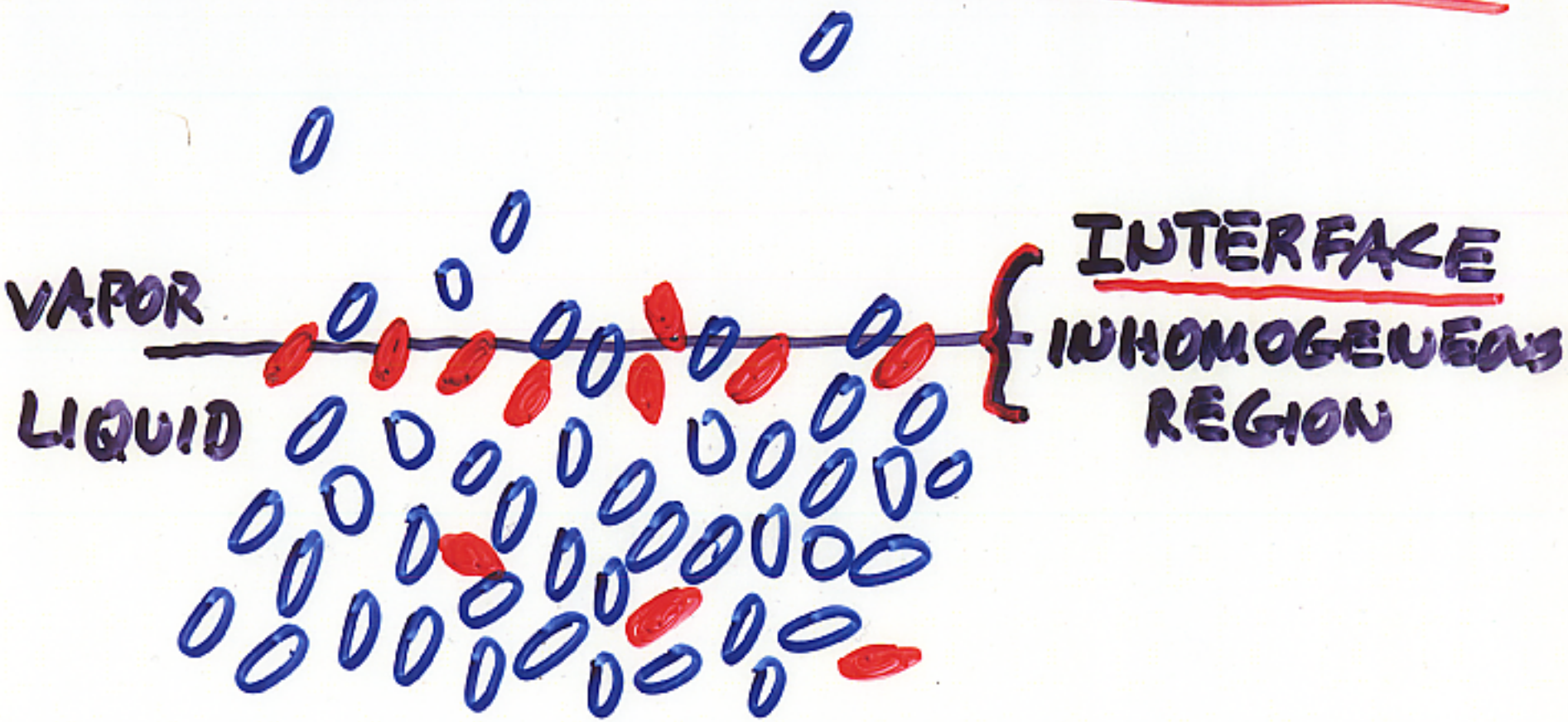
CHEMICAL AND PHYSICAL PROPERTIES OF LIQUID INTERFACES



SECOND HARMONIC GENERATION AS A SELECTIVE PROBE OF INTERFACE

SHG [redacted]: LIQ/VAPOR INTERFACE

- BINARY SOLUTIONS

- SOME ISSUES

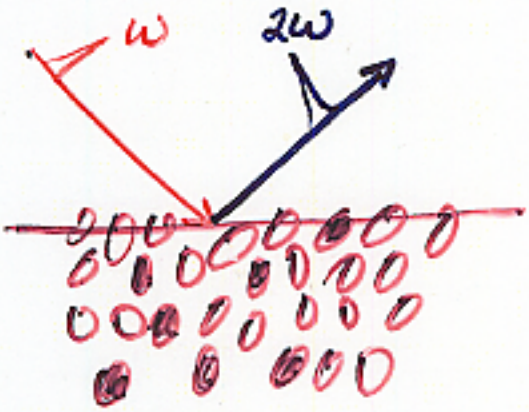
- MOLECULAR ORIENTATION
- COMPOSITION
- SPECTROSCOPY
- CHEMICAL REACTIONS
- DYNAMICS

SPECTROSCOPY OF INTERFACES

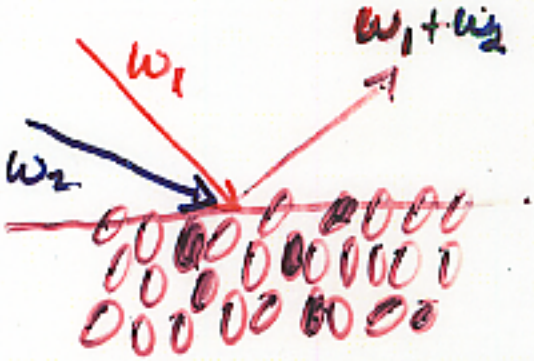
- BULK MOLECULES OVERWHELM SPECTROSCOPY OF INTERFACE MOLECULES

$\Downarrow$

- SECOND HARMONIC AND SUM FREQUENCY GENERATION ARE INTERFACE SELECTIVE METHODS



SECOND HARMONIC



SUM FREQUENCY

$$E_{\omega_1+\omega_2} \sim P_{\omega_1+\omega_2} = \chi^{(2)} E_{\omega_1} E_{\omega_2} \; ; \; \chi^{(2)} \sim N_s \langle \alpha^{(2)} \rangle_{ORIENT}$$

SYMMETRY AND SECOND HARMONIC GENERATION

CENTROSYMMETRIC SYSTEM

$\Downarrow$

INVERSION SYMMETRY

$\Downarrow$

$$P \rightarrow -P \quad ; \quad E \rightarrow -E$$

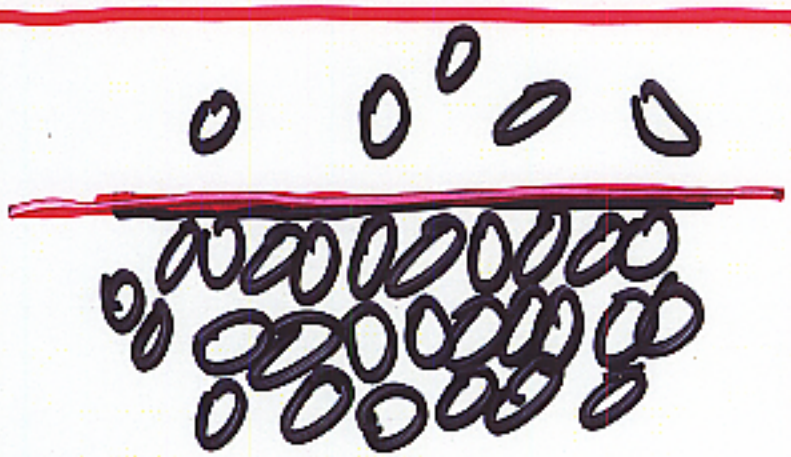
$\Downarrow$

$$P^{(2)} = \chi^{(2)} E E$$

$$-P^{(2)} = \chi^{(2)} (-E)(-E) = P^{(2)}$$

$$\therefore \quad \chi^{(2)} = 0$$

WHAT HAPPENS AT SURFACE OF CENTROSYMMETRIC MEDIUM?



