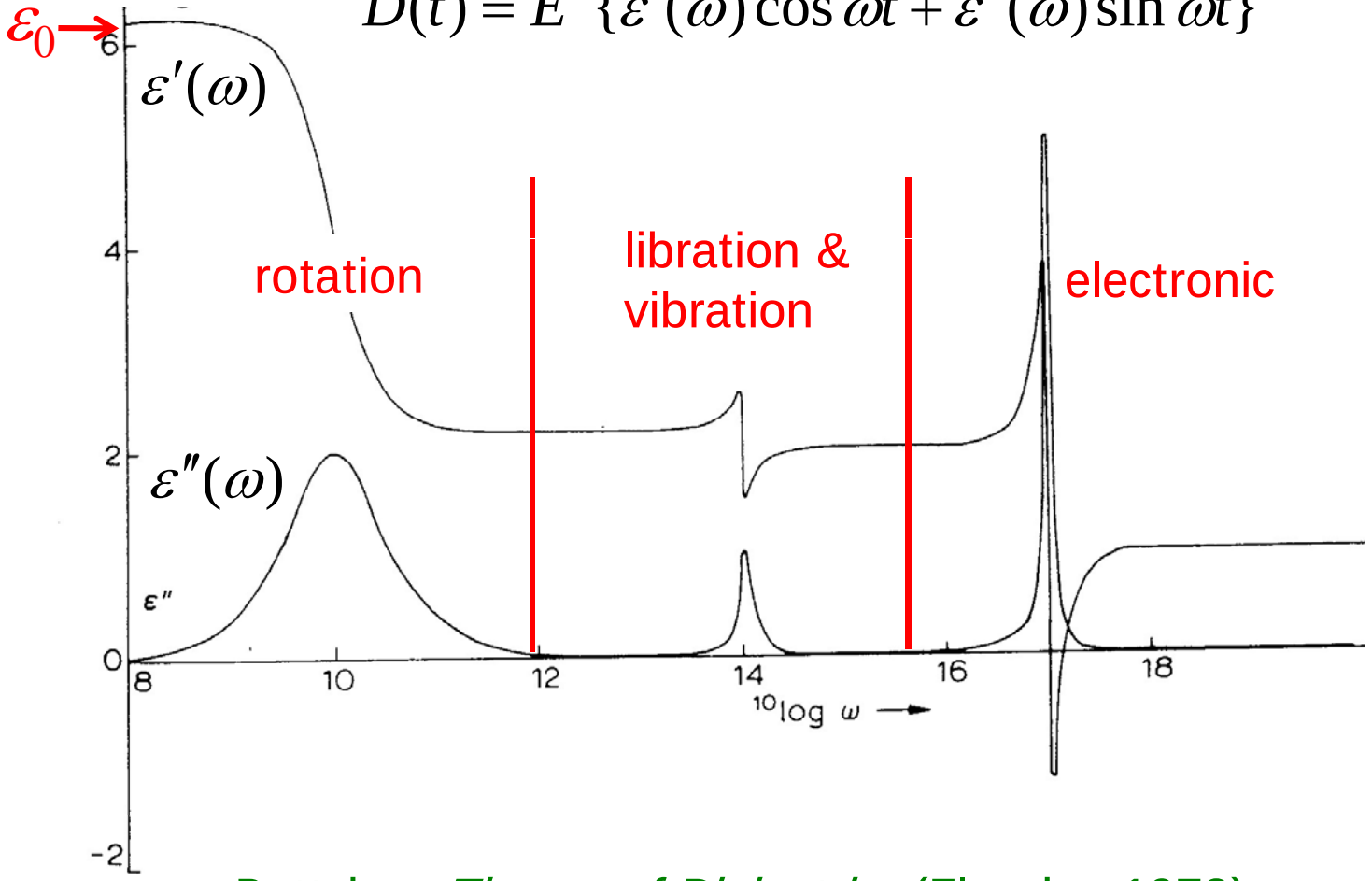


Dielectric Response $\varepsilon(\omega)$

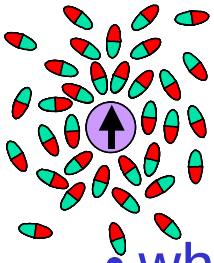
$$\vec{E}(t) = \vec{E}^0 \cos \omega t \qquad 4\pi\vec{P}(t) = \vec{D}(t) - \vec{E}(t)$$

$$\vec{D}(t) = \vec{E}^0 \{\varepsilon'(\omega) \cos \omega t + \varepsilon''(\omega) \sin \omega t\}$$





Bottcher, *Theory of Dielectrics* (Elsevier, 1973)



$S_\nu(t)$ and $\varepsilon(\omega)$

- when the static electrical u-v interaction can be written:

$$U_{el} = -\Phi_m^2 \chi_m(\varepsilon_0)$$

solute $q,\mu,Q,\ldots$ — solvent susceptibility

- the solvation response to a change in Φ_m is approximately:

$$S_m(t) = L_p^{-1}\left\{\left[\tilde{\varepsilon}(0) - \tilde{\varepsilon}(p)\right]/\, p\right\} \qquad \tilde{\varepsilon}(p) = \hat{\varepsilon}(i\omega) \qquad \hat{\varepsilon}(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$

inverse Laplace transform

- for example:

$$\chi_q(\varepsilon_0) = \frac{1}{a\varepsilon_0}$$

$$\chi_\mu(\varepsilon_0) = \frac{2}{a^3}\frac{\varepsilon_0 - 1}{2\varepsilon_0 + 1}$$

for Debye type $\varepsilon(\omega)$

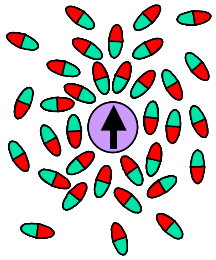
$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau_D}$$

