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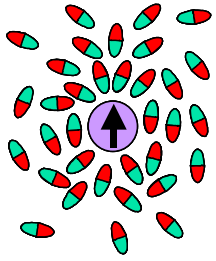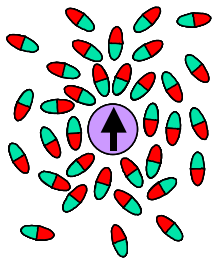
I. Background and Fundamentals

II. Polar Solvation Dynamics

III. Other "Simple" Environments

IV. Complex Environments, Biological and Otherwise

III. Other "Simple" Environments

- ❏ Nonpolar Solvation (SCFs)
- ❏ Glasses
- ❏ H-Bonding Dynamics
- ❏ Ionic Solutions & Ionic Liquids
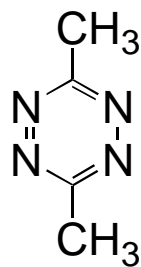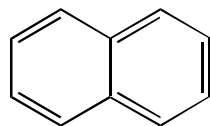- ❏ The Solvent's Perspective

Nonpolar Solvation
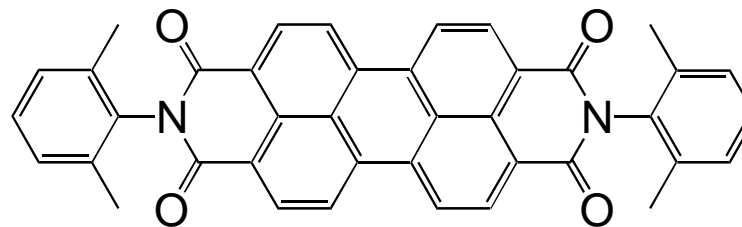
- polar solutes in nonpolar solvents:

   Ar, CCl4, CS_2, ...

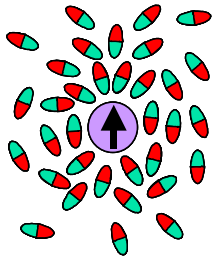   (not multipolar solvents like benzene, dioxane, ...)

- solutes whose S_1-S_0 change does not involve a large change in permanent charge moments
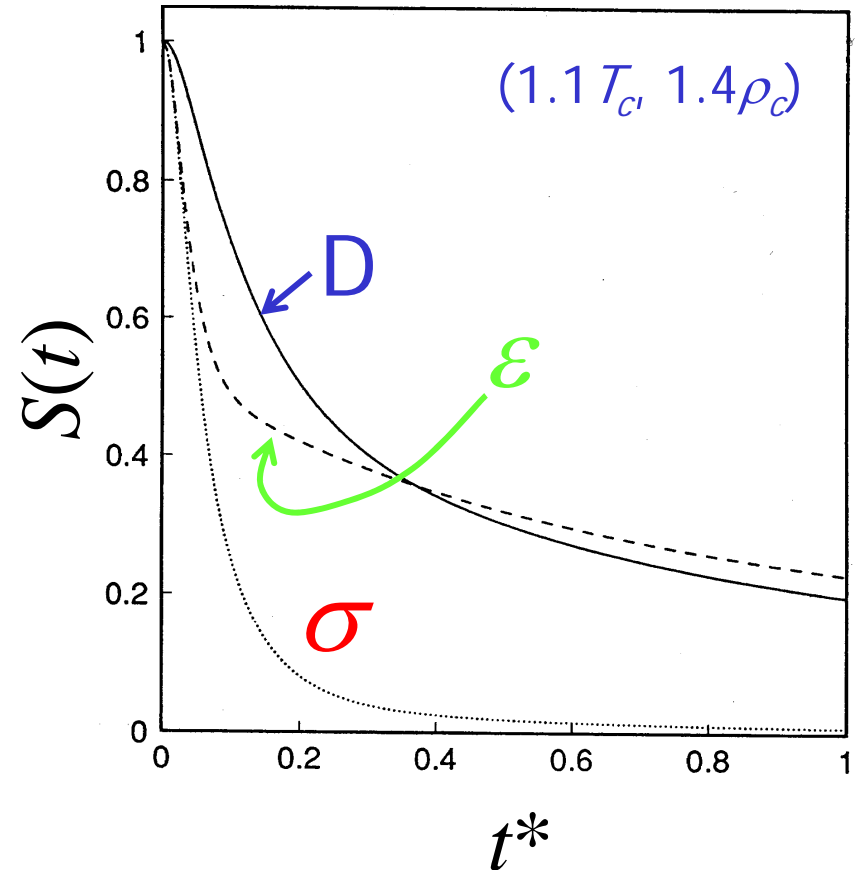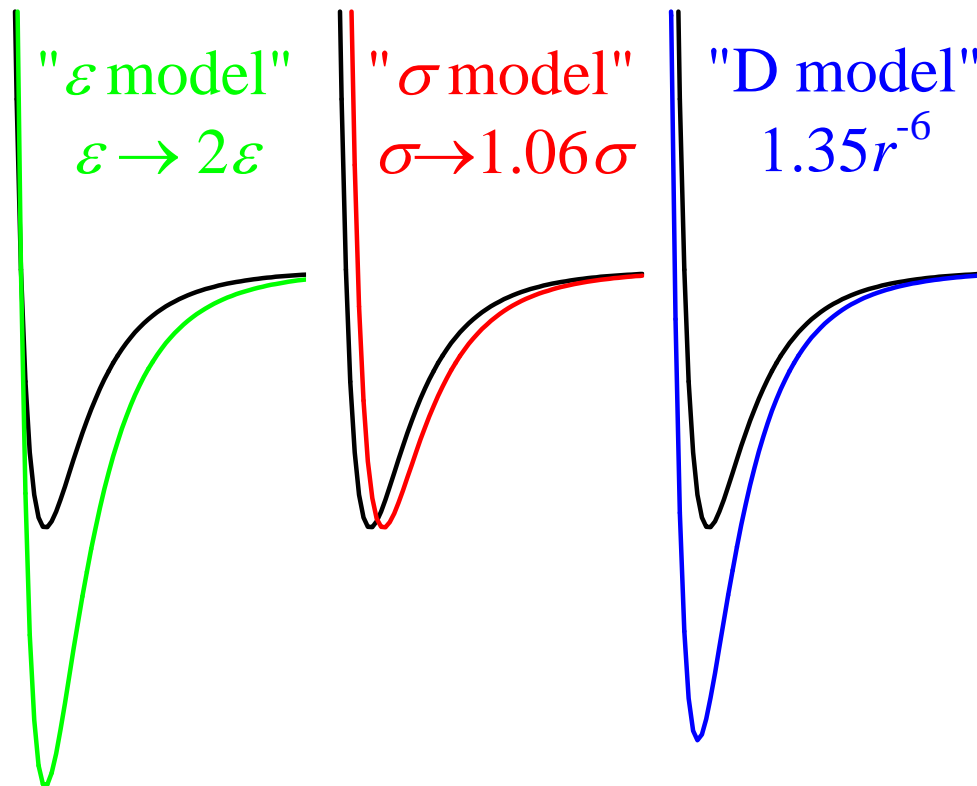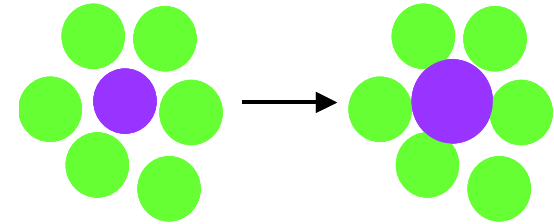
(?)   (??)

LJ Models - Simulation & Theory
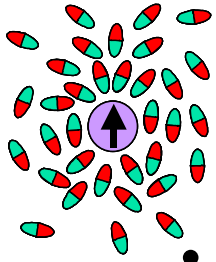
LJ Potential: $u(r) = 4\varepsilon \left\{ \left(\dfrac{\sigma}{r} \right)^{12} - \left(\dfrac{\sigma}{r} \right)^{6} \right\}$

"ε model"
$\varepsilon \to 2\varepsilon$

"σ model"
$\sigma \to 1.06\sigma$

"D model"
$1.35 r^{-6}$

$(1.1\, T_{c},\ 1.4\, \rho_c)$

$S(t)$

D

ε

σ

t^*

Stephens, Saven, & Skinner, J. Chem. Phys. **106**, 2129 (1997).

MCT Theory

- LJ system well suited to analytical theory (Skinner, Bagchi, Reichman, Egorov...)

- Most advanced is Mode Coupling Theory (MCT) of Egorov & Reichman:

  - linear response treatment of $<\delta v \delta v(t)>$

  - early (free streaming) dynamics from t^4 expansion

  - later dynamics from MCT formalism

$$C_{\mathrm{MCT}}(t) = \frac{1}{2\pi^2\rho} \int_0^\infty dk\, k^2 V(k)^2 F_s(k,t) F(k,t)$$

  - essentially *ab initio* theory using structure from inhomogeneous integral equation theory
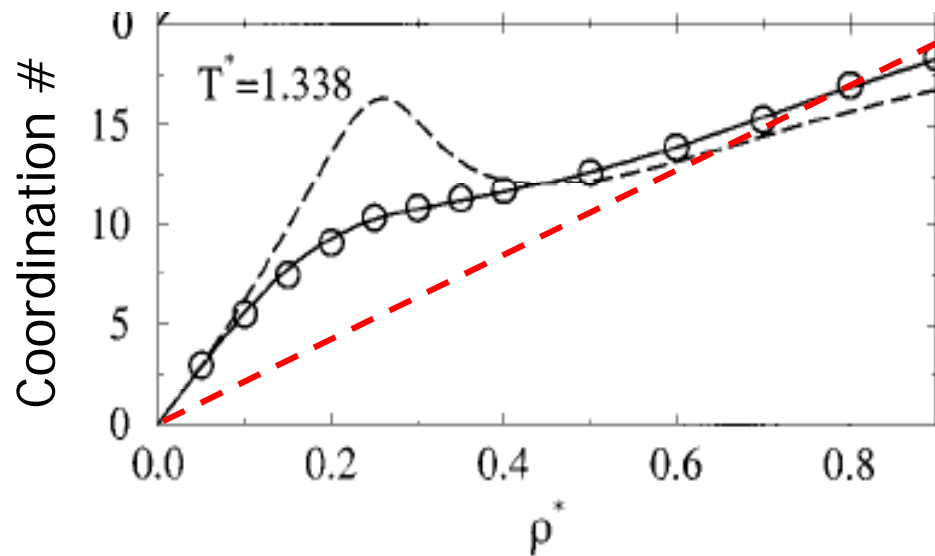
Egorov, J. Chem. Phys. **118**, 10643 (2003); Egorov, Denny, & Reichman, J. Chem. Phys. **116**, 5080 (2002).
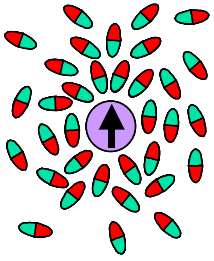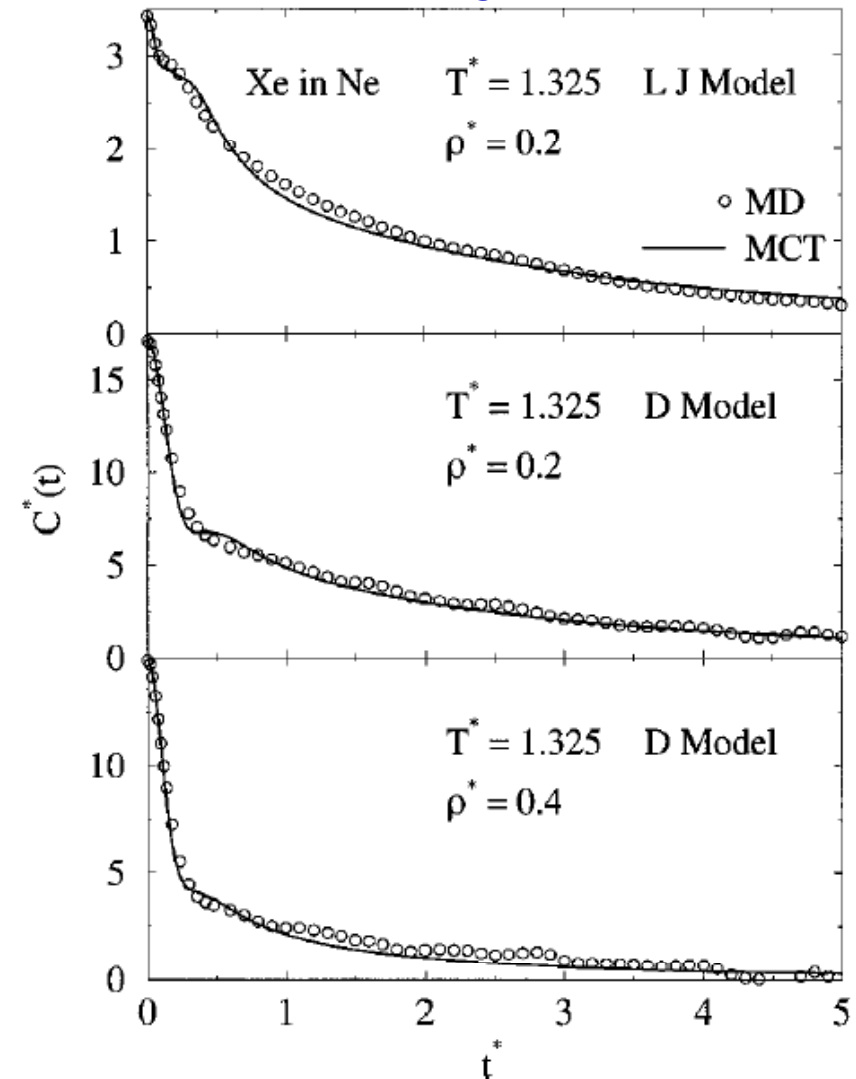
MCT & Simulation

- Xe in supercritical Ne
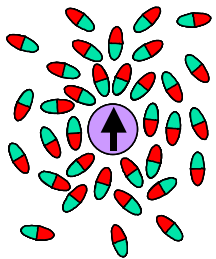- $T = 1.01 T_c$
- $\rho = 0.63, 1.26\rho_c$