INVERSION SYMMETRY IS BROKEN

$\therefore \chi^{(2)} \neq 0$ BY SYMMETRY

$\Downarrow$

SHG SURFACE SENSITIVE TOO

$\Downarrow$

STUDIES OF

SOLID SURFACES

ADSORBATES ON SOLIDS

ELECTRODE

SURFACTANTS ON LIQUIDS

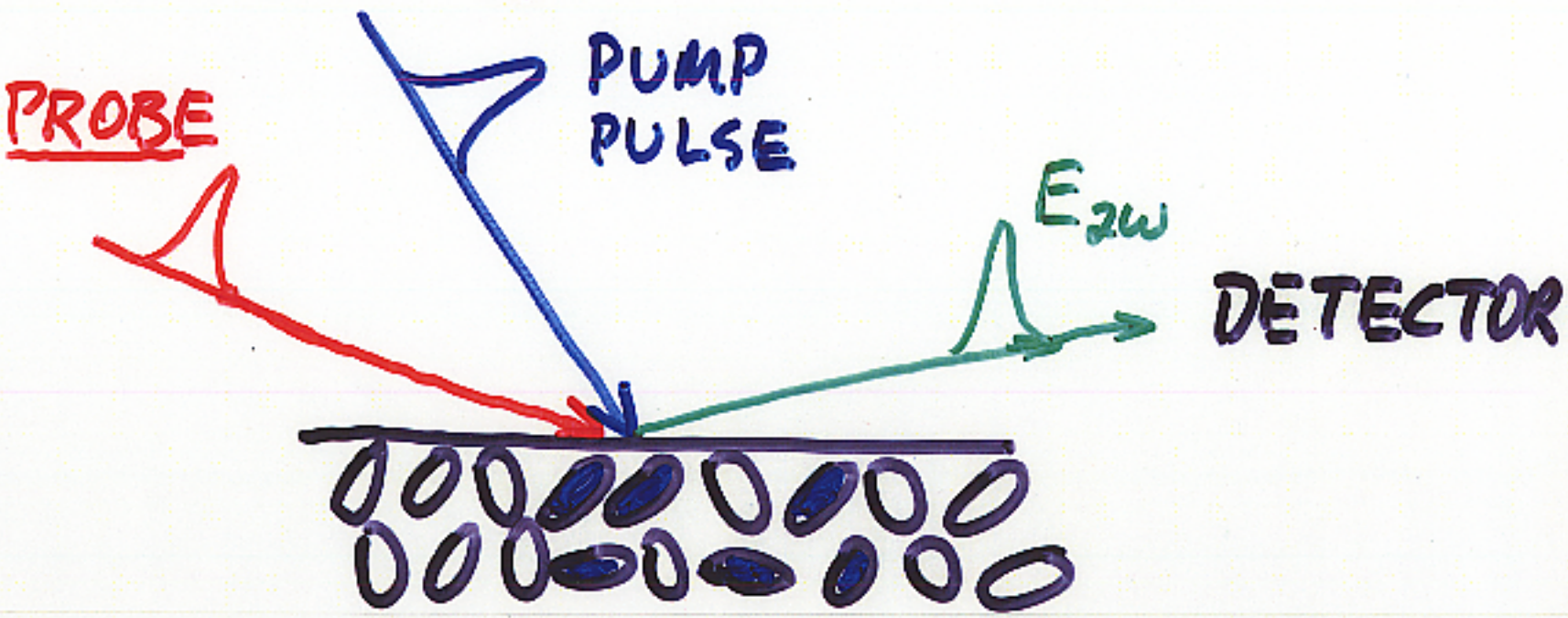
METHOD TO STUDY INTERFACE DYNAMICS

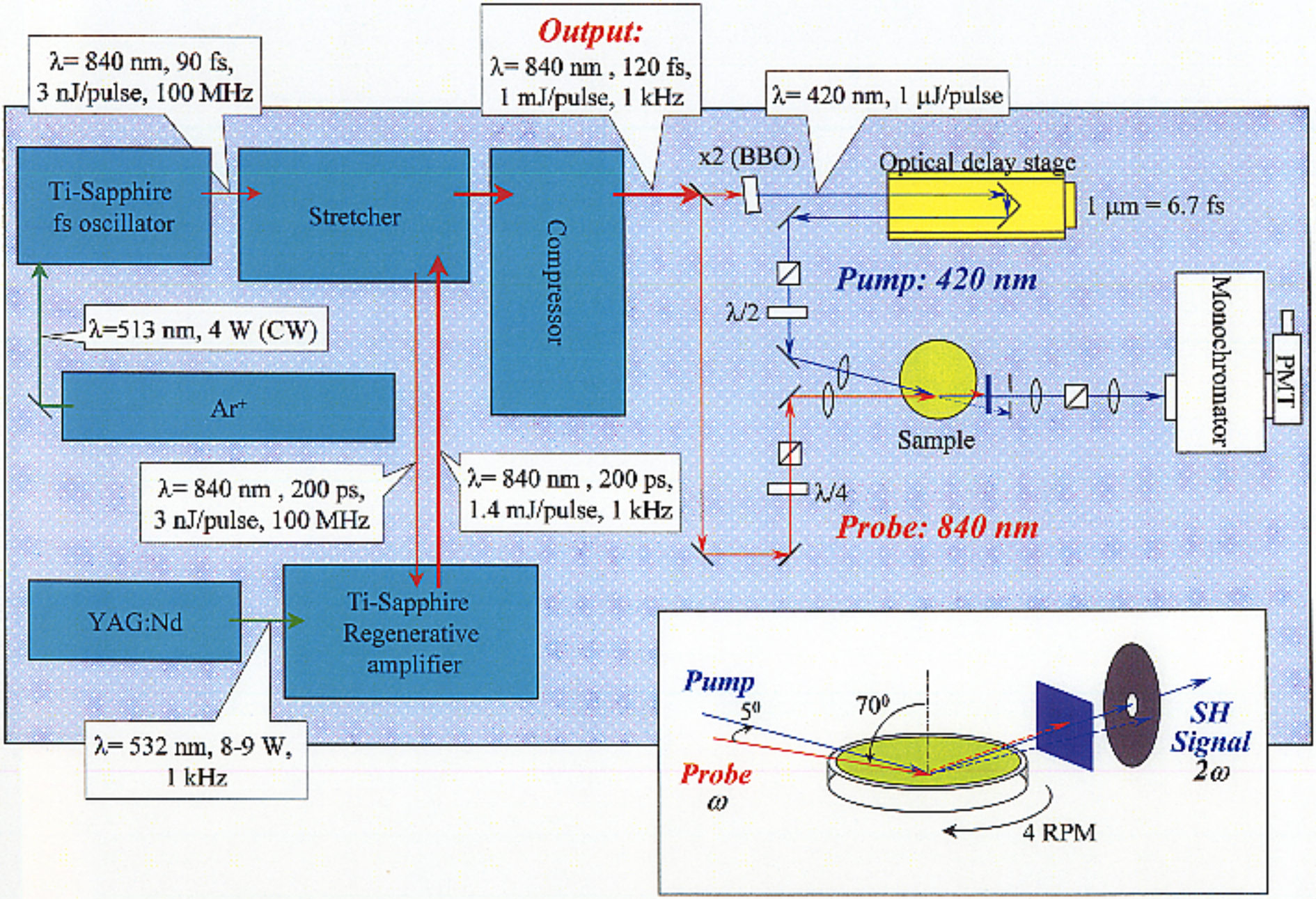
PERTURB SYSTEM WITH A PUMP PULSE

⇓

MONITOR DYNAMICS BY SECOND HARMONIC GENERATION WITH A TIME-DELAYED PROBE PULSE

⇓

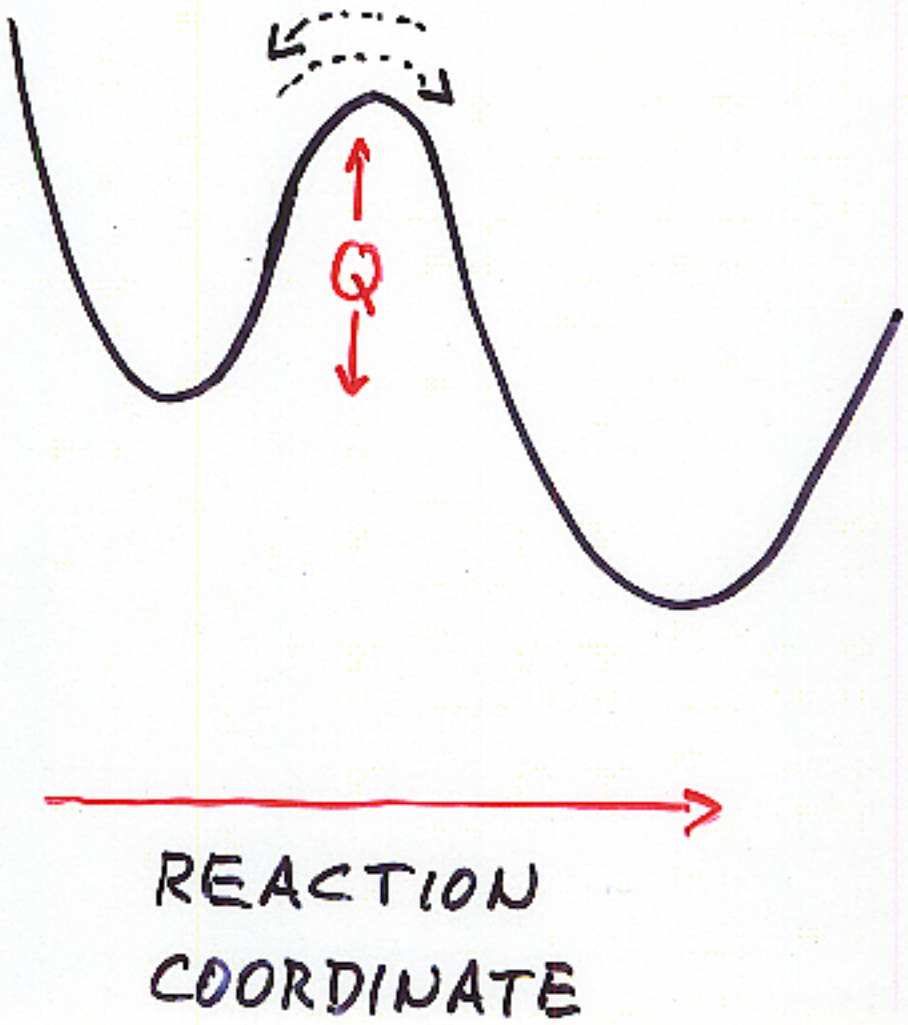



λ= 840 nm, 90 fs,
3 nJ/pulse, 100 MHz
Output:
λ= 840 nm , 120 fs,
1 mJ/pulse, 1 kHz
λ= 420 nm, 1 μJ/pulse
Ti-Sapphire
fs oscillator
Stretcher
Compressor
x2 (BBO)
Optical delay stage
1 μm = 6.7 fs
Pump: 420 nm
λ/2
λ=513 nm, 4 W (CW)
Ar+
Monochromator
PMT
Sample
λ/4
Probe: 840 nm
λ= 840 nm , 200 ps,
3 nJ/pulse, 100 MHz
λ= 840 nm , 200 ps,
1.4 mJ/pulse, 1 kHz
YAG:Nd
Ti-Sapphire
Regenerative
amplifier
λ= 532 nm, 8-9 W,
1 kHz
Pump
5⁰
70⁰
Probe
ω
SH
Signal
2ω
4 RPM

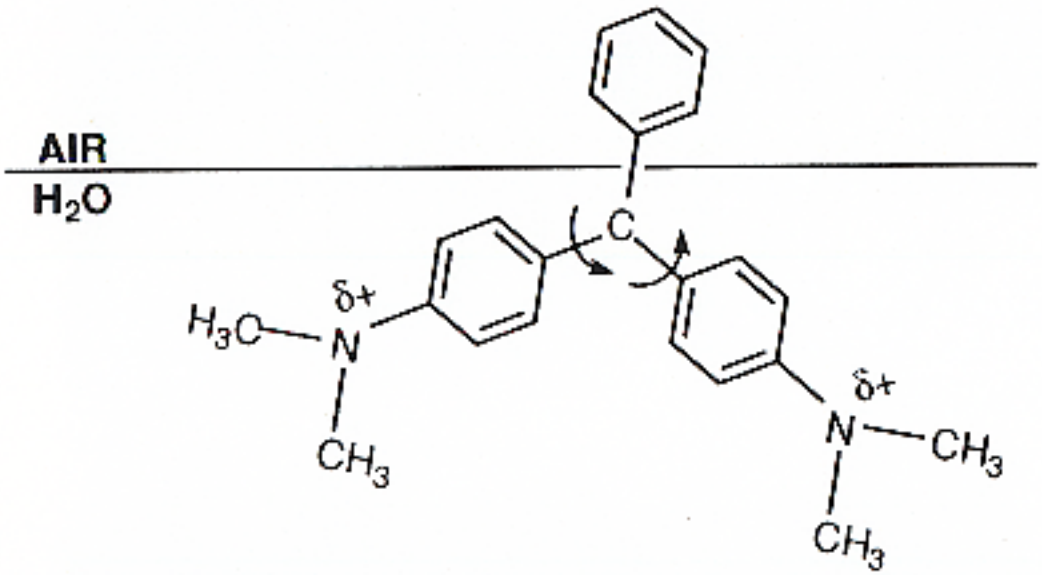
ROLE OF SOLVENT IN CHEMICAL REACTIONS

⇓

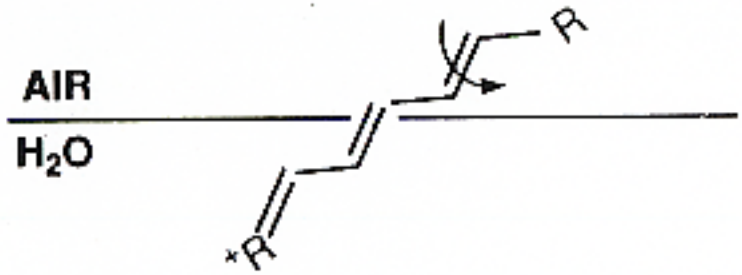
BARRIER CROSSING MODEL



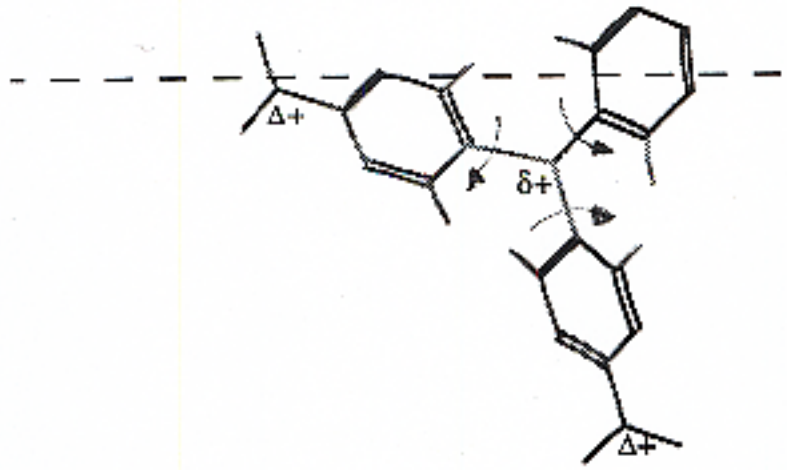
ISOMERIZATION MOTIONS AT AIR/H_2O INTERFACE