$$S_m(t) = \exp(-t/\tau_m)$$

$$\tau_q = \frac{\varepsilon_\infty}{\varepsilon_0}\tau_D = "\tau_L"$$

longitudinal relaxation time

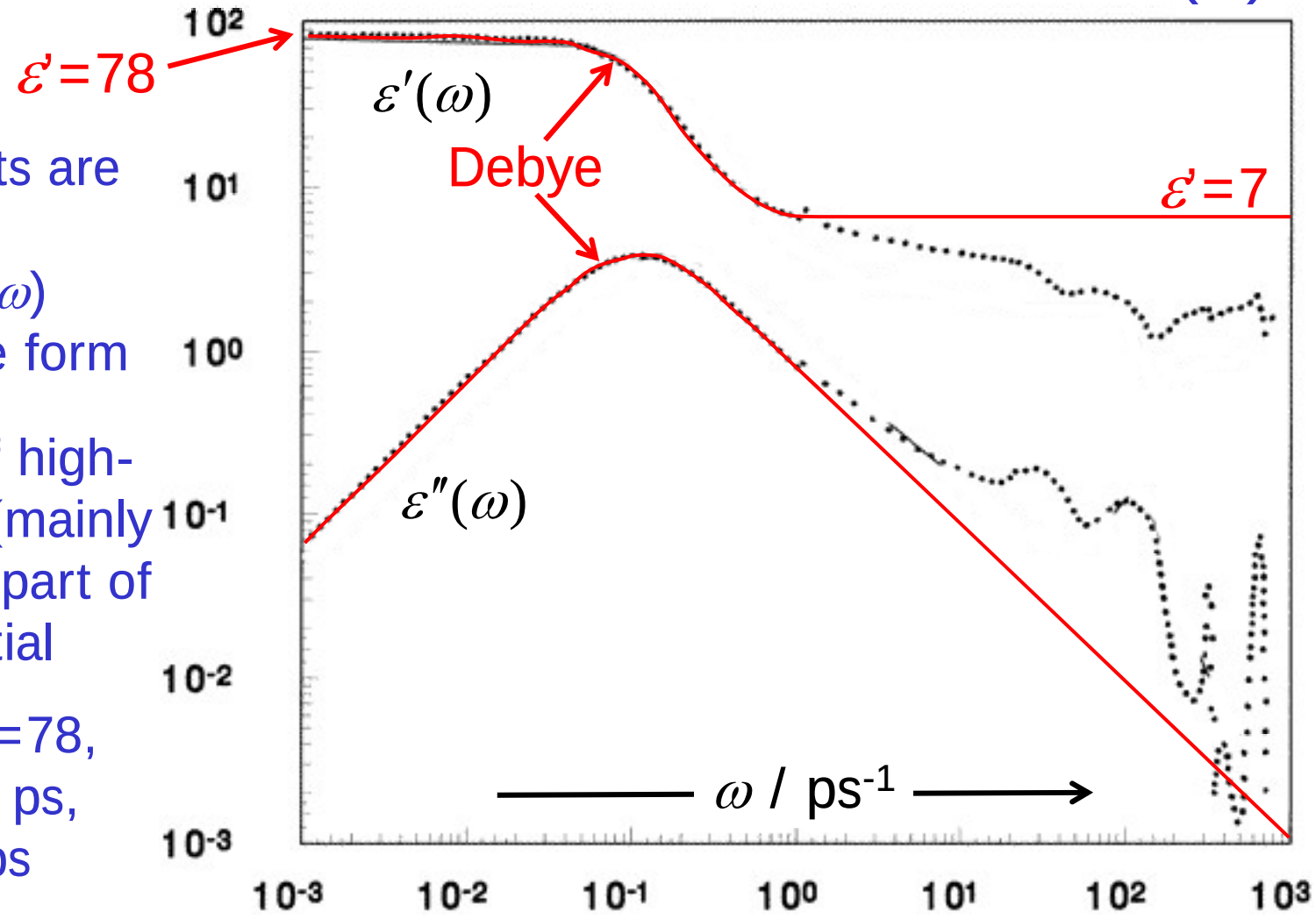
$$\tau_\mu = \frac{2\varepsilon_\infty + 1}{2\varepsilon_0 + 1}\tau_D$$



Non-Debye $\varepsilon(\omega)$

- real solvents are show more complex $\varepsilon(\omega)$ than Debye form
- inclusion of high-frequency (mainly librational) part of $\varepsilon(\omega)$ essential
- if Debye ε_0=78, ε_∞~7, τ_D=8 ps, so τ_μ~0.8 ps

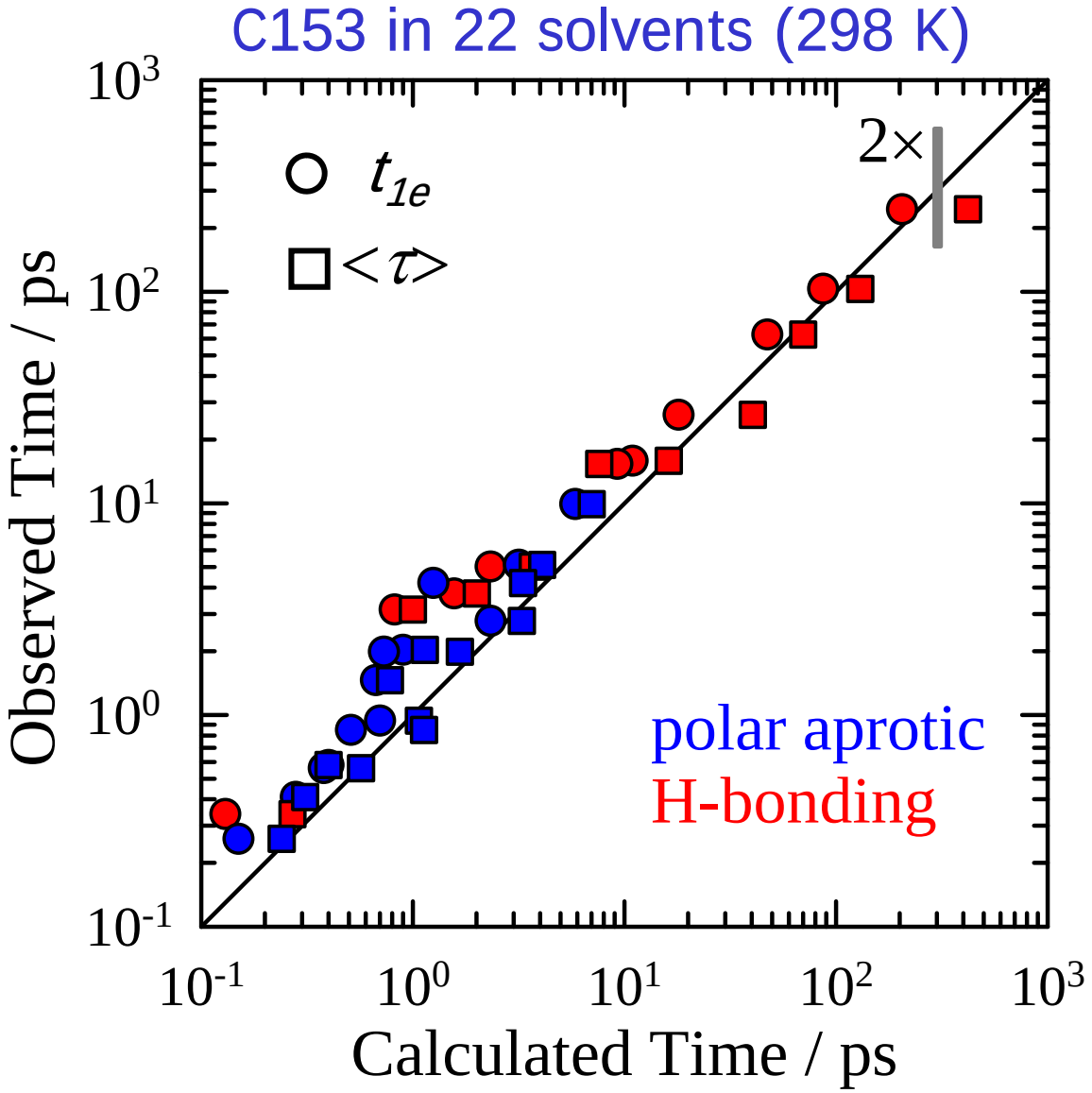
Water $\varepsilon(\omega)$

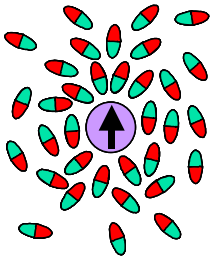


Trokhymchuk et al., J. Phys. Chem. 1996, 100, 1411(1996).

$\varepsilon(\omega)$ Predictions

- characteristic times predicted to within a factor of 2 for wide range of solvents near room T
- no distinction with H-bonding

