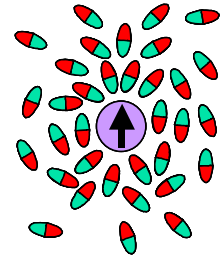# Solvation Dynamics: Fundamentals and A Survey of Results in Simple and Complex Environments
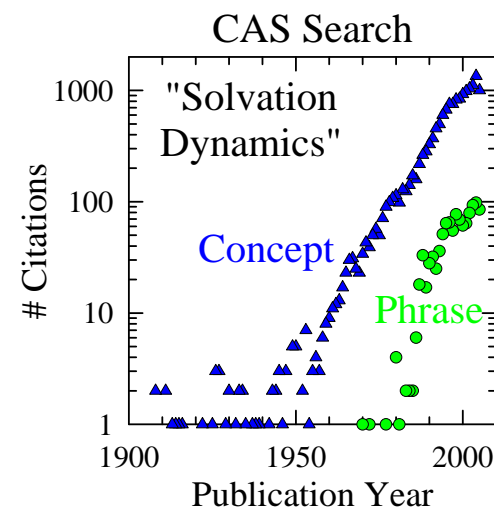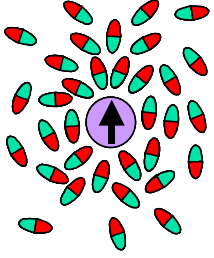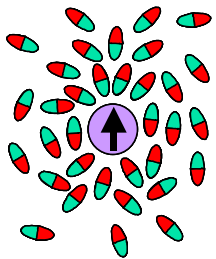
I. Background and Fundamentals

II. Polar Solvation Dynamics

III. Other "Simple" Environments

IV. Complex Environments, Biological and Otherwise

CAS Search

I. Background & Fundamentals

❑ Solvation Energies & Solvatochromism

❑ The Dynamic Stokes Shift

❑ Measurement Techniques

❑ Linear Response (Interlude)
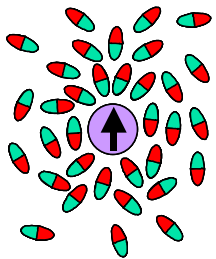
❑ 3PEPS Measurements

❑ Why Study?

Intermolecular Interactions

- **repulsive:**
  - exchange-repulsion
- **attractive:**
  - ionic
  - H-bonding
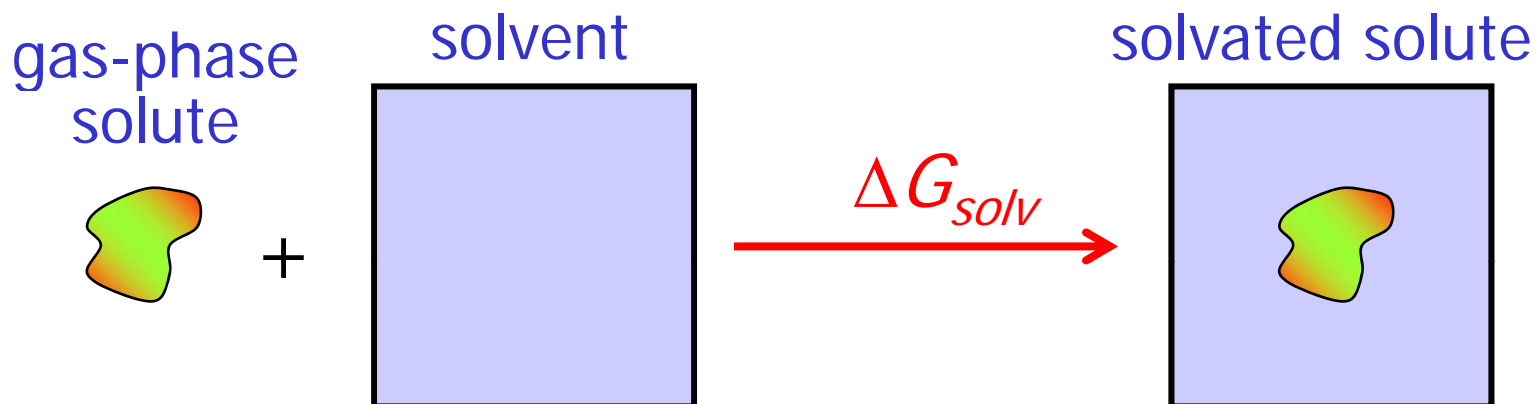 - dispersion
  - electrostatic
  - induction

typical strength ↑

"solvation" describes the sum total of solute + solvent interactions -- usually a complicated mix
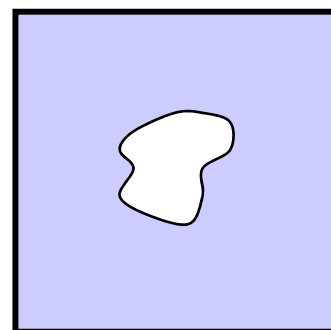
Solvation Energies - ΔG_{solv}
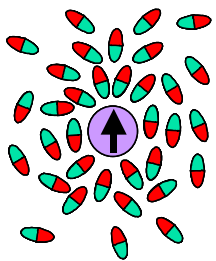
The Solvation Process:

gas-phase solute   solvent   solvated solute

$+$ ΔG_{solv}

Interpretation: ------------------------------
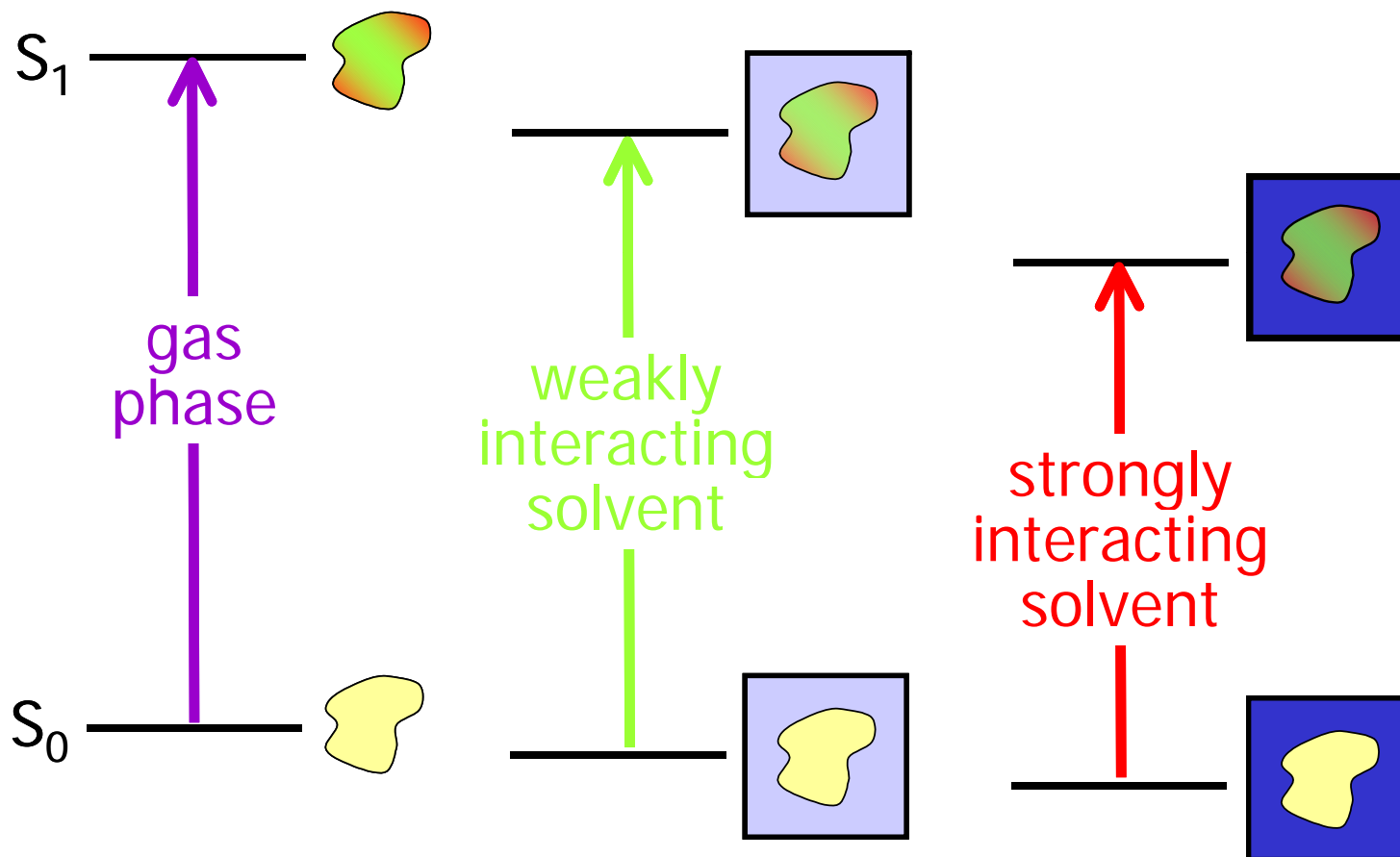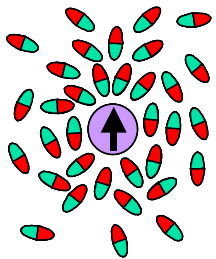
cavity formation
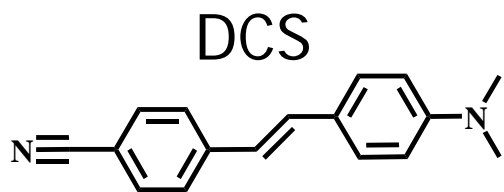(repulsion)

u-v attraction
(dispersion, μ-μ, etc.)

Solvatochromism - $h\nu = \Delta\Delta G_{solv}$

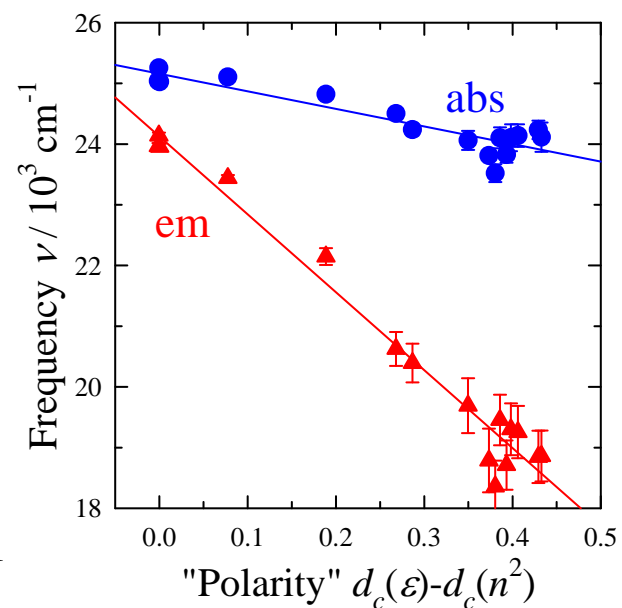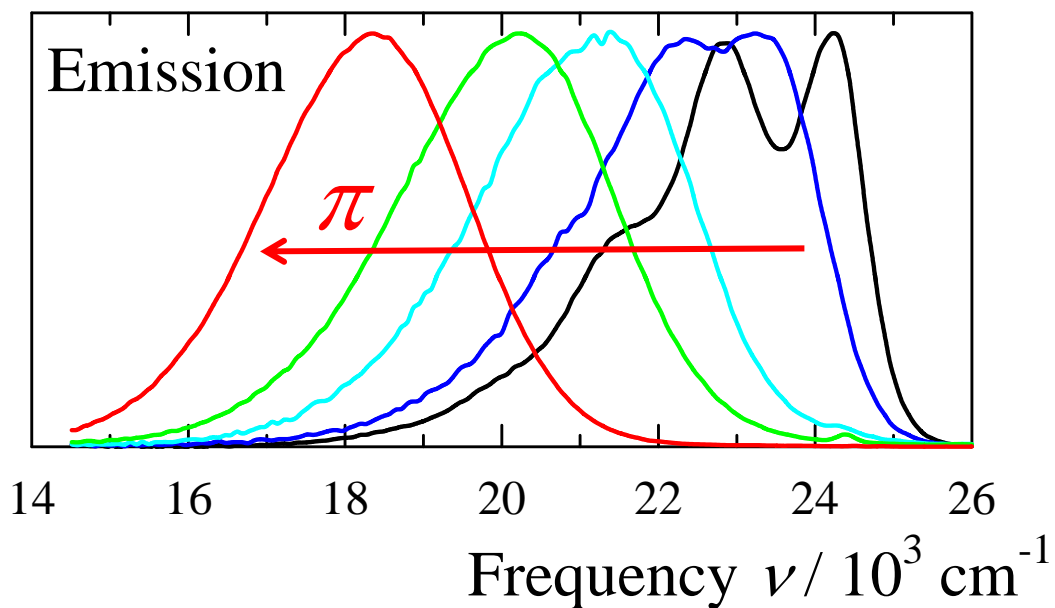spectral shifts are differential solvation energies $\Delta\Delta G$

Example Data - DCS Probe
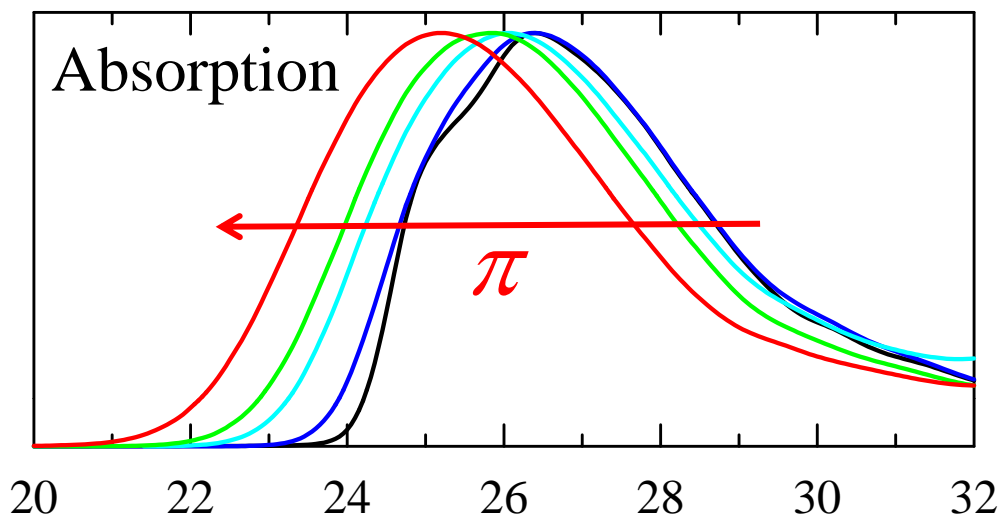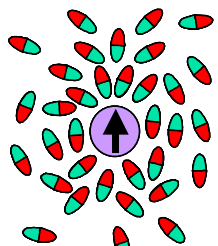
DCS

n-hexane
CF$_2$Cl-CFCl$_2$
dioxane

THF
DMSO

Absorption

π

20   22   24   26   28   30   32

Emission

π

14   16   18   20   22   24   26

Frequency ν / 10^3 cm^{-1}

Frequency ν / 10^3 cm^{-1}

26

abs

em

24

22

20

18

0.0   0.1   0.2   0.3   0.4   0.5

"Polarity" $d_c(\varepsilon)$-$d_c(n^2)$

Solvatochromic Polarity Scales

π_{az}

Reichardt, Chem. Rev. 94, 2319 (1994).
"From the total of 78 solvatochromic and solvatofluorchromic compounds in Table 1, which have been proposed and used as potential empirical solvent polarity indicators, up to now only ca. 18 of them have been really used to establish definite, UV/vis/near-IR spectroscopically derived scales of solvent polarity…"

$E_T(30)$

RPM

Z

S

χ_R

LMCT

χ_B

Py

π^*
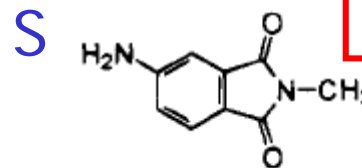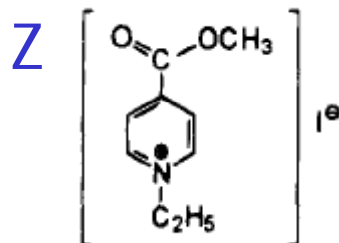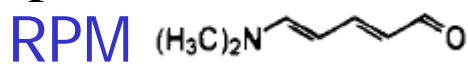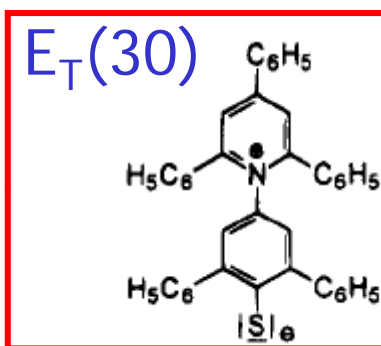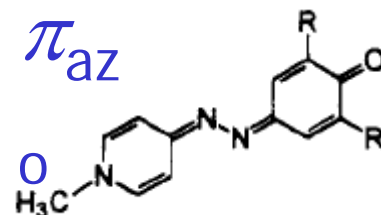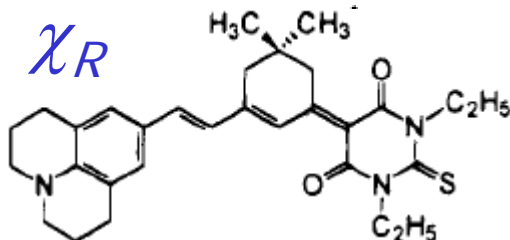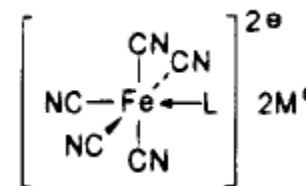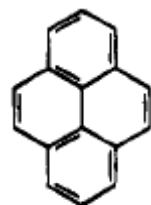
	15	16	17	18
R^1	C_2H_5	OCH_3	NEt_2	H
R^2	H	H	H	NEt_2

Solvatochromic Polarity Scales

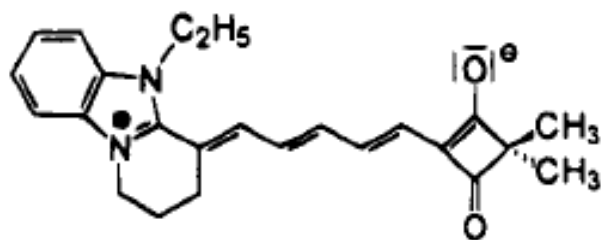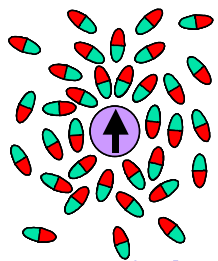## Reichardt (cont.)