Solvation Structure

Coordination #

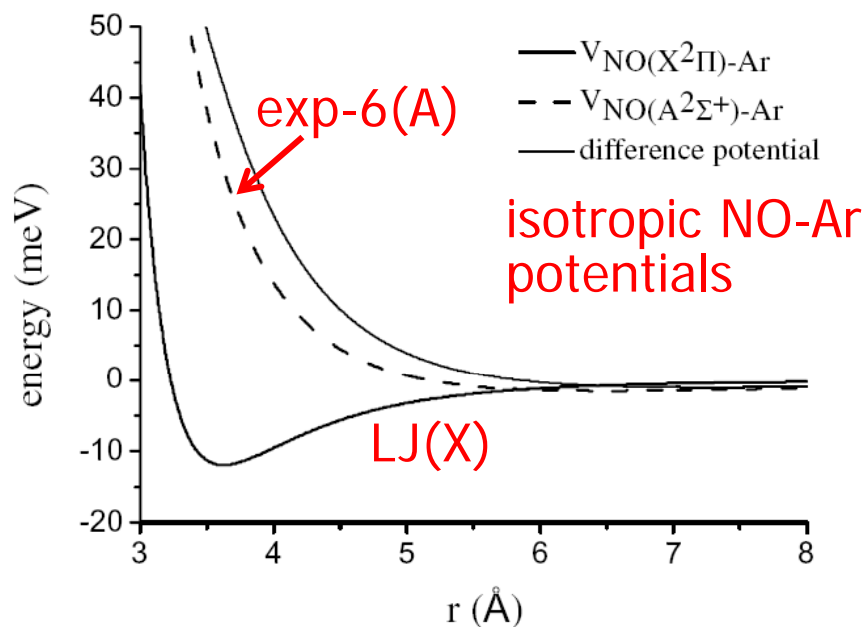Egorov, J. Chem. Phys. **118**, 10643 (2003); **112**, 7138 (2000).
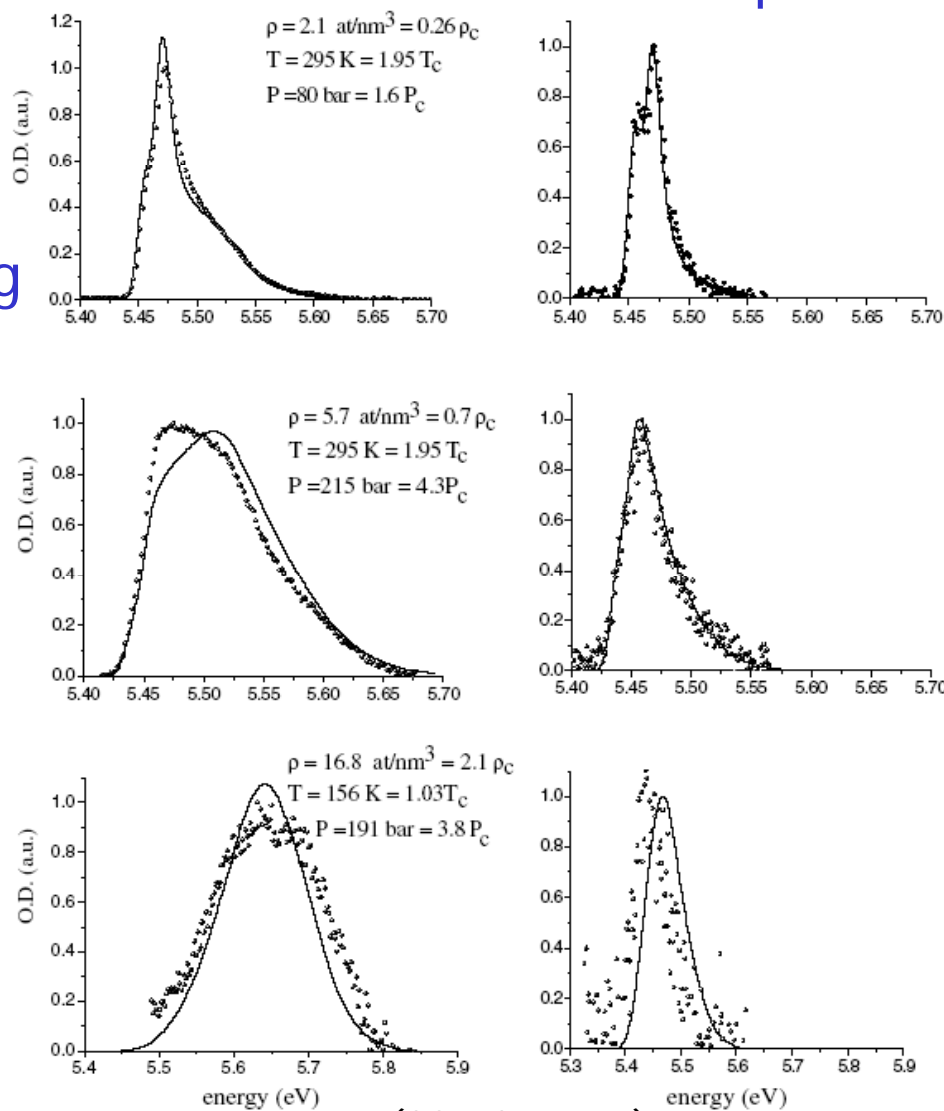
Solvation Dynamics
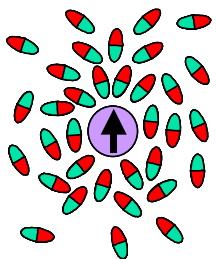
Linear Response & Size Change

- several groups noted that changes in solute size can lead to the breakdown of linear response

- Chergui & co. studied the Rydberg $X^2\Pi \rightarrow A^3\Sigma_+$ transition of NO in Ar

exp-6(A)

isotropic NO-Ar potentials

LJ(X)

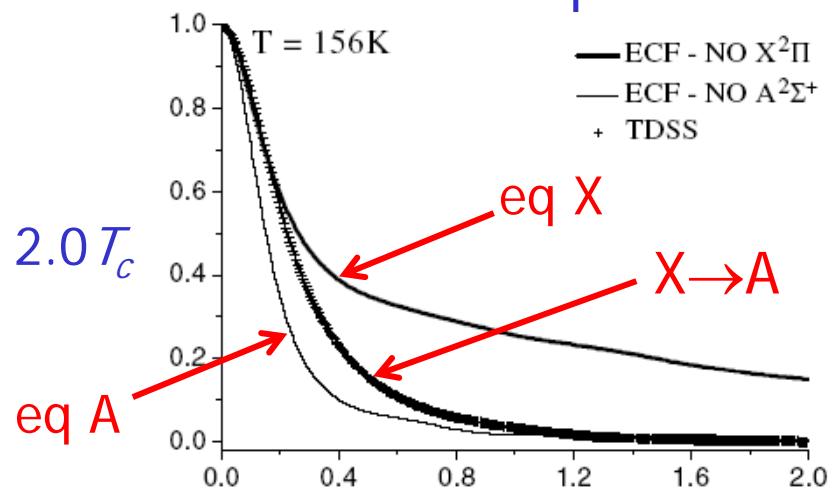Chergui & Co., Chem. Phys. **308**, 13 (2005).

(230-210 nm)

Simulated Structure Dynamics

Radial Distributions

Solvation Response Fns

$NO(X^2\Pi)$

- - - $T = 295K$
— $T = 156K$

$g_{NO-Ar}(r)$

ground state X

$0.7\rho_c$, $2.0\,T_c$

$T = 156K$

— ECF - NO $X^2\Pi$
— ECF - NO $A^2\Sigma^+$
+ TDSS

eq X

X→A

eq A

$NO(A^2\Sigma^+)$

$g_{NO-Ar}(r)$

Rydberg state A

$r\,(\text{Å})$

$0.7\rho_c$, $1.03\,T_c$

$T = 295K$

- - ECF - NO $X^2\Pi$
----- ECF - NO $A^2\Sigma^+$
+ TDSS

$t\,(ps)$
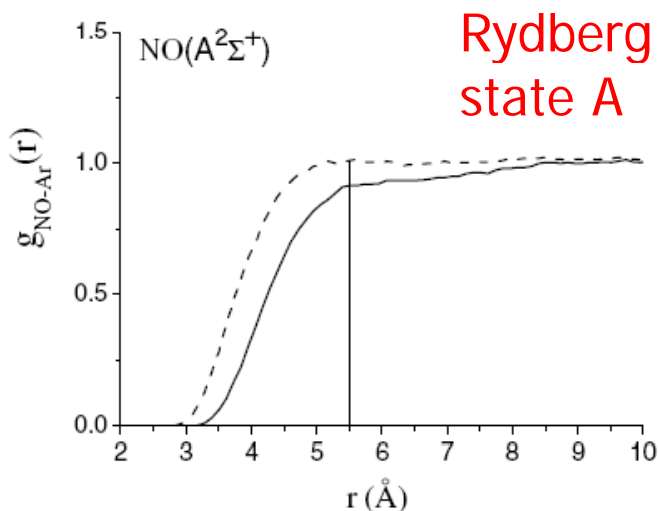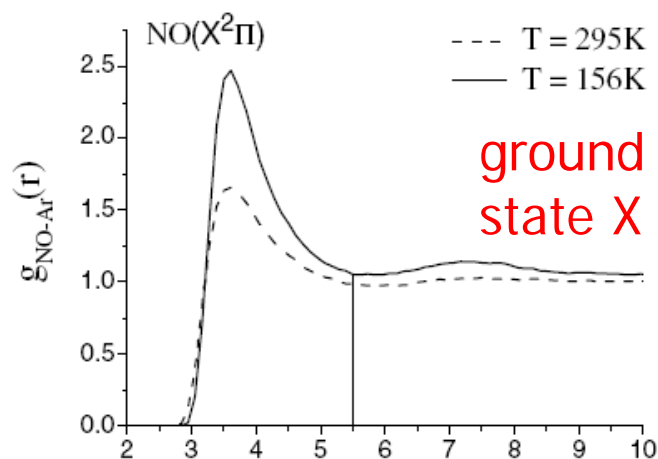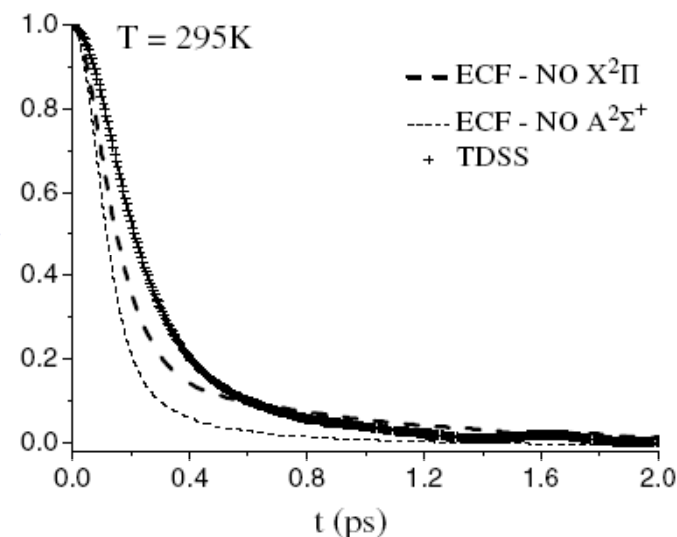
Chergui & Co., Chem. Phys. **308**, 13 (2005).
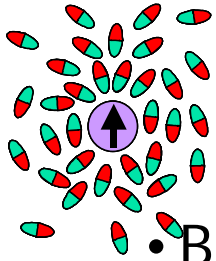
Viscoelastic Continuum Model

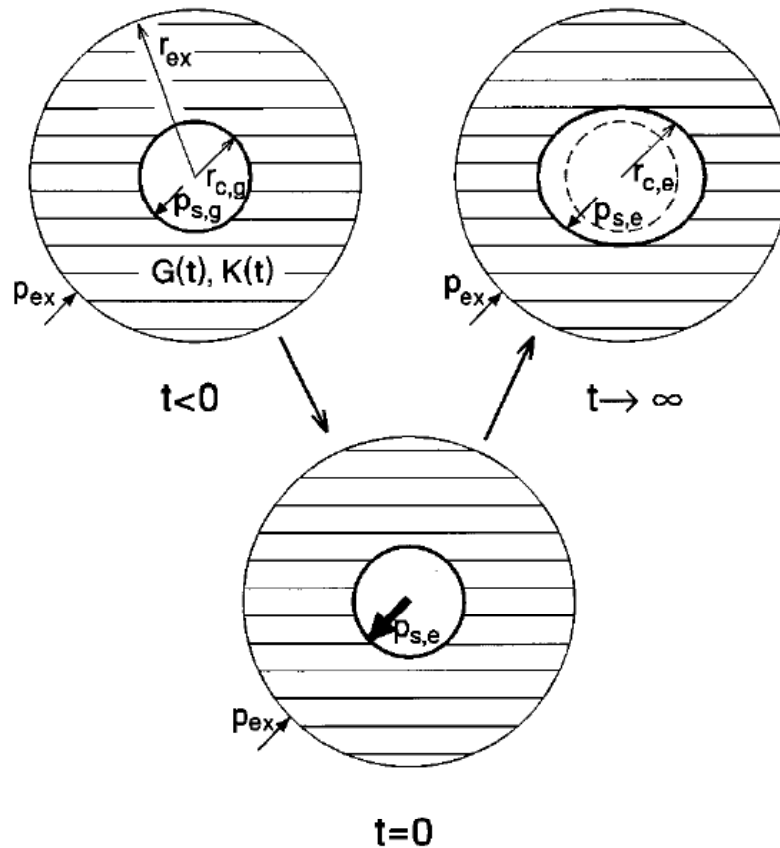- Berg developed a model of "mechanical solvation dynamics" roughly the equivalent of the dielectric continuum model for polar solvation dynamics

Solute:
   r_c radius (& shape ρ)
   K_s force constant
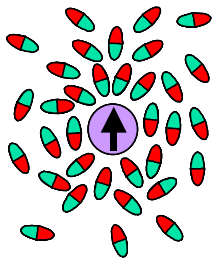
Solvent:
   $G(t)$ - shear modulus
   $K(t)$ - compression modulus

$G(t)$ is time-domain rep. of $\eta(\omega)$

$$\eta = \int_0^\infty G(t)\, \mathrm{d}t$$

$K(t)$ "force constant" of solvent

Berg, J. Phys. Chem. A **102**, 17 (1998).

VEC Model (cont.)

- for a spherical change in solute size and a Maxwell type mechanical solvent response

$$G(t) = G_\infty e^{-t/\tau_s} \qquad K(t) = K_0 + (K_\infty - K_0)e^{-t/\tau_s}$$

- a biphasic solvation response is predicted:

$$R_0(t) \approx \underbrace{(1-f)R_0{}^{ph}(t/\tau_{ph})}_{\substack{\text{phonon} \\ \text{component}}} + \underbrace{fR_0{}^{st}(t/\tau_s)}_{\substack{\text{structural} \\ \text{component}}}$$