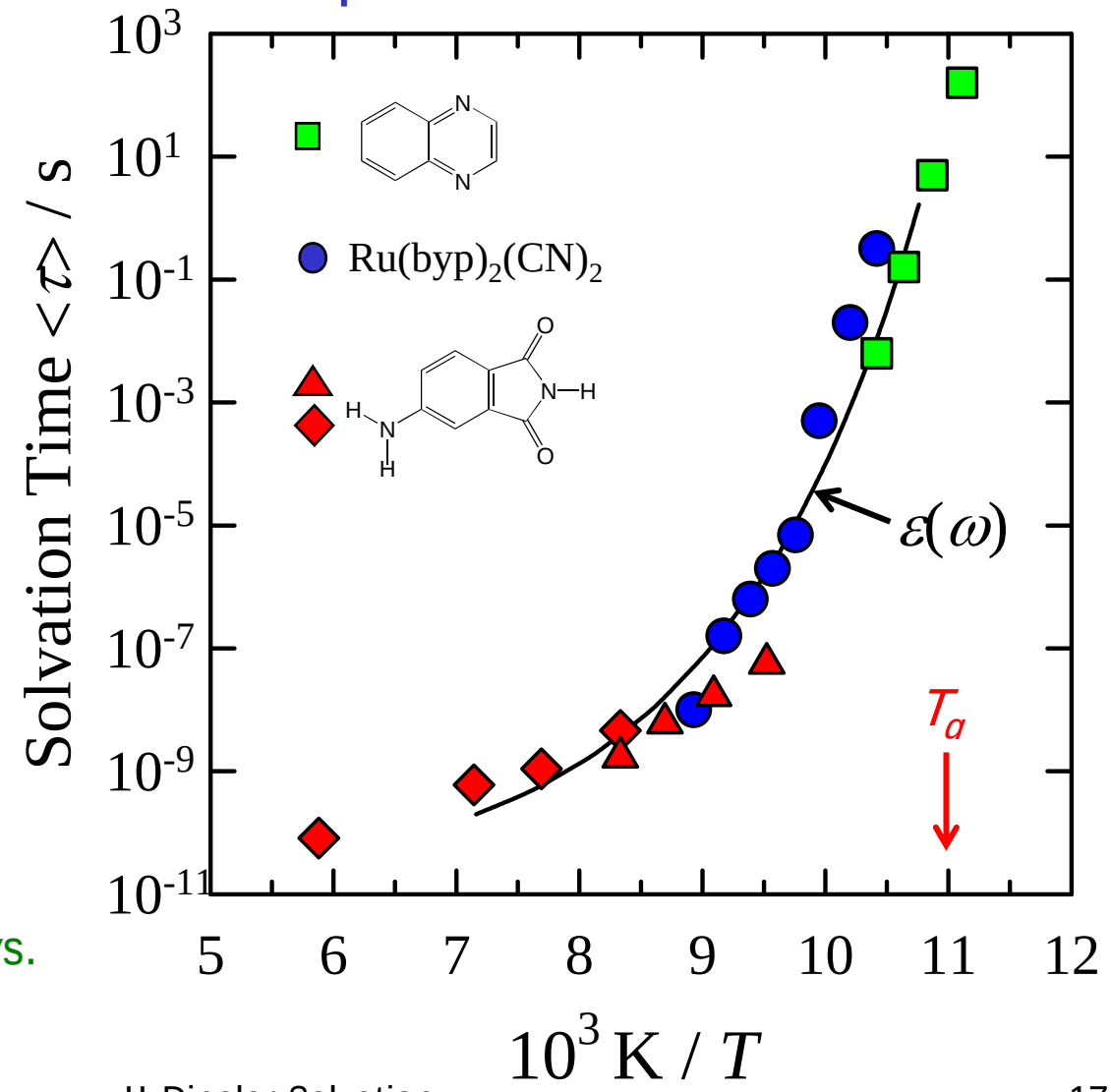




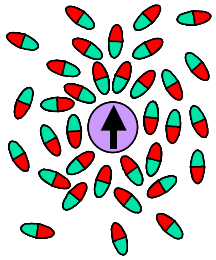
Temperature Dependence

- connection to $\varepsilon(\omega)$ persists over wide T range
- but few examples

T dependence in m-THF

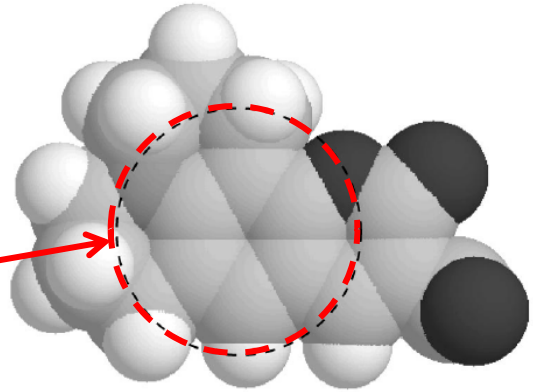


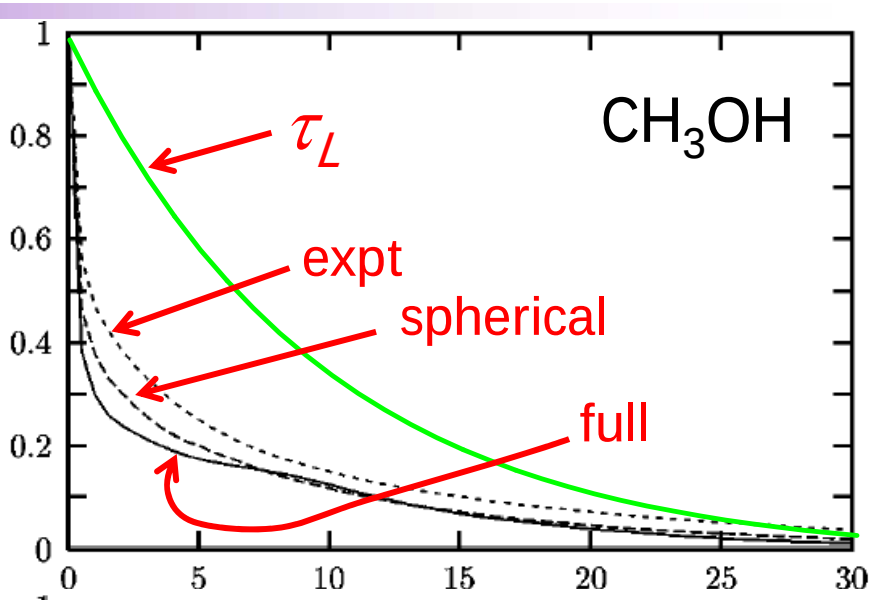
Richert,...Maroncelli, Chem. Phys. Lett. **229**, 302 (1994).