Z vs $E_T(30)$ - a favorable case

"…Most of these scales are based on the spectral data of a single standard probe (or reporter) molecule. They are, therefore, of somewhat limited value in the correlation analysis of other solvent-dependent processes because they respond to a combination of nonspecific and specific solute/solvent interactions, which are typical for the chemical structure of the probe molecule, i.e. its ability to register dispersion, dipole/dipole, hydrogen-bond, and other possible intermolecular interactions."
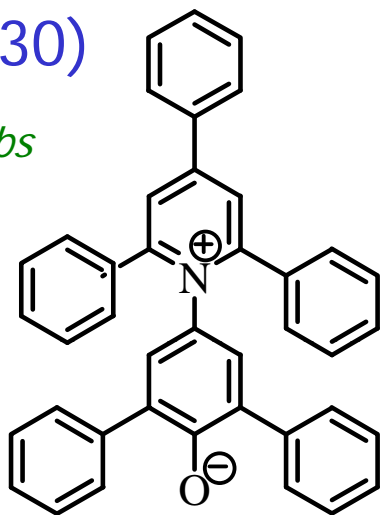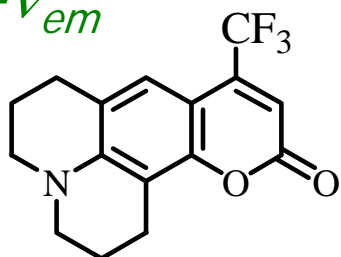
More Typical: $E_T(30)$ & H-Bonding

$E_T(30)$

ν_{abs}

π^*

ν_{abs}

C153

$\nu_{abs} - \nu_{em}$

CF$_3$

AN
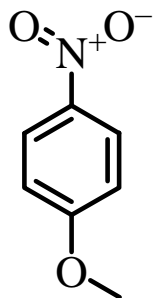
δ_{NMR}
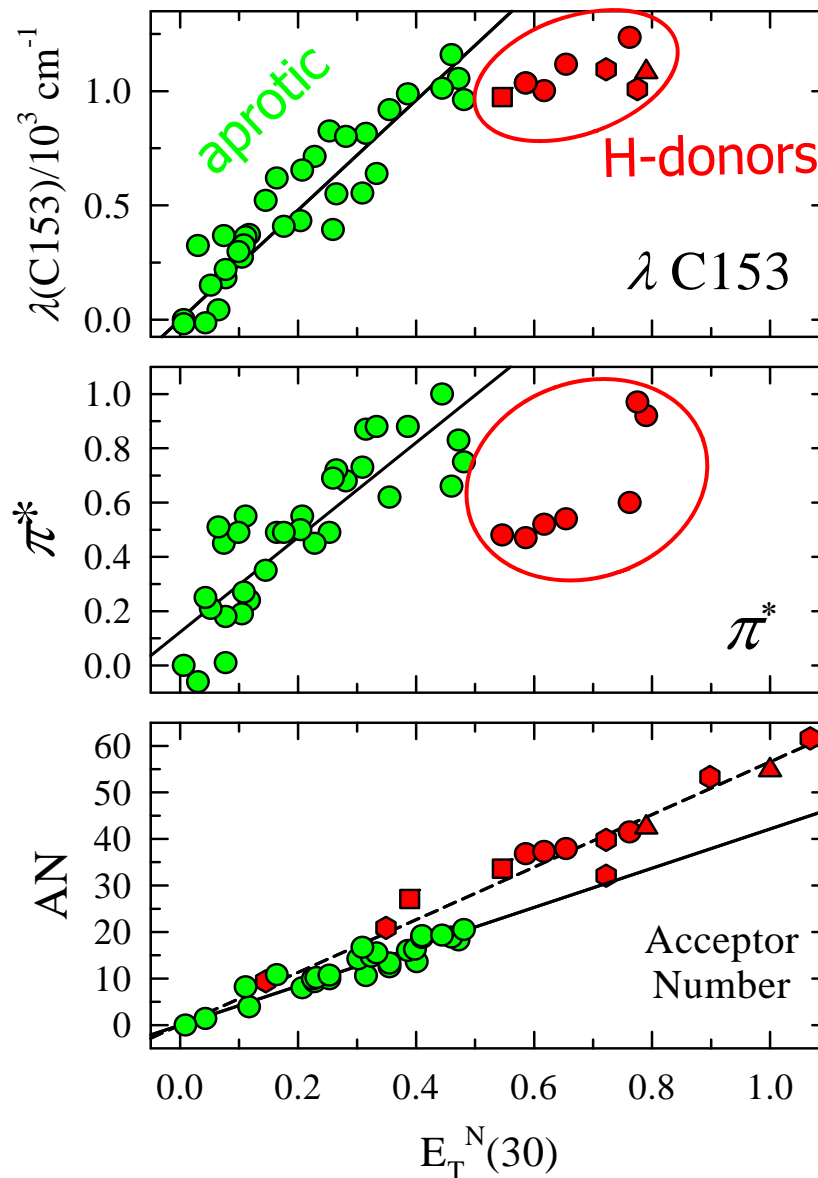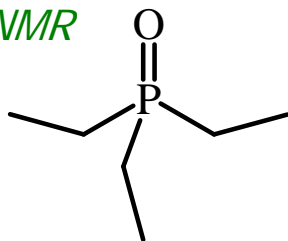
A Refinement

What's wrong with this picture?

Absorption and Emission Shifts are Different

The Stokes Shift (DCS)

Energy

S_1

S_0

ν_{abs}

ν_{em}

Solvation Coordinate

hexane ~ gas

em   abs

solv $\Delta\nu \sim 0$

THF

$\Delta\nu$

DMSO

$\Delta\nu$

Frequency $\nu / 10^3 \text{ cm}^{-1}$

16   18   20   22   24   26   28   30
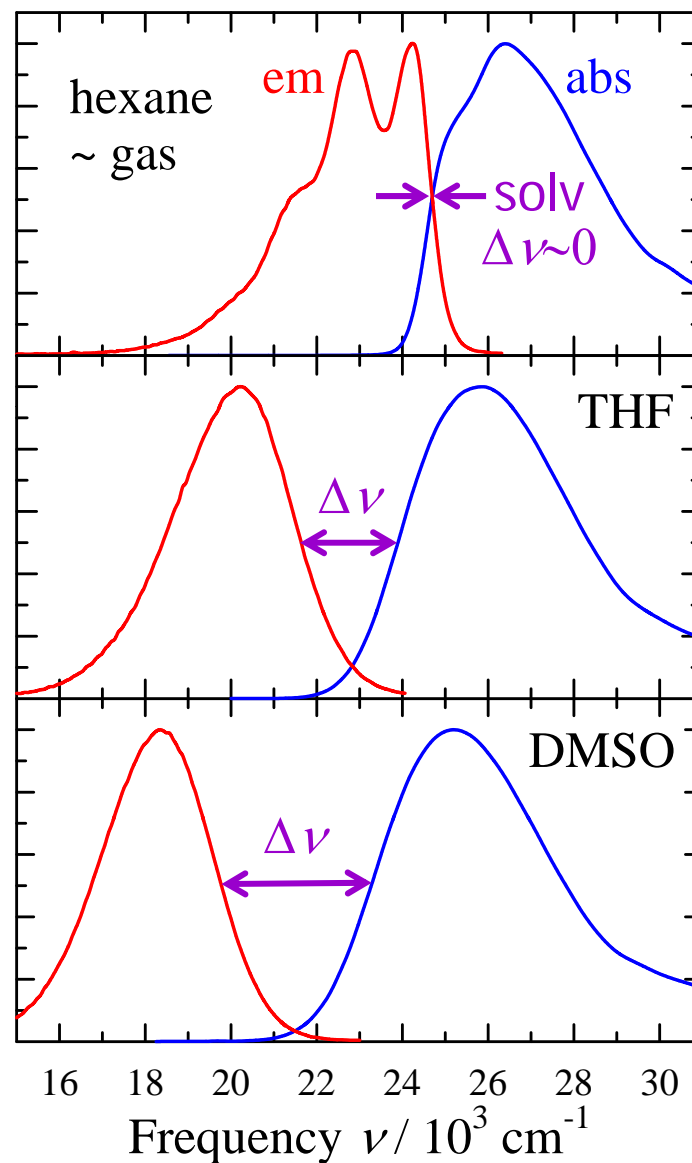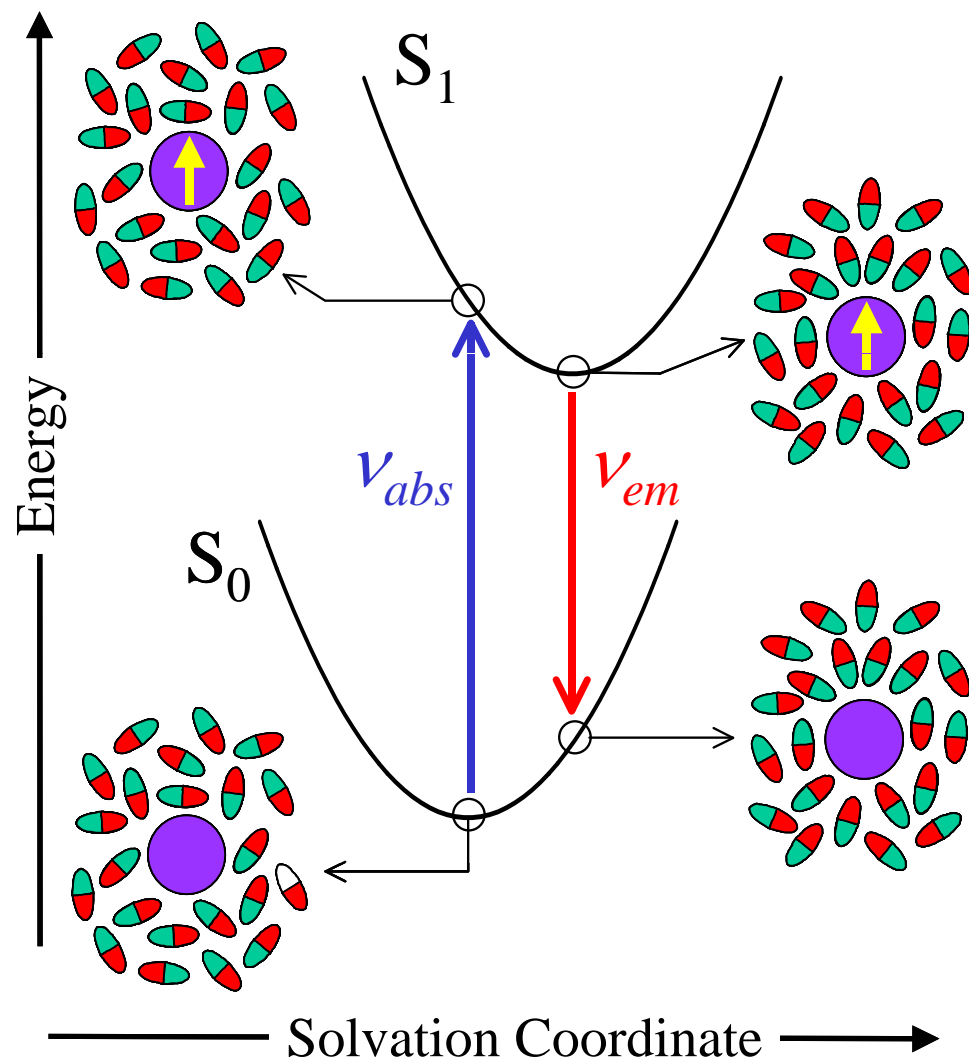
Shift Energetics

Abs. & Em. Frequencies:

$$h\nu_{abs} = F_1^{FC} - F_0^{eq}$$

$$h\nu_{em} = F_1^{eq} - F_0^{FC}$$

nuclear
+
electronic

Stokes Shift:

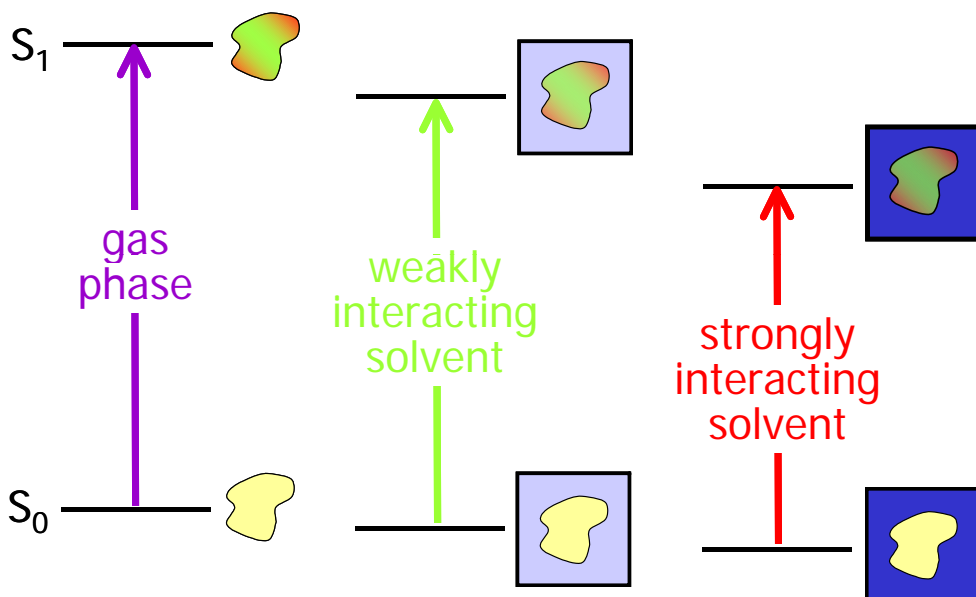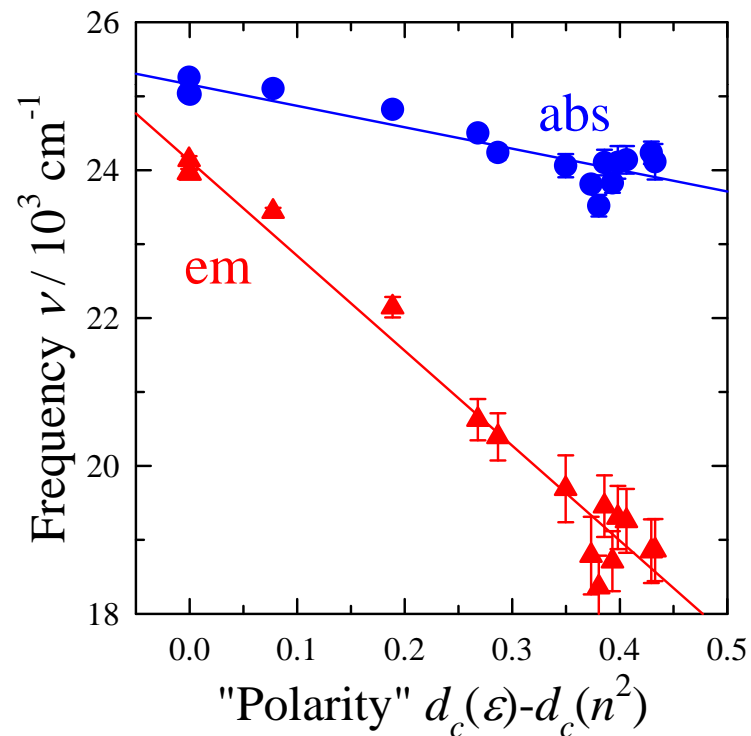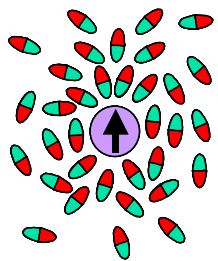$$h\Delta\nu = h\nu_{abs} - h\nu_{em}$$

$$= (F_1^{FC} - F_1^{eq}) - (F_0^{FC} - F_0^{eq})$$

$$= 2\lambda$$

"nuclear reorganization energy"

$\Delta\nu$ is not sensitive to solvent electronic polarizability, only its "nuclear polarizability"

For Example, Dielectric Models

$$h\nu_{abs} = h\nu^0_{abs} + A_{abs}d_c(n^2) + C_{abs}\{d_c(\varepsilon) - d_c(n^2)\}$$

$$h\nu_{em} = h\nu^0_{em} + A_{em}d_c(n^2) + C_{em}\{d_c(\varepsilon) - d_c(n^2)\}$$
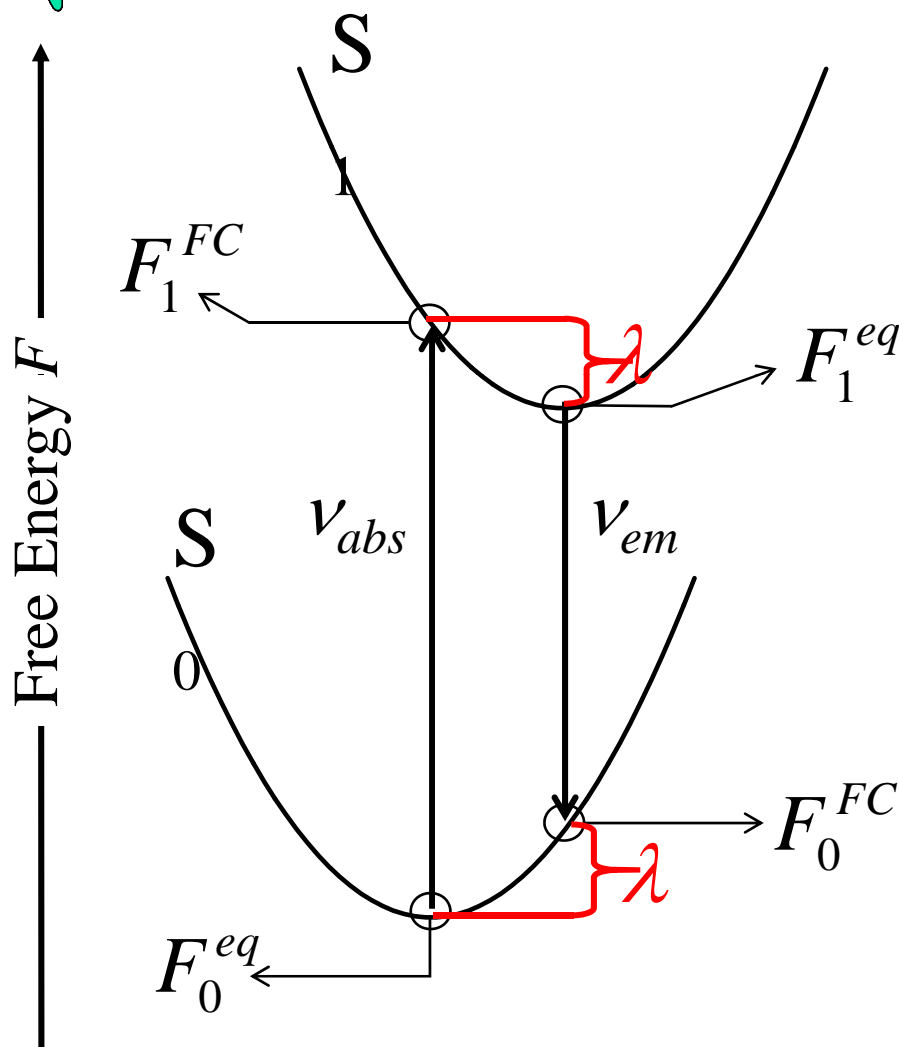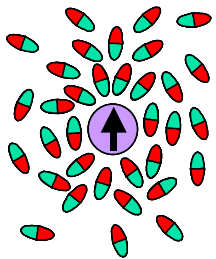
gas　　electronic　　nuclear

$$h\Delta\nu = h\Delta\nu^0 + [2(\vec{\mu}_1 - \vec{\mu}_0)^2 a^{-3}]\{d_c(\varepsilon) - d_c(n^2)\}$$

solute properties　　solvent nuclear response

solute factors: $c \equiv \alpha/a^3$

$$A_{abs} = A_{em} = -(\mu_1^2 - \mu_0^2)a^{-3} \quad C_{abs} = -2\vec{\mu}_0 \cdot (\vec{\mu}_1 - \vec{\mu}_0)a^{-3} \quad C_{em} = -2\vec{\mu}_1 \cdot (\vec{\mu}_1 - \vec{\mu}_0)a^{-3}$$

solvent dielectric functions: $\quad d_c(x) \equiv \dfrac{d_0(x)}{1 - 2cd_0(x)} \quad d_0(x) \equiv \dfrac{x-1}{2x+1}$

C153 $\Delta\nu$ and π^*
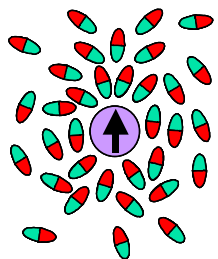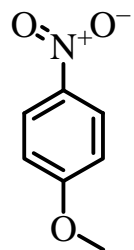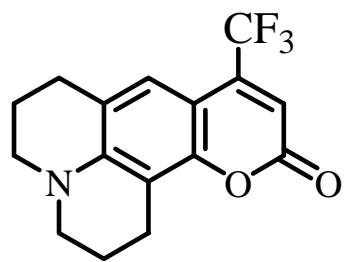
CF$_3$ structure (coumarin 153) and O=N$^+$-O$^-$ / OCH$_3$ (4-nitroanisole) structures
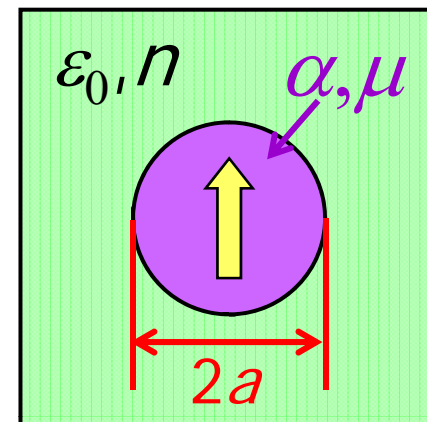
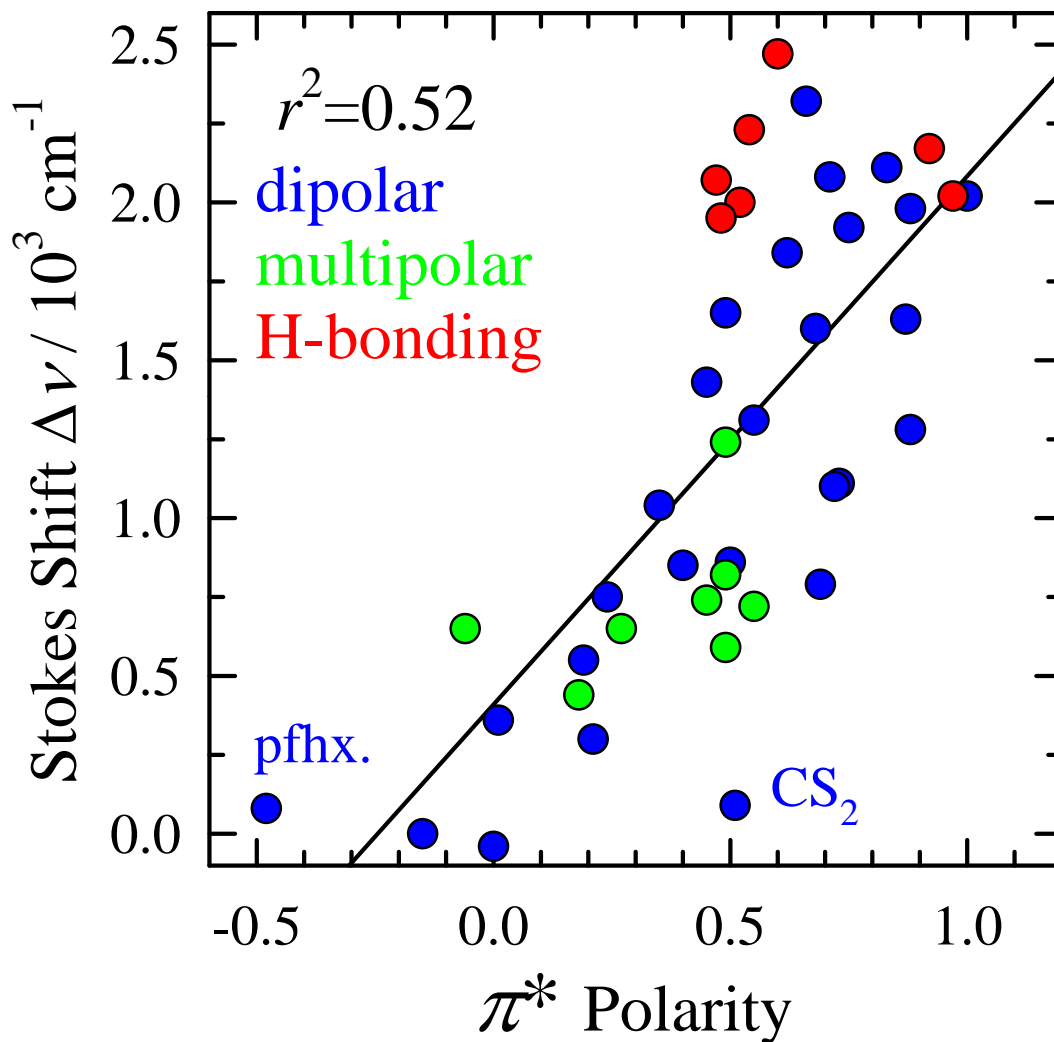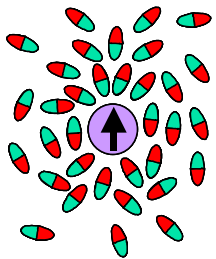- $\Delta\nu$ (or λ) of C153 provides excellent measure of non-specific solvent nuclear polarity

- correlation with π^* scale is quite poor because the latter is strongly affected by electronic polarizability

$r^2=0.52$

dipolar
multipolar
H-bonding

pfhx.