$$R_0{}^{ph}(t) = \exp\left(\frac{-t}{\tau_{ph}}\right)\left[\cos\left(\frac{t}{\beta\tau_{ph}}\right) - \beta\sin\left(\frac{t}{\beta\tau_{ph}}\right)\right] \qquad R_0(t) = \exp\left[\frac{-t}{\tau_s/(1-f)}\right]$$
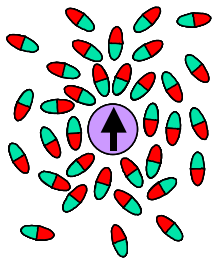
$$f = \frac{{}^4/_3 G_\infty}{K_s + {}^4/_3 G_\infty} \qquad \tau_{ph} = \frac{1+\beta^2}{2\beta^2}\tau_1 \qquad \beta^2 = 3\frac{M_\infty + (K_s - K_\infty)}{M_\infty - 3(K_s - K_\infty)}$$
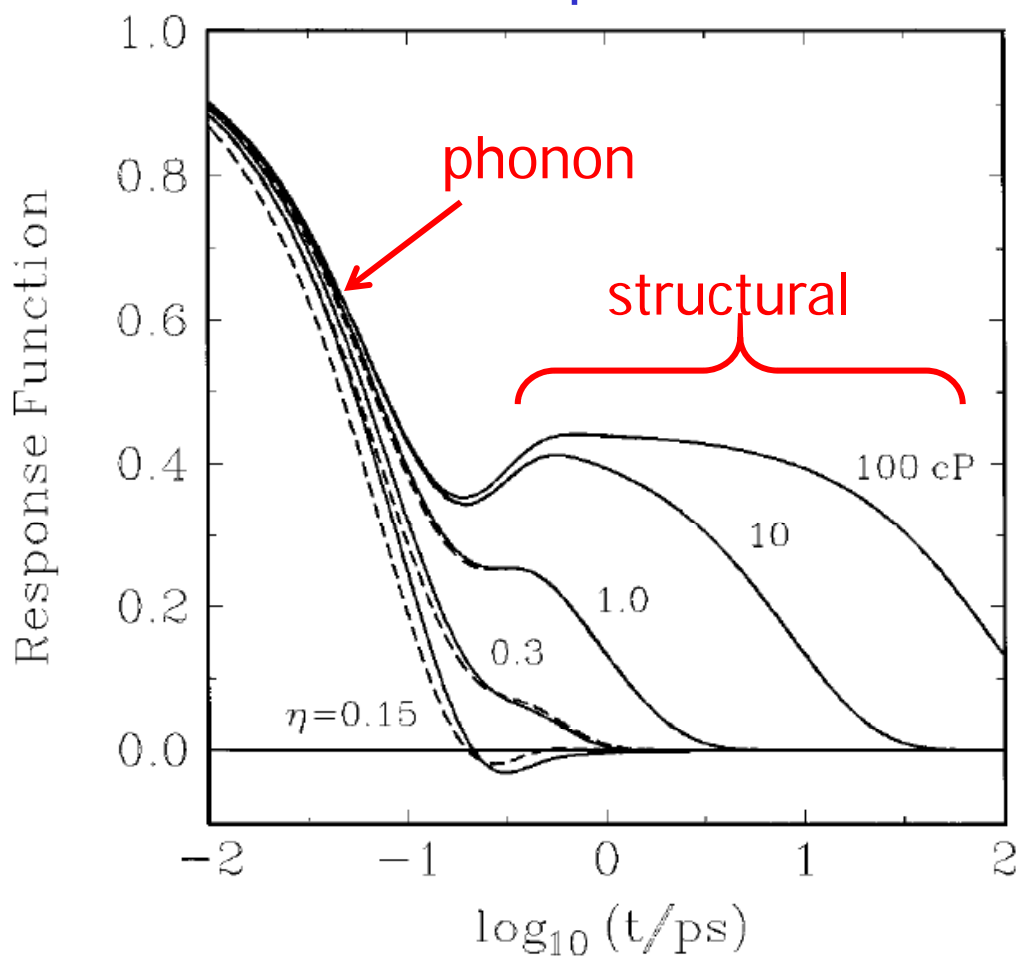
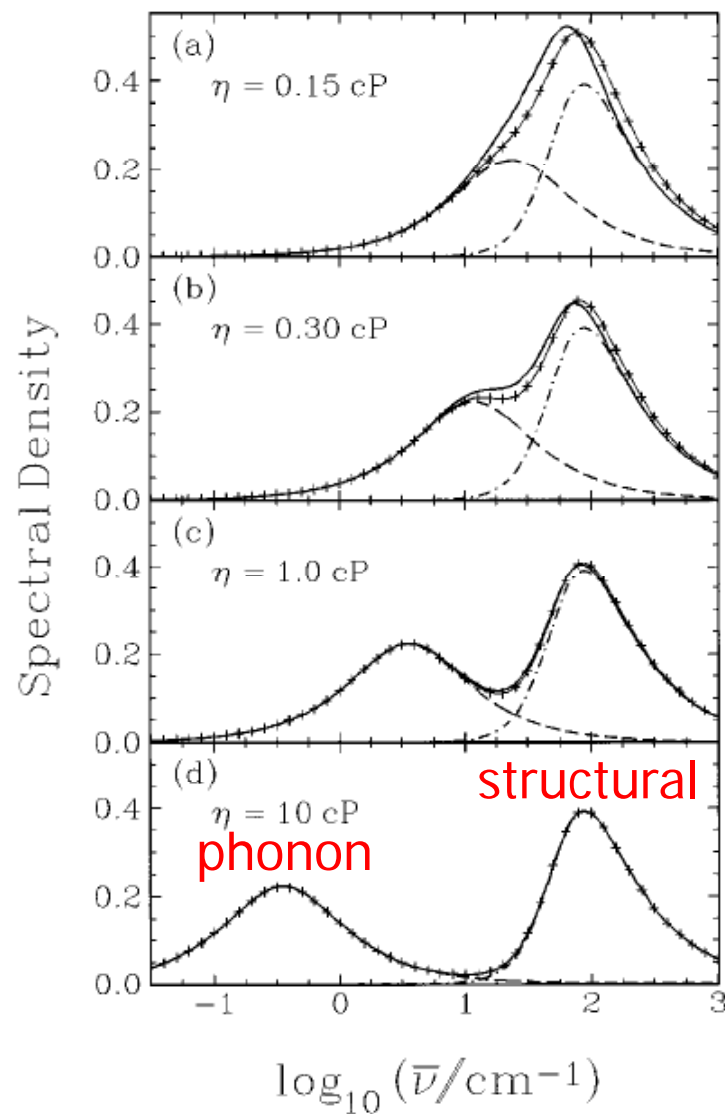$$M_\infty = K_\infty + \tfrac{4}{3}G_\infty \qquad\qquad \text{Berg, J. Phys. Chem. A } \mathbf{102}, 17 \text{ (1998).}$$

VEC Model Predictions

Solvation Response Fns.

Spectral Densities

phonon

structural

100 cP

10

1.0

0.3

$\eta = 0.15$

$\log_{10}(t/ps)$

(a) $\eta = 0.15$ cP

(b) $\eta = 0.30$ cP

(c) $\eta = 1.0$ cP

(d) $\eta = 10$ cP

structural

phonon

$\log_{10}(\overline{\nu}/cm^{-1})$

Berg, J. Phys. Chem. A **102**, 17 (1998).

Tetrazine in PC

PC= $\varepsilon=65$
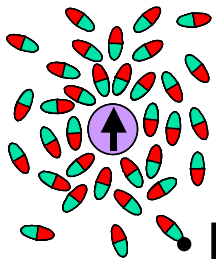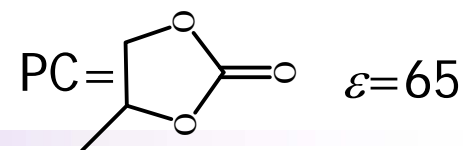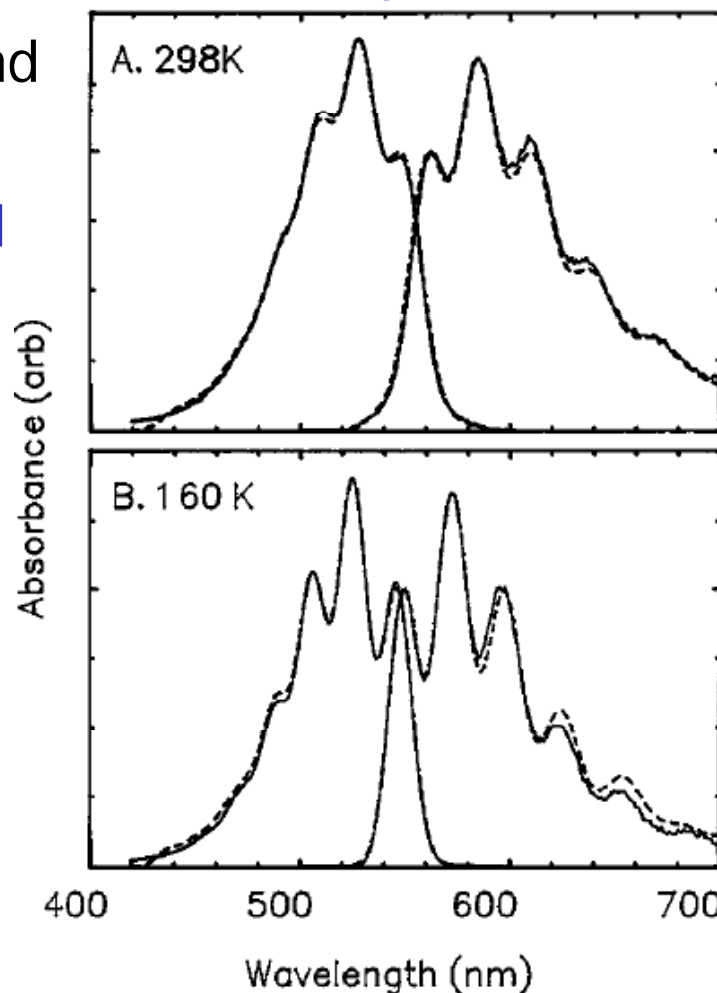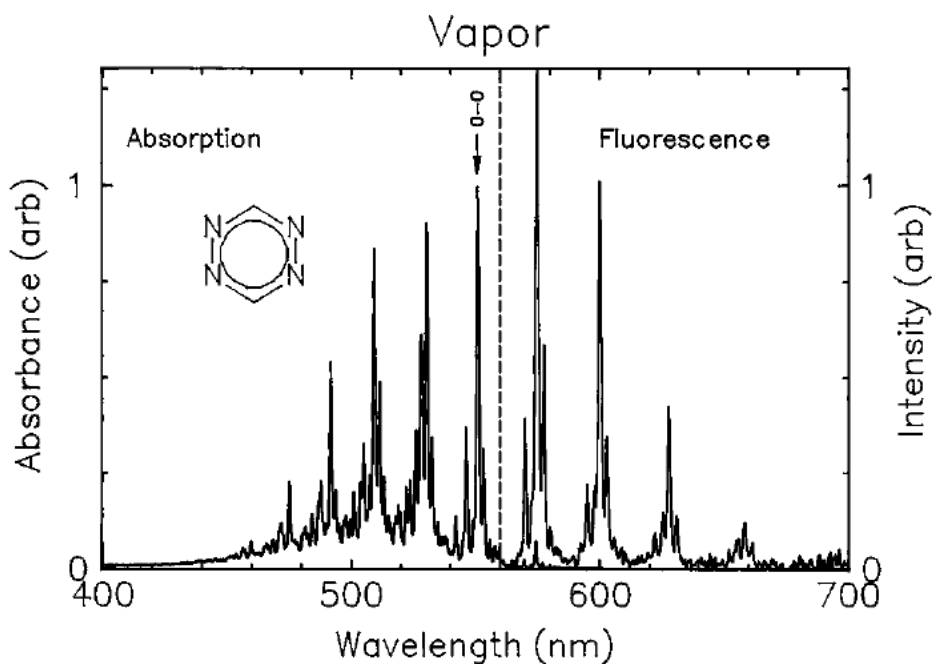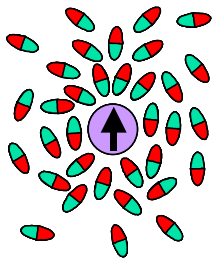
- Berg & Co. used VEC model to interpret solvation dynamics of tetrazine and dimethyl tetrazine in butylbenzene and propylene carbonate vs *T*

Fits of SS Spectra (in PC)

- transient absorption (~1 ps) analyzed with 36 mode vibronic model
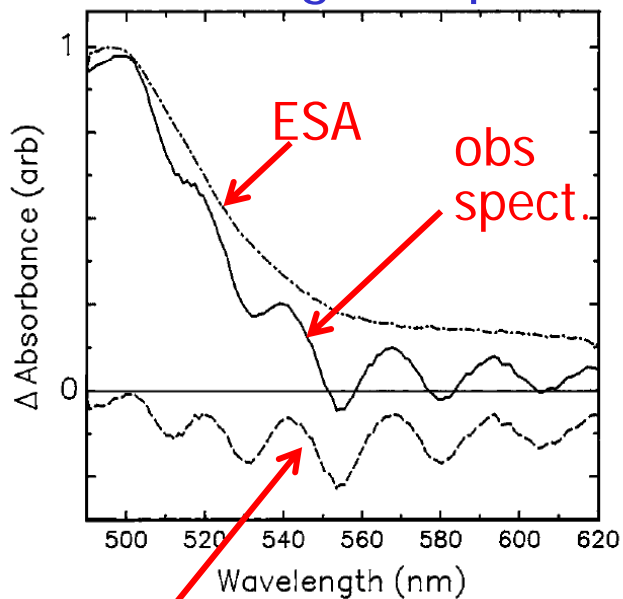

Vapor

Absorption Fluorescence

A. 298K

B. 160 K

Ma, ...Berg, J. Chem. Phys. **103**, 9146 (1995); Fourkas *et al*. **99**, 8552 (1993).
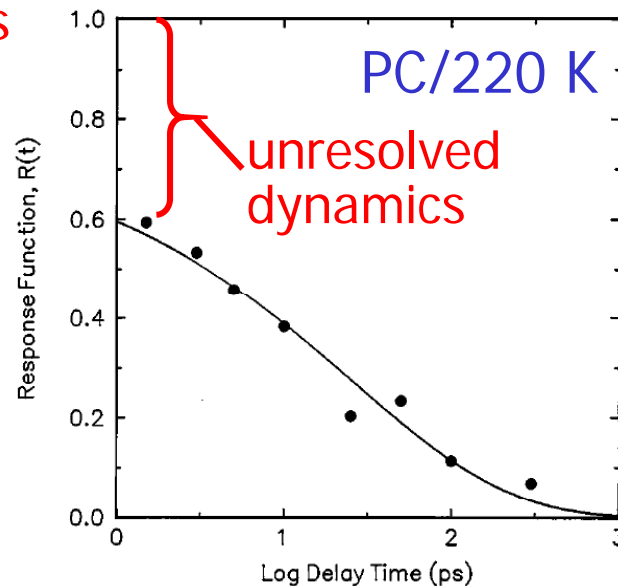
Spectral Analysis

Correcting TA Spectra

Hole-Burning Spectra PC/220 K
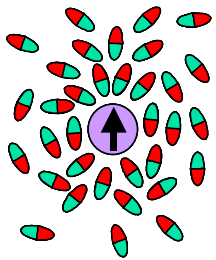

ESA

obs spect.

difference =
"hole burning spectrum"