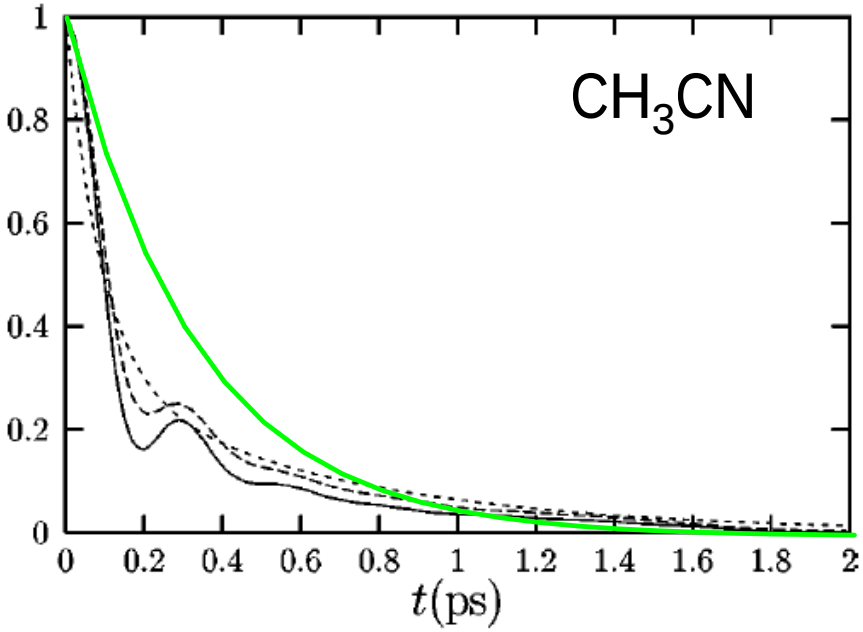


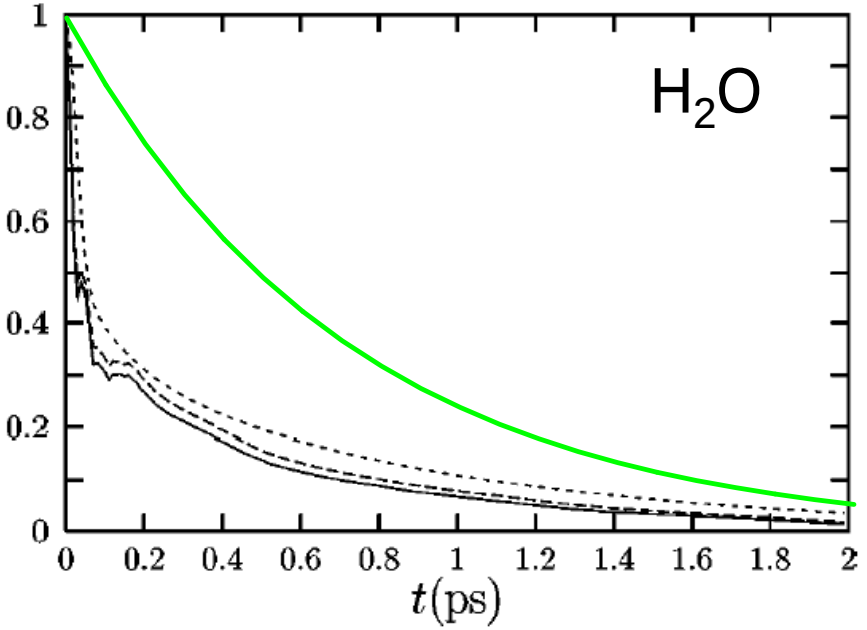
More Sophisticated $\varepsilon(\omega)$ Calcs.

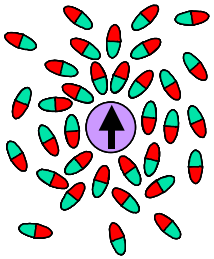
Song & Chandler, J. Chem. Phys. **108**, 2594 (1998)







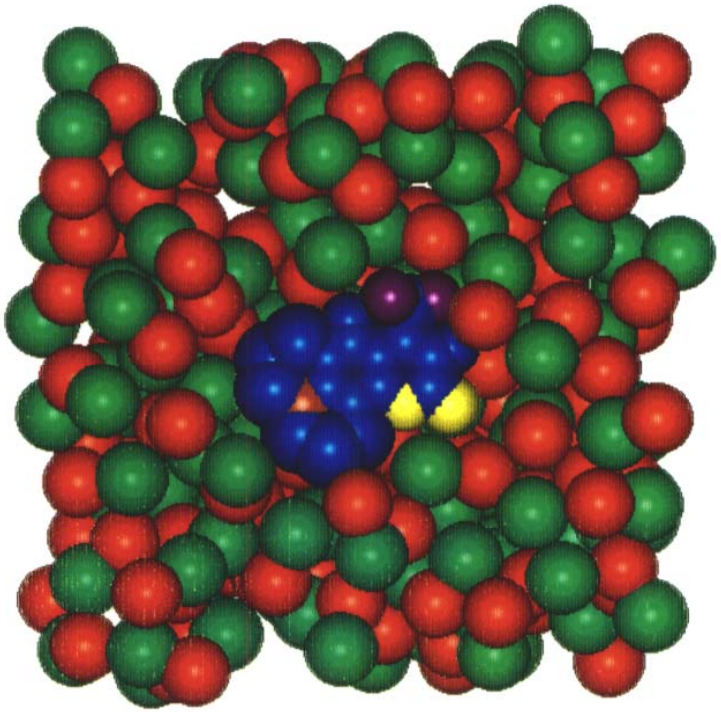




Key Points

- solvation in many solvents is remarkably rapid >1 ps
- but >10^3 variation in t_{1e} at room T
- biphasic, with many solvents showing a pronounced fast component
- highly non-exponential, esp. in alcohols
- essential features captured by dielectric continuum models

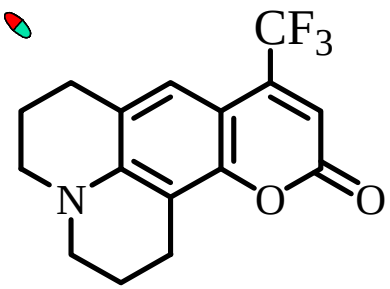
Computer Simulations

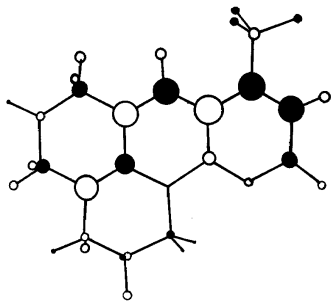


- (usually) classical dynamics, pair-wise additive potentials (LJ+q), ...
- 1 solute and 250-1000 solvent molecules
- equilibrium and non-equilibrium dynamics

Ando, Benjamin, Berkowitz, Brown, Callis, Fonseca, Ladanyi, Hynes, Kim, Nitzan, Patey, Rossky, Schwartz, Stratt, ...

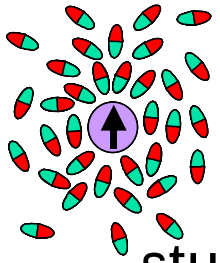
Simulation & Experiment





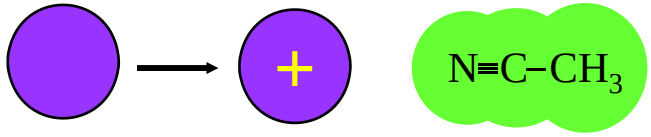
- standard solvent models
- solute q, Δq from Ψ

Kumar&Maroncelli, JCP 103, 3038 (1995); Jimenez et al., Nature 369, 471 (1994).