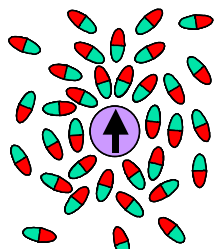CS$_2$

Stokes Shift $\Delta\nu / 10^3$ cm^{-1}

π^* Polarity

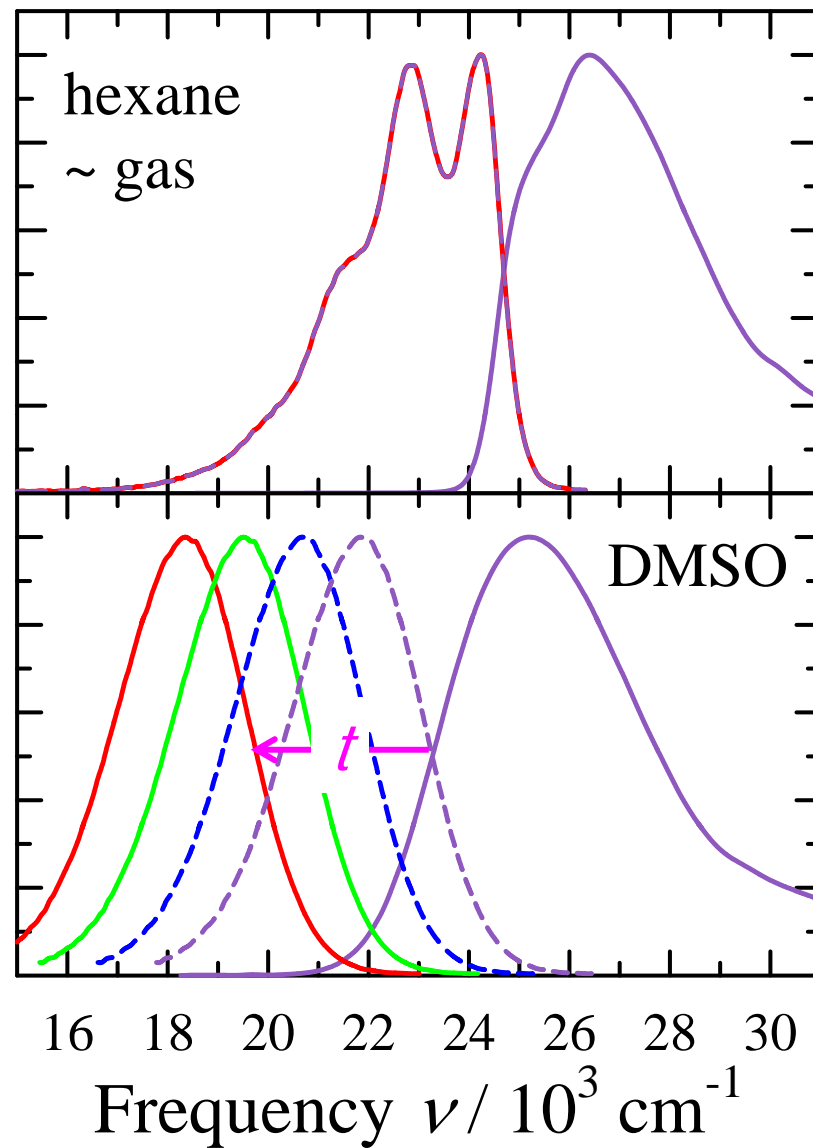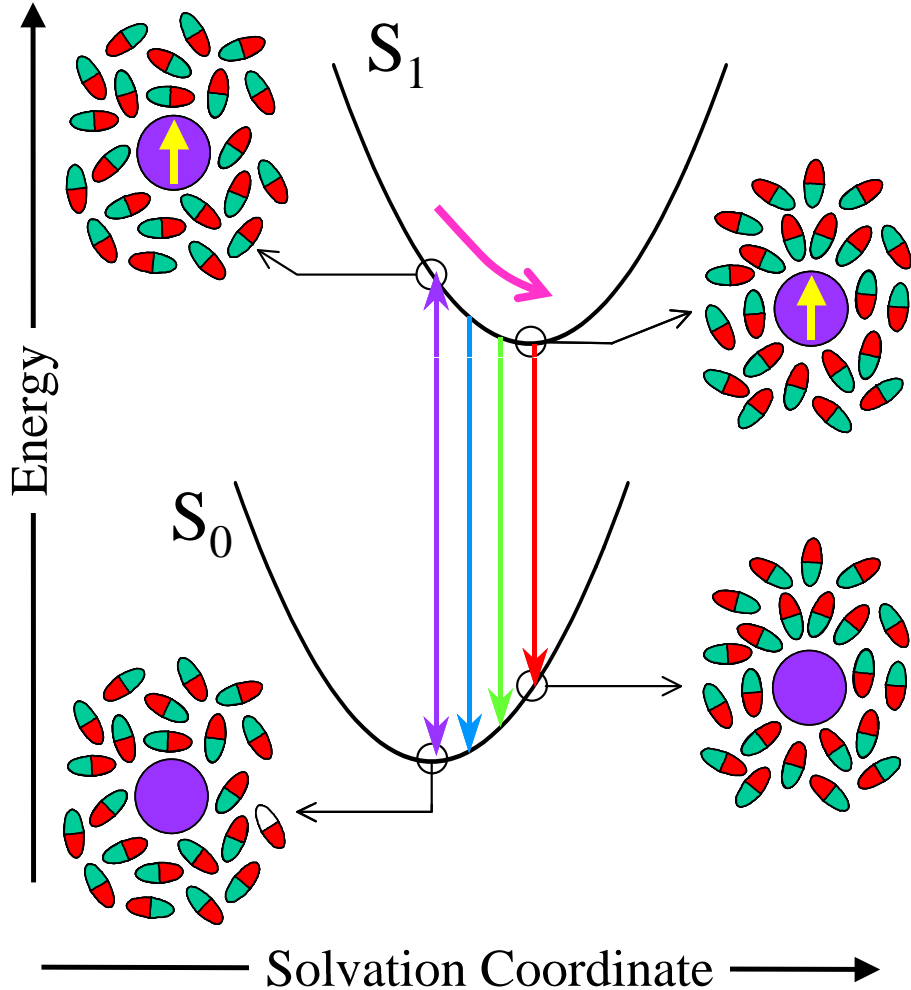Reynolds, Maroncelli, J. Phys. Chem. **100**, 10337 (1996)

Key Points:

- solvation energies reflect a complex mix of interactions (attractive & repulsive)

- solvatochromism is a differential measurement; what is measured are those interactions that change between S_0 and S_1

- many scales of solvatochromic polarity exist each emphasizing a certain mix

- ν_{abs} & ν_{em} depend on both the electronic and nuclear solvent polarizabilities; $\Delta\nu$ depends only on the nuclear part (i.e. the polarization requiring nuclear solvent motions)

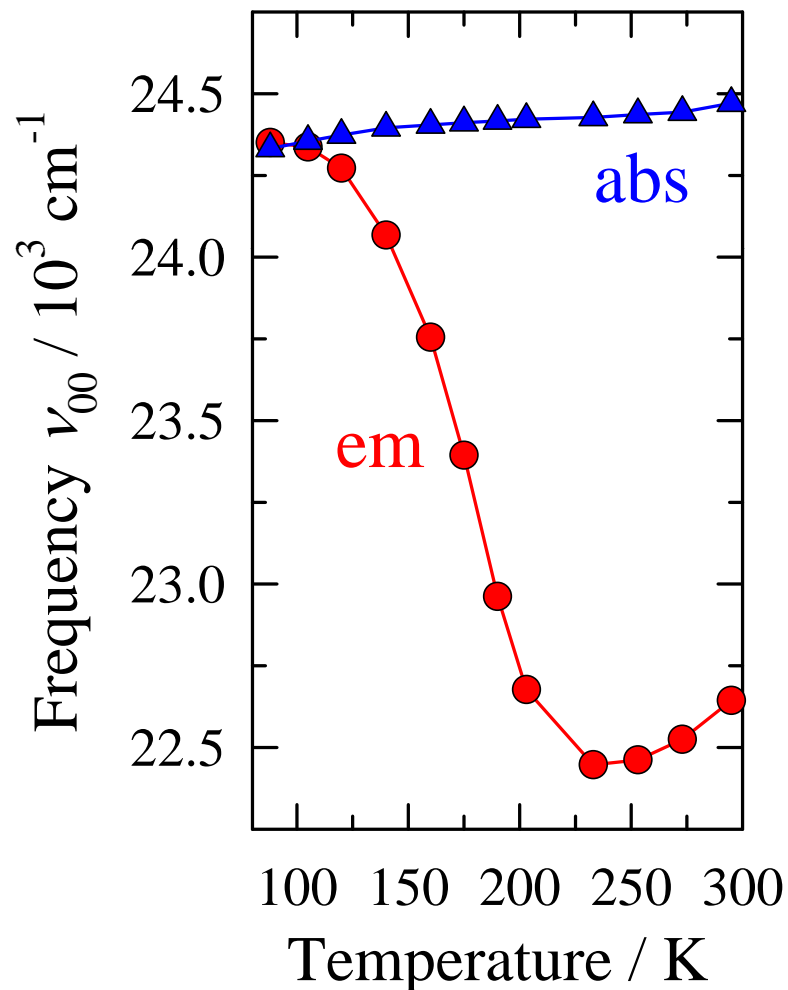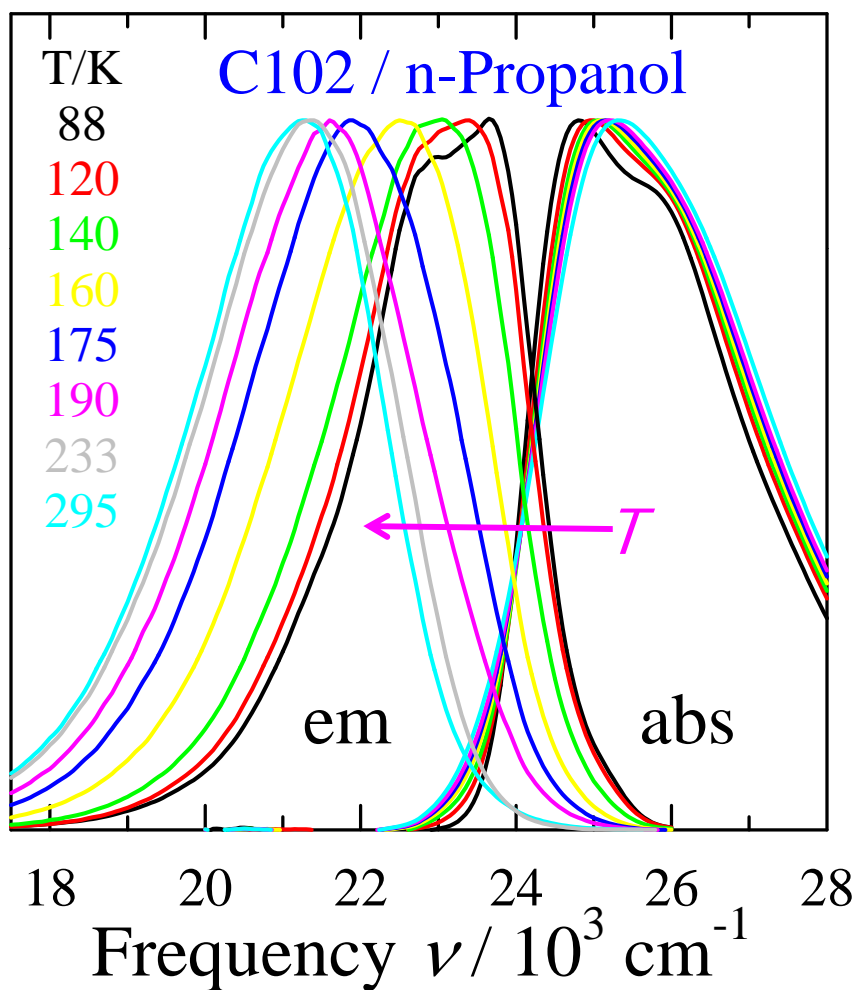# The Dynamic Stokes Shift

Energy

S₁

S₀

Solvation Coordinate

hexane
~ gas

DMSO

t

Frequency ν / 10^3 cm^{-1}
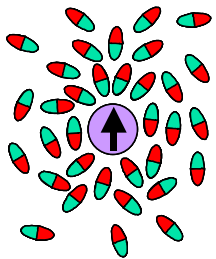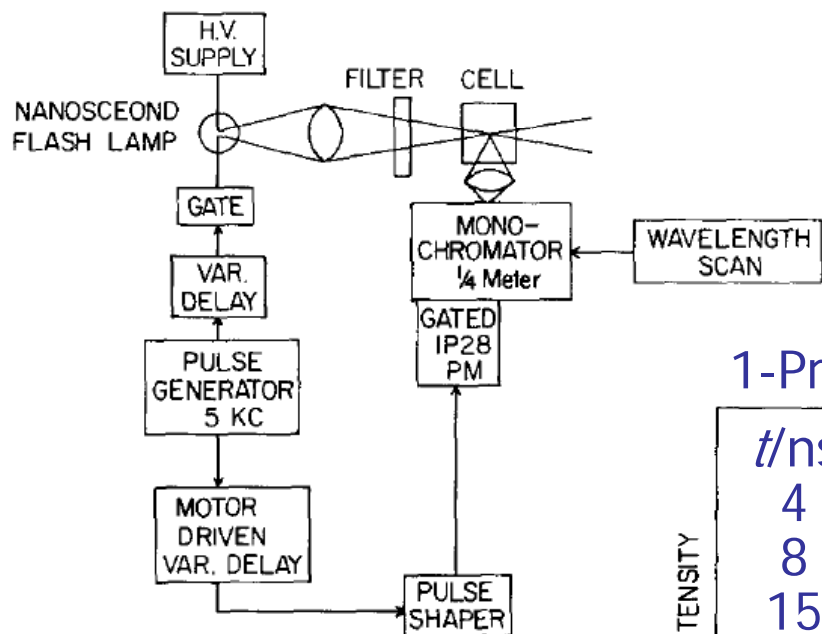
16   18   20   22   24   26   28   30
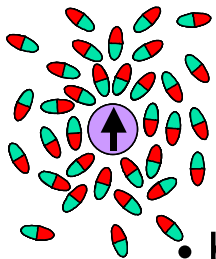
First Observations: T-dep.

- before time-resolved spectra, solvation dynamics detected via time-temperature connection first expressed by Bakhshiev ~1961

C102 / n-Propanol

T/K
88
120
140
160
175
190
233
295

Time-Resolved Experiments

1-Propanol 298 K

4-AP probe

stroboscopic fluorimeter

1-Propanol 203 K

t/ns
4
8
15
23

t
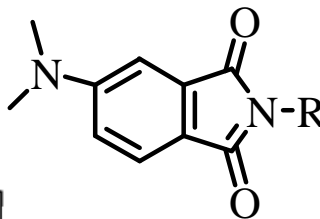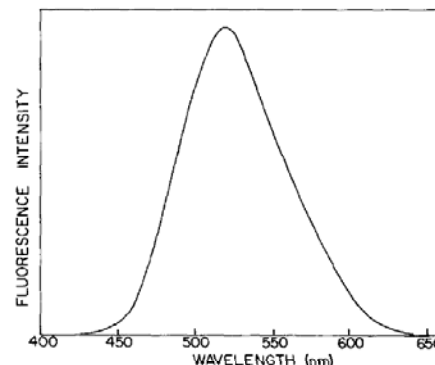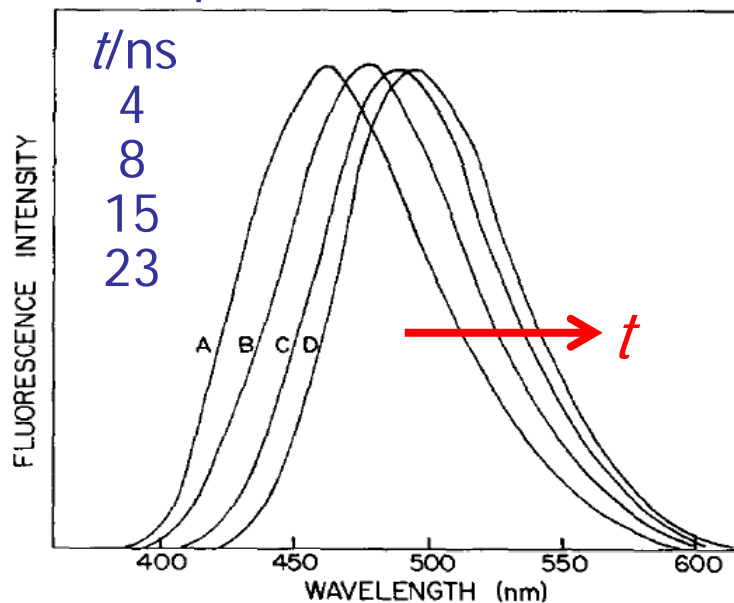
Ware & Co: Chem. Phys. Lett. **2**, 356 (1968); J. Chem. Phys. **54**, 4729 (1971).