1.5 ps

SE   GSB

50 ps

Spectral Response

PC/220 K

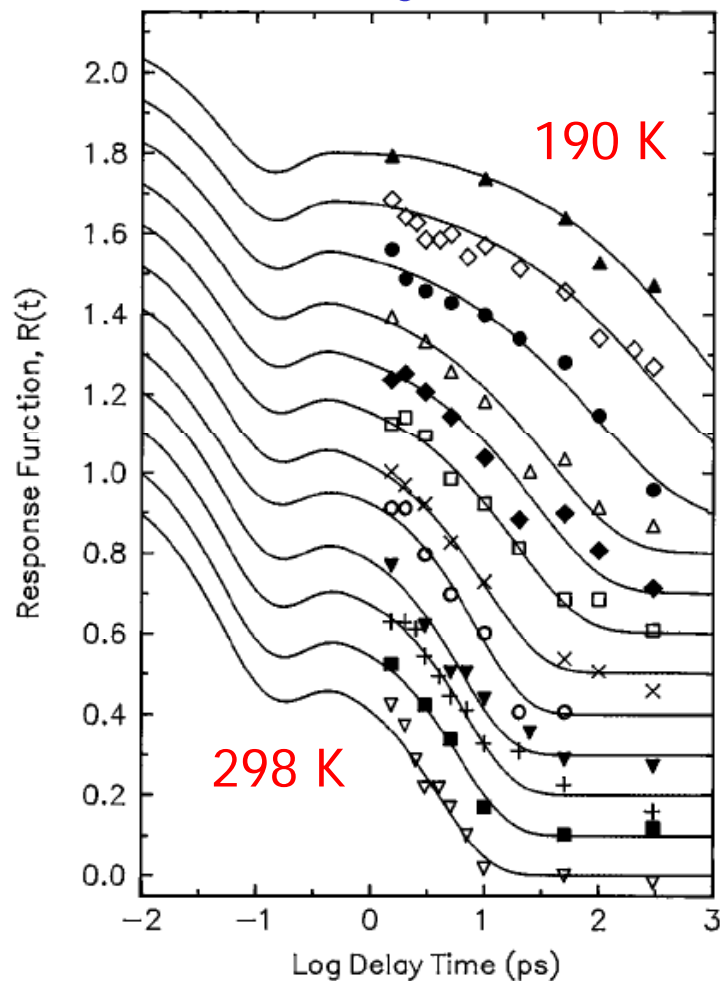unresolved
dynamics

ESA = excited-state absorption
GSB = ground-state bleach (hole)
SE = stimulated emission
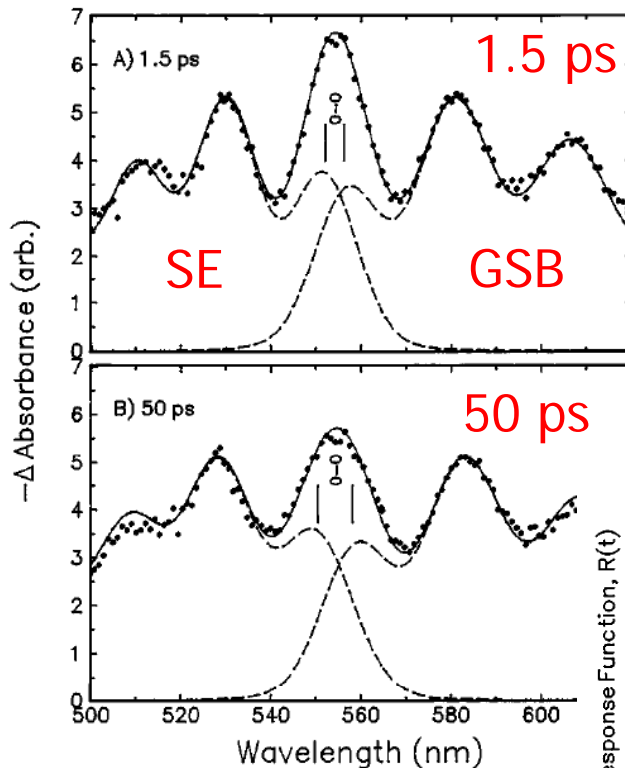
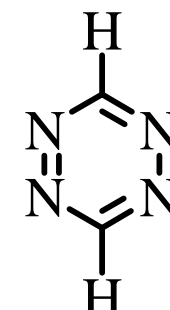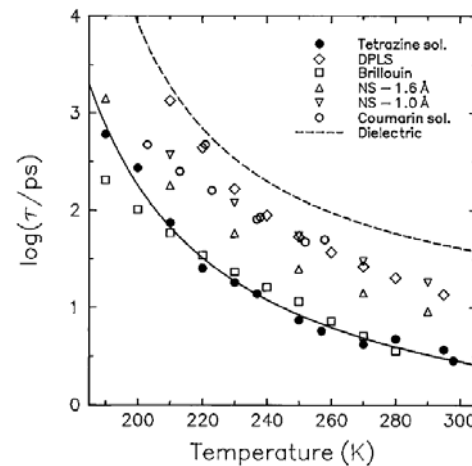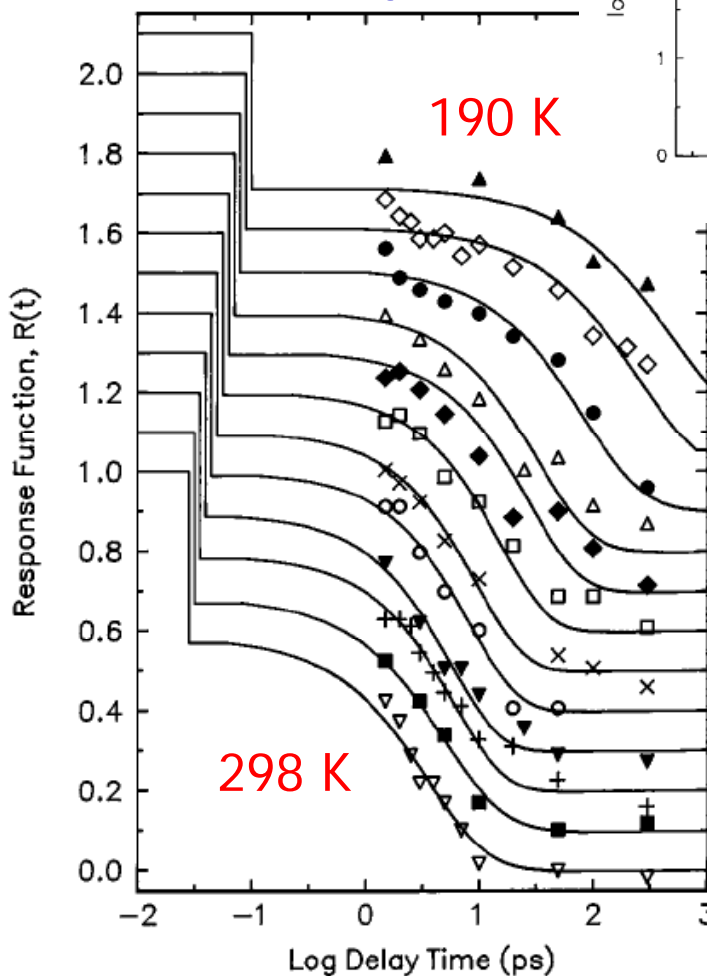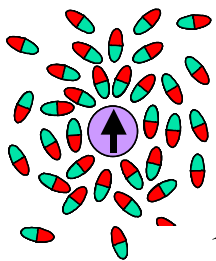# Mechanical or Dielectric?

$\Delta\nu = 325$ cm^{-1} in PC; 125 cm^{-1} in BB

VEC Analysis

$\varepsilon(\omega)$ Analysis

A 3PEPS Example?
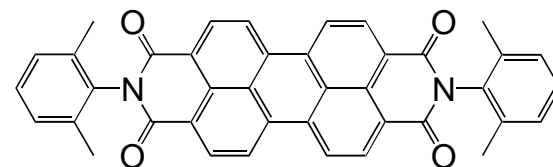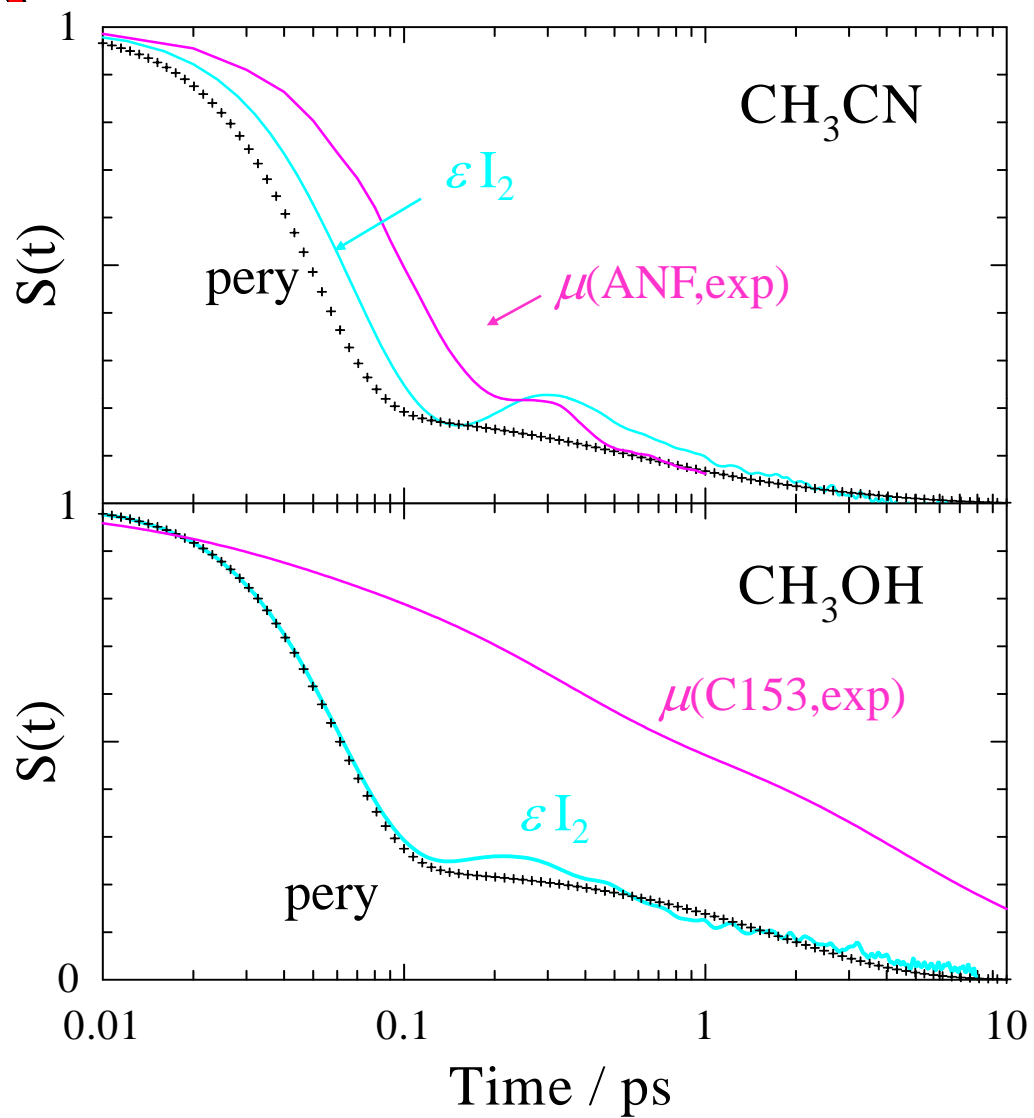
Larsen, Ohta, & Fleming, J. Chem. Phys. 111, 8971 (1999).
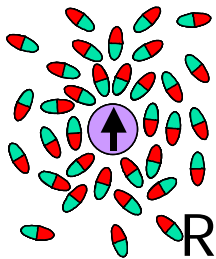
Nonpolar Solvation in Glasses

Richert & Co. have studied solvation dynamics near the glass transitions in a number of solute + solvent combinations using time-resolved phosphorescence

- time-resolved phosphorescence

- excimer laser + gated diode array

- IRF~100 ns; times to s range
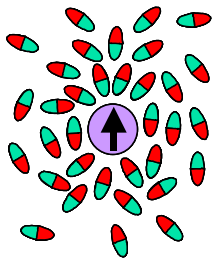
SS Phosp. Spectra

QX/mTHF $\nu(t)$

Richert, JCP **113**, 8404 (2000).
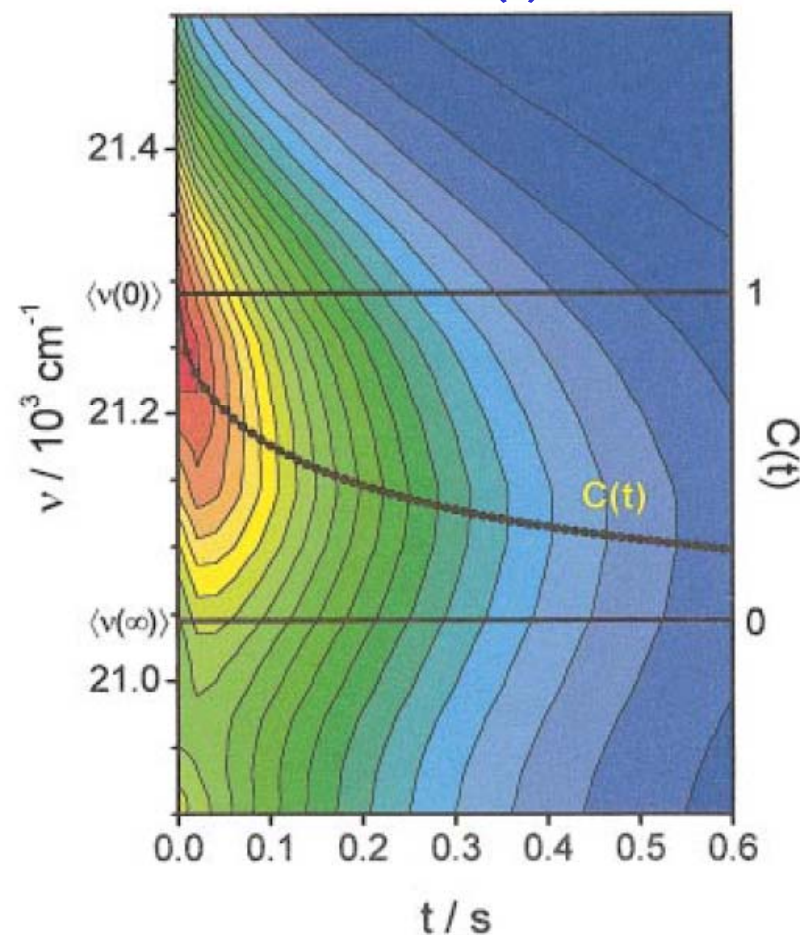
A Definitive Example

- compared solvation of QX(polar) and NA(nonpolar)
- similar dynamics in most solvents, not in 1-PrOH

"QX"-quinoxolane
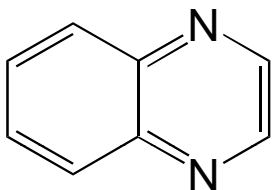
$\mu_0 = 0.44$ D
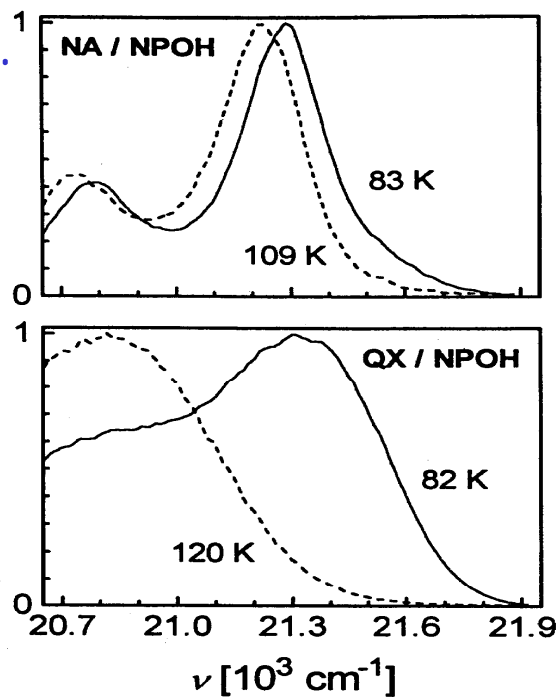$\Delta\mu = 1.31$ D
$\Delta\nu = 490$ cm^{-1}

"NA"-naphthalene
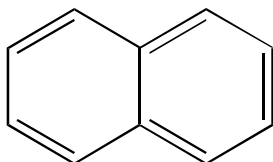
$\mu_0 = 0.00$ D
$\Delta\mu = 0.15$ D(?)
$\Delta\nu = 60$ cm^{-1}

Richert, JCP **113**, 8404 (2000).