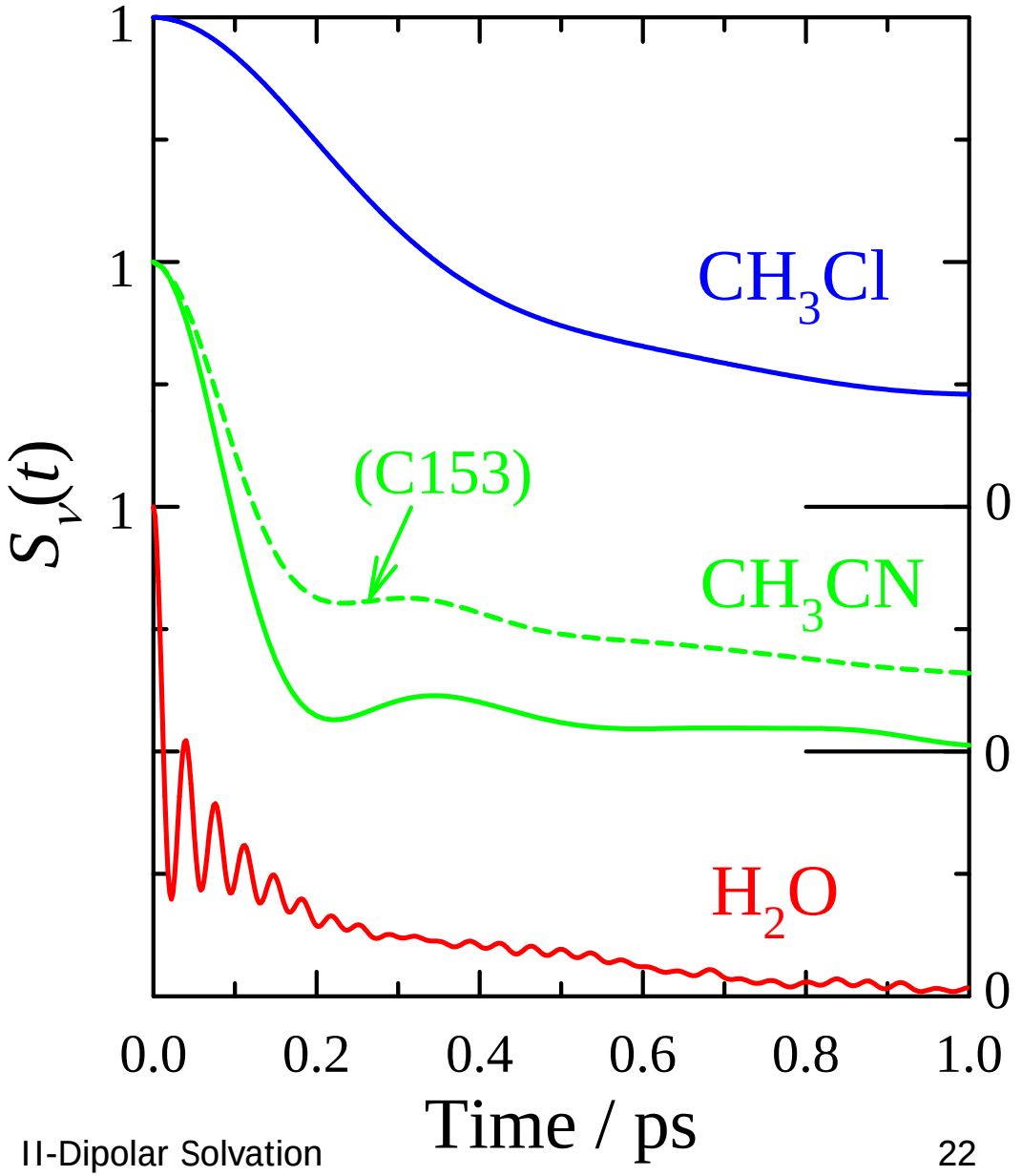
MD of Simple Solutes

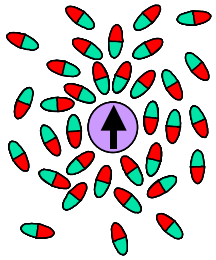
studies of simple solutes afforded many insights



($m=\infty$)

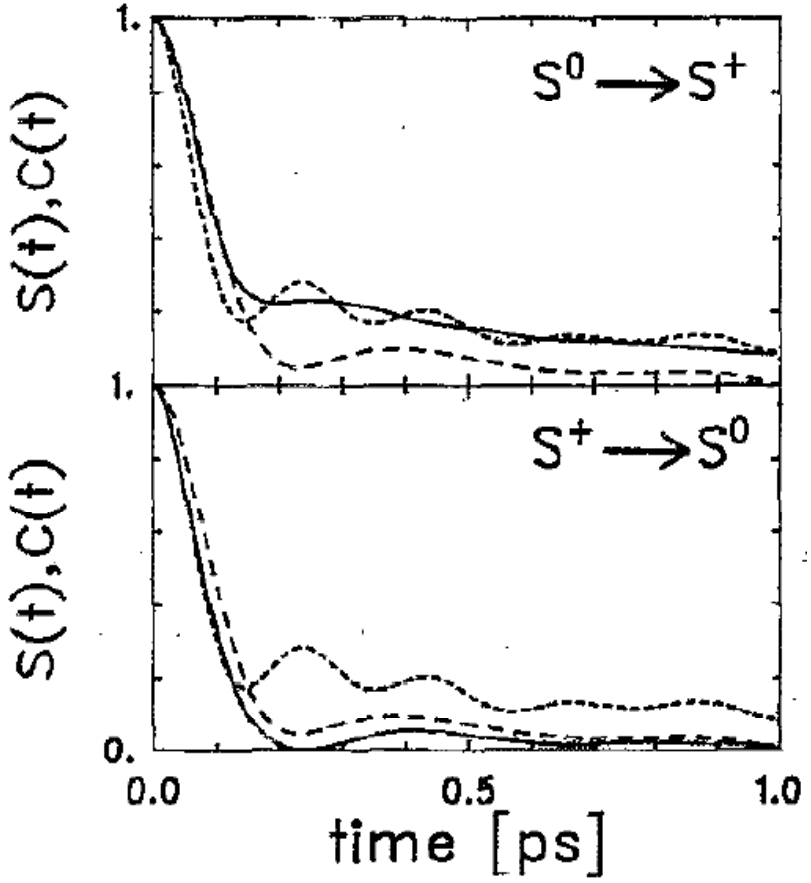
- often linear response
- prominent “inertial” or “Gaussian” decay
- mainly solvent rotation
- speed tied to solvent polarity



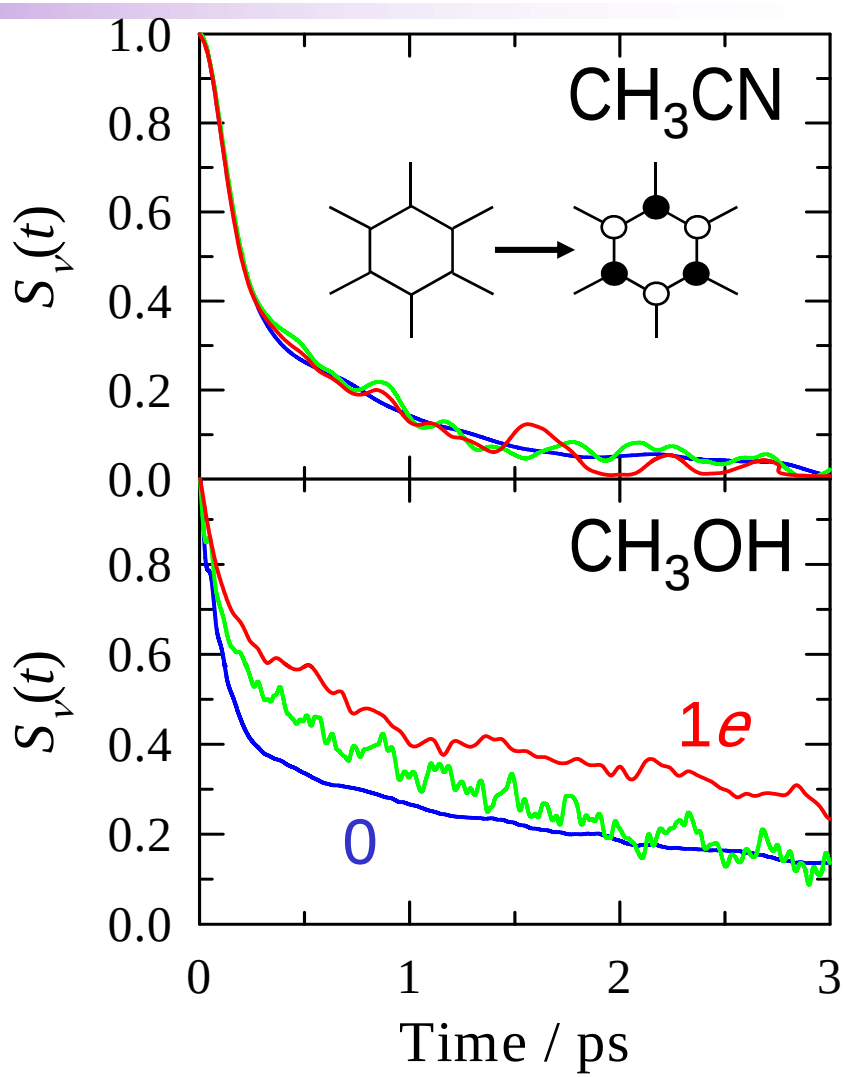


Linear Response?