Early Protein Dynamics

TNS

TNS probe adsorbed to bovine serum albumin protein @ 273 K
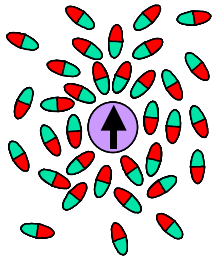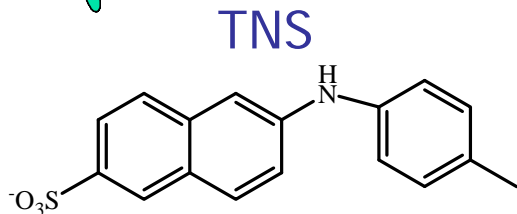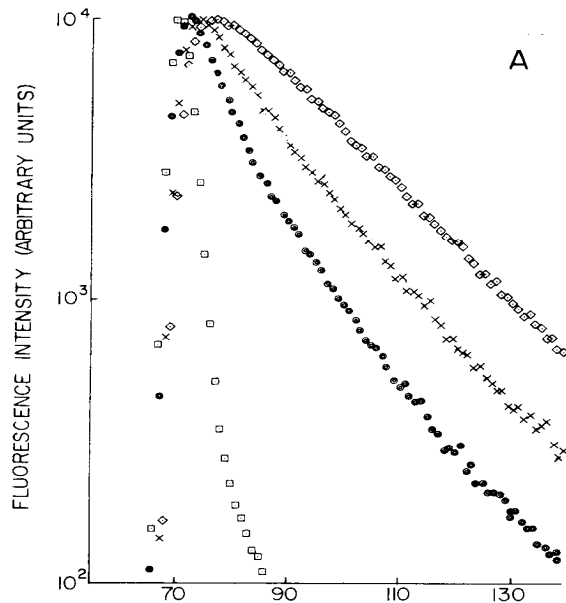
time resolved spectra

TCSPC decays

t=2,6,20 ns

$\lambda(t)$ data

0.42 ns/ch
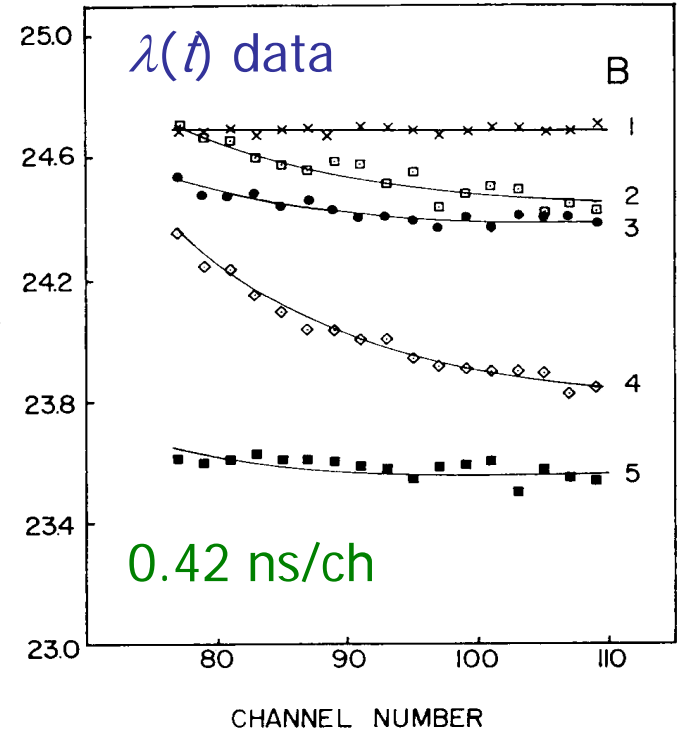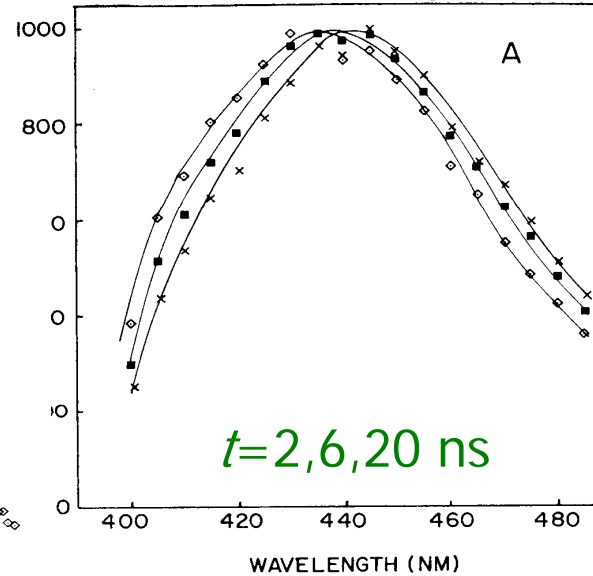
1 – EtOH 273K
2 - protein 273 K
3 - protein 323 K
4 - glycerol 273 K
5 - glycerol 323 K

Brand & Gohlke, J. Biol. Chem. **246**, 2317 (1971).
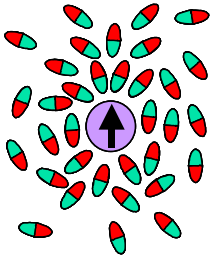
Modern Measurement Techniques

Spontaneous Emission Methods:
- phase fluorimetry
- time-correlated single-photon counting
- streak-camera

} IRF>20 ps

- fluorescence upconversion
- Kerr-gating

Stimulated Emission:
- transient absorption /stimulated emission or hole burning

Other:
- photon echo (3PEPS) measurements
- THz & RAPTORS (solvent's perspective)

} <1 ps

TCSPC

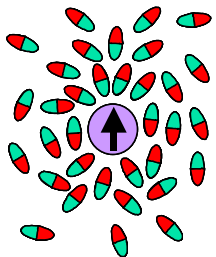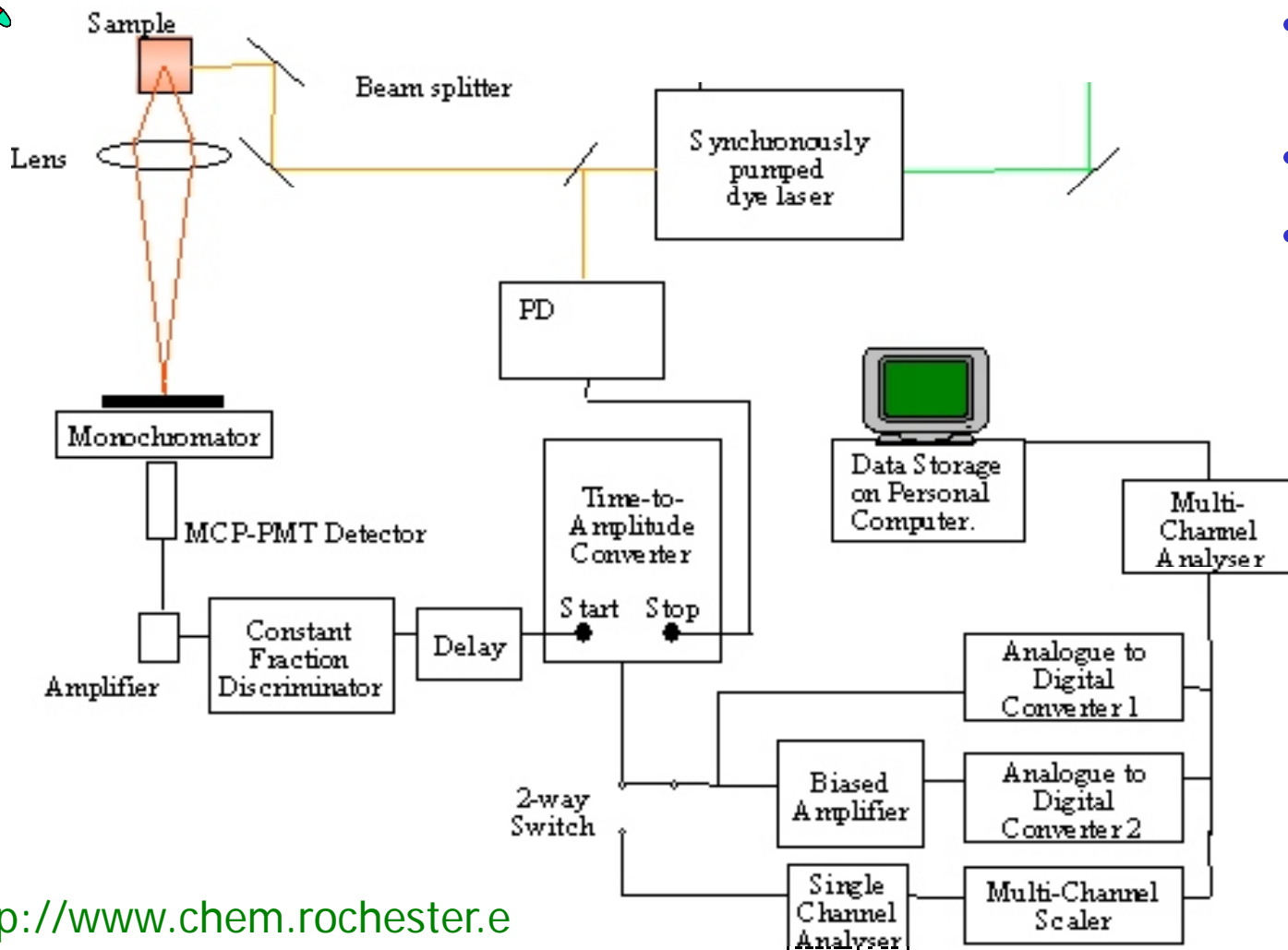- timing is electronic
- $\delta t > 20$ ps
- inherently single λ

http://www.chem.rochester.edu/~stc/tcspc.htm

Fluorescence Upconversion

mixing pulse

ω_2

emission

ω_1

Nonlinear crystal

upconverted emission

$\omega_1 + \omega_2$
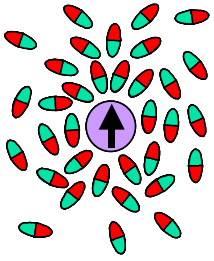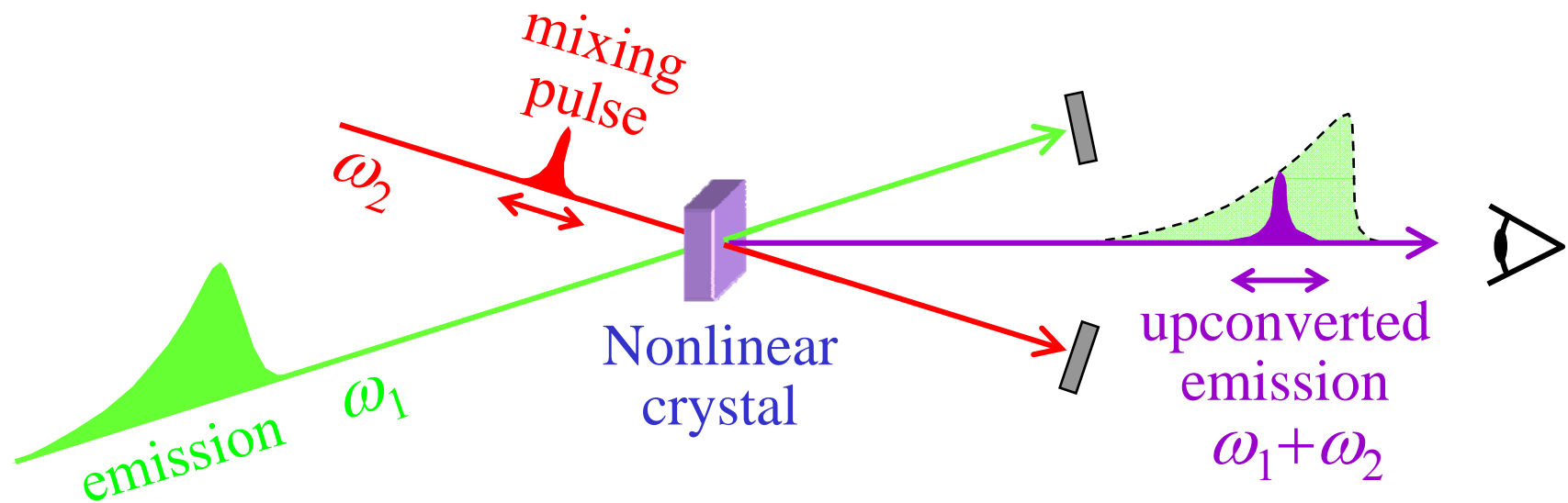
- better than 100 fs IRF possible (but hard)

A. Single Wavelength Version

unamplified Ti:saph
390 nm pump
440-700 em.
IRF 120 fs fwhm
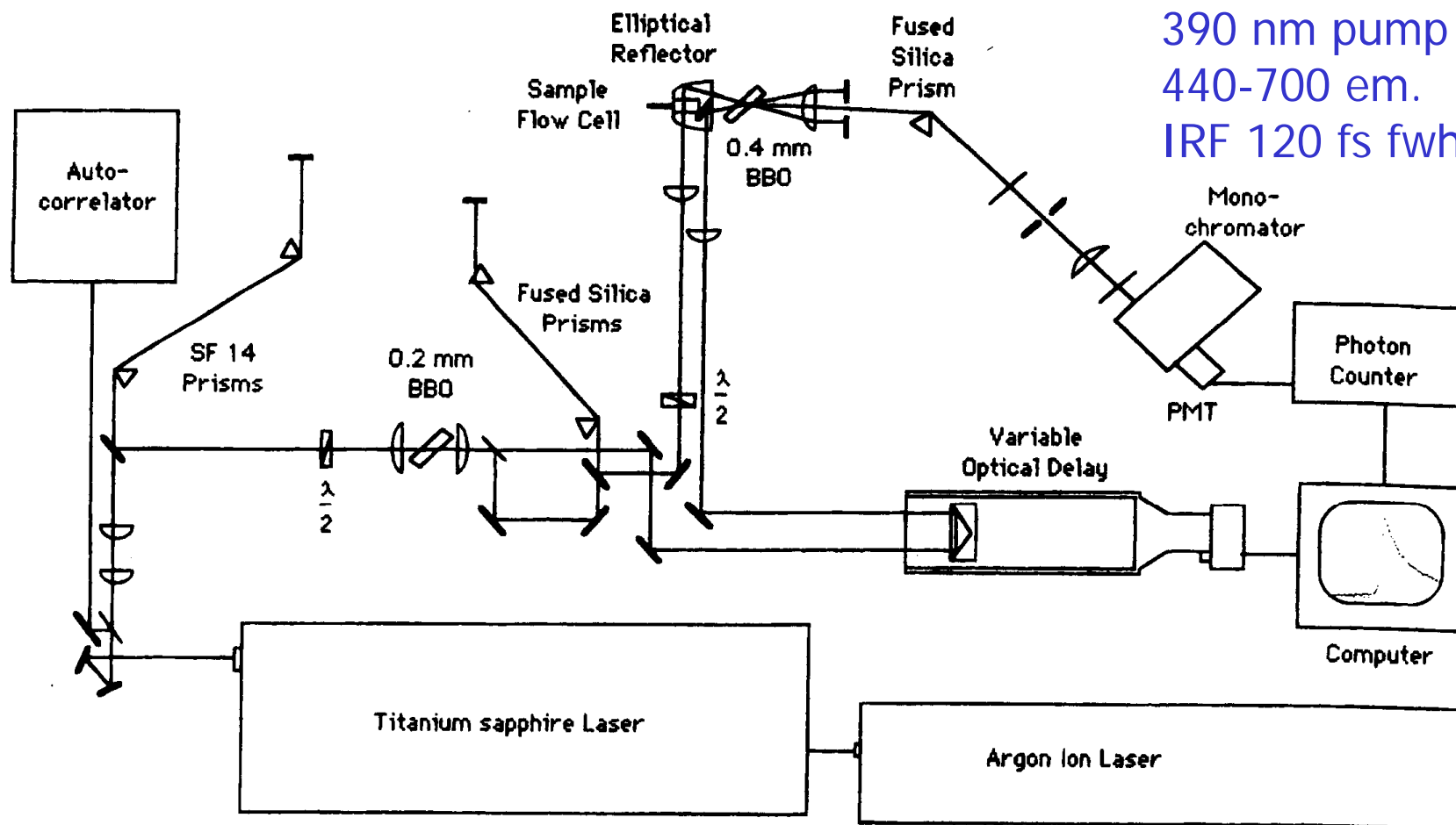
Horng *et al.*, J. Phys. Chem. **99**, 17311 (1995); after Fleming & co.

Representative Data - 1λ upcv

Single λ Decay & Fit
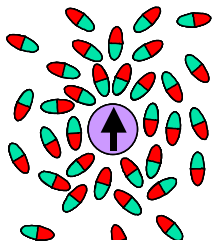

4 exp

.02

.2

2 ps/ch

IRF

Horng *et al.*, J. Phys. Chem. **99**, 17311 (1995)
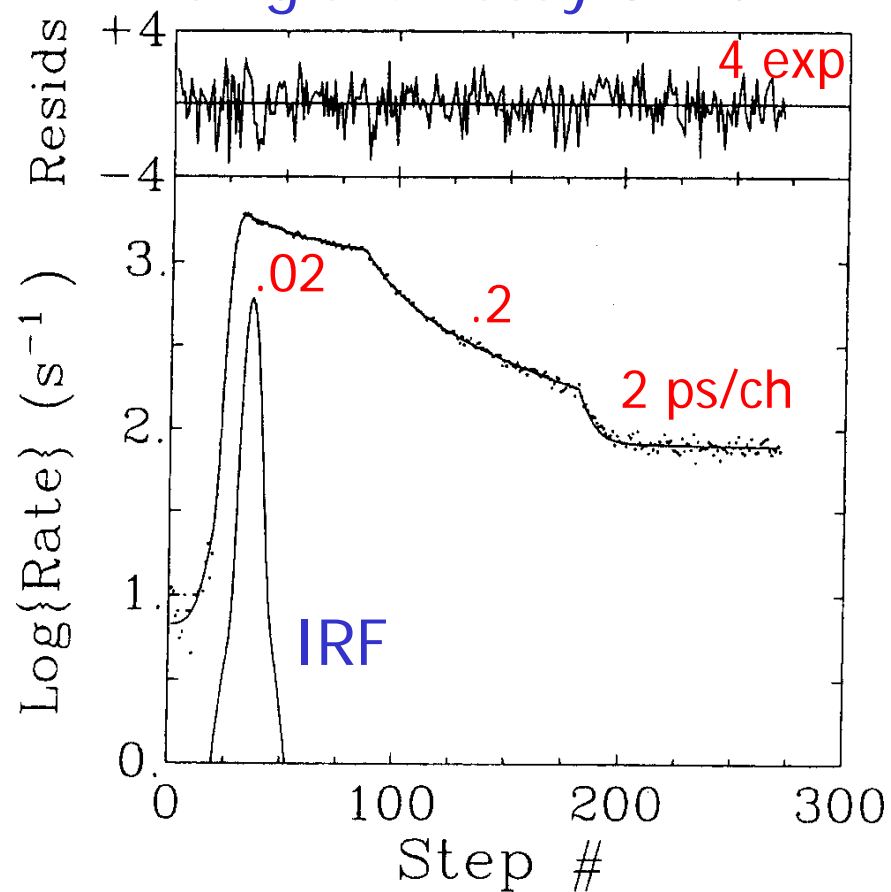
Decays Across Spectrum

λ

Frauchiger, Castner, J. Phys. Chem. B, **106** (30), 7463

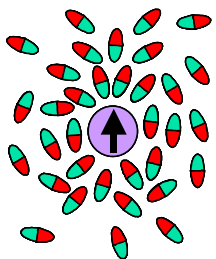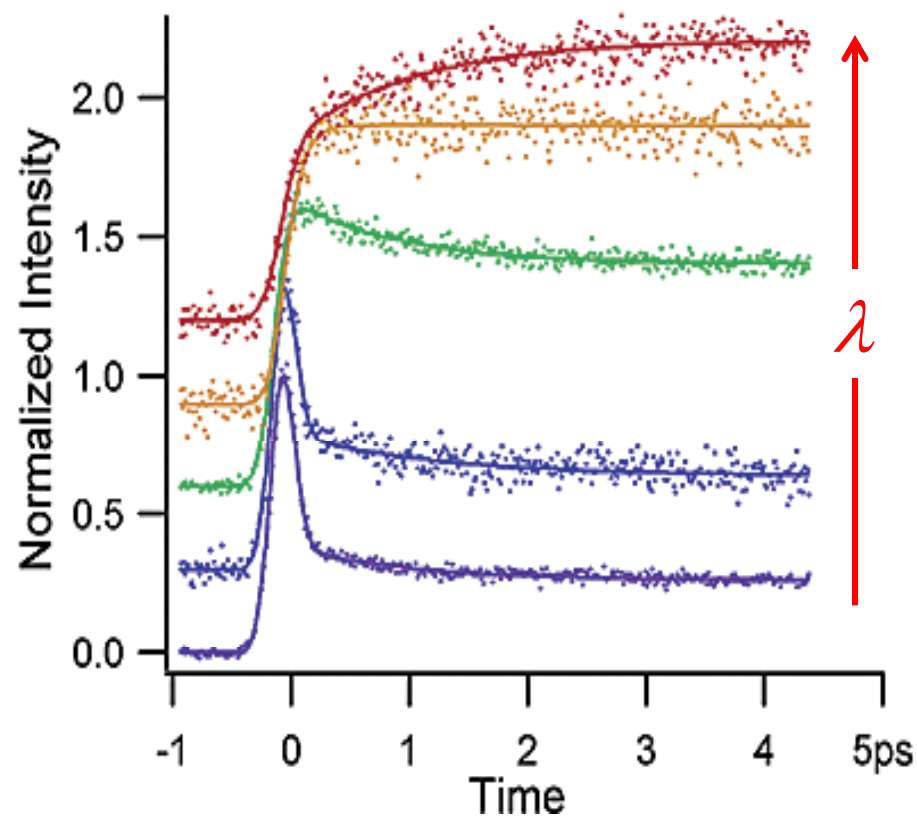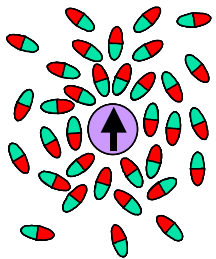# "Spectral Reconstruction" & Fitting