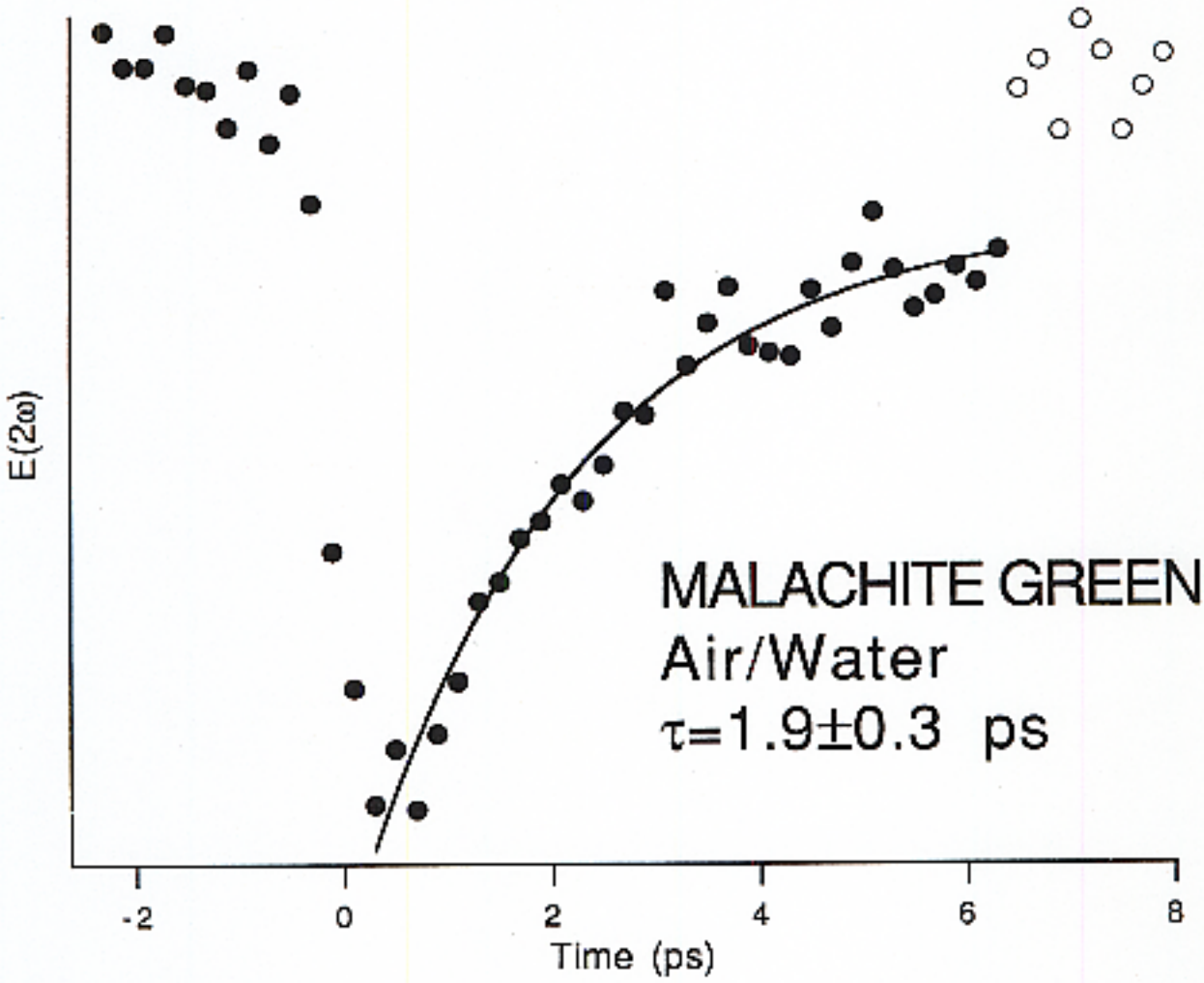


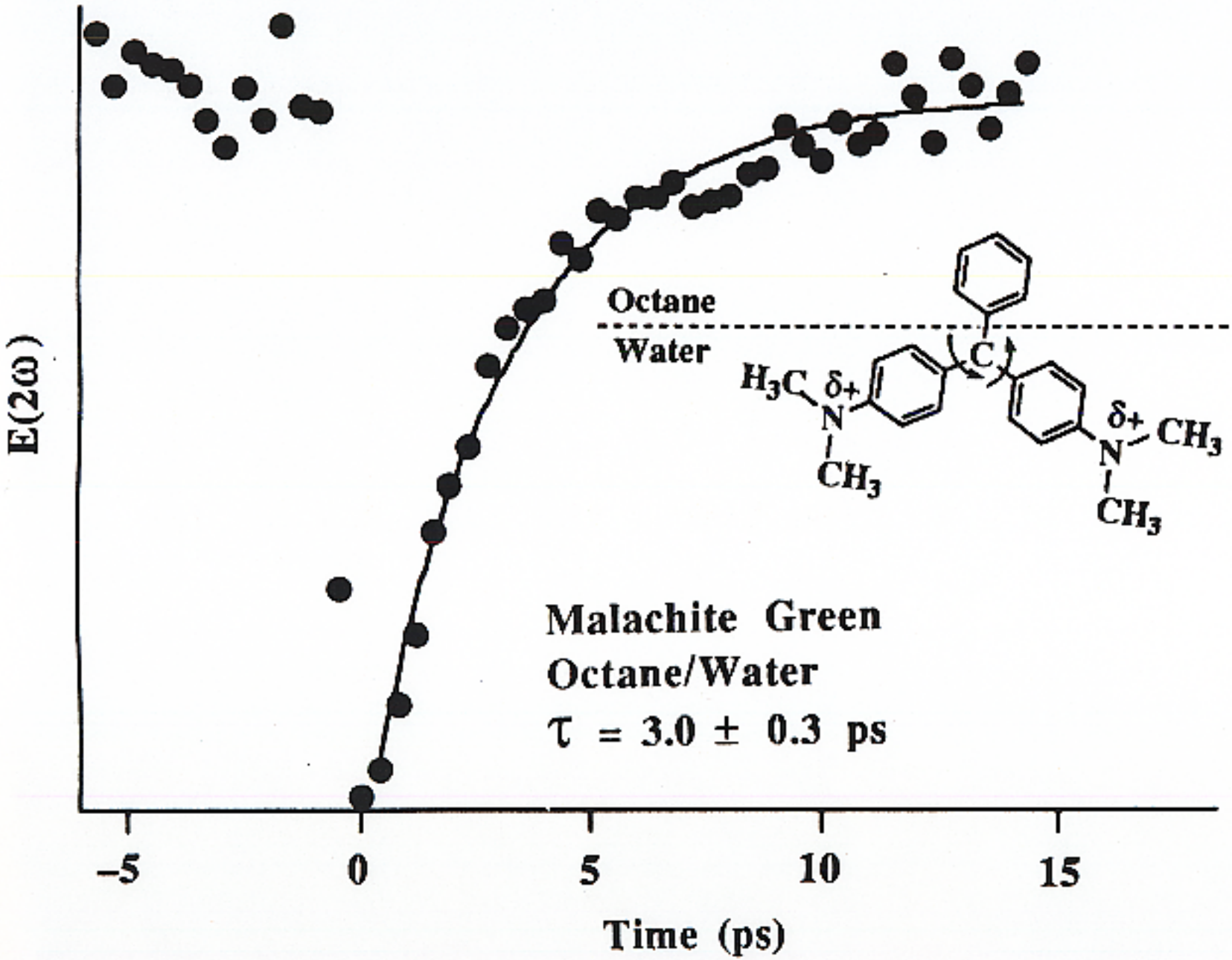
MG

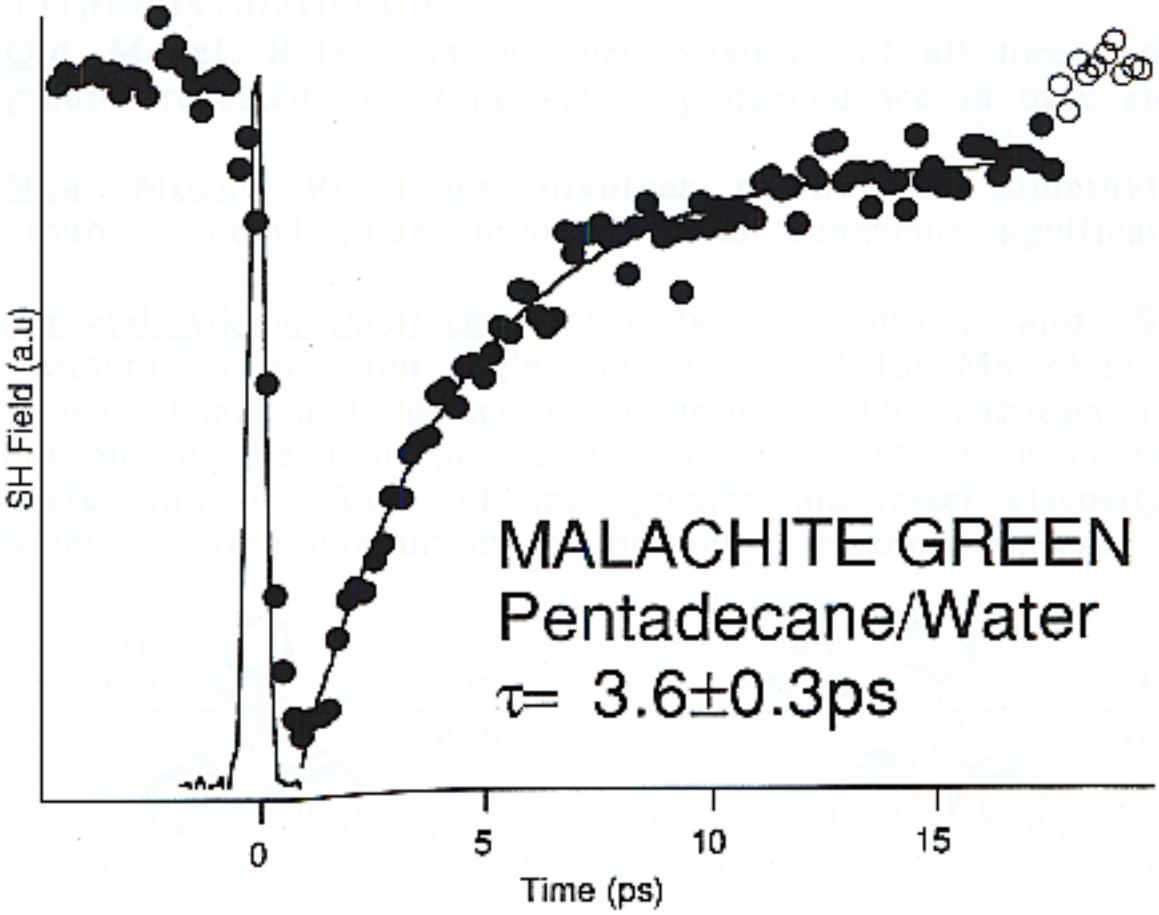


DODCI


Δ+
δ+
Δ+


E(2ω)
MALACHITE GREEN
Air/Water
τ=1.9±0.3 ps
-2
0
2
4
6
8
Time (ps)


E(2ω)
Octane
Water
H3C δ+ N CH3
C
δ+ CH3 N CH3
Malachite Green
Octane/Water
τ = 3.0 ± 0.3 ps
–5
0
5
10
15
Time (ps)


SH Field (a.u)
MALACHITE GREEN
Pentadecane/Water
τ= 3.6±0.3ps
0
5
10
15
Time (ps)

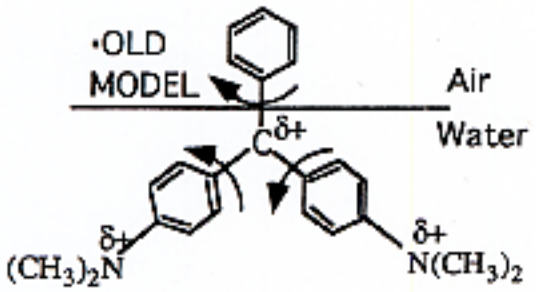
Conclusions

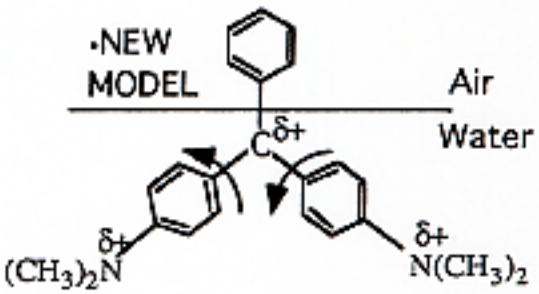
• New model for barrierless relaxation of Triphenylmethanes.