Atomic Solute in CH_3CN

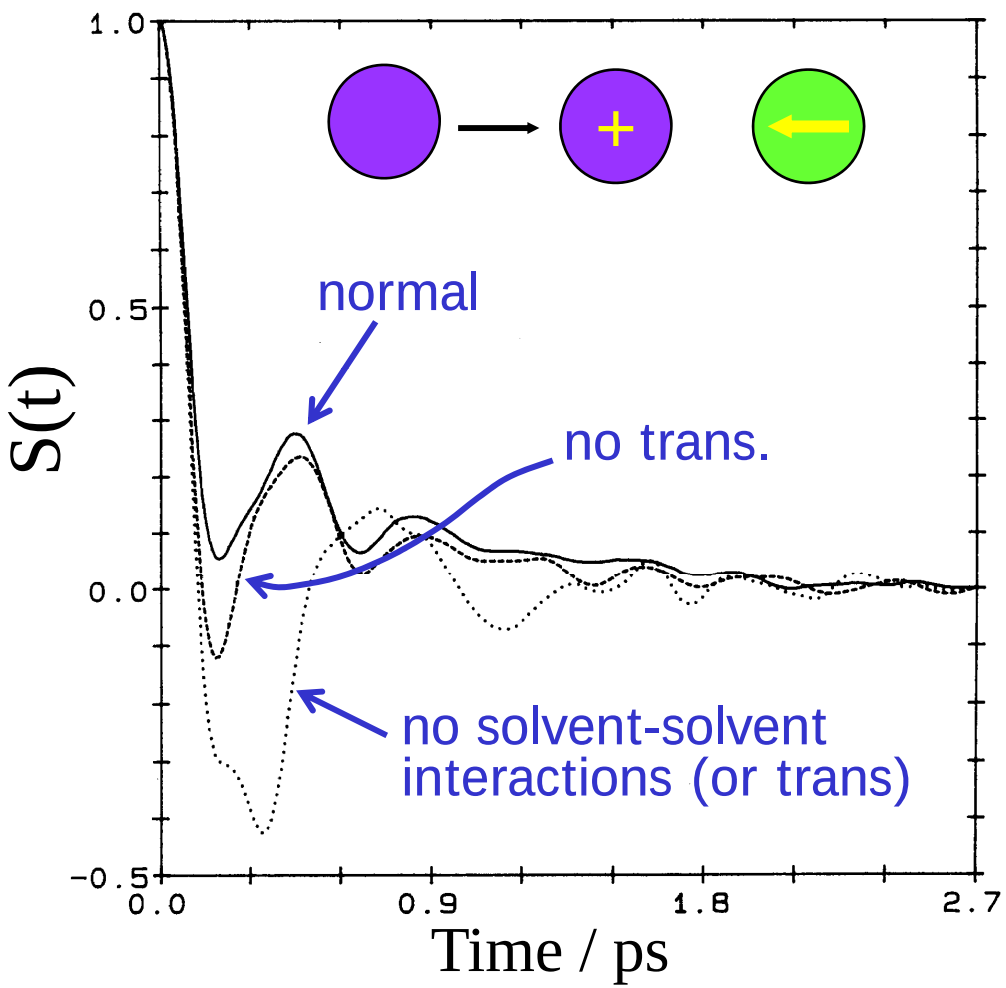


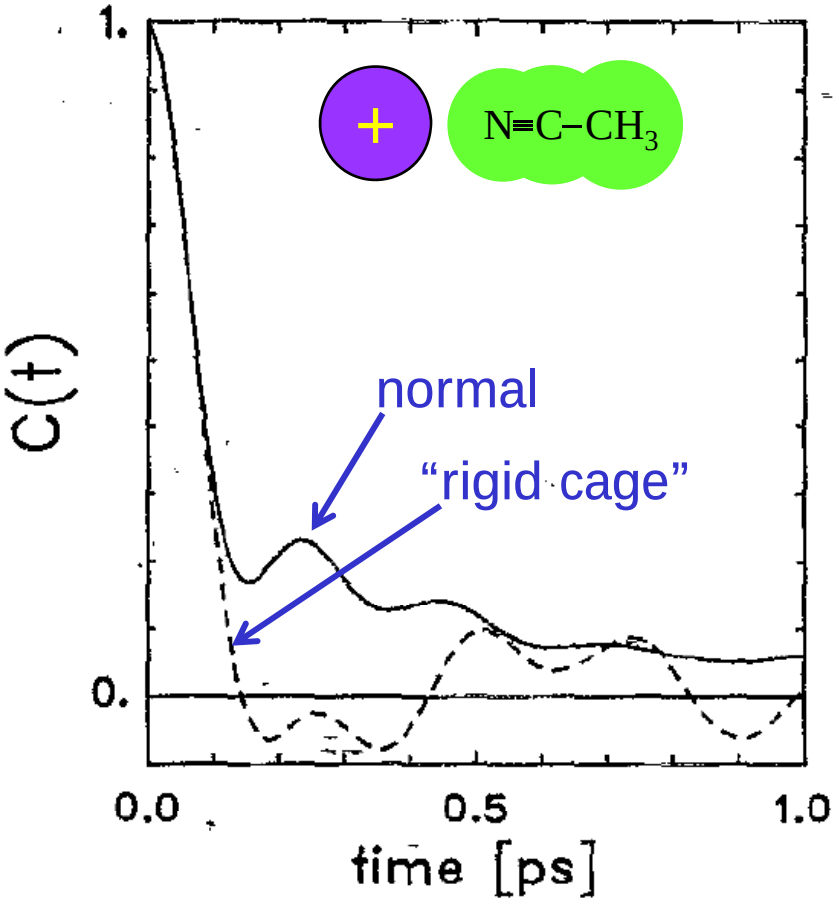
except for large Δq or specific interactions response is linear



Maroncelli, JCP **94**, 2084 (1991);
Kumar & Maroncelli, JCP **103**, 3038 (1995)

The Initial Gaussian



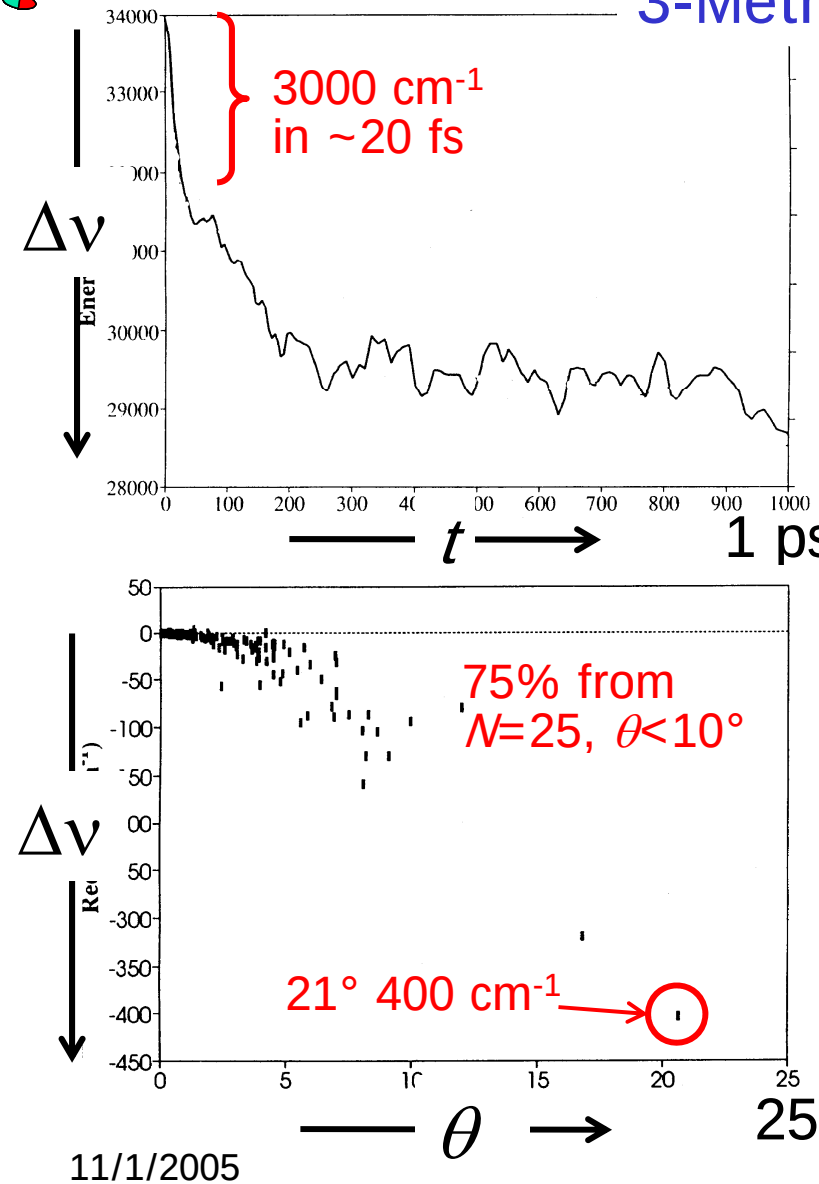


Perera & Berkowitz, J. Chem. Phys. **97**, 5253 (1992); Maroncelli, JCP **94**, 2084 (1991);