Normalization

$$F(\lambda_i, t) \propto \left\{ \frac{F_{SS}(\lambda_i)}{\int_0^\infty I(\lambda_i, \tau) d\tau} \right\} I(\lambda_i, t)$$
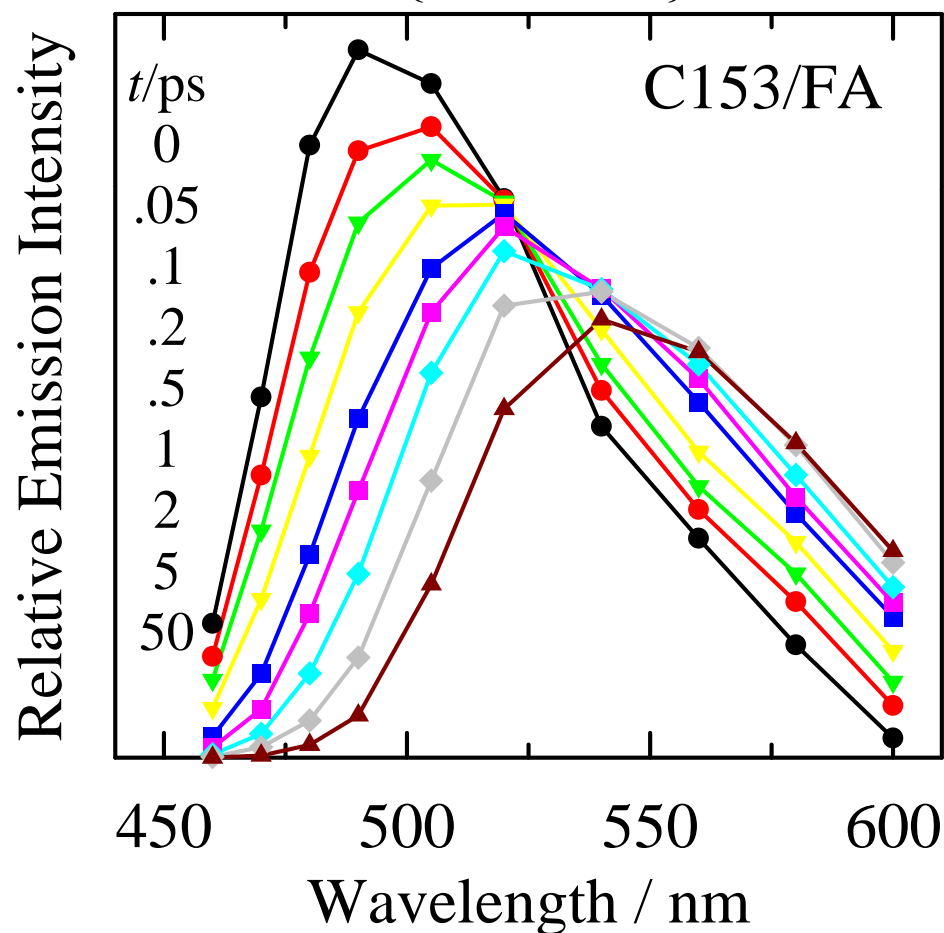
Log-Normal Fits

$$F(\nu; t) = h \begin{cases} \exp[-\ln(2)\{\ln(1+\alpha)/\gamma\}^2] & \alpha > -1 \\ 0 & \alpha \leq -1 \end{cases}$$

$$\alpha \equiv 2\gamma(\nu - \nu_p)/\Delta$$

C153/FA

t/ps
0
.05
.1
.2
.5
1
2
5
50

Relative Emission Intensity

Wavelength / nm

(B)

Frequency (10^3 cm^{-1})
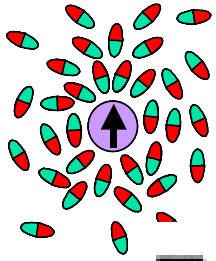
Broadband Upconversion
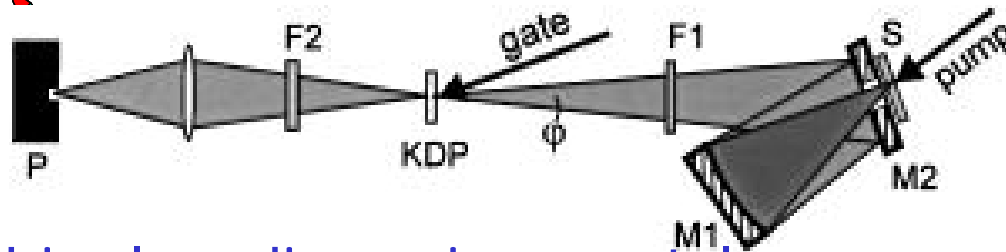
- thin, low dispersion crystal (100μ KDP)
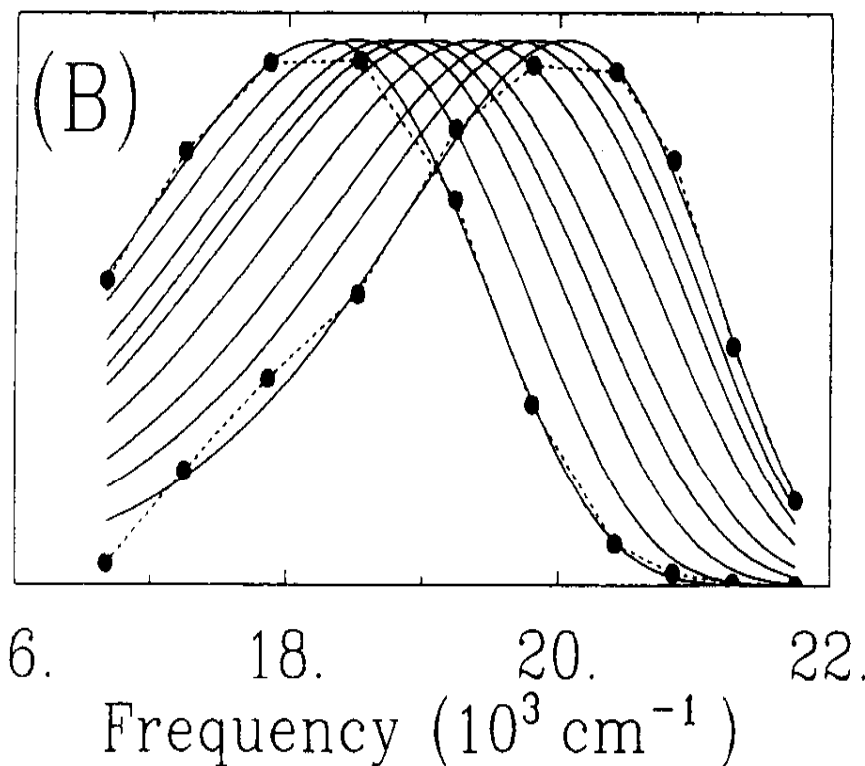- gate at long λ = 1300 nm (Cr: Forsterite laser)
- amplified pulses required
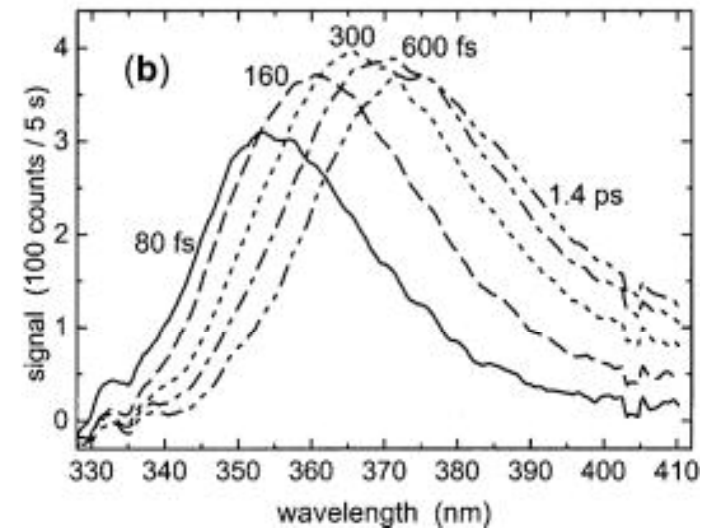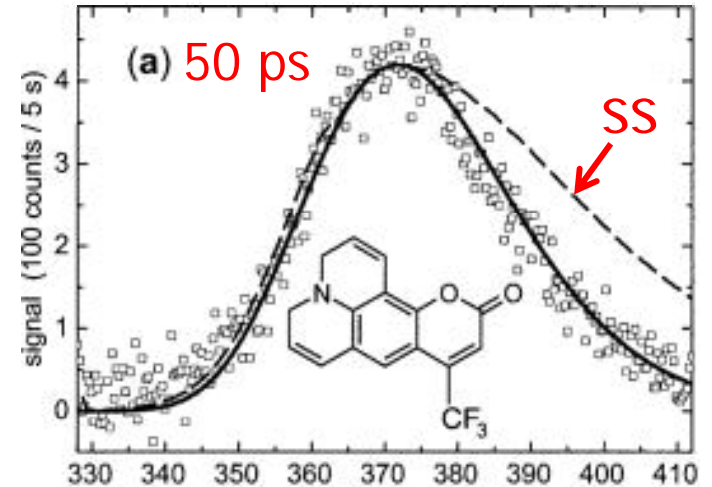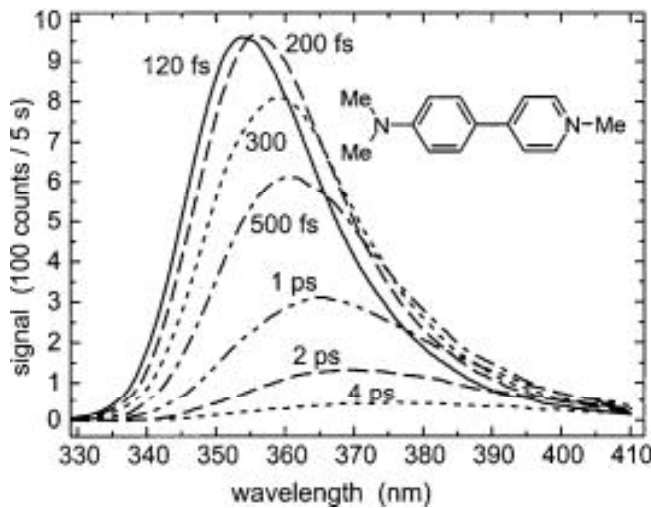
Schanz,... Ernsting, Appl. Phys. Lett. 79, 566 (2001).
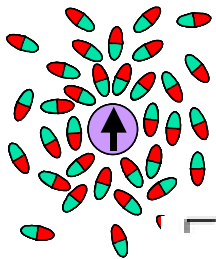
"FLUPS" (FLuorescence UPconversion Spectroscopy)

- pulse tilting
- nearly dispersion-free collection
- prism based spectrograph
- 80 fs IRF, 10,000 cm^{-1} range
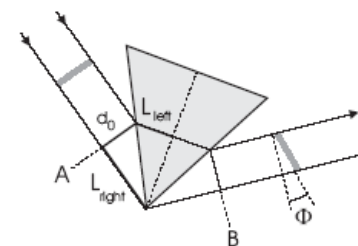
Zhao, ...Ernsting, Phys. Chem. Chem. Phys. **7**, 1716 (2005)
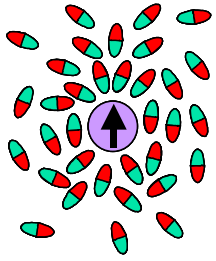
Kerr-Gated Emission Spectroscopy

45° gate pulse

emission

0°

Kerr medium

90°

gated emission
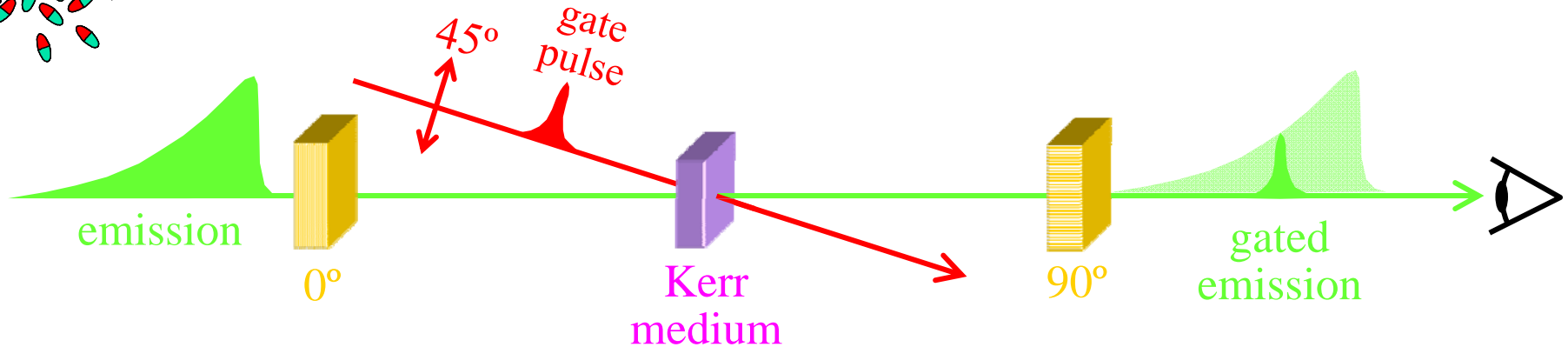
- 1969 Duguay & Hansen
  1970 Rentzepis & Co. } 1st reports
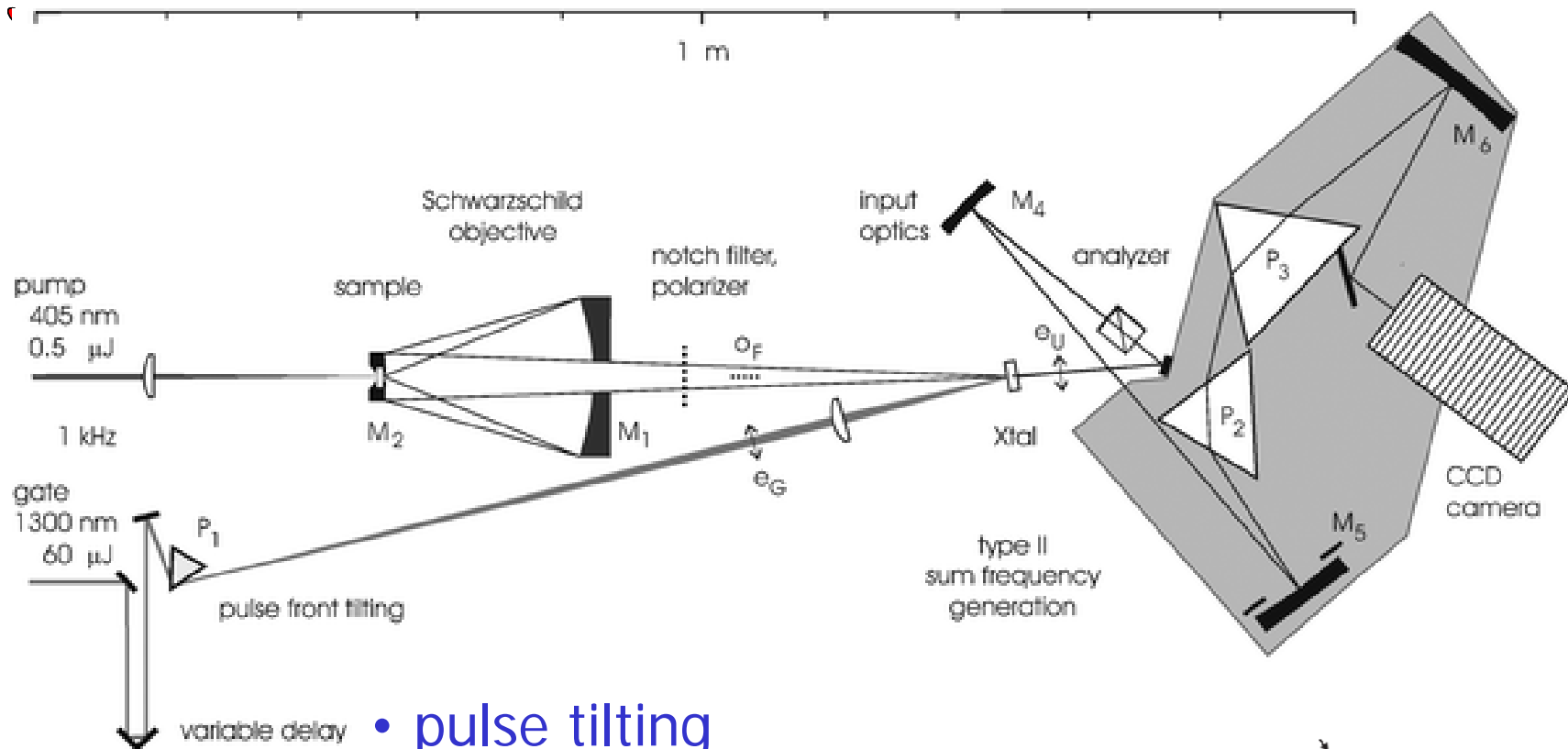
- 1987 Rulliere & Co.   "ps fluorimeter" ($\delta t \sim 25$ ps)

- 2000 Kanematsu & Co.
- 2000 Takeda *et al*.   } recent versions using optical
- 2003 Schmidt *et al*.   glasses & crystals; $\delta t < 200$ fs

- 2002 Matousek *et al*.   Raman spectroscopy

KGE Spectrometer
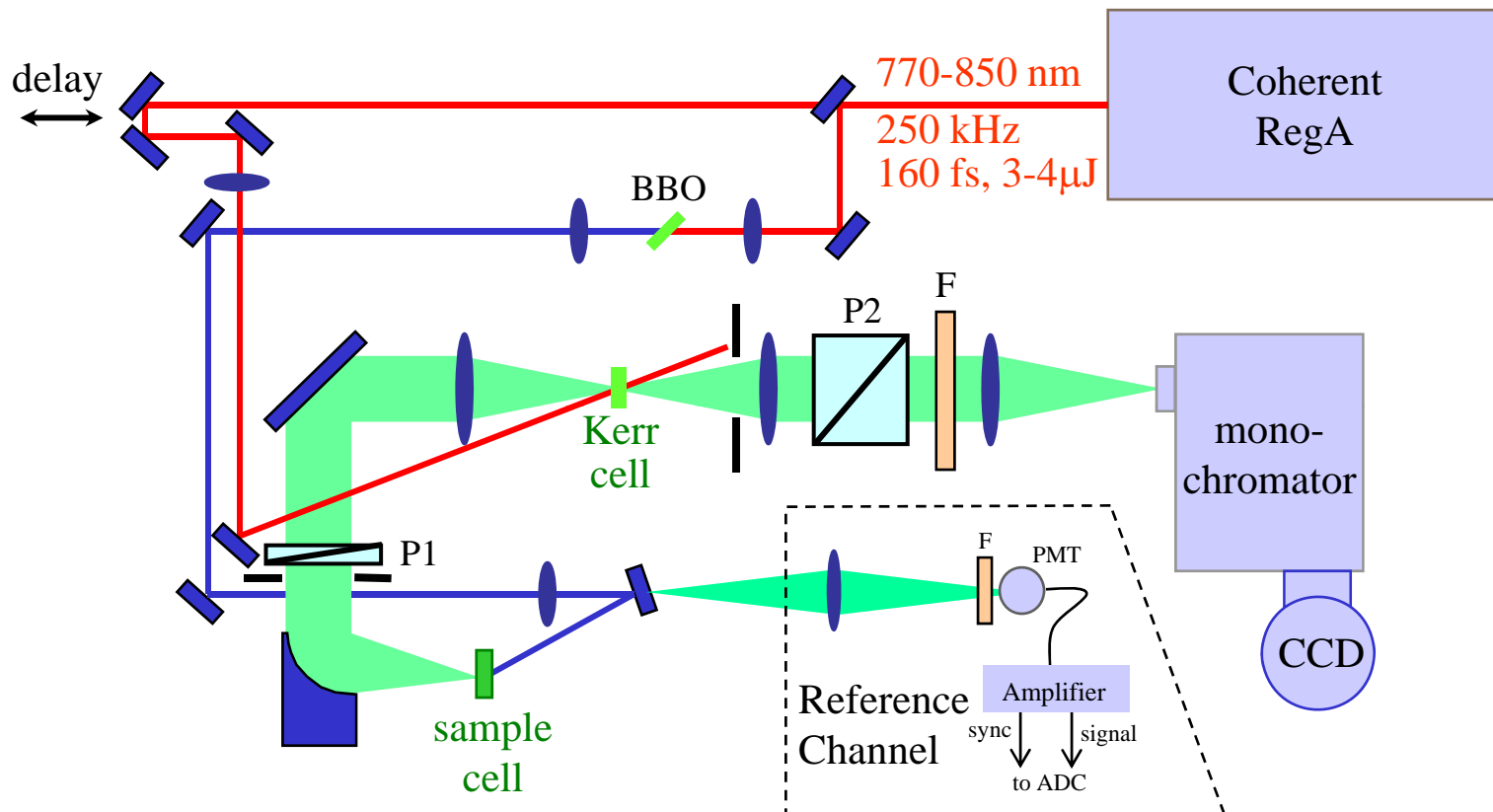
- tuned for ns lifetime solutes
- 1 mm benzene Kerr medium

Arzhantsev & Maroncelli, Appl. Spectroscop. **59**, 206 (2005).