Old Model: Relaxation involves rotations of all three aromatic groups, revealed by strong viscosity dependence in bulk studies.

New Model: Relaxation involves rotation of dimethylamino groups. Phenyl group motion does not contribute significantly.

Air and Alkane Interfaces: Similar dynamics, and Second Harmonic polarization angles, are observed for Malachite Green at Air, Octane and Pentadecane interfaces. This suggests that the motion of the hydrophobic phenyl ring, which projects into phases (air or alkane) of both greater and lesser viscosity than water, is not important in the photoisomerization process.

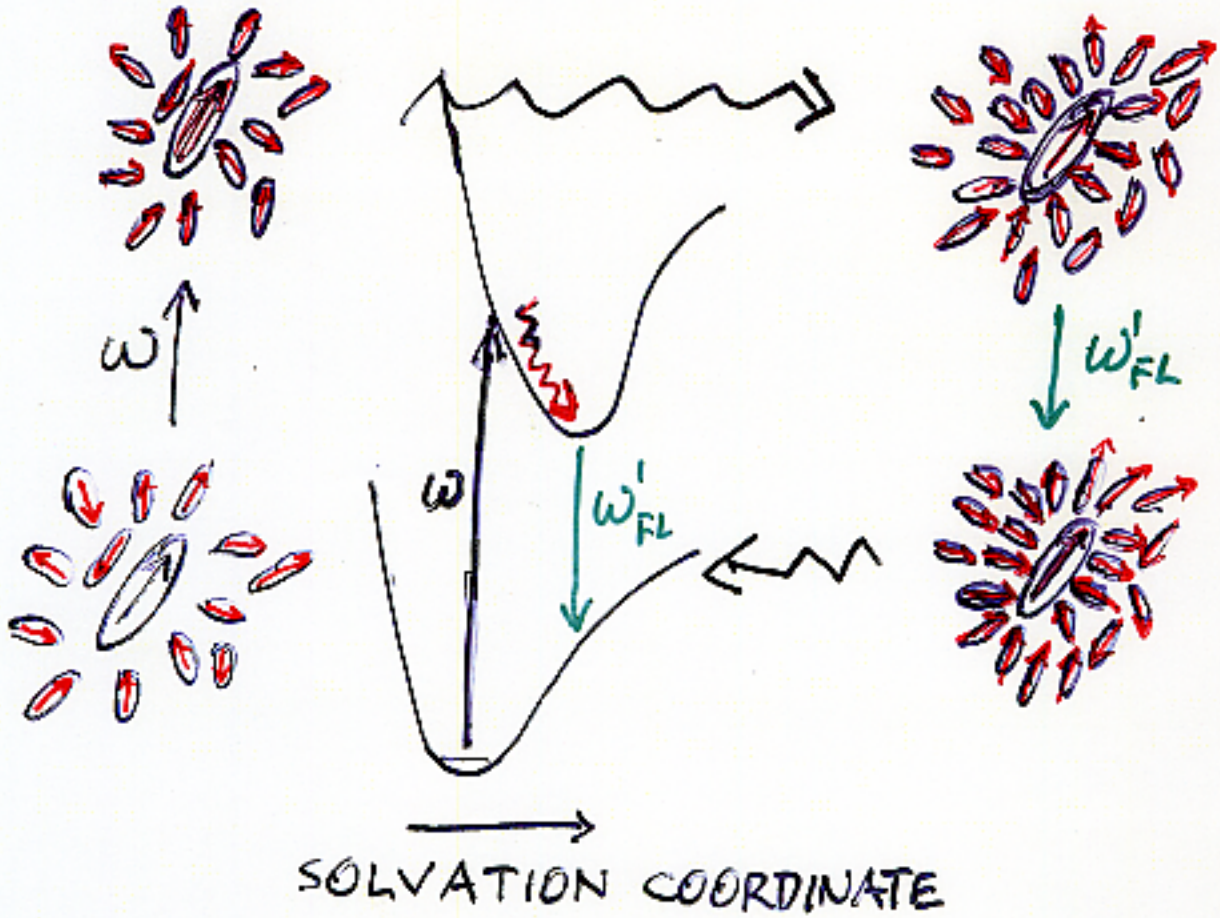




Silica/Aqueous Interface: Relaxation slower than at Air/Aqueous and Alkane/Aqueous interfaces. Suggests that water molecules are even more structured at this interface due to polarizing effect of surface SiOH groups.

Interfaces can thus be used to orient molecules and probe the effects of specific groups on ultrafast dynamical processes.

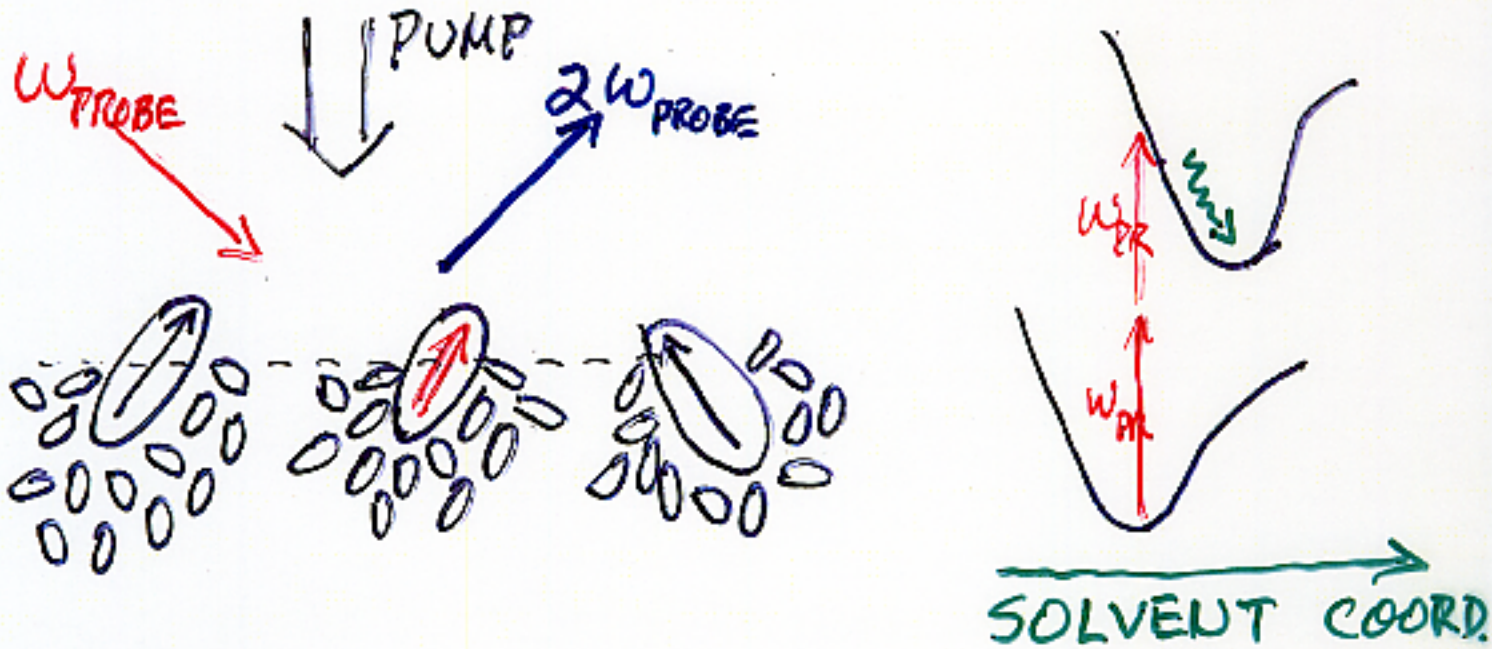
EXCITED STATE SOLVATION



- SOLVENT MOLECULES MOVE IN RESPONSE TO CHANGE IN SOLUTE DIPOLE MOMENT ON PHOTOEXCITATION

- SOLVATION DYNAMICS IN BULK LIQUID REGION OBSERVED BY TIME DEPENDENT FLUORESCENT SHIFT.

INTERFACE SOLVATION DYNAMICS USING SECOND HARMONIC GENERATION



- SOLVENT RESPONDS ONLY TO EXCITED SOLUTE MOLECULES

- $$I_{2\omega}^{1/2} \sim \chi^{(2)} = N_{S_0}\alpha^{(2)}_{S_0} + N_{S_1}\alpha^{(2)}_{S_1}(t)$$

$$\alpha^{(2)}_{S_1}(t) \sim \sum \frac{\langle S_1|\vec{\mu}|S_0\rangle\langle S_0|\vec{\mu}|S_n\rangle\langle S_n|\vec{\mu}|S_1\rangle}{(\omega_{S_1S_0} - 2\omega_{PR} + i\Gamma_{S_1S_0})(\omega_{S_nS_1} - \omega_{PR} + i\Gamma_{S_nS_1})}$$

$$\chi^{(2)}(t) = N_{TOTAL}\alpha^{(2)}_{S_0} - N_{S_1}(\alpha^{(2)}_{S_0} - \alpha^{(2)}_{S_1})$$

$\alpha^{(2)}_{S_1}(t)$ DECREASES AS RESONANCE DECREASES.

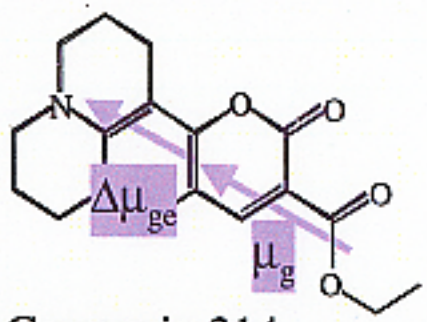
Experimental method

Time Resolved Second Harmonic Generation (TRSHG) spectroscopy of a solvatochromic probe dye coumarin 314.