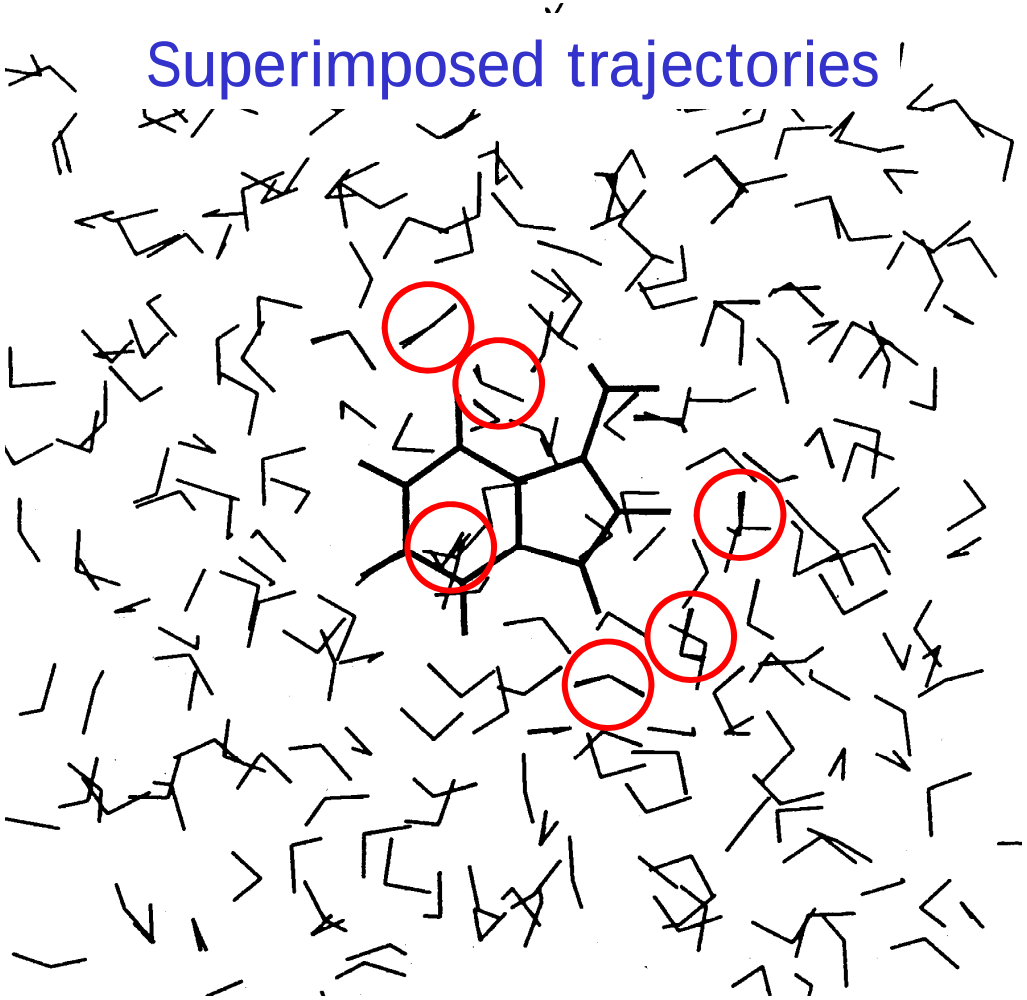
initial gaussian decay is “free-streaming” rotational motion

Little time, little motion

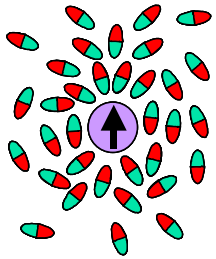
3-Methyindole / water



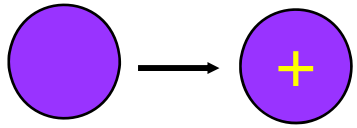
Superimposed trajectories



Muiño & Callis, J. Chem. Phys. **100**, 4093 (1994)