Solvatochromism
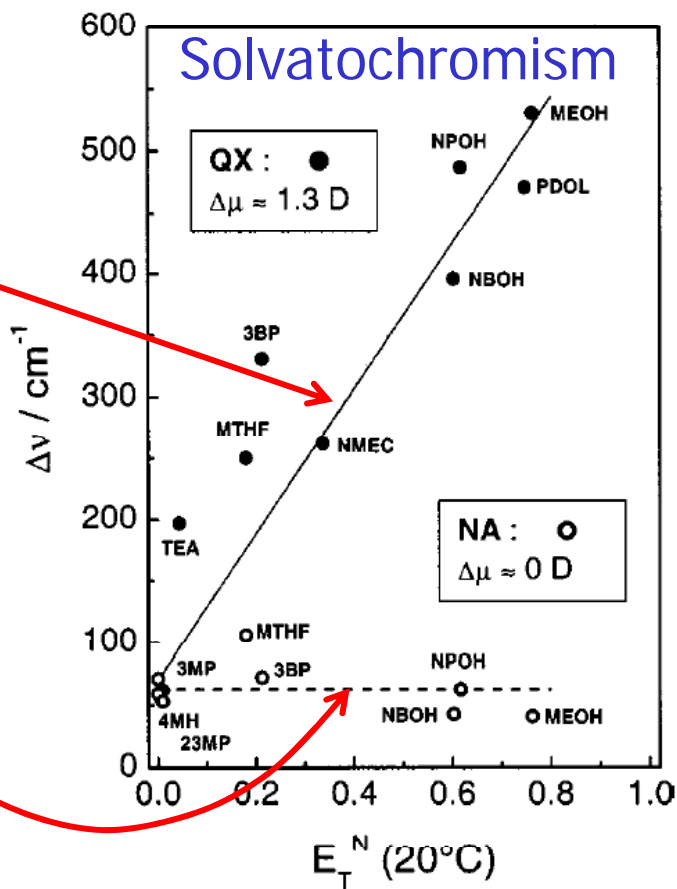
S(t) 1-PrOH 102 K
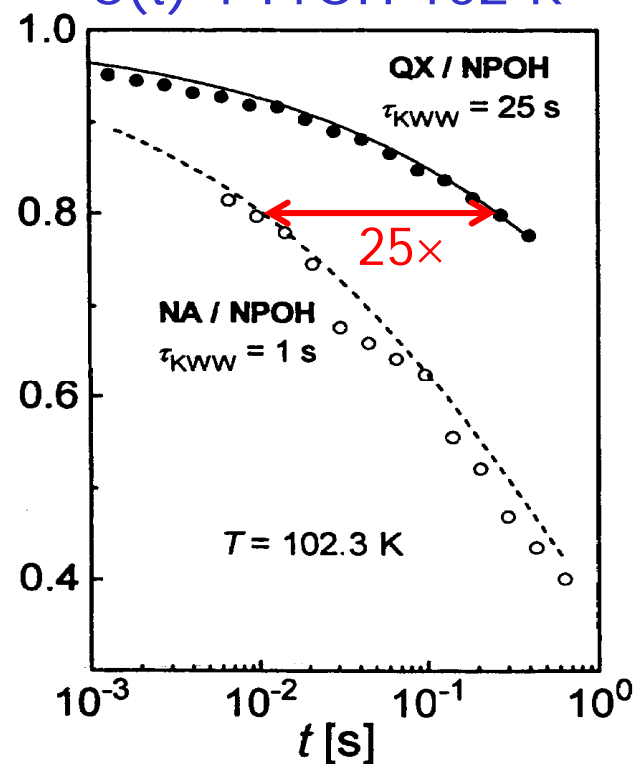
$\tau_{diel}/\tau_{mech} \sim 21$
$\tau_{QX}/\tau_{NA} \sim 25$

Other Glassy Behavior

Richert & Co. also used time-dependence of spectral width to explore dynamic heterogeneity

KWW form:

$$S(t) = \exp\{-(t/\tau)^{\beta}\}$$

t-T Superposition

$S(t)$ in mTHF (QX)

$S(t/\tau)$
$\beta=0.5$

KWW fit

scale
time by τ

Richert, JCP **113**, 8404 (2000).
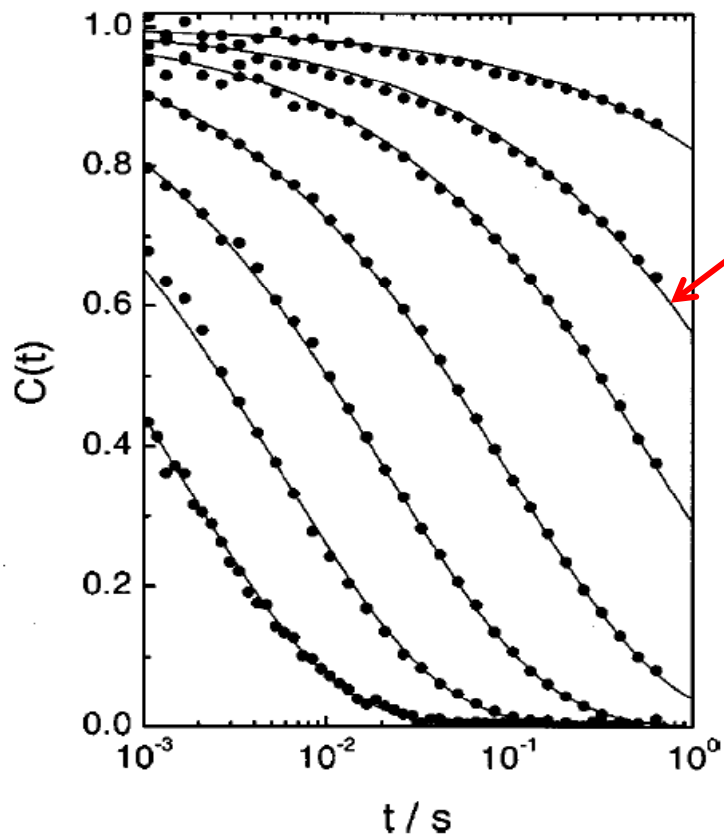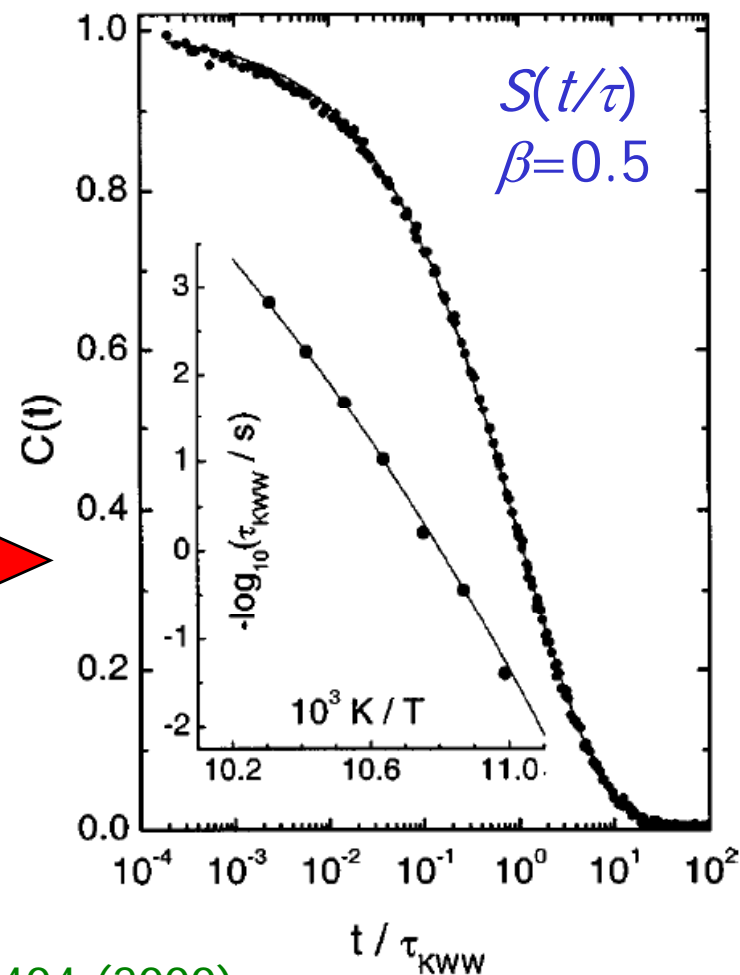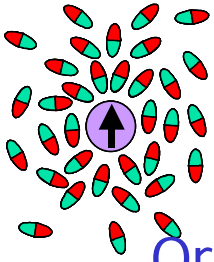
Dynamic Heterogeneity

Origin of Complex Dynamics

Motion in 2d Soft-Sphere Glass

HOMOGENEOUS   HETEROGENEOUS

ENSEMBLE AVERAGE

$\log \phi$ time   = $\log \phi$ time
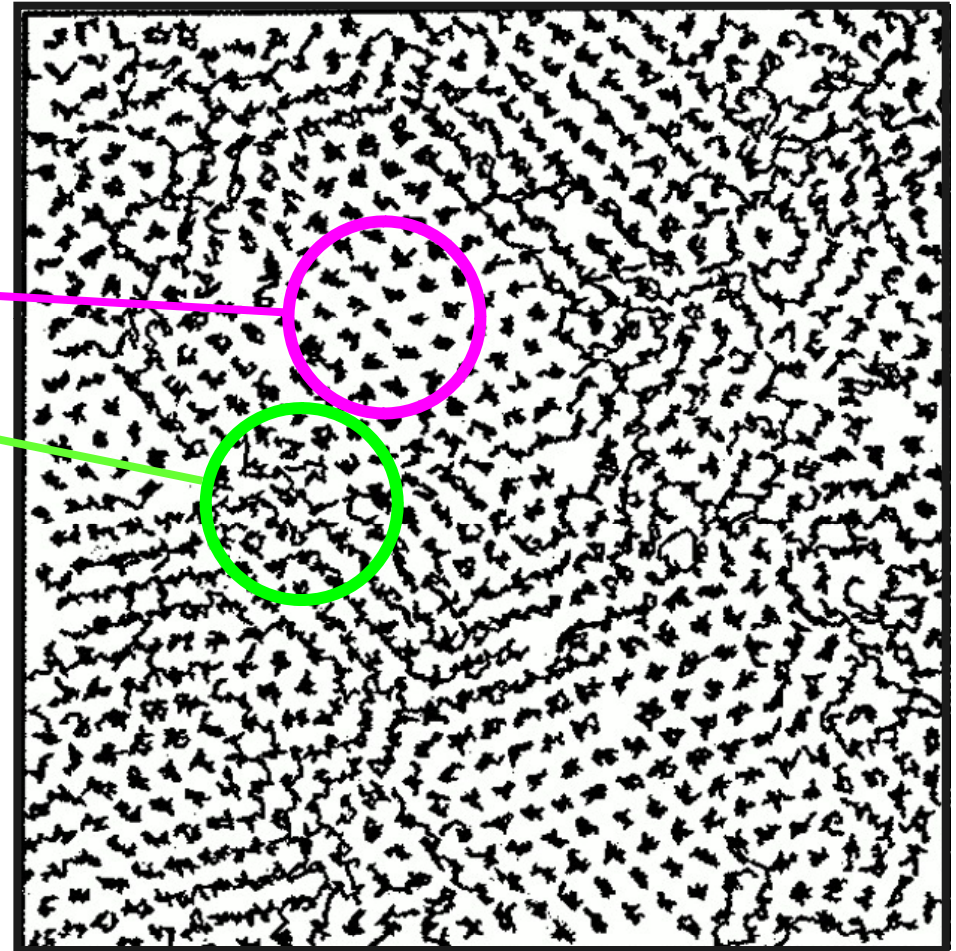
Richert, J. Phys. Chem. B **101**, 6323 (1997).   Hurley & Harrowell, Phys. Rev. E **52**, 1694 (1995).
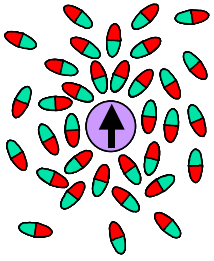
Detecting Dynamic Heterogeneity

- $\sigma_{inh}(t)$ is the inhomogeneous broadening of the spectrum at t

- assume that the solvation response ($C(t)=S(t)$) is a superposition:

$$C(t) = \exp[-(t/\tau_{KWW})^{\beta_{KWW}}]$$

$$= \int_0^\infty g(\tau)\exp[-(t/\tau)^{\beta_{intr}}]d\tau.$$

- then $\sigma_{inh}(t)$ should follow:

$$\frac{\sigma_{inh}^2(t) - \sigma_0^2}{\Delta\nu^2} = \rho(t) = C(2^{1/\beta_{intr}}t) - C^2(t)$$

- in mTHF near T_g: $\boxed{\beta_{intr}=1.00\pm.08}$

Richert, JCP **113**, 8404 (2000).

Hydrogen Bonding Dynamics

- a few experimental studies have focused on measuring dynamics of solute-solvent H-bonding:

  A. J. Benigno, E. Ahmed, and M. Berg, "The Influence of Solvent Dynamics on the Lifetime of Solute-Solvent Hydrogen Bonds," *J. Chem. Phys.* **104,** 7382-7394 (1996).

  E. Nibbering, F. Tschirschwitz, C. Chudoba, and T. Elsaesser, "Femtochemistry of Hydrogen Bonded Complexes after Electronic Excitation in the Liquid Phase: The Case of Coumarin 102," *J. Phys. Chem. A* **104,** 4236-4246 (2000).

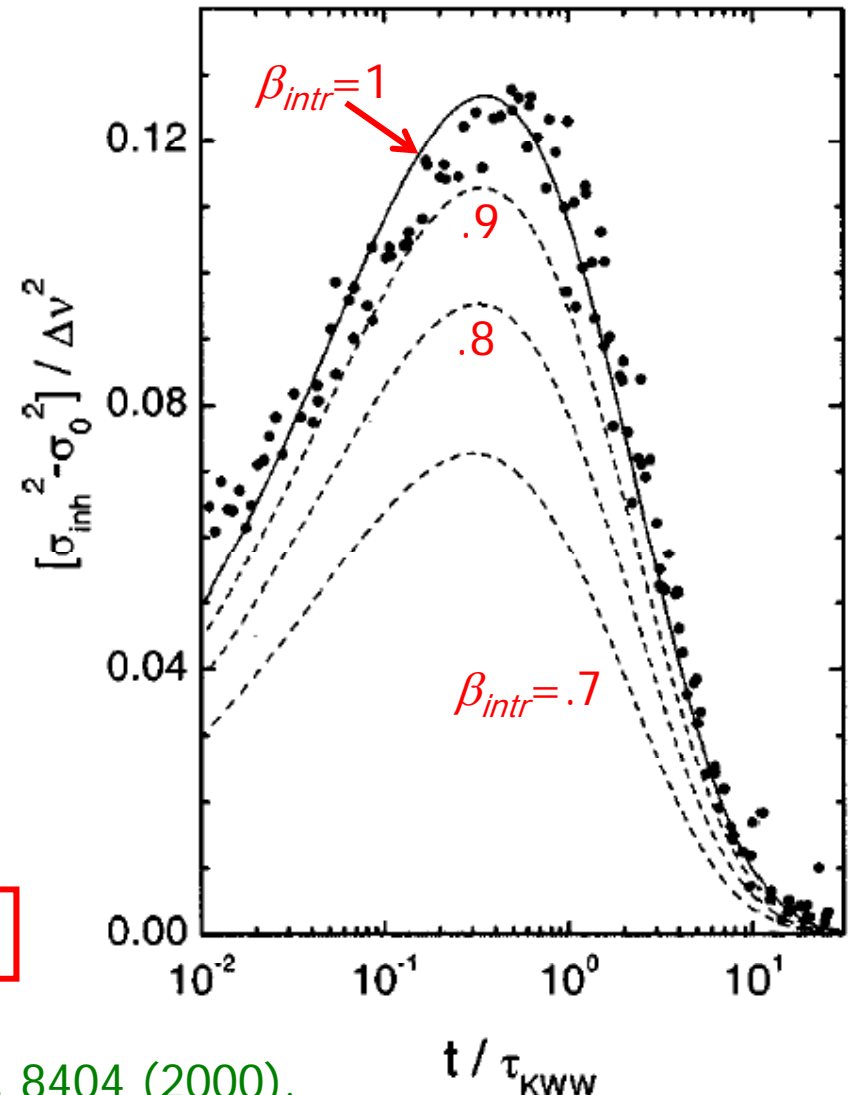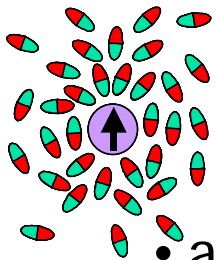 D. K. Palit, T. Zhang, S. Kumazaki, and K. Yoshihara, "Hydrogen-Bond Dynamics in the Excited State of Coumarin 102-Aniline Hydrogen-Bonded Complex," *J. Phys. Chem. A* **107,** 10798-10804 (2003).