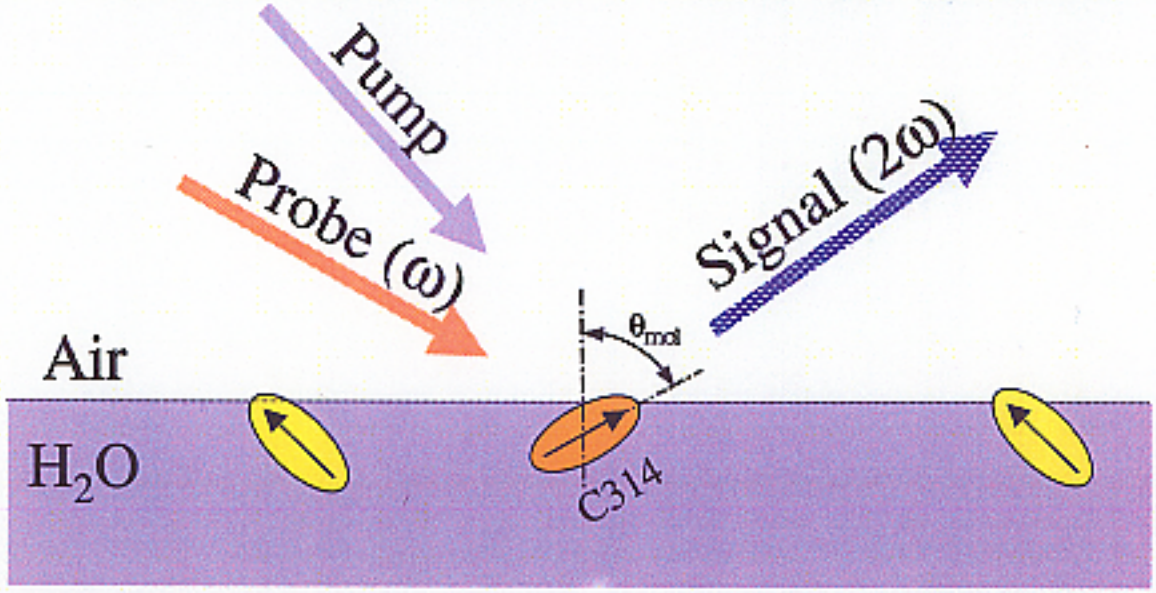
Surface selectivity
SHG detects only dye molecules adsorbed at the interface

Spectroscopic selectivity
Resonantly enhanced SHG

Ultrafast time resolution
fs pump-probe experiment

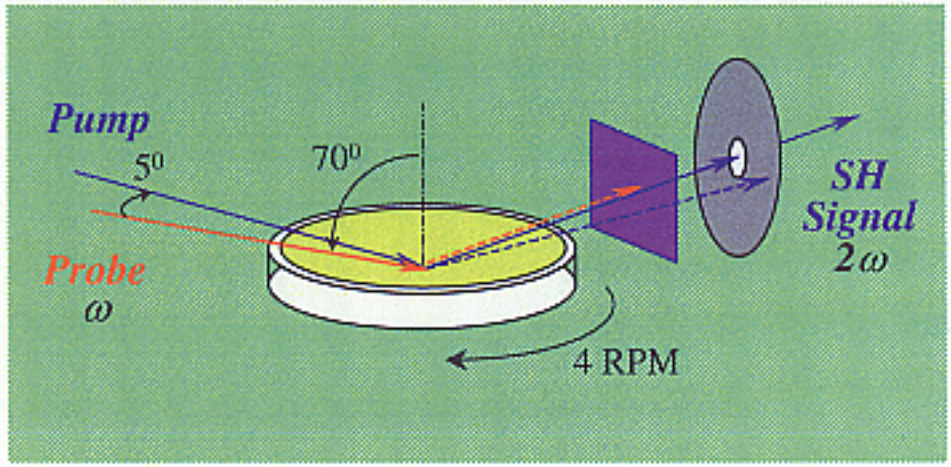


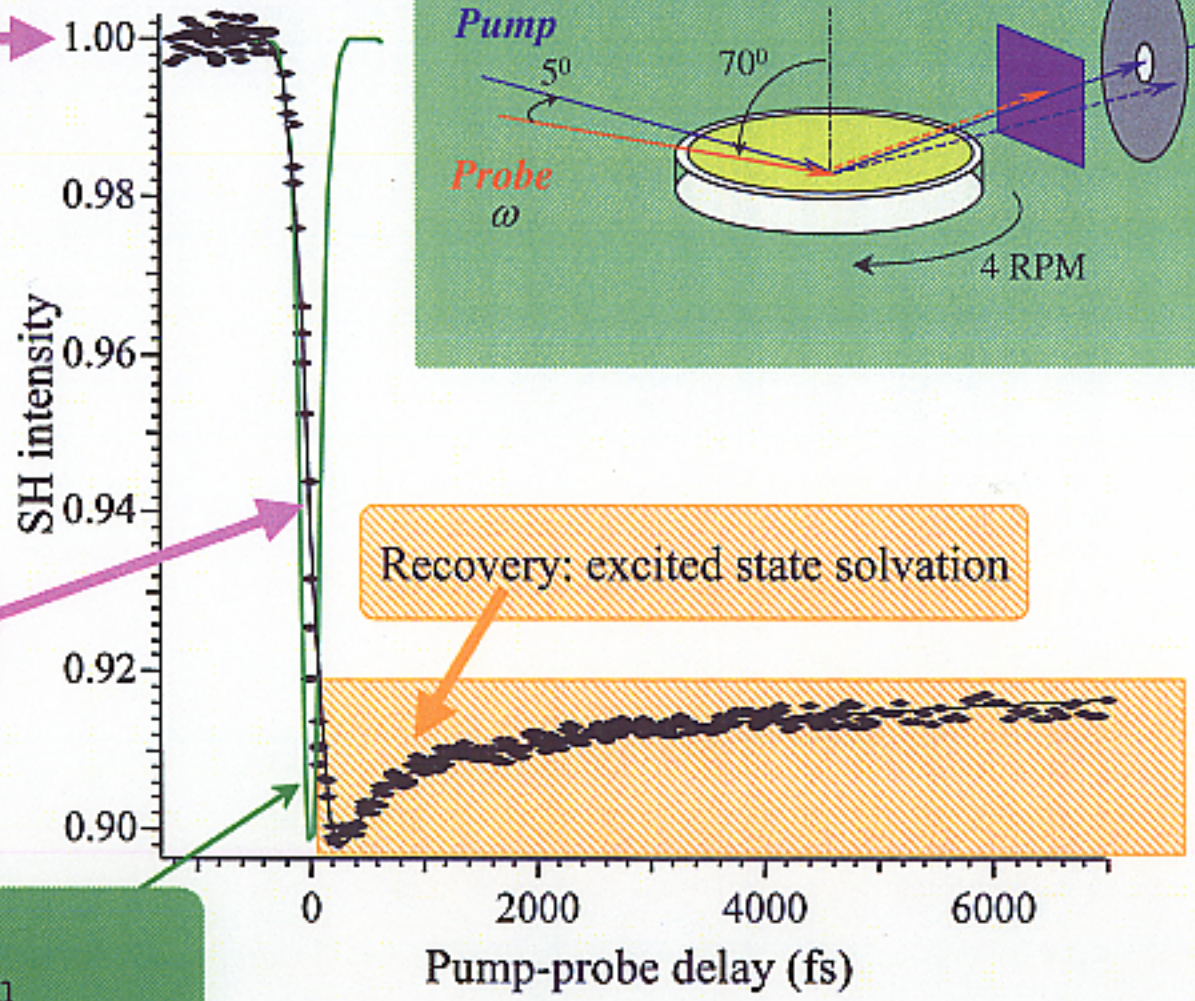
Coumarin 314



TRSHG: coumarin 314 at the air/water interface

SH signal level before the pump pulse excitation (100% population in the ground state)



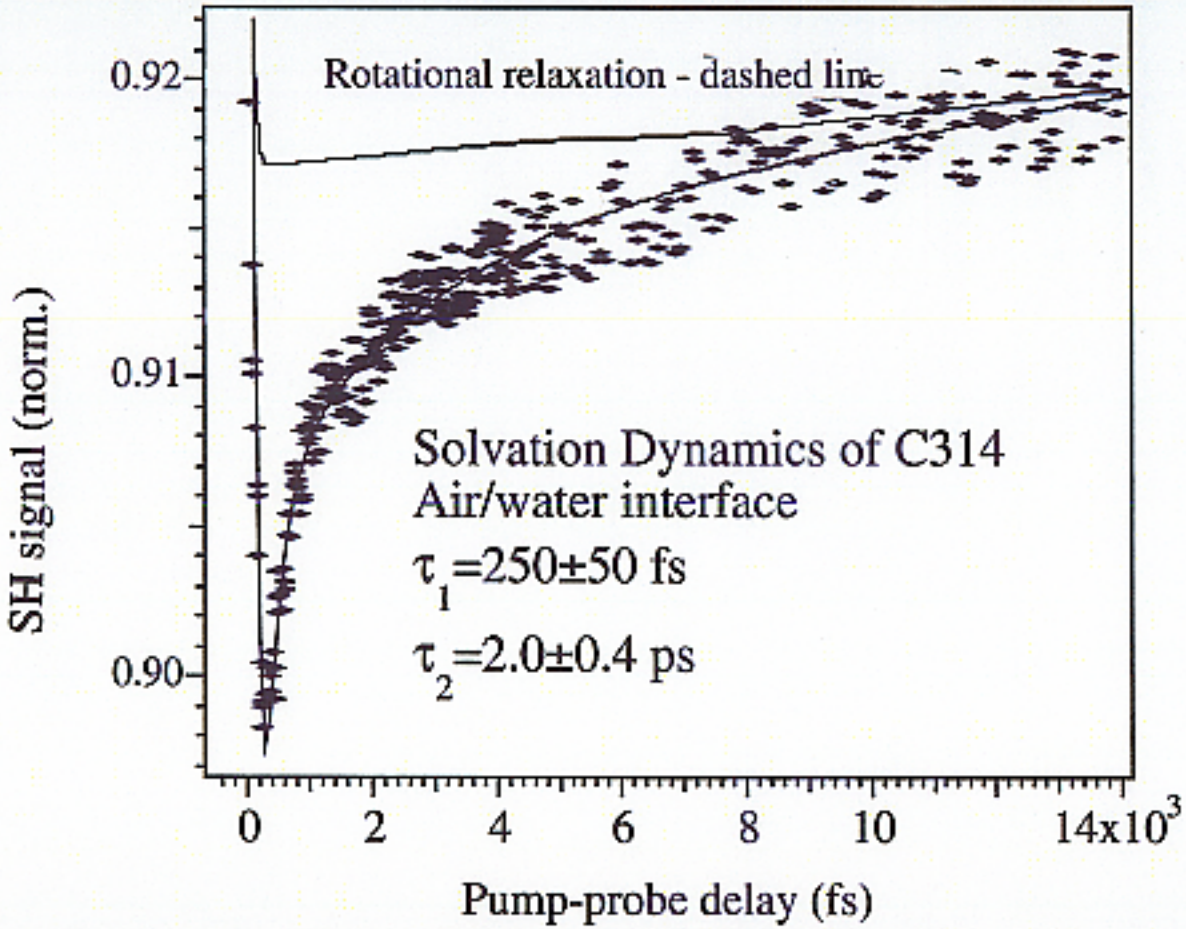


Bleach: population transfer to the excited state

Recovery: excited state solvation

Pump-probe cross-correlation (surface sum frequency generation)