Limitations of KGE

IRF limited ~200 fs

Long τ_{fl} Challenging

fused silica

< 300 fs

benzene

450 fs

Relative Intensity

Time / ps

C153
τ_{fl}=6 ns
$t>0$ $t<0$
signal

DCS
0.6 ns

Relative Intensity

Wavelength / nm
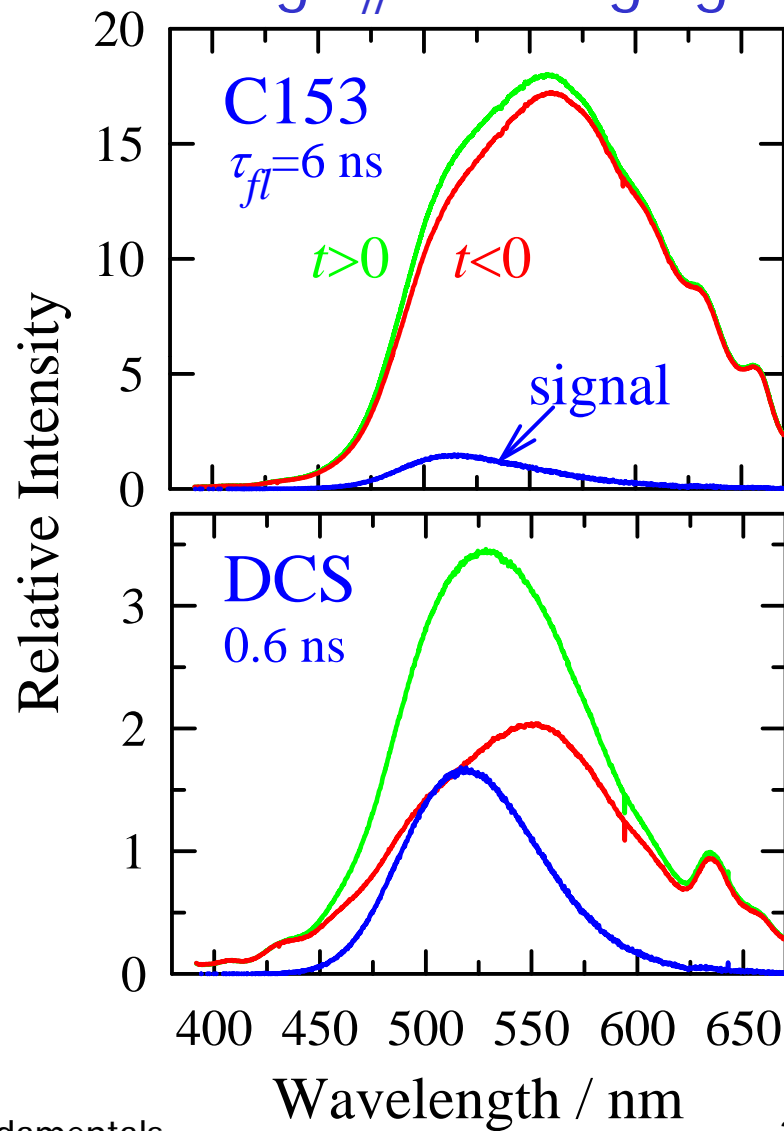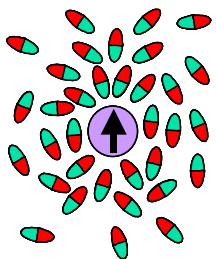
Performance Comparisons

C153/acetone

"Raw" Spectra

After Fitting

Relative Intensity

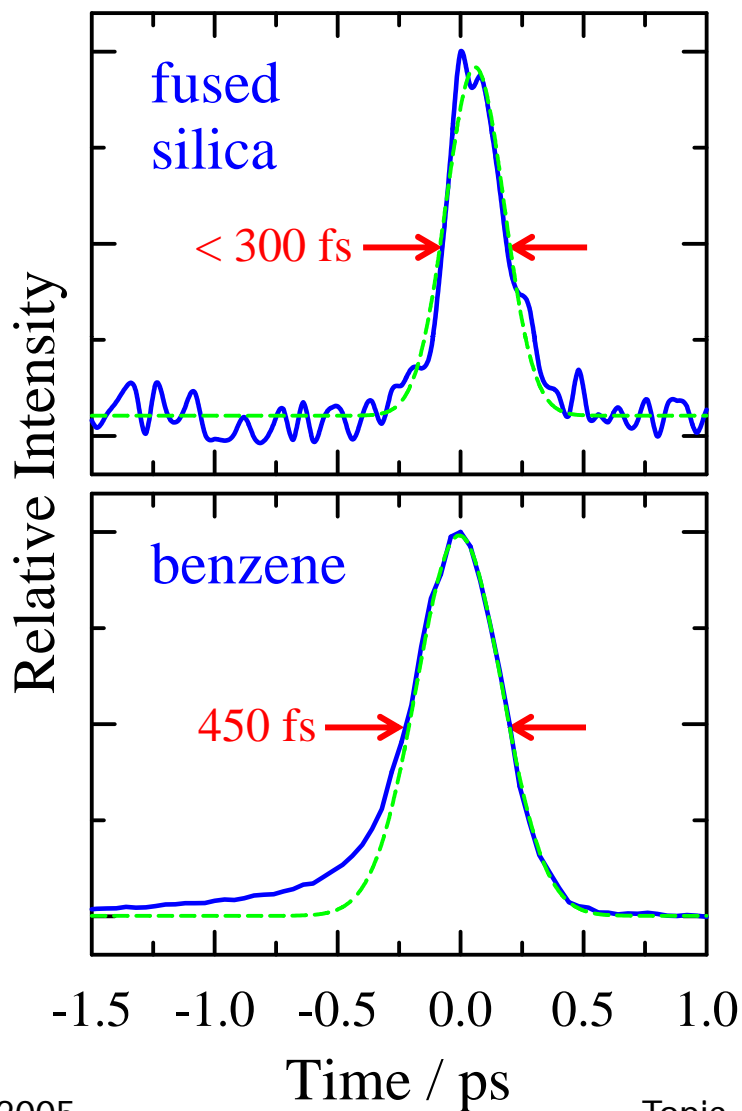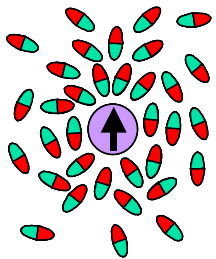Frequency / 10^3 cm^{-1}

16 17 18 19 20 21 22 23

t / ps
-1
-.5
-.2
0
.1
.2
.5
1
2
5
50

.05
.1
.2
.5
1
2
5
50

KGE vs Upcv

Peak Frequency ν_p / 10^3 cm^{-1}

acetone

CH$_3$CN

(ν shifted)

DMSO

Time / ps

0.0   0.5   1.0   1.5   2.0
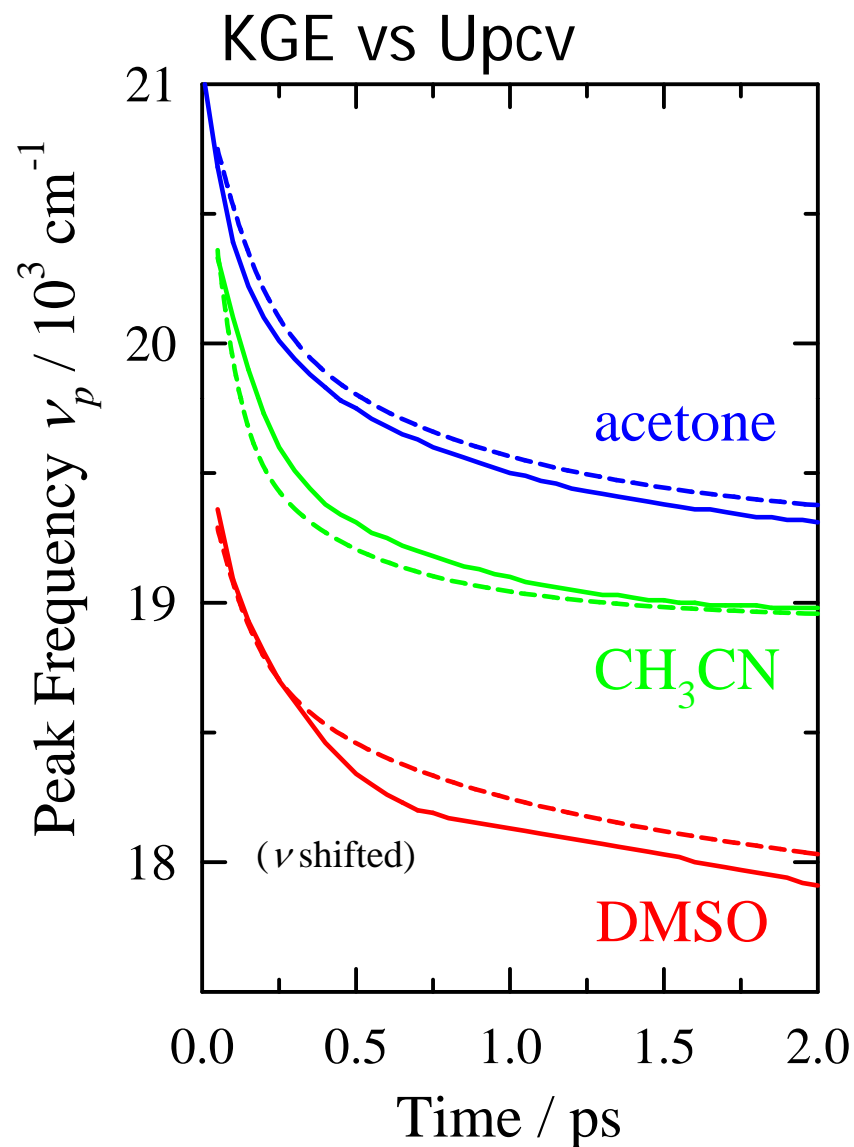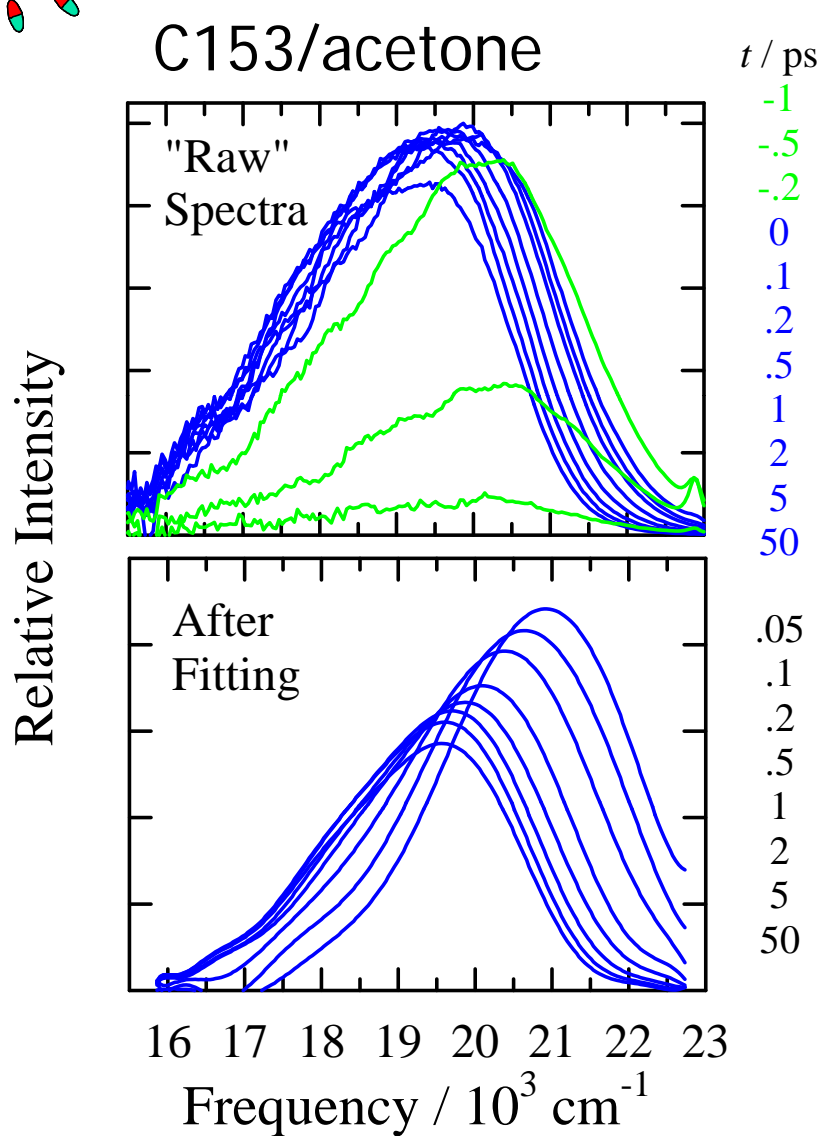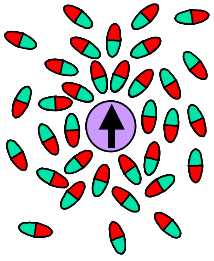
KGE current status

DCS in SC CHF$_3$ 1.6ρ_c
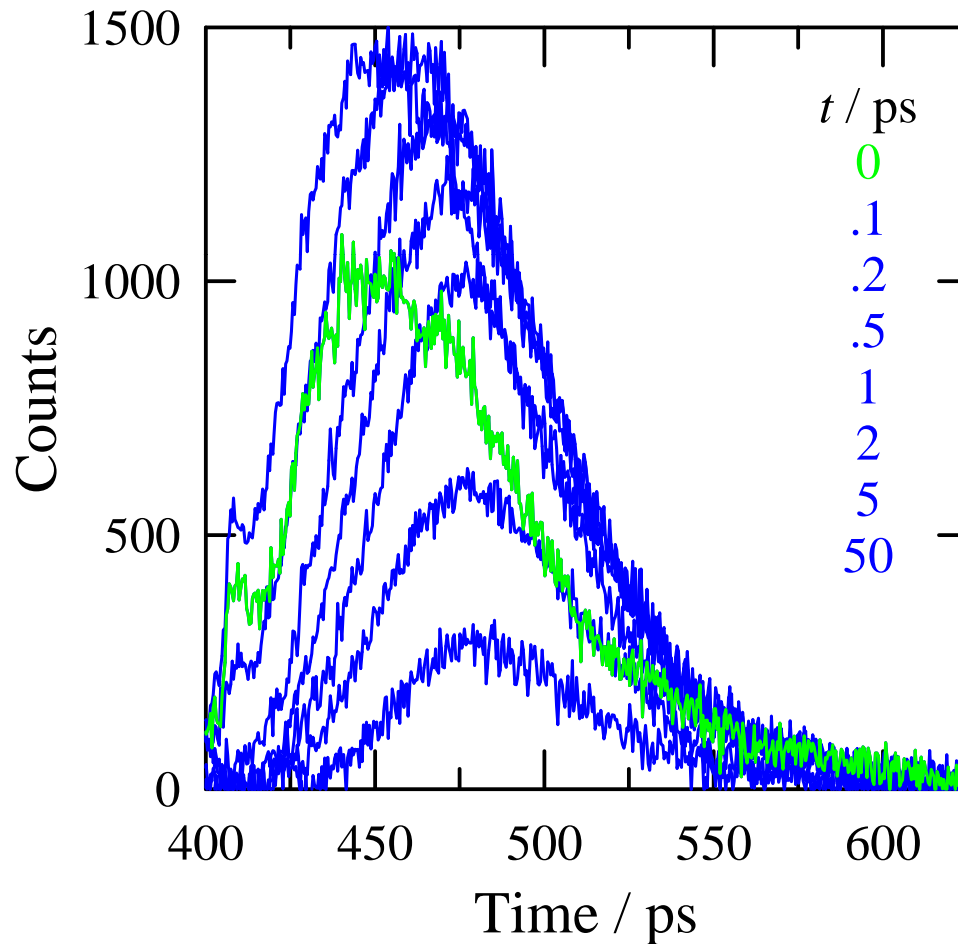
Current Performance:
+ 400-675 nm range
+ sample OD << 1

- IRF limited (450 fs)
- spectral correction large (6-fold)
- hard for τ>2 ns

Stimulated Emission (TA)

800 nm, 35 fs
180 Hz, .6mJ

540 nm
50 fs
Pump

400 nm
10 µJ

dual spectrographs
512 diode arrays
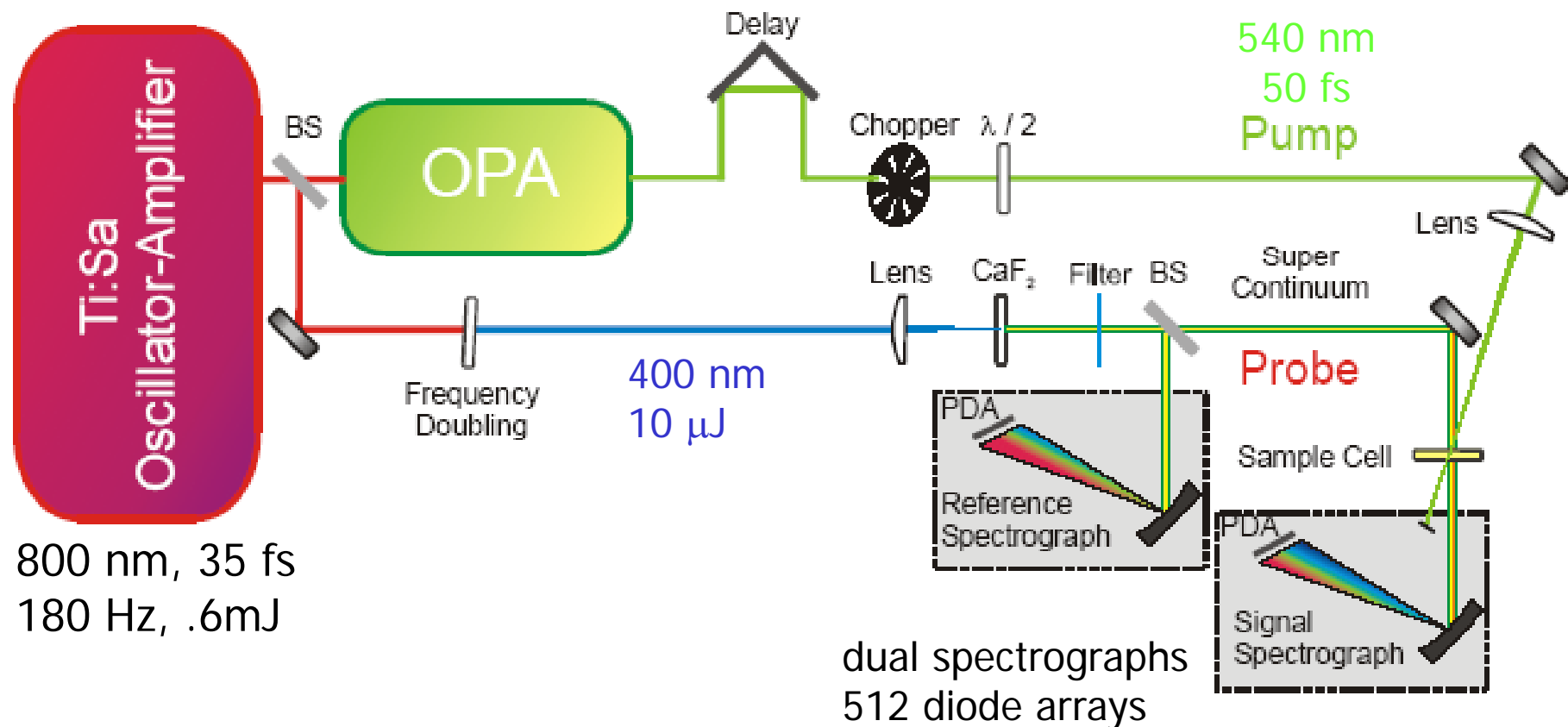
- 20 fs effective resolution