  E. Pines, D. Pines, Y.-Z. Ma, and G. R. Fleming, "Femtosecond pump-probe measurements of solvation by hydrogen-bonding interactions," *ChemPhysChem* **5,** 1315-1327 (2004).

- especially interesting are the UV pump + IR probe studies of Nibbering & Co. and Yoshihara & Co. who find H-bond rupture of C102+H-bonded partners CHCl3, phenol, & aniline all indicate <250 fs H-bond rupture
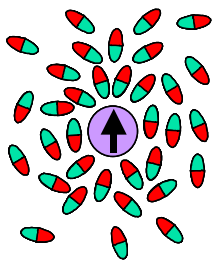
C102 + Phenol H-Bond Dynamics

CH₃

C102 C=O stretch

phenol O-H stretch
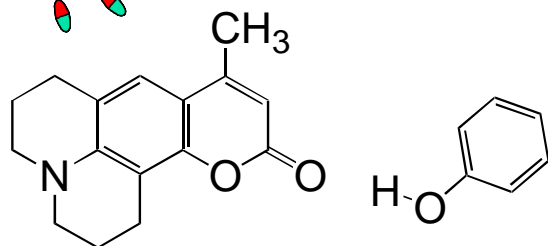
- C102 in C_2Cl_4 with added phenol 10mM

- estimate 92% C102 complexed and 44% 1:1, rest 1:n

- UV pump, IR probe IRF 200 fs

$S_0 \rightarrow S_1$ causes H-bond rupture in <200 fs

(a) C_2Cl_4 +phenol

(b) — ■ — 0.4 ps   — · — · 0.7 ps
    — — 1 ps   — · · 1.5 ps
    · · · · 2 ps   — ● — 5 ps

t

1700   1750   1800
Frequency (cm⁻¹)

Absorbance

Phenol H-bonded x15 free (a)

C102 + Phenol x3 (b)

t x3 (c)

3400   3600
Frequency (cm⁻¹)
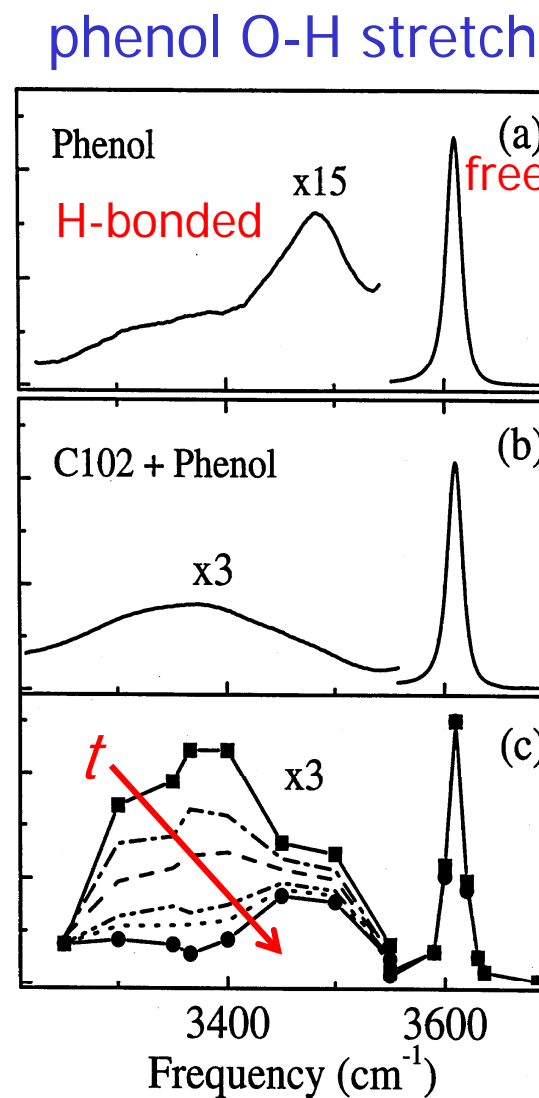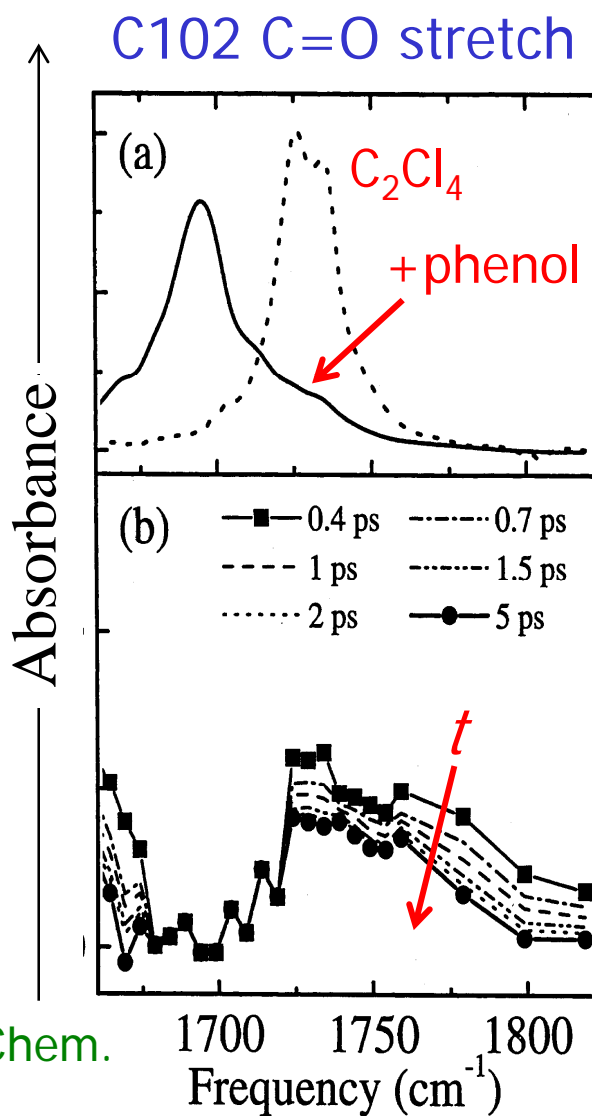
Nibbering & Co., J. Phys. Chem. A 103, 5625 (1999).

11/2/2005   III-Other Simple   22

A Comparable(?) Simulation

Phelps, Weaver, & Ladanyi, Chem. Phys. **176**, 575 (1993).

Ionic Solutions

Chapman & Maroncelli surveyed the solvatochromism & solvation dynamics of several dyes in (non-aqueous) ionic solutions
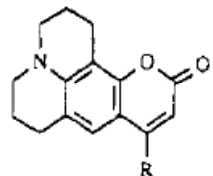
Cu102 R=CH$_3$
Cu153 R=CF$_3$
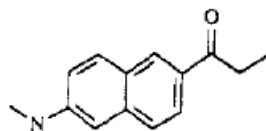
"Prodan"
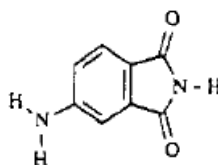
4-AP

SS Spectra C102/ CH$_3$CN/NaClO$_4$

(a)
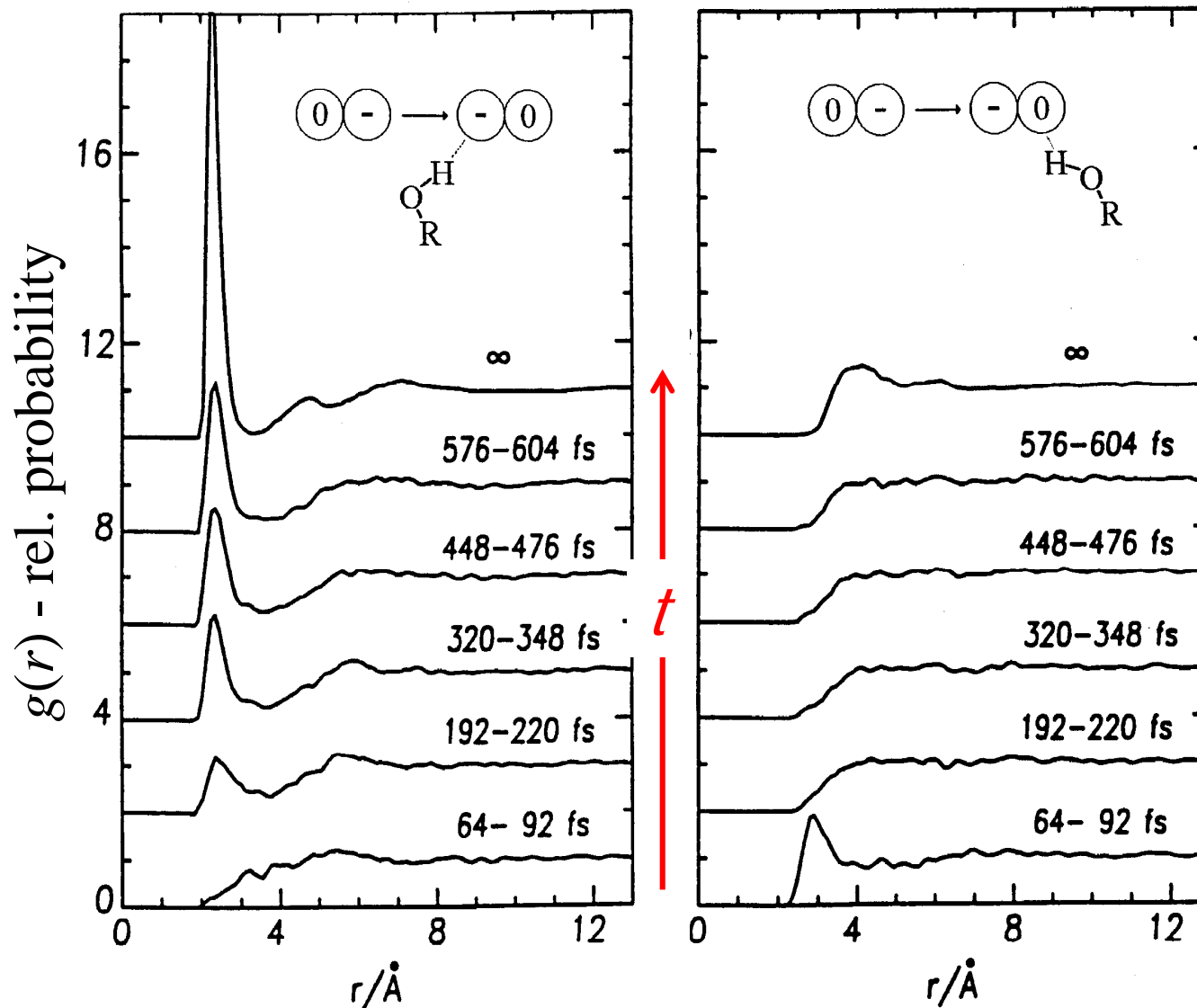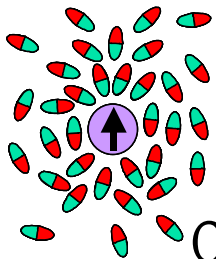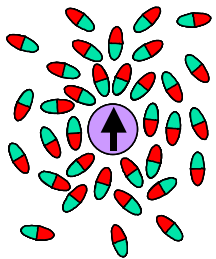0M
0.1M
0.25M
0.5M
1.0M
2.0M

(b)
0M
0.1M
0.25M
0.5M
1.0M
2.0M
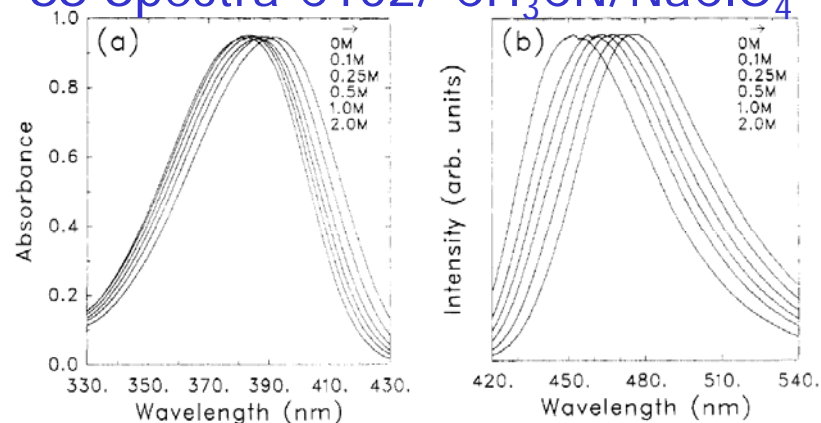
Shifts in C102/ CH$_3$CN/XClO$_4$ Solns.
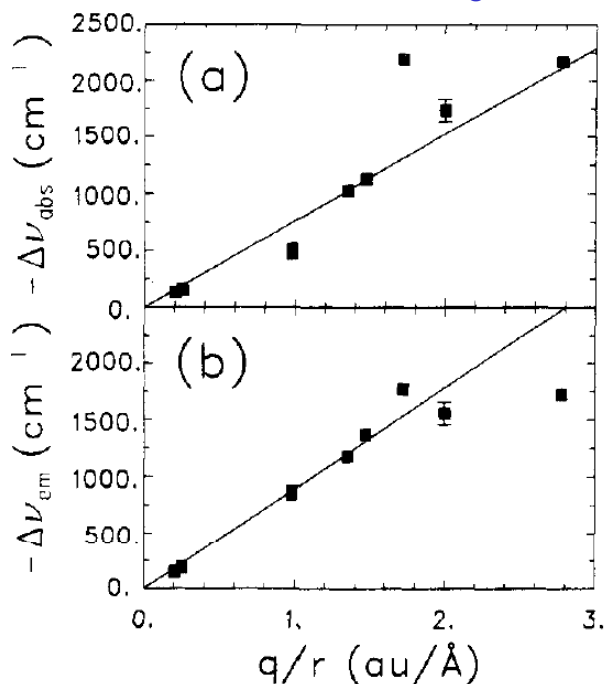
salt[a]	$r_+,$[b] Å
(CH$_3$CN)	
Bu$_4$N$^+$	4.94
Et$_4$N$^+$	4.00
Na$^+$/ClO$_4^-$	1.02
Na$^+$/SCN$^-$	1.02
Li$^+$	0.74
Ba^{2+}	1.36
Sr^{2+}	1.16
Ca^{2+}	1.00
Mg^{2+}	0.72

- SS spectra shift continuously with ion conc.

- shift mainly related to cation charge/size ratio

Chapman & Maroncelli, J. Phys. Chem. **95**, 9095 (1991).

Ionic Solutions (cont.)