Solvation dynamics at the air/water interface

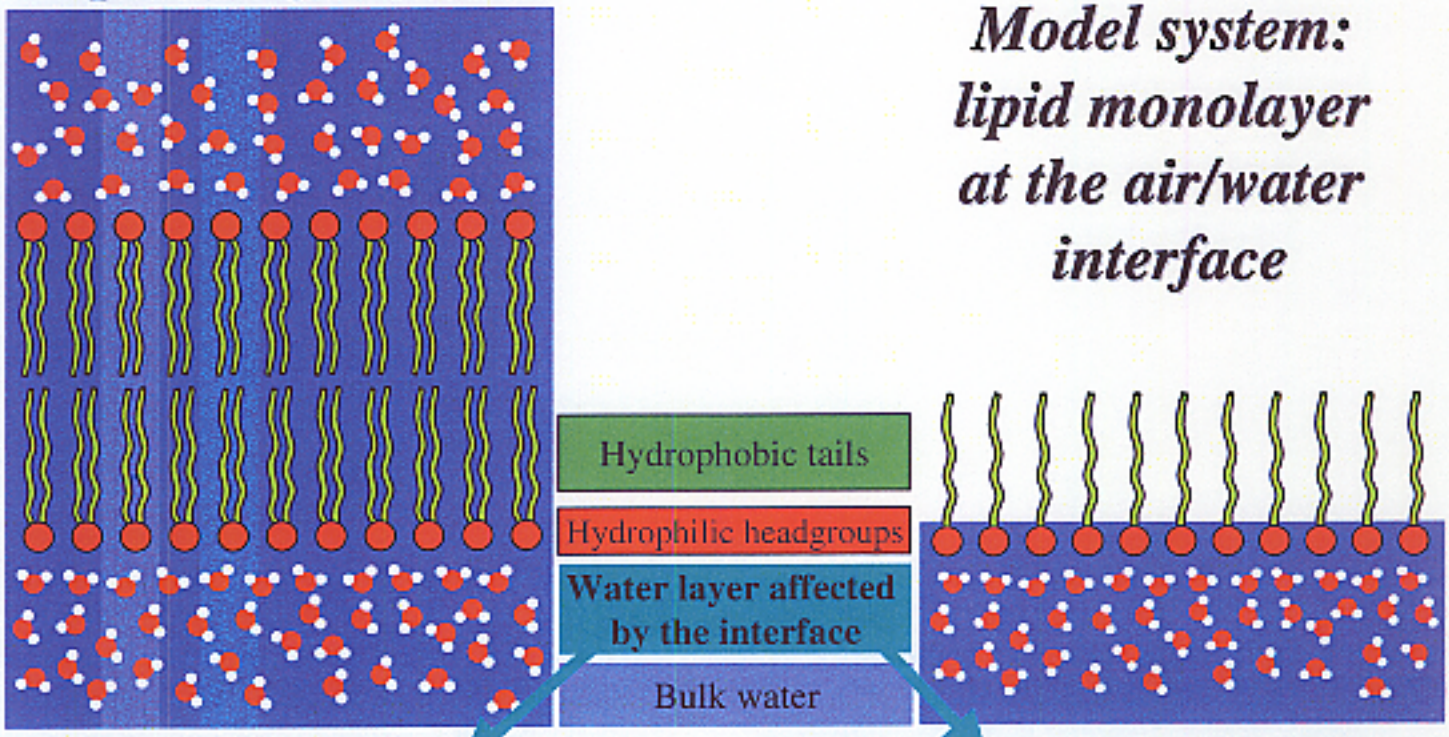


Diffusive solvation components in bulk water: τ_1=130-290 fs; τ_2=0.69-1.2 ps.

Note: the 25 fs inertial solvation component is not observed here due to limited time resolution

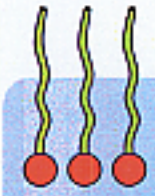
Biological interface: lipid bilayer/water

Model system: lipid monolayer at the air/water interface



H_2O molecules bonding to the interfacial moieties (e.g., hydrogen bonds)

At electricallycharged interfaces, alignment of water dipoles along the field lines may affect structure, hydrogen bond patterns of water, and therefore dynamics



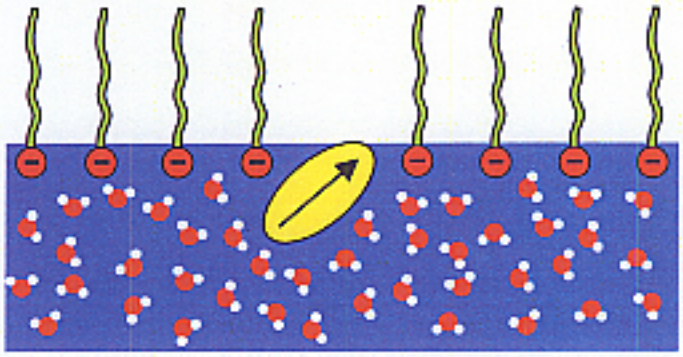
= carboxyl (-COOH) ; hydroxyl (-OH) amine ($-NH_2$)
carboxylate ($-COO^-$) ; sulfate ($-OSO_3^-$); phosphate ($-OPO_3^-$)
ammonium ($-NH_3^+$); trimethyammonium ($-N(CH_3)^+$)
etc.

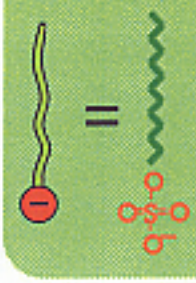
Solvation influences both chemical equilibria and chemical dynamics

Static solvation:
Free energies of chemical species
Reaction equilibria
Adsorption-desorption equilibria

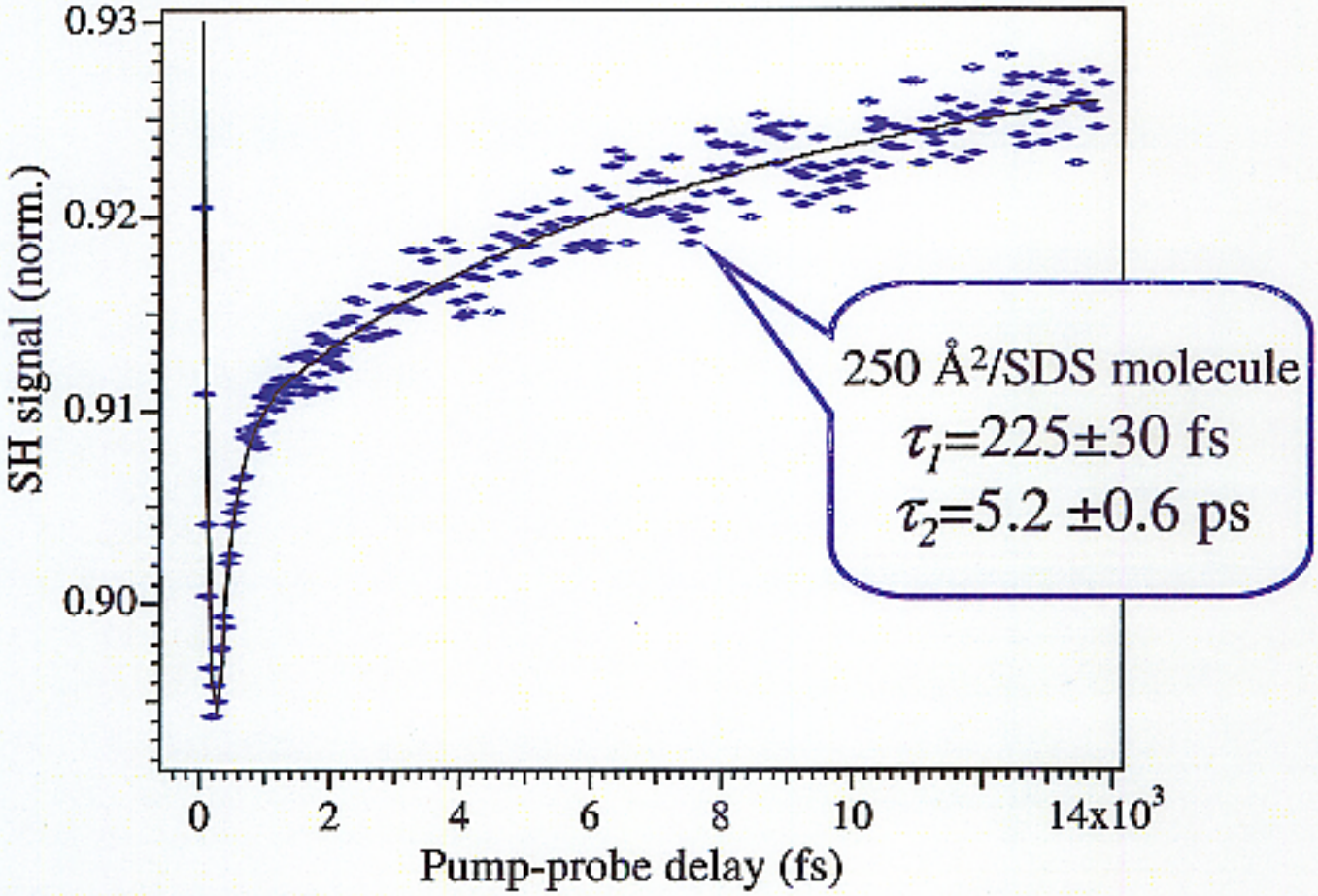
Solvation dynamics:
Fluctuating reaction barriers
⇒affects *reaction rates*
e.g. electron transfer: Marcus theory