A Simple Interpretation

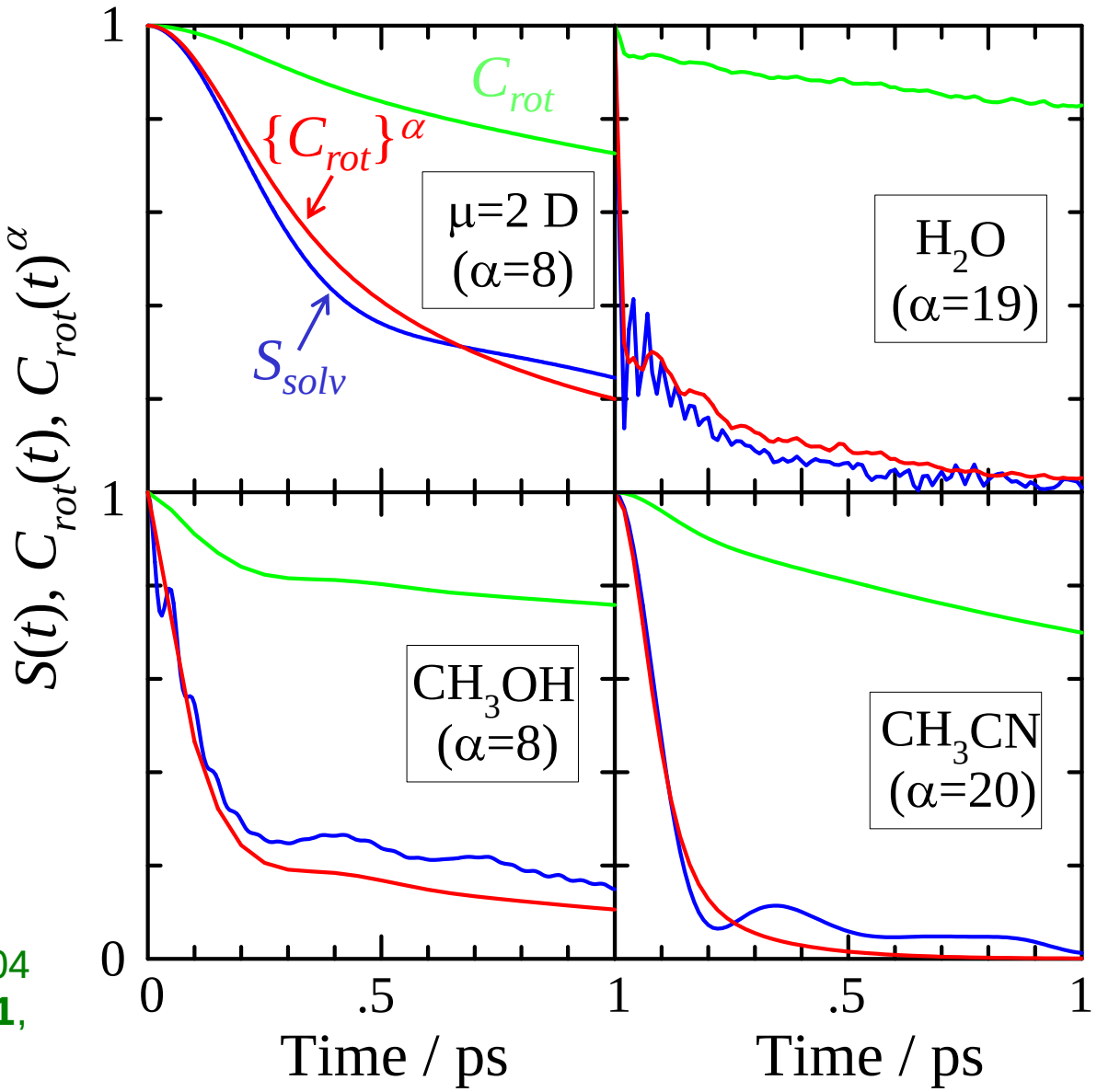


$$S_{solv}(t) \cong \{C_{rot}(t)\}^{\alpha}$$

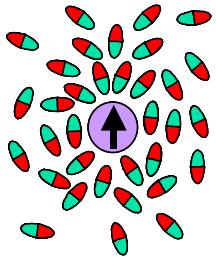
$$C_{rot}(t) = \langle \hat{\mu} \cdot \hat{\mu}(t) \rangle$$

$$\alpha = \frac{4\pi\mu^2\rho}{3k_BT}(1-1/\varepsilon)^{-1}$$

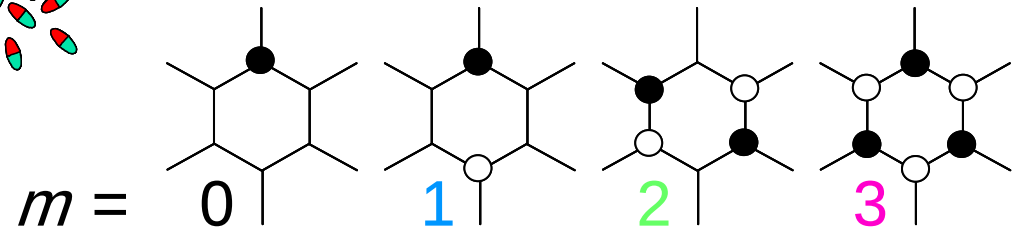
Polar solvation is solvent rotation. Greater coupling (α) means less motion is required & thus greater speed.

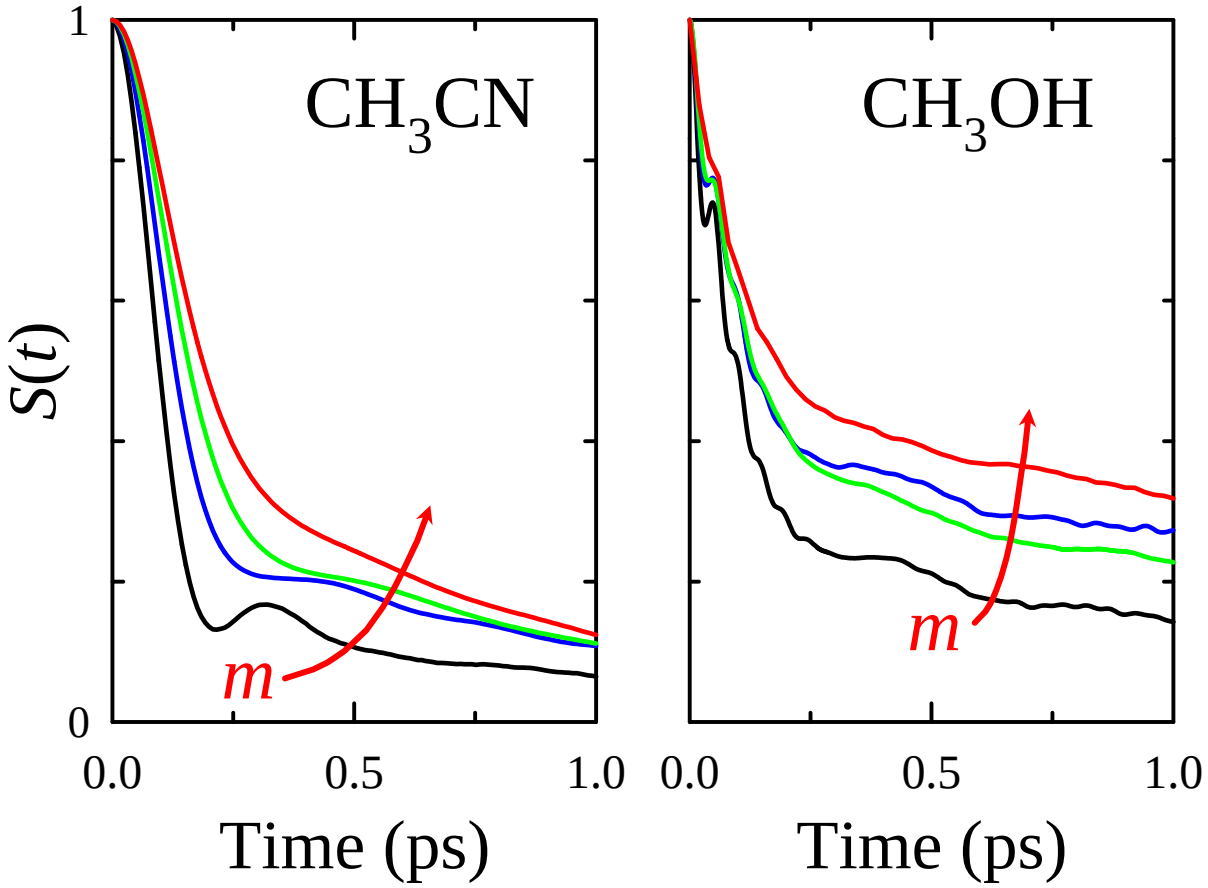


Maroncelli *et al.*, J. Phys. Chem. **97**, 13 (1993); also JCP **109**, 3204 (1998); and Raineri et al. JCP **101**, 6111 (1994).



Character of Δq Matters



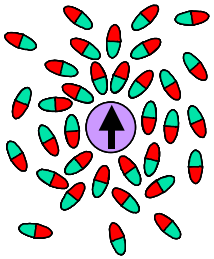


As solute multipole m increases:

- spatial range ↓
- response ↓
- collectivity "α" ↓
- translation ↑
- effect of solute motion ↑

Kumar & Maroncelli, JCP **103**, 3038 (1995)

Ladanyi & Maroncelli, JCP **109**, 3204 (1998).



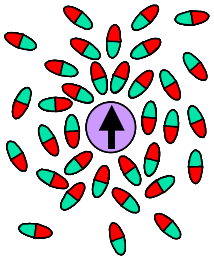
Molecular Theories

- extend $\varepsilon(\omega)$ to $\varepsilon(k,\omega)$
- site-site formulation for realistic systems
- *ab initio* treatment of Stockmayer model

F. O. Raineri and H. L. Friedman, "Solvent Control of Electron Transfer Reactions," *Adv. Chem. Phys.* **107,** 81-189 (1999).

B. Bagchi and R. Biswas, "Polar and Nonpolar Solvation Dynamics, Ion Diffusion, and Vibrational Relaxation: the Role of Biphasic Solvent Response in Chemical Dynamics," *Adv. Chem. Phys.* **109,** 207-433 (1999).

V. Kapko and S. A. Egorov, "Polar solvation dynamics in supercritical fluids: A mode-coupling treatment," *J. Chem. Phys.* **121,** 11145-11155 (2004).



Key Points

- computer simulations show that:
  - initial Gaussian decay is free streaming motion (rotation)
  - extreme speed is result of collective nature of solvation - small-amplitude motion has large effect in presence of high polarity α
  - multipole character of Δq matters
- molecular theories can now reproduce simulation & experiment