- expected fast ion atmosphere relaxation; instead slow ns dynamics were the norm

C102/THF + 1M X Solutions

X=NaClO$_4$

NaClO$_4$ /THF

X=MeOH, PC

MeOH /THF   PC/THF

C102/CH$_3$CN+NaClO$_4$

"true" $\nu(0)$

CH$_3$ CN dynamics

$\nu(0)$

ion dynamics

$\nu(\infty)$
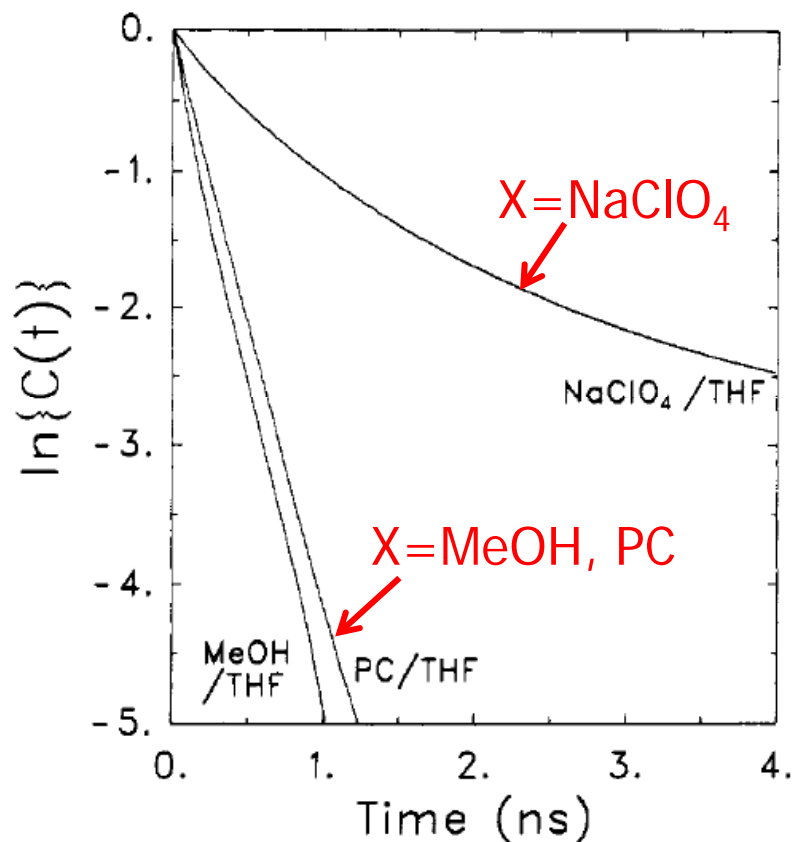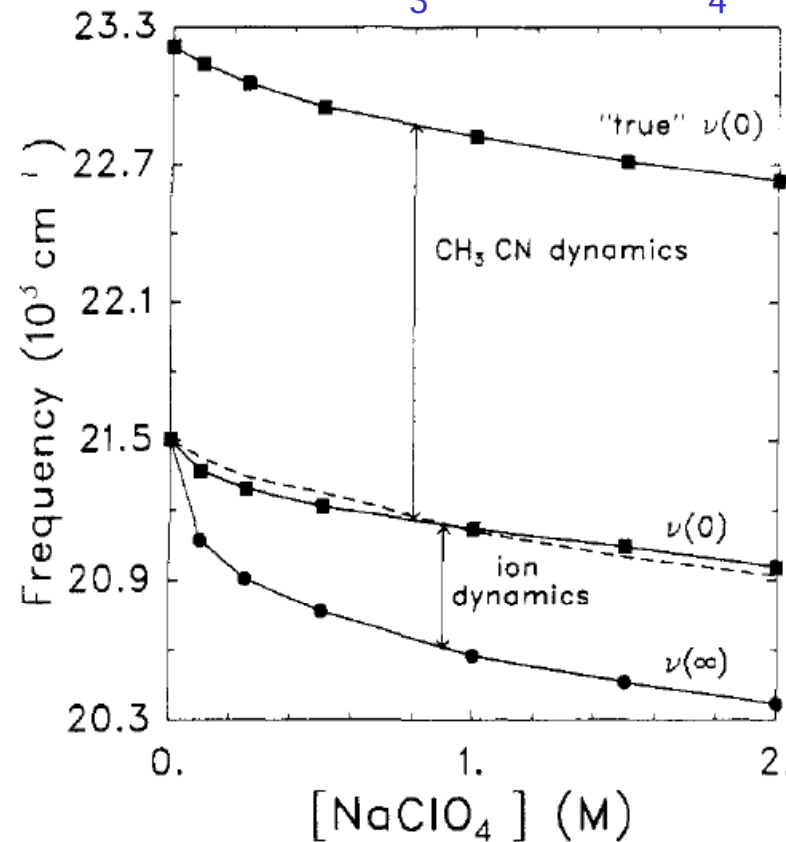
- background solvent dynamics unaffected by ions?
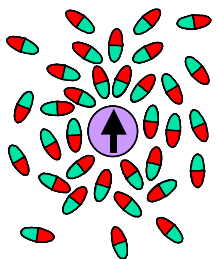
Model of Ion-Probe Dynamics

C102/CH$_3$CN+NaClO$_4$
λ_{exc} Dependence
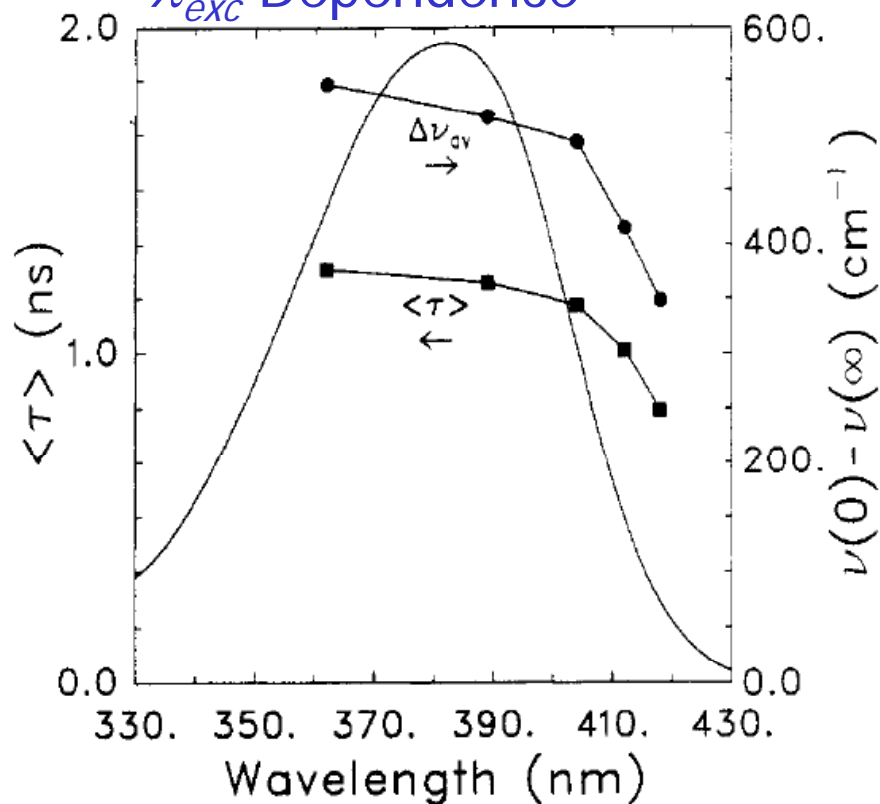
Multiple Equilibria Model

$$PS_nI_0 \rightleftharpoons PS_{n-1}I_1 \rightleftharpoons \ldots PS_{n-j}I_j \ldots \rightleftharpoons PS_1I_{n-1} \rightleftharpoons PS_0I_n$$
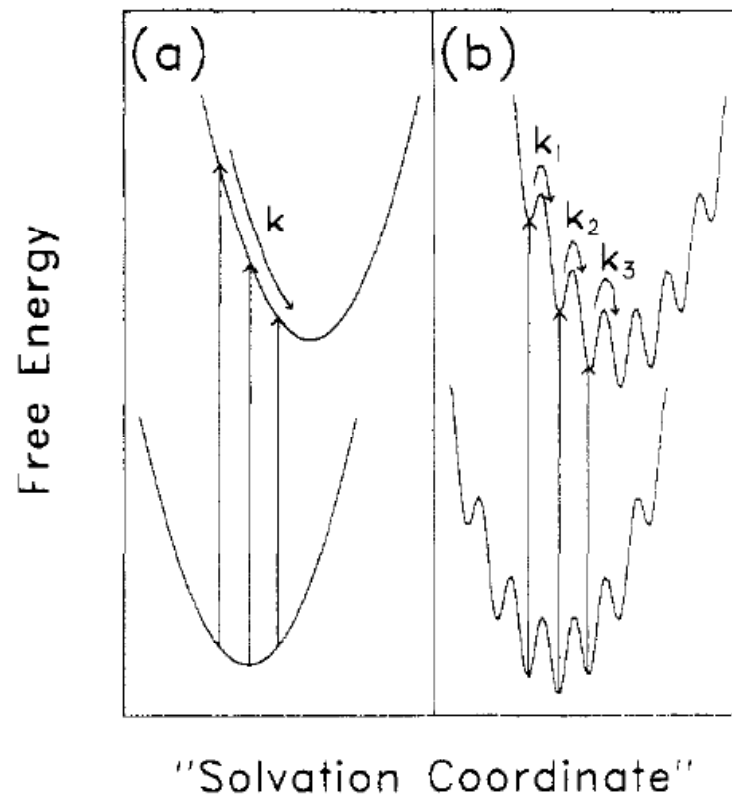
P=probe,
S=solvent mol.
I=ion

Ionic Liquids

Ionic Liquids Studied
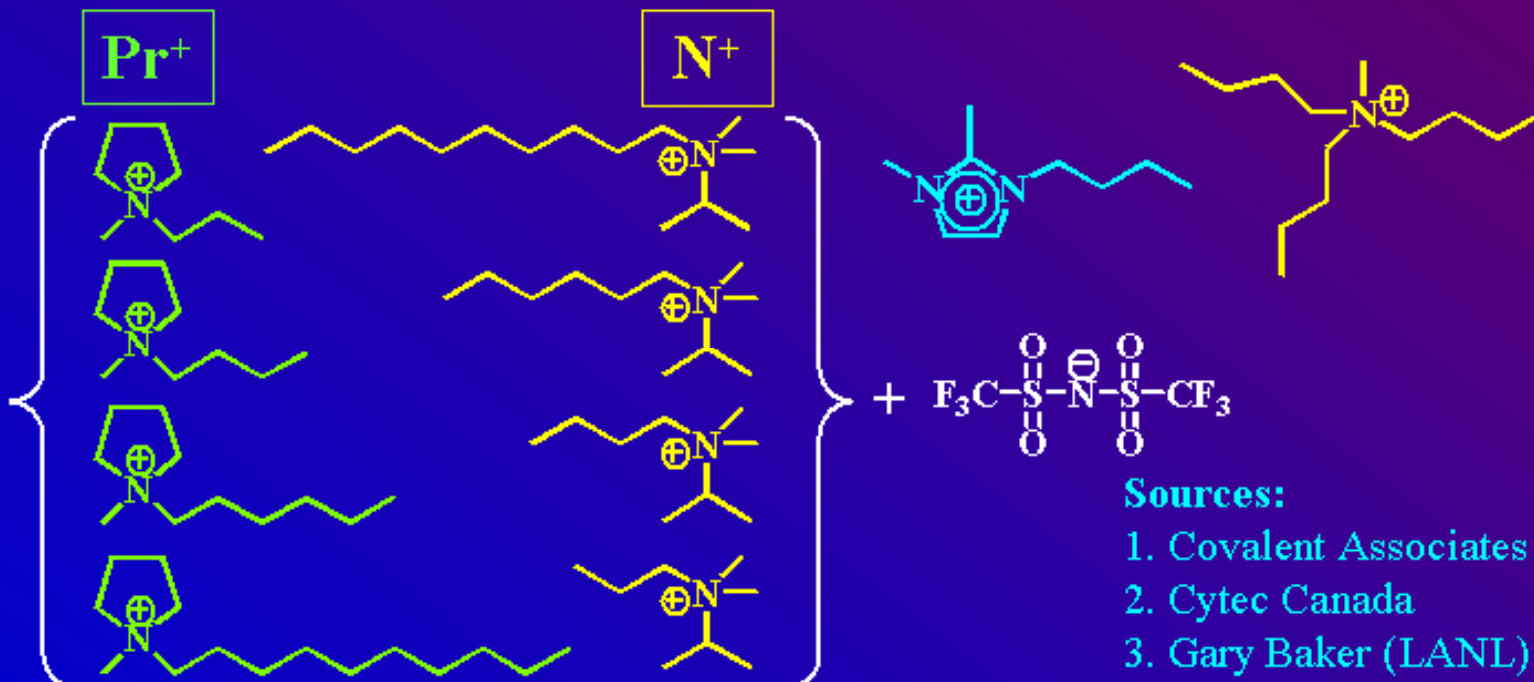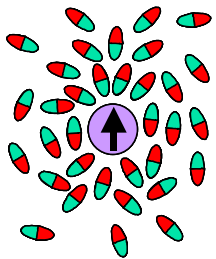
Ionic Liquids (cont.)

The Solvation Response

- normalized response:

$$S_v(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)}$$

- stretched exponential fits:

$$S_v(t) \cong \exp\{-(t/\tau_0)^\beta\}$$

Anion	τ_0/ps	β
PF_6^-	34	.31
Tf_2N^-	59	.44
Tf_3C^-	310	.39

➤ broad distribution of relaxation times: 200 fs - 2 ns

DCS in $[Im_{41}^+][X^-]$ 25 °C

Tf_3C^-

Tf_2N^-

PF_6^-

$S_v(t)$

Time / ps
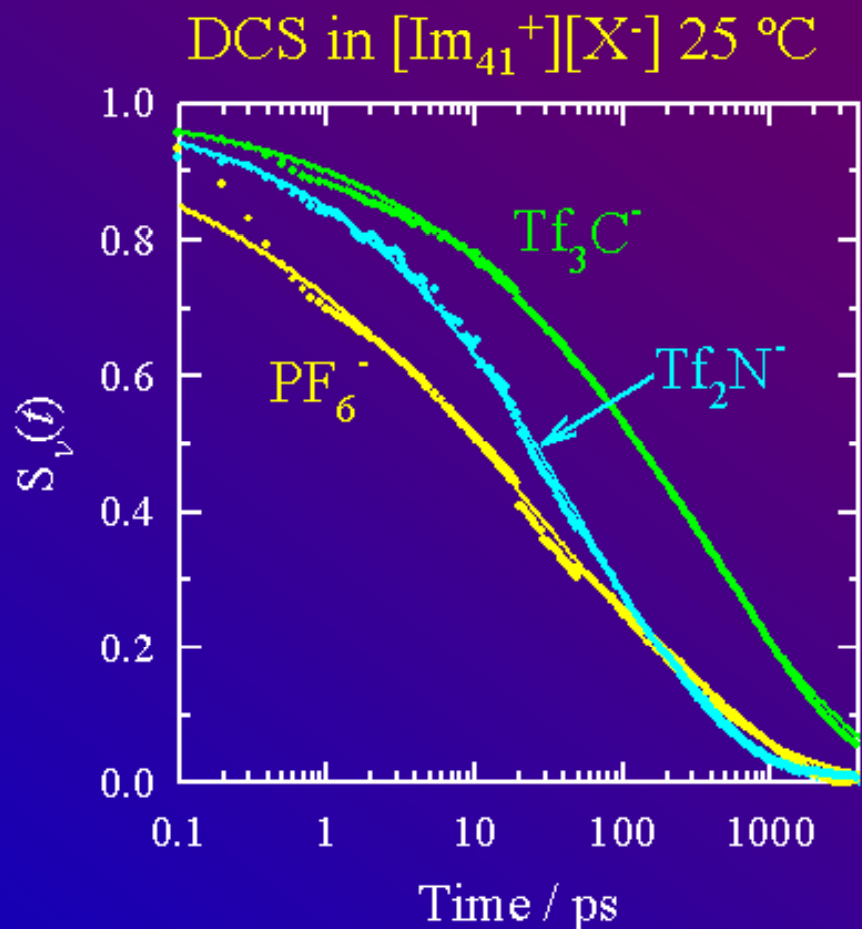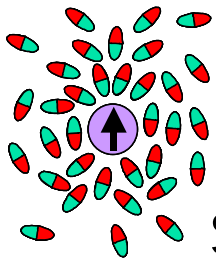
The Solvent's Perspective

Several techniques have recently been developed that look at how the solvent sense a perturbation to a dissolved solute

- Schmuttenmaer & Co. have tried time-resolved THz spect.