Effect of surface charge density on solvation dynamics

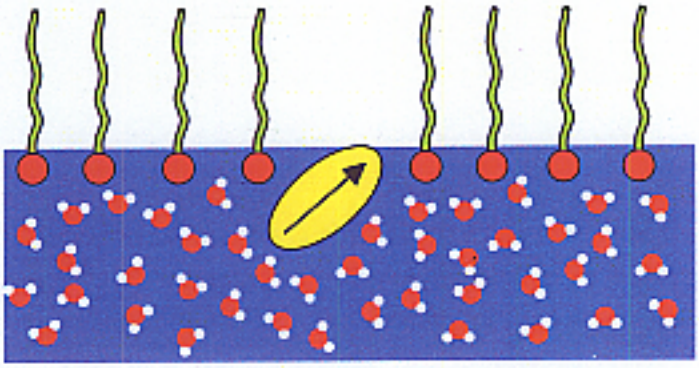


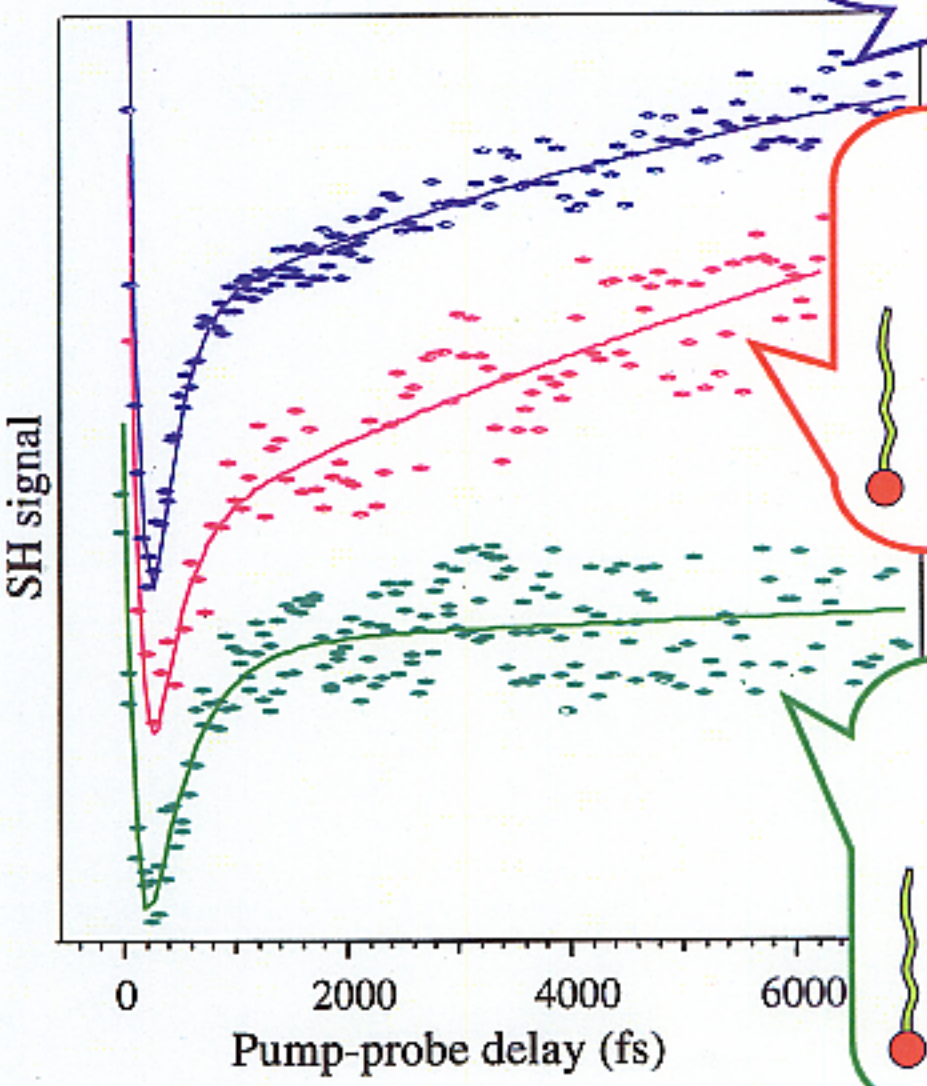


Anionic surfactant
Sodium Dodecyl
Sulfate (SDS)
$CH_3(CH_2)_{11}OSO_3^-$



Effect of surface charge vs. structure on solvation dynamics





Anionic surfactant (sulfate) SDS

$CH_3(CH_2)_{11}OSO_3^-$

250 Å²/SDS molecule

τ_1=225±30 fs

τ_2=5.2 ±0.6 ps

Anionic surfactant (carboxylate)

Stearic acid (pH=10.0)

$CH_3(CH_2)_{16}COO^-$

200 Å²/molecule

τ_1=250±70 fs

τ_2=5.5 ±2.1 ps

Neutral surfactant (carboxyl)

Stearic acid (pH=3.0)

$CH_3(CH_2)_{16}COOH$

200 Å²/molecule

τ_1=400±60 fs

No τ_2

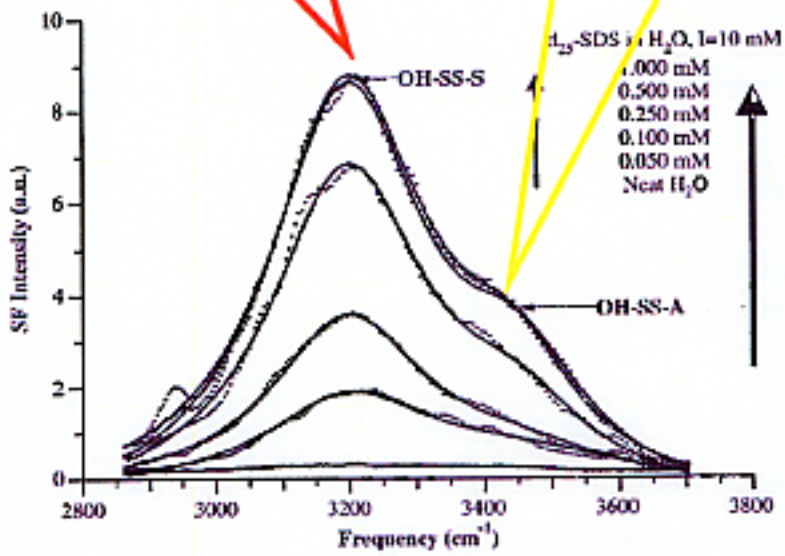
Water Structure - Solvation Dynamics Correlation

VSFG spectroscopy of water at a charged interface

D. E. Gragson and G. L. Richmond, *JACS* **1998**, *120*, p. 366.

OH-SS-S band
(~3200 cm^{-1})
Stronger H-bonded water
(ice-like structures,
tetrahedral coordination)

OH-SS-A band
(~3400 cm^{-1})
Weaker H-bonded water
(water-like structures,
nearly tetrahedral coordination)

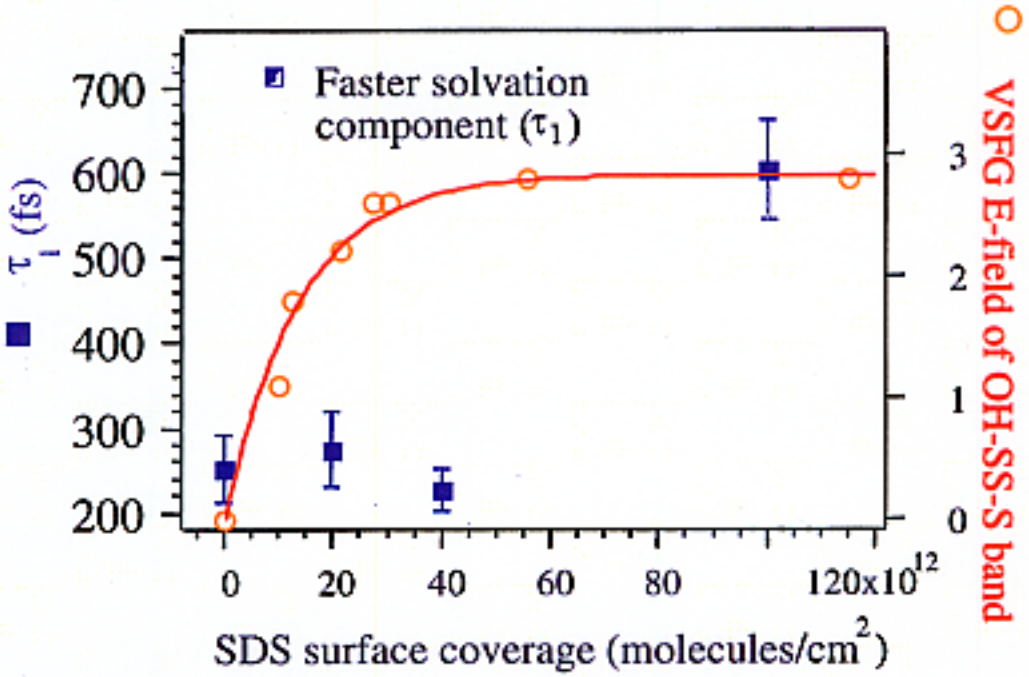


Increasing coverage of anionic surfactant (SDS)

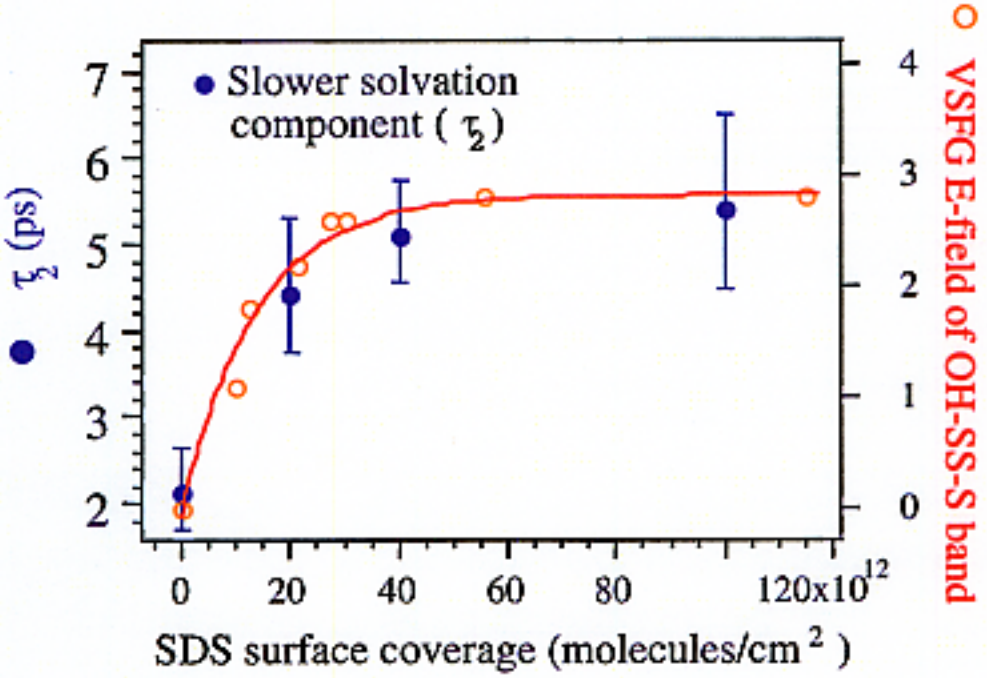
Solvation dynamics timescales vs. VSFG spectra

of water at an anionic interface (SDS)

as a function of surface charge



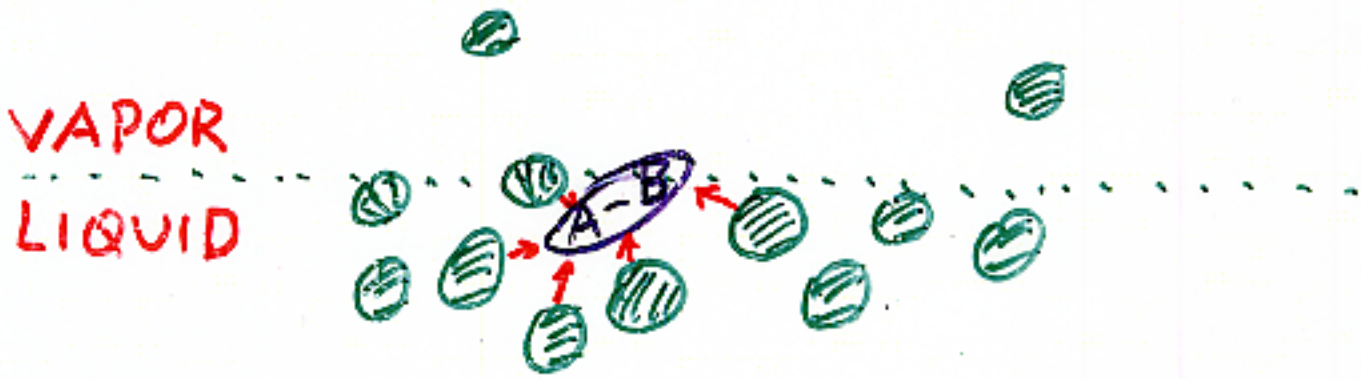
Strongly H-bonded water structures

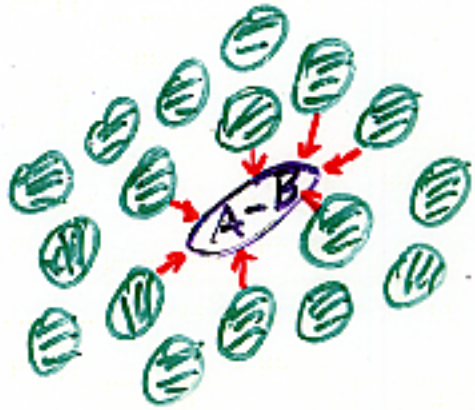


Strongly H-bonded water structures

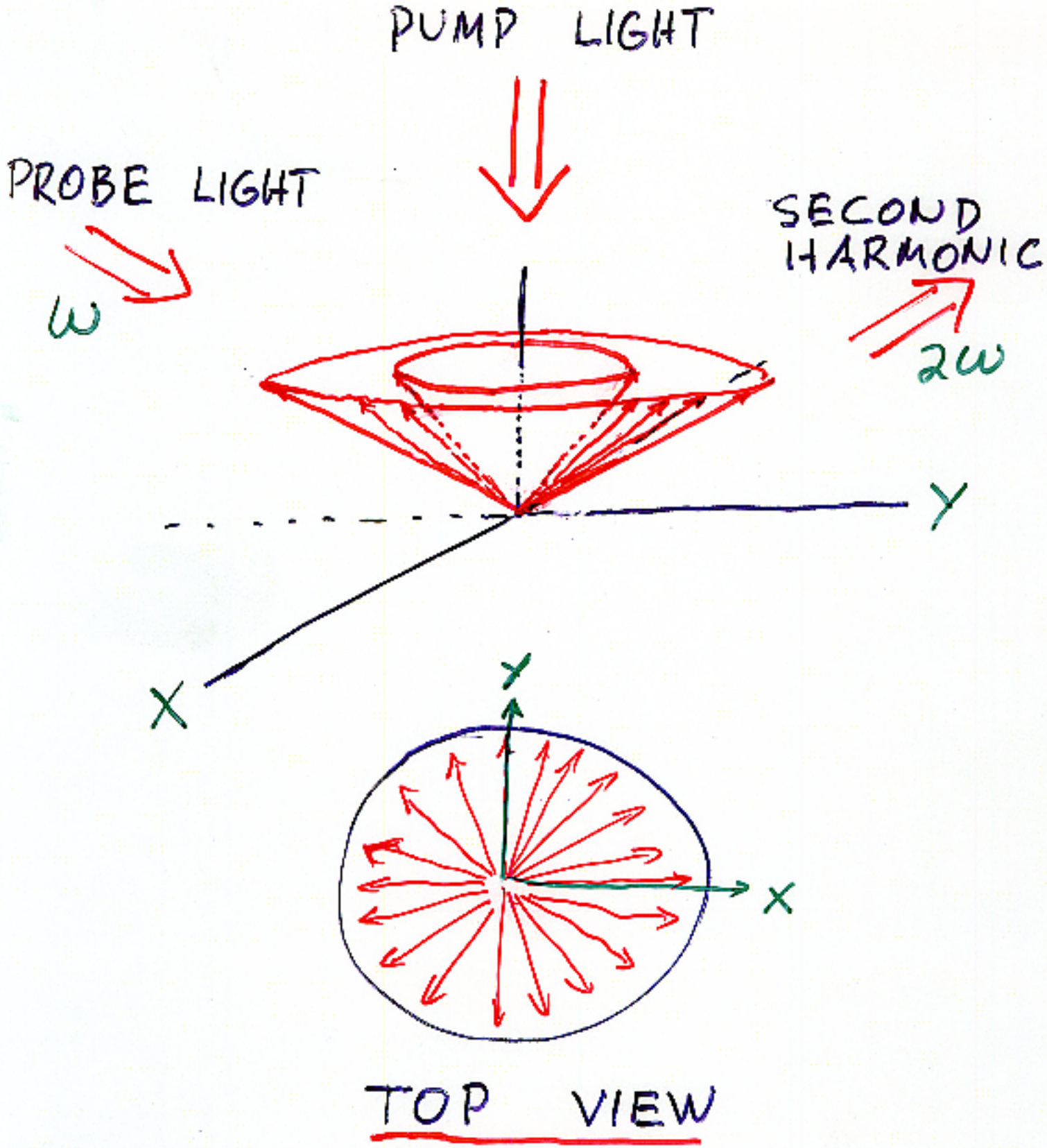
MOLECULAR ROTATION AT LIQUID INTERFACES

- THE ANISOTROPIC FORCES AT A LIQUID INTERFACE CAN DIFFER FROM THE BULK LIQUID

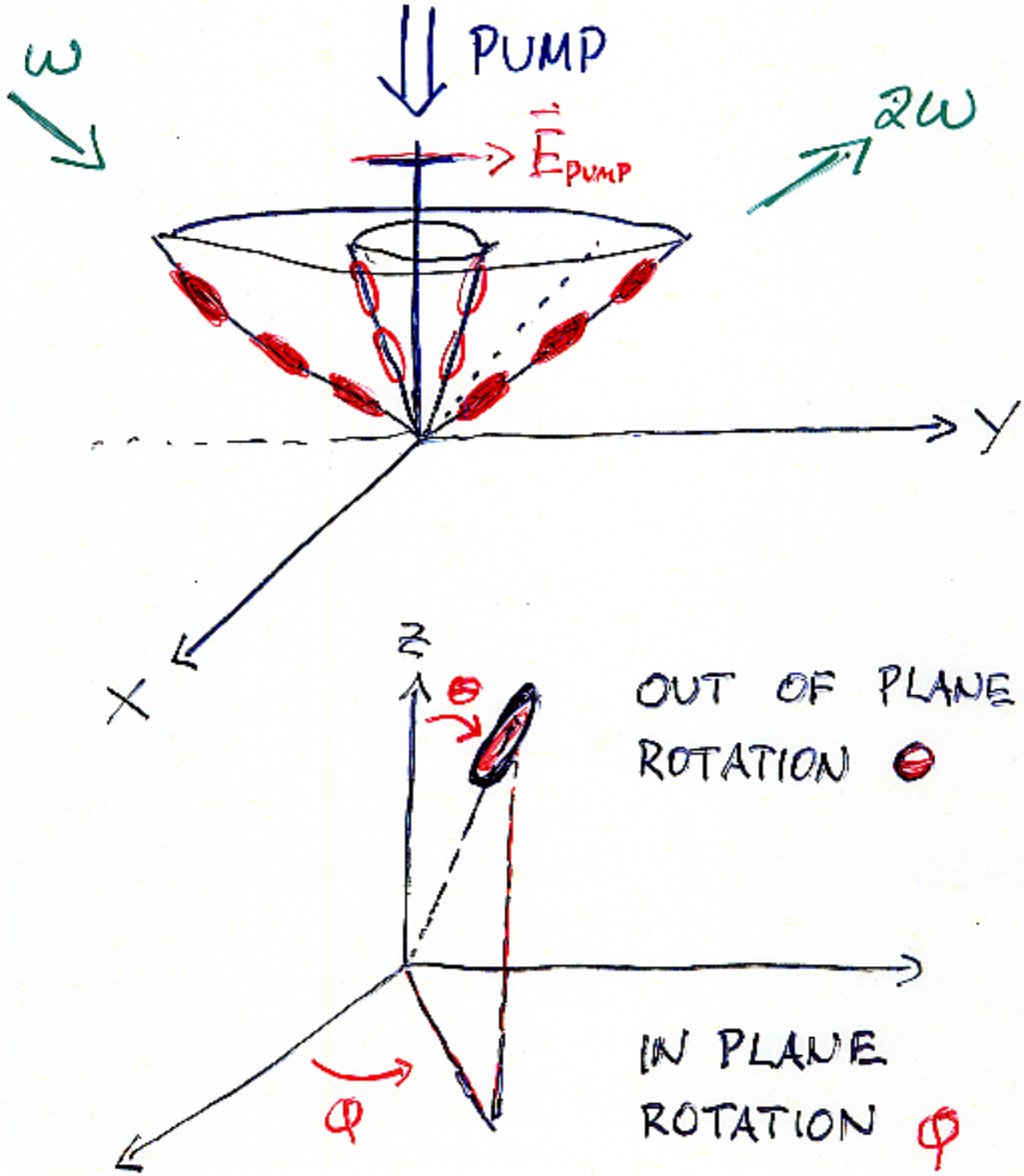




BULK LIQUID


PUMP LIGHT
PROBE LIGHT
ω
SECOND HARMONIC
2ω
Y
X
Y
X
TOP VIEW

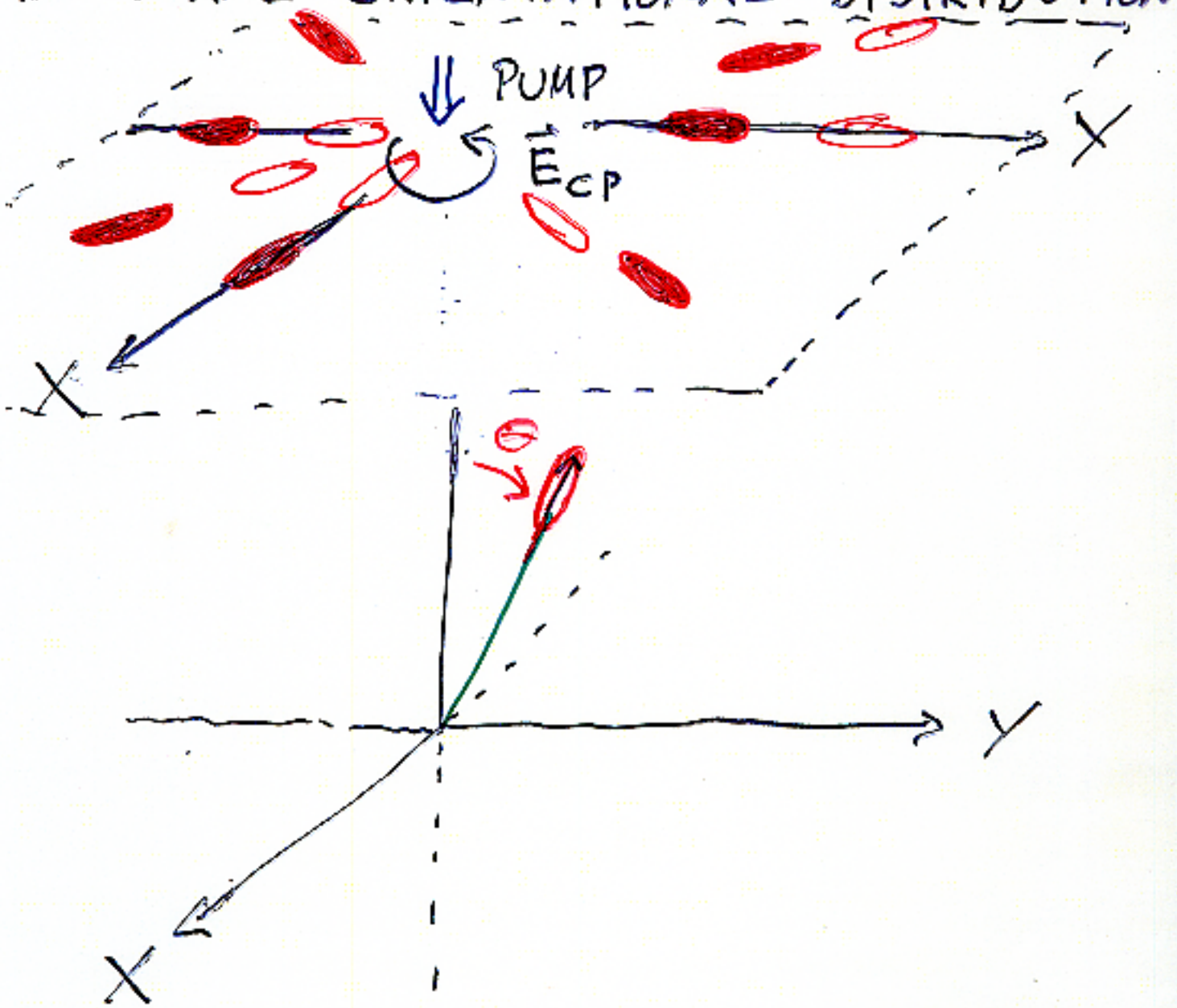
POLARIZED PHOTOEXCITATION PERTURBS ORIENTATIONAL DISTRIBUTION AT INTERFACE



WAY TO ELIMINATE IN-PLANE MOTION, φ, FROM DYNAMICS