Lustres, Ernsting, Angew. Chem. **44**, 5635 (2005)
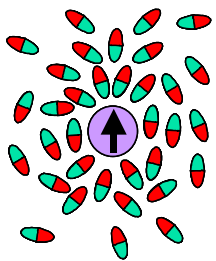
Sample data: MQ/MeOH

- easier than upconversion but signal is GSB+ESA+SE

MQ in CH_3OH

Lustres, Ernsting, Angew. Chem. **44**, 5635 (2005)

• with care SE component can be extracted

ESA

ΔOD / 10^{-3}

bleach

SE

λ / nm

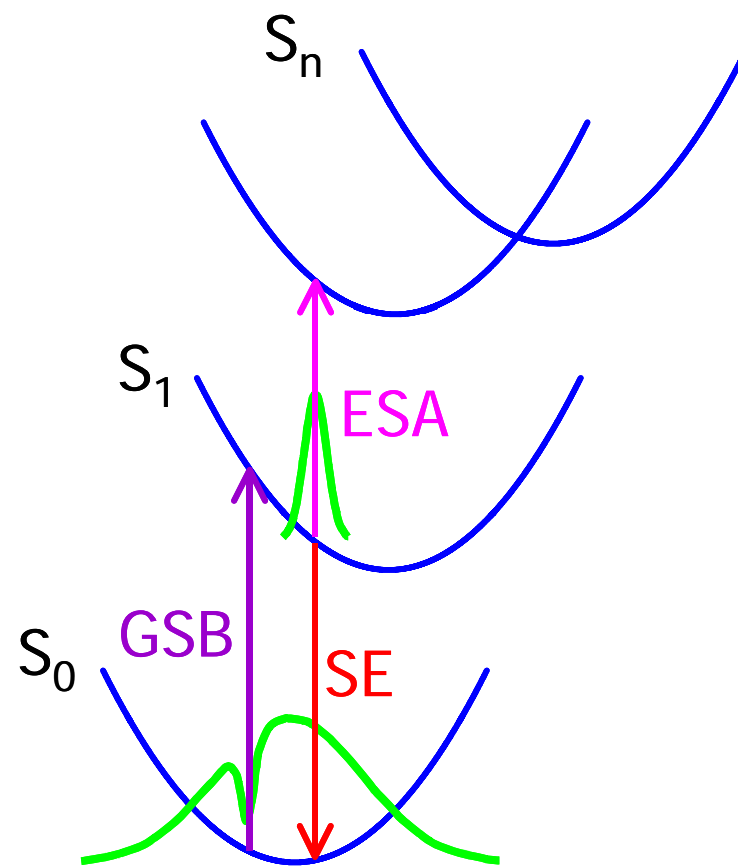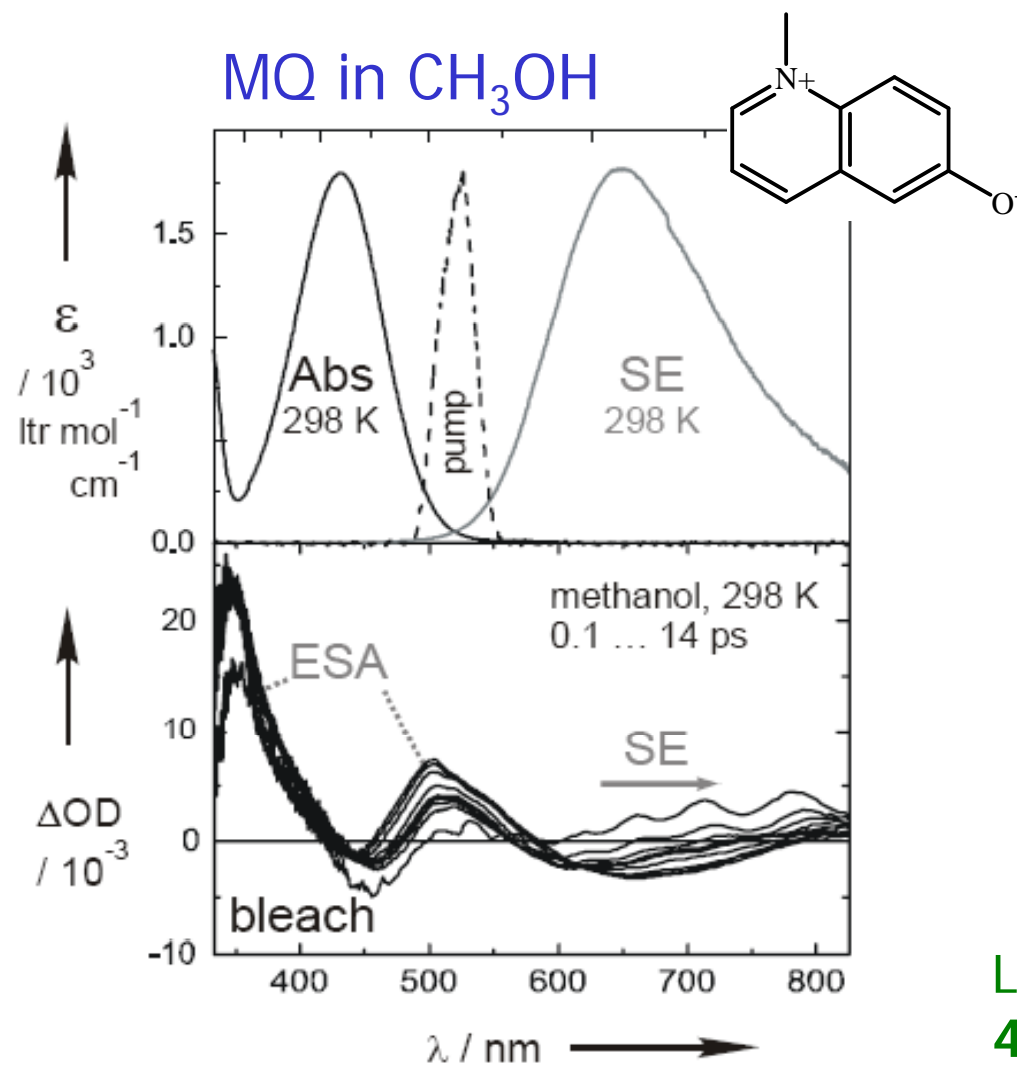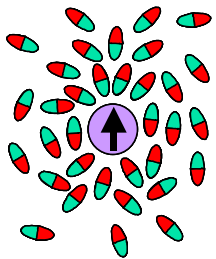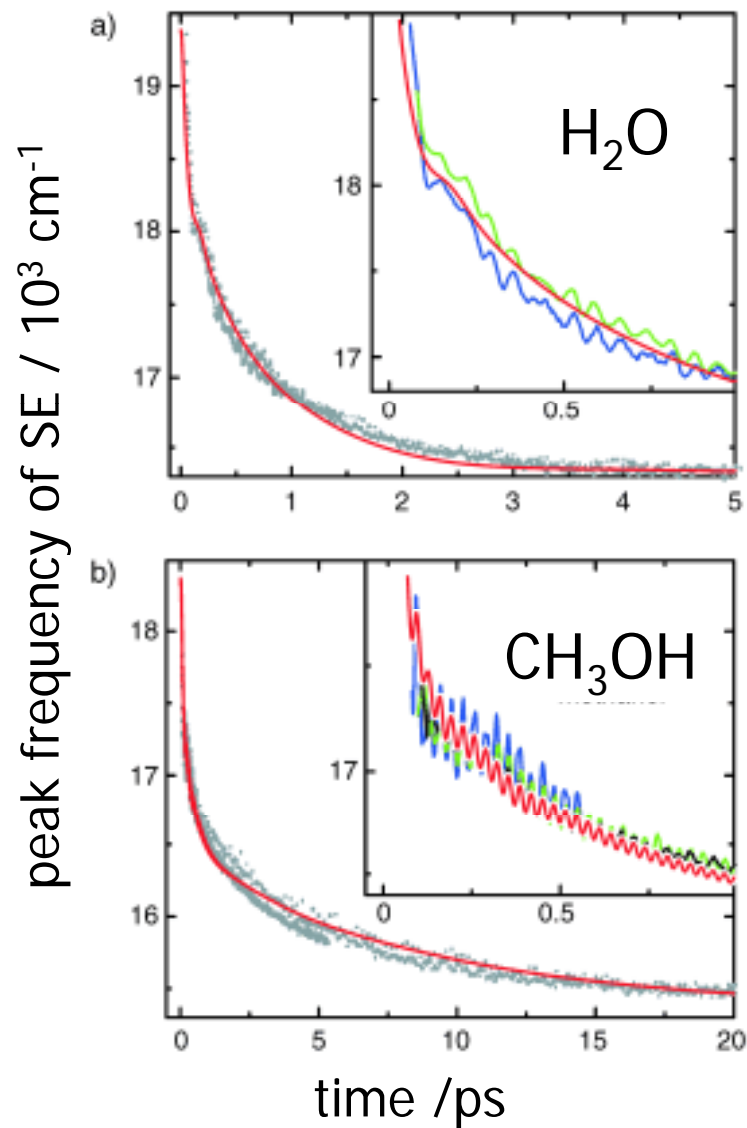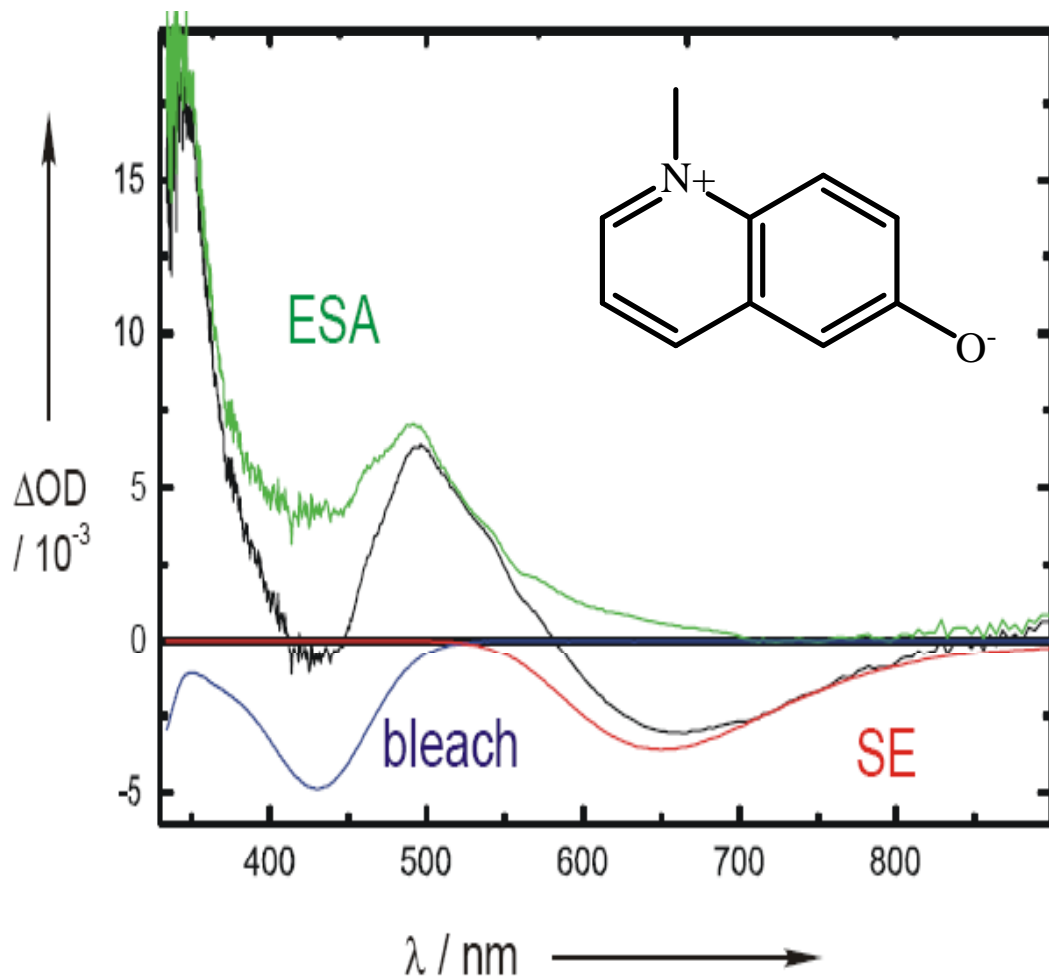peak frequency of SE / 10^3 cm^{-1}

a)

H$_2$O

b)

CH$_3$OH

time /ps
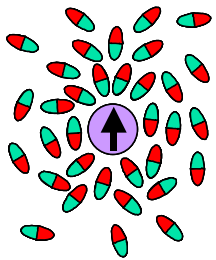
Response and Fluctuations

- $v(t)$ measures the non-equilibrium response of the solute + solvent system to perturbation caused by solute excitation

- linear response theory relates this non-equilibrium response to time-dependent fluctuations in the unperturbed system

$$\hat{H}(t) = \hat{H}_0 + V(t) \qquad V(t) = " \vec{F} \cdot \Delta \vec{\mu}(t) "$$

pert. due to
$S_0 \rightarrow S_1$ change

solvent "field"

solute change

linear solute-solvent coupling
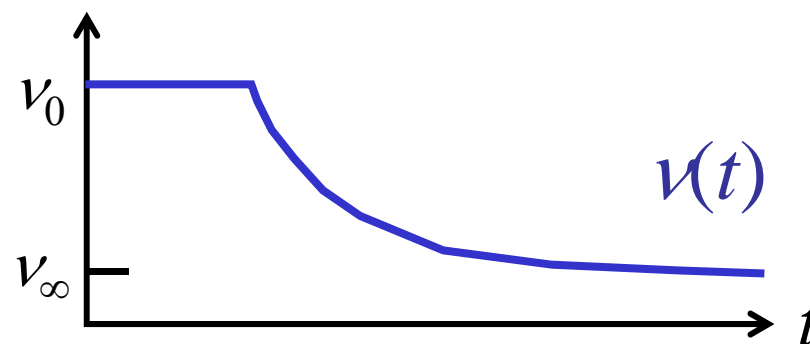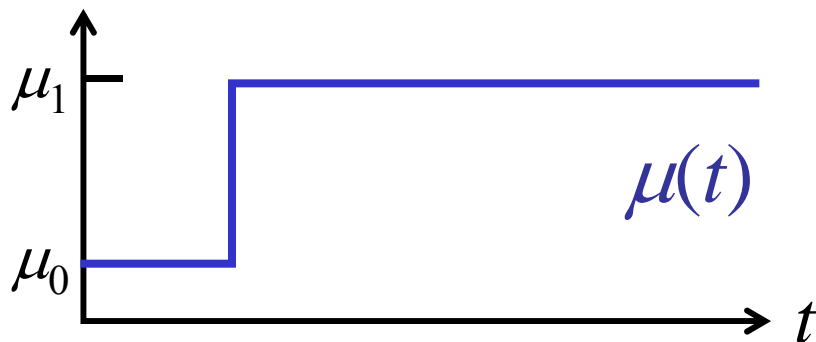
- use time-dependent perturbation theory to expand response $(v(t))$ to first order in $V(t)$
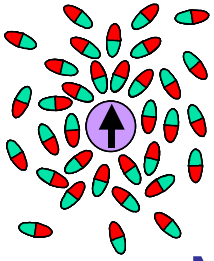
Linear Response Predictions

Non-Equilibrium Response	Equilibrium Fluctuations
$h\nu(t) = \left\langle \Delta E(t) \right\rangle_{ne}$	$h\delta\nu(t) = \Delta E(t) - \left\langle \Delta E \right\rangle_{eq}$

magni-
tude
$$\Delta\nu = \nu(0) - \nu(\infty) \quad \longleftrightarrow \quad \left\langle \delta\nu \right\rangle_{eq} / k_B T$$
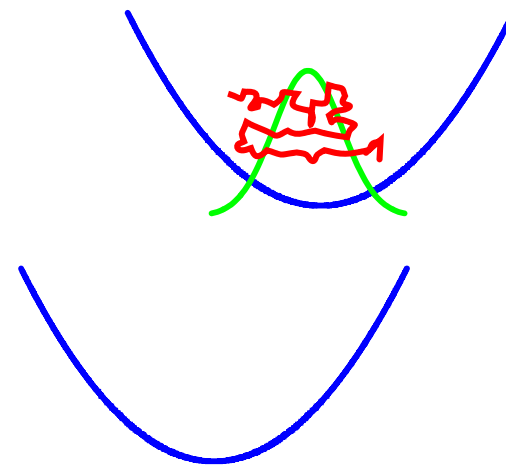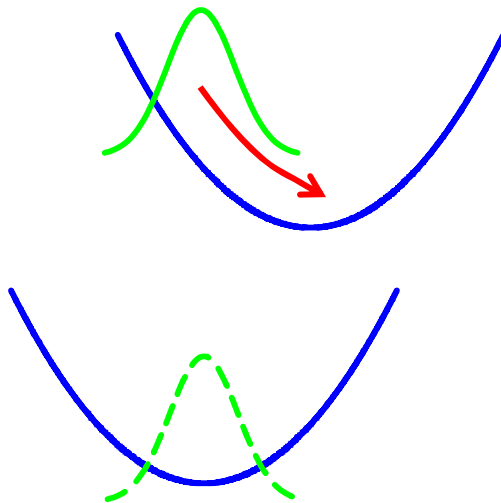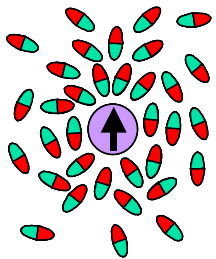
time
dep.
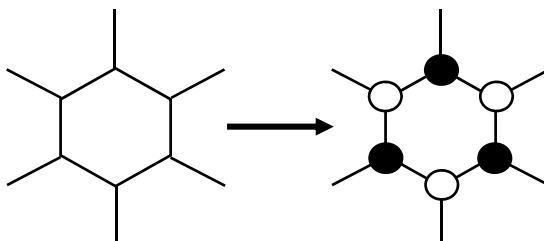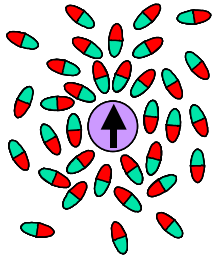$$S_\nu(t) = \{\nu(t) - \nu(\infty)\}/\Delta\nu \quad \longleftrightarrow \quad C_\nu(t) = \left\langle \delta\nu(0)\delta\nu(t) \right\rangle_{eq} \Big/ \left\langle \delta\nu \right\rangle_{eq}$$

A Simulation Example
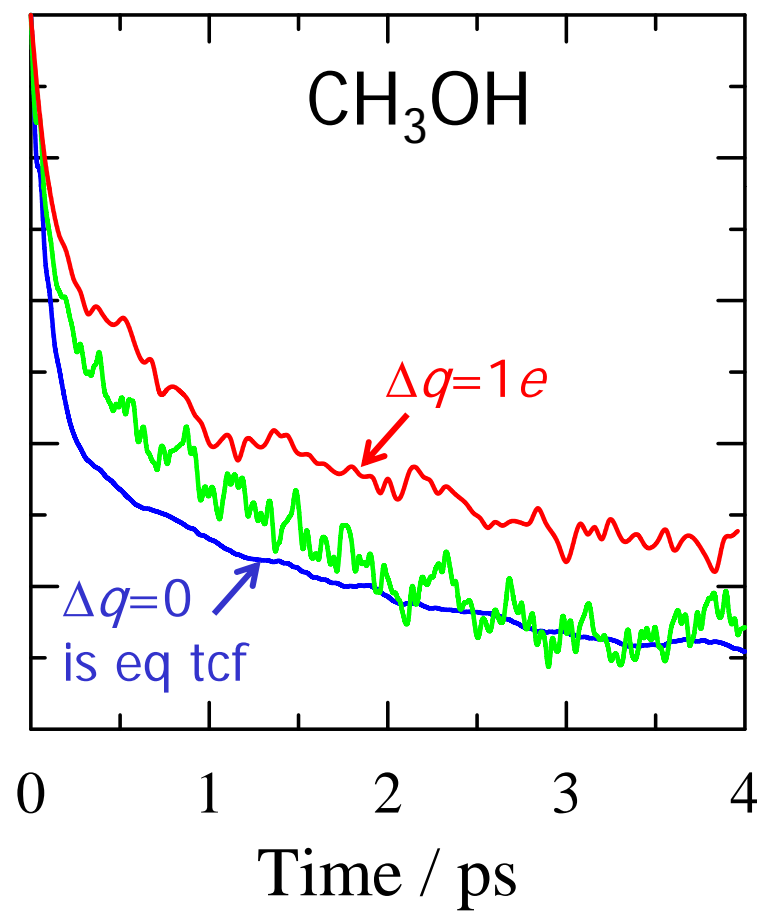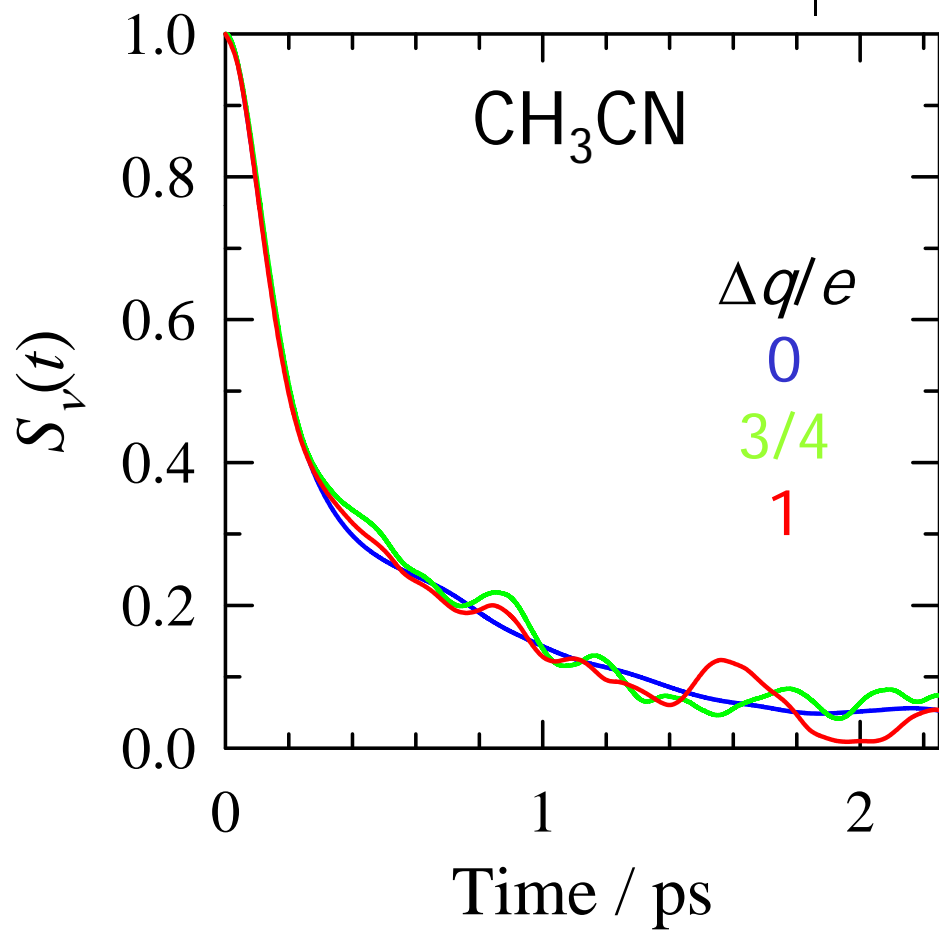
3PEPS: The Echo Idea

Fig. 1. Ray optics analogy for the three-pulse stimulated photon echo experiment. The rays represen the phase evolution of the quantum system. (*a*) After the initial pulse ($\tau = 0$), the rays fan out with slopes determined by the value of the offset from the mean frequency of individual members of the inhomogeneou distribution. The second pulse (first lens) collimates the rays by converting the superposition into a population state. The third pulse (second lens) refocuses the rays by converting the population state to the Hermitian conjugate of the first superposition state. The echo intensity is proportional to the square of the field amplitude and thus depends on the amount of constructive interference generated by the third (rephasing) pulse. For a wide inhomogeneous distribution, the constructive interference is restricted to a very short time interval at around $t = \tau$ depicted by the sharpness of focus produced by the second lens. (*b*) The disruption of the smooth phase evolution during the population period, T, and during the two coherence periods (τ and t) leads to a loss of refocusing ability. Thus, by recording the photon echo as a function of the population period, the fluctuations in the inhomogeneous distribution ("spectral diffusion") can be followed.
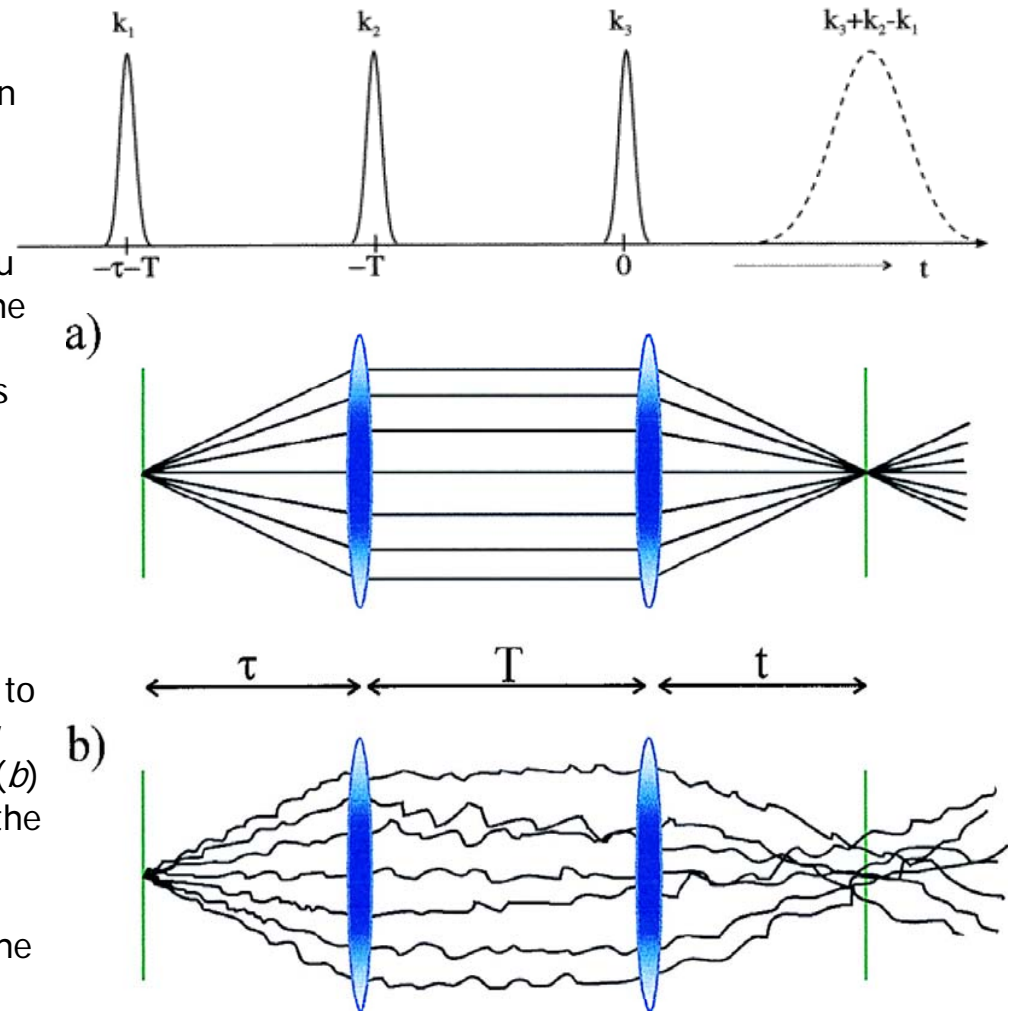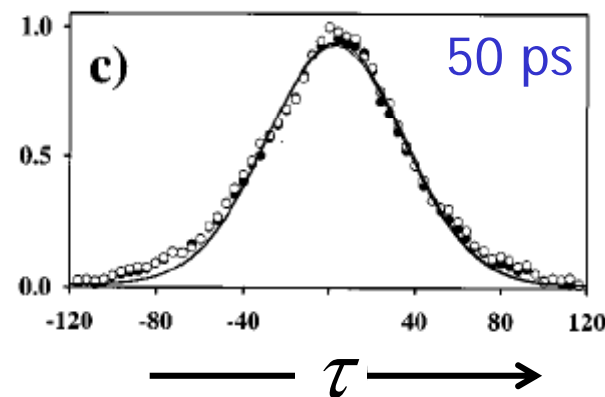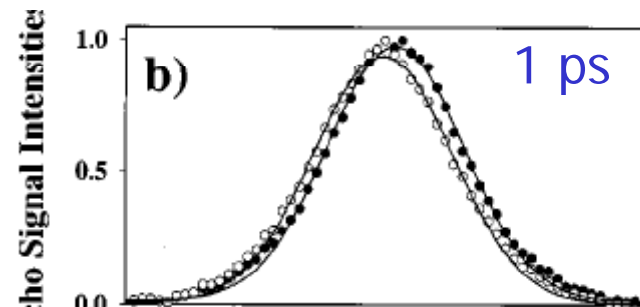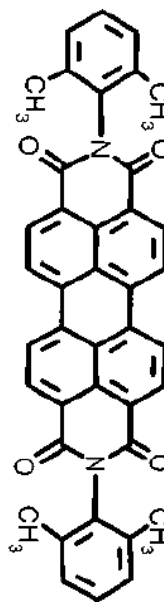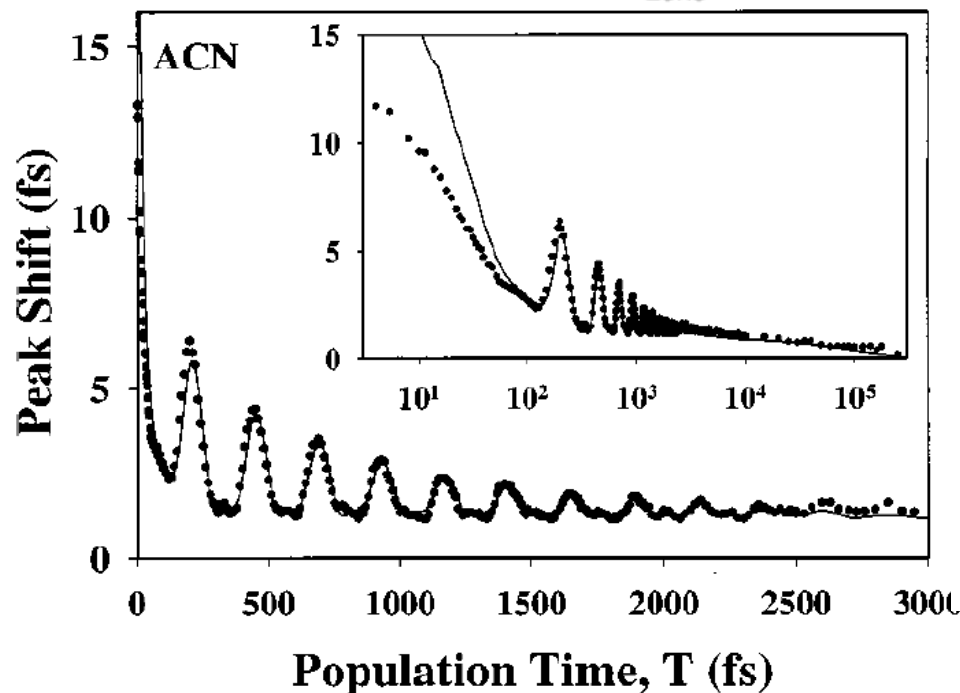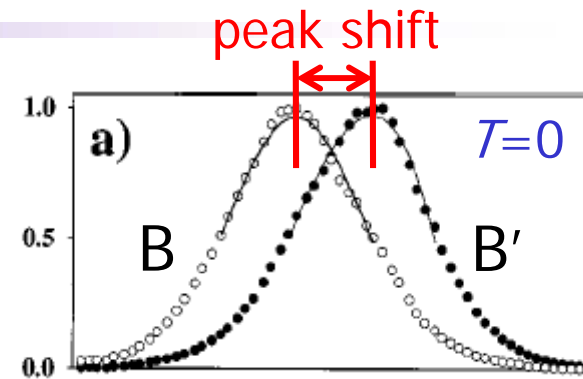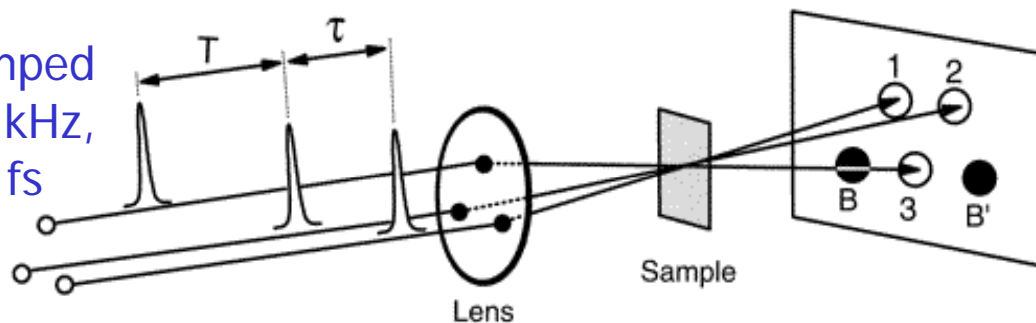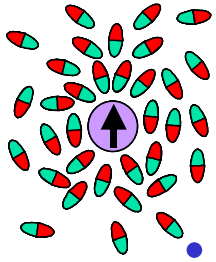
Fleming, Proc. Natl. Acad. Sci. USA **95**, 15161 (1998).
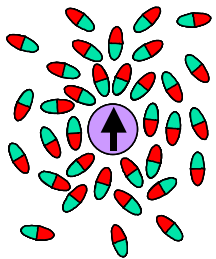
3PEPS - The Experiment

peak shift

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

B   B′   *T*=0

1 ps

50 ps

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

3PEPS - Interpretation

- peak shift $\tau^*(T)$ qualitatively like frequency tcf $M(t)$, but complex analysis required for quantitative results

$$M(t) = \frac{\langle \Delta\omega(0)\Delta\omega(t)\rangle}{\langle \Delta\omega^2\rangle}$$

$$M(t) = \lambda_g \exp[-(t/\tau_g)^2] + \sum_i \lambda_{\text{sol},i} \exp[-(t/\tau_{\text{sol},i})]$$

$$+ \sum_{i=1}^{2} \lambda_{\text{vib},i} \exp[-(t/\tau_{\text{vib},i})]\cos[\omega_{\text{vib},i}t + \phi_{\text{vib},i}]$$
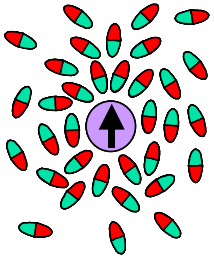
Input model M(t)
solvent + intra vib

Fit to:

$$\sigma_A(\omega) = \int_{-\infty}^{\infty} dt \, \exp[-i(\omega - \omega_{eg})t]\exp[-g(t)]$$ absorption spectrum

$$P^{(3)}(\tau, T, t') \propto \int_0^\infty dt_3' \int_0^\infty dt_2' \int_0^\infty dt_1' \sum_{i=1}^{4} R_i(t_1', t_2', t_3') \mathbf{E}_1^*(\mathbf{k}_1, t_1)\mathbf{E}_2(\mathbf{k}_2, t_2)\mathbf{E}_3(\mathbf{k}_3, t_3)$$ 3PEPS

with $R_1(=R_4) = \exp\{-g^*(t_1') + g(t_2') - g^*(t_3') - g^*(t_1' + t_2') - g(t_2' + t_3') + g^*(t_1' + t_2' + t_3')\}$
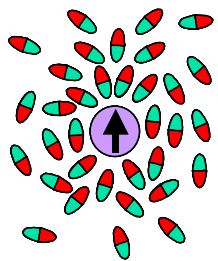
$$g_i(t) = i\lambda_i \int_0^t dt_1 \, M_i(t_1) + \langle \Delta\omega_i^2\rangle \int_0^t dt_1 \int_0^{t_1} dt_2 \, M_i(t_2)$$

Joo,...Fleming, J. Chem. Phys. 104, 6089 (1996).

Summary

- many measurement options available for both single channel and complete spectral coverage

- measuring spontaneous emission gets more difficult as IRF gets shorter

- transient absorption and 3PEPS measurements offer alternatives with very high time resolution but at the cost of added complexity of interpretation
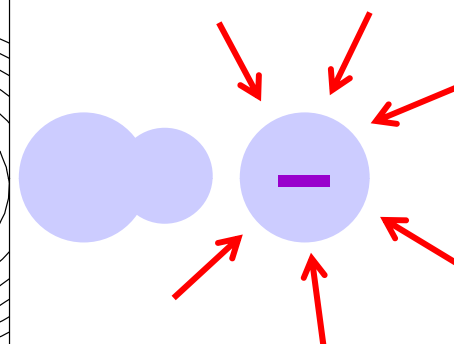
Why Solvation Dynamics?
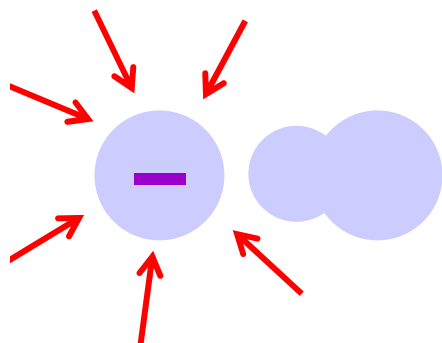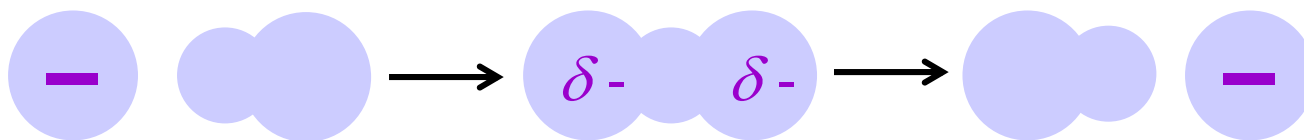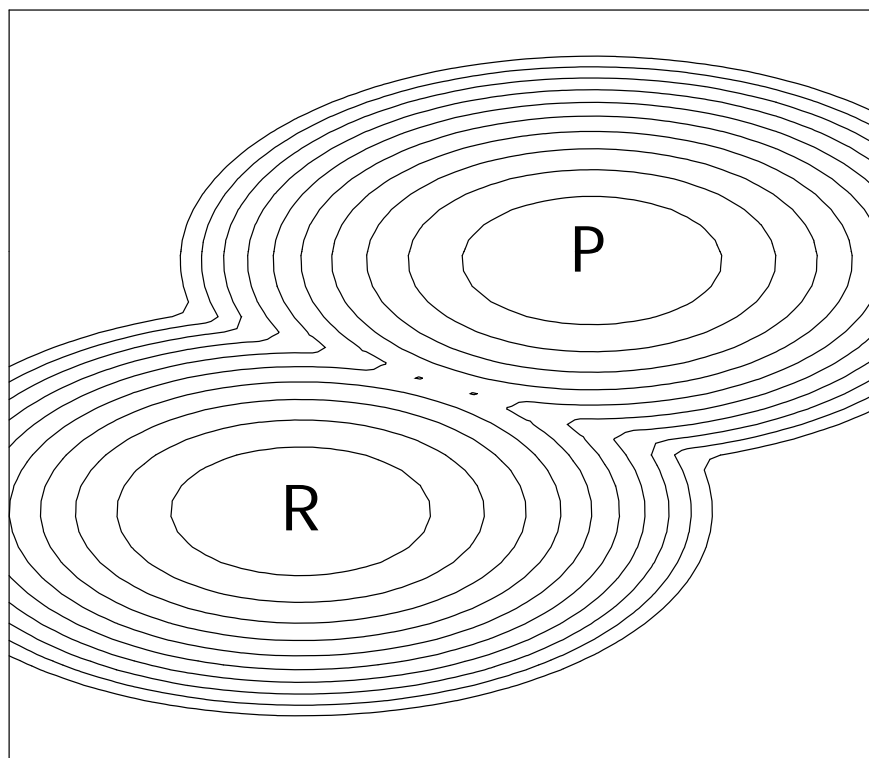
Like it or not, solvent is part of the reaction coordinate!