Ti:Sapphire Regenerative Amplifier
1 kHz, 100 fs, 1W average power

Transmitter beam variable delay line

1

Chopper Pos. 1

THz transmitter

sample in cryostat

30% R, 70% T beamsplitter

Chopper Pos. 2

3

Pump beam variable delay line

beamsplitting polarizer

THz beam

polarizer

balanced detectors

THz receiver

2

Receiver beam variable delay line

THz Abs of TBNC/CHCl$_3$

after exc.

eq. solvent

TBNC

Frequency (cm^{-1})

- 10mM TBNC/CHCl$_3$
- 1-5% solvent affected by exc.

Interpretation:

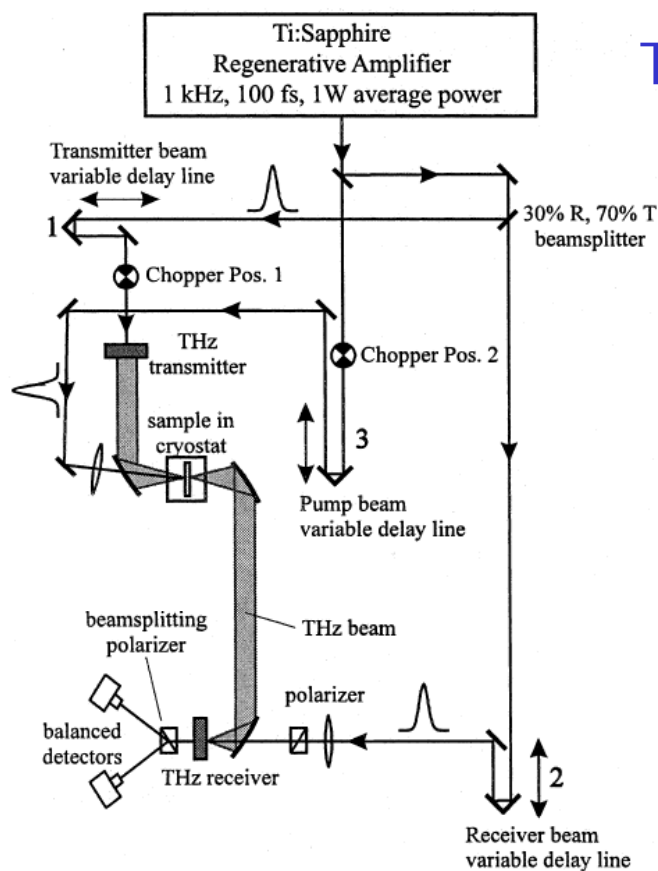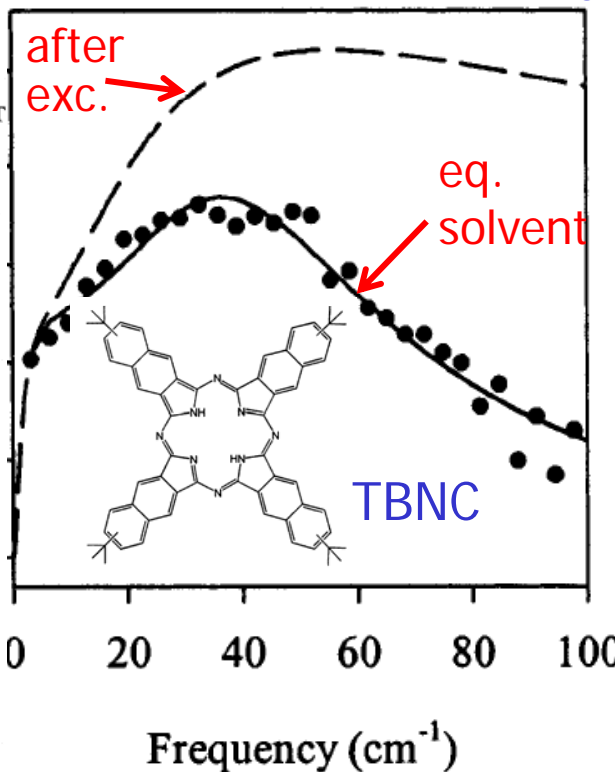"Prior to excitation of the dye molecules, the solvent is undergoing librational motion. Upon photoexcitation, the nearby solvent molecules must reorient to the new charge distribution, and their librational motion becomes ill-defined, which is why the mode becomes overdamped. After a few picoseconds, they have reoriented and can resume their usual librational motion."

Beard,…Schmuttenmaer, J. Phys. Chem. B **106**, 7146 (2002).
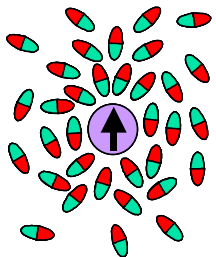
"RaPTORS"

Blank & Co. developed "Resonant Pump Third-Order Raman probe Spectroscopy" = RaPTORS

$k_s = k_{nr1} - k_{nr2} + k_{nr3}$

E_{nr2} E_{nr3}
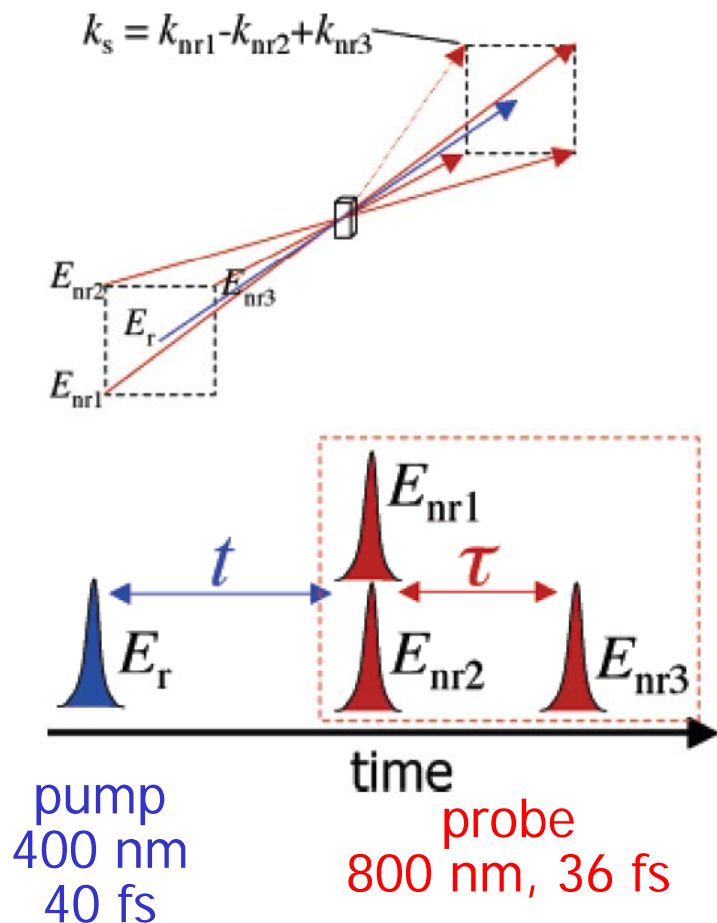
E_r

E_{nr1}

- excite solute resonantly and record non-resonant low-frequency Raman response of solvent after delay t
- C102 in CH_3CN (.5mM)
- IRF = 140 fs

E_{nr1}

t τ

E_r E_{nr2} E_{nr3}

time

pump
400 nm
40 fs

probe
800 nm, 36 fs

Underwood & Blank, J. Phys. Chem. A 109, 3295 (2005).

III-Other Simple

RaPTORS (Cont.)

Solvent-Only Response $R(\omega)$ **& B.O. Fit**

Brownian Oscillator:

$$G_i(\tau) = \eta_i \sin(\Omega_i \tau) \exp(-\Lambda_i \tau)$$

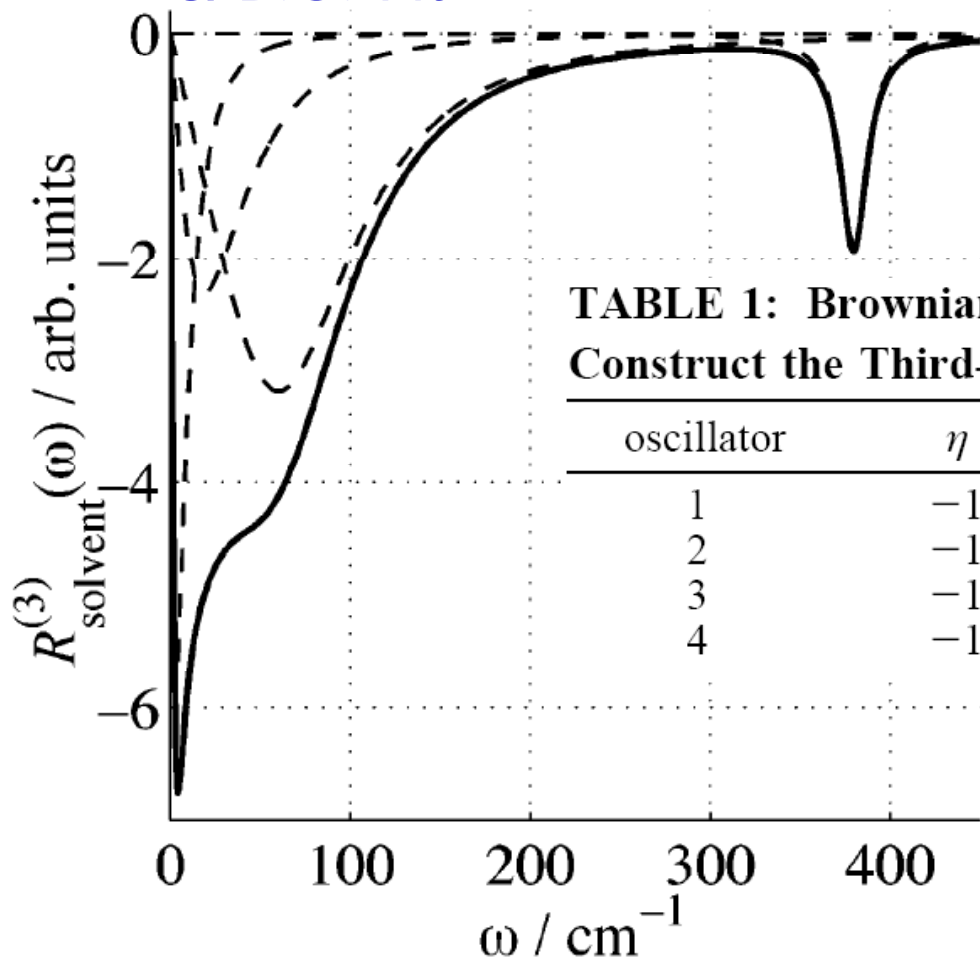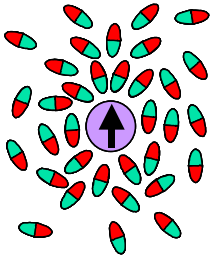$$\Omega_i = \sqrt{\omega_i^2 - \Lambda_i^2} \quad \Lambda_i = \gamma_i/2$$

TABLE 1: Brownian Oscillator Fitting Parameters Used To Construct the Third-Order Response Function, $R_{solvent}^{(3)}(\tau)^a$

oscillator	η	$\alpha^{(1)}$	ω/cm^{-1}	γ/cm^{-1}
1	-1	0.30	9.48	28.0
2	-1	0.71	36.5	81.2
3	-1	1.57	78.9	111.4
4	-1	1.15	379	18.4

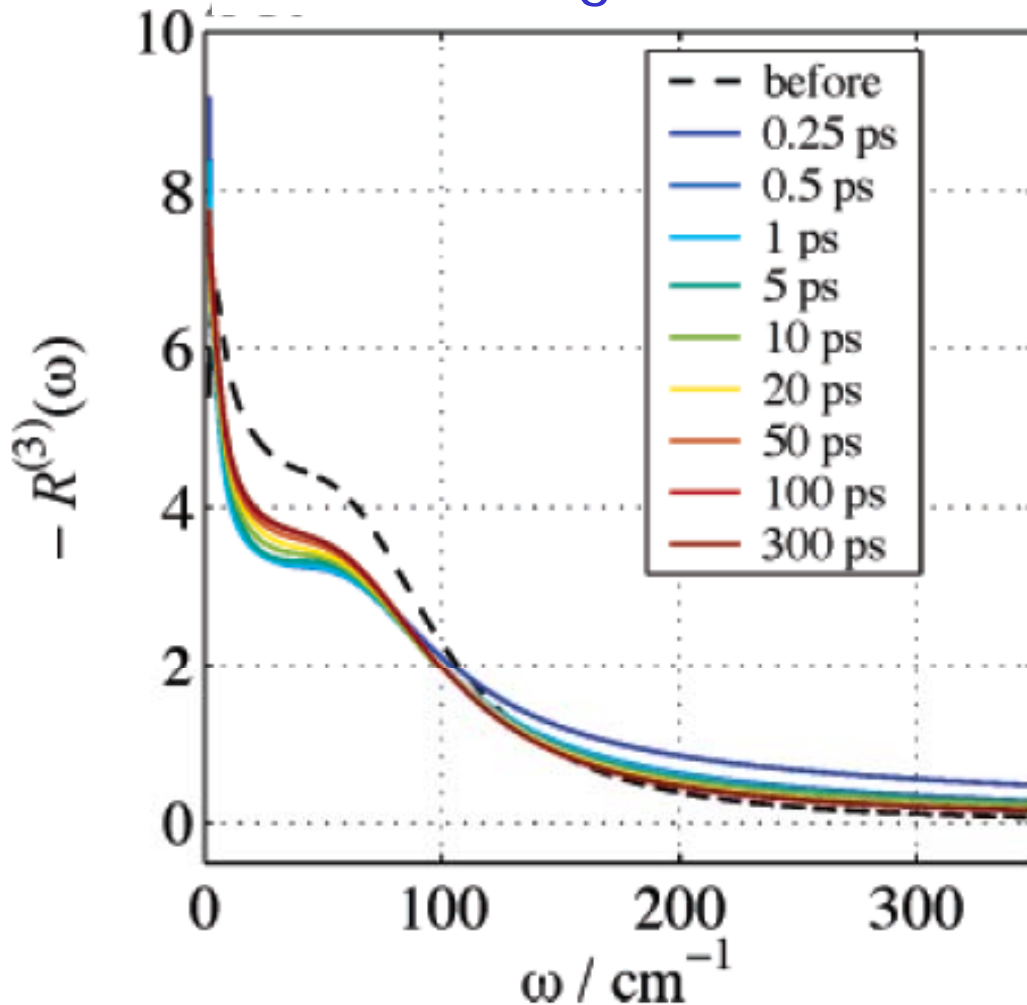**Interpretation:**
1-diffusive reorientation
2-collision induced
3-librations
4-intramolecular mode

RaPTORS (Cont.)

Estimated Response $R(\omega)$ of Interacting Fraction

- large fraction <100 fs
- diff. persists >300 ps
- change similar to change upon decreasing T = increasing ρ

- excitation causes electectrostriction effect
- longer time relaxation reflects longer distance scales
- differences imply breakdown of linear response

Underwood & Blank, J. Phys. Chem. A 109, 3295 (2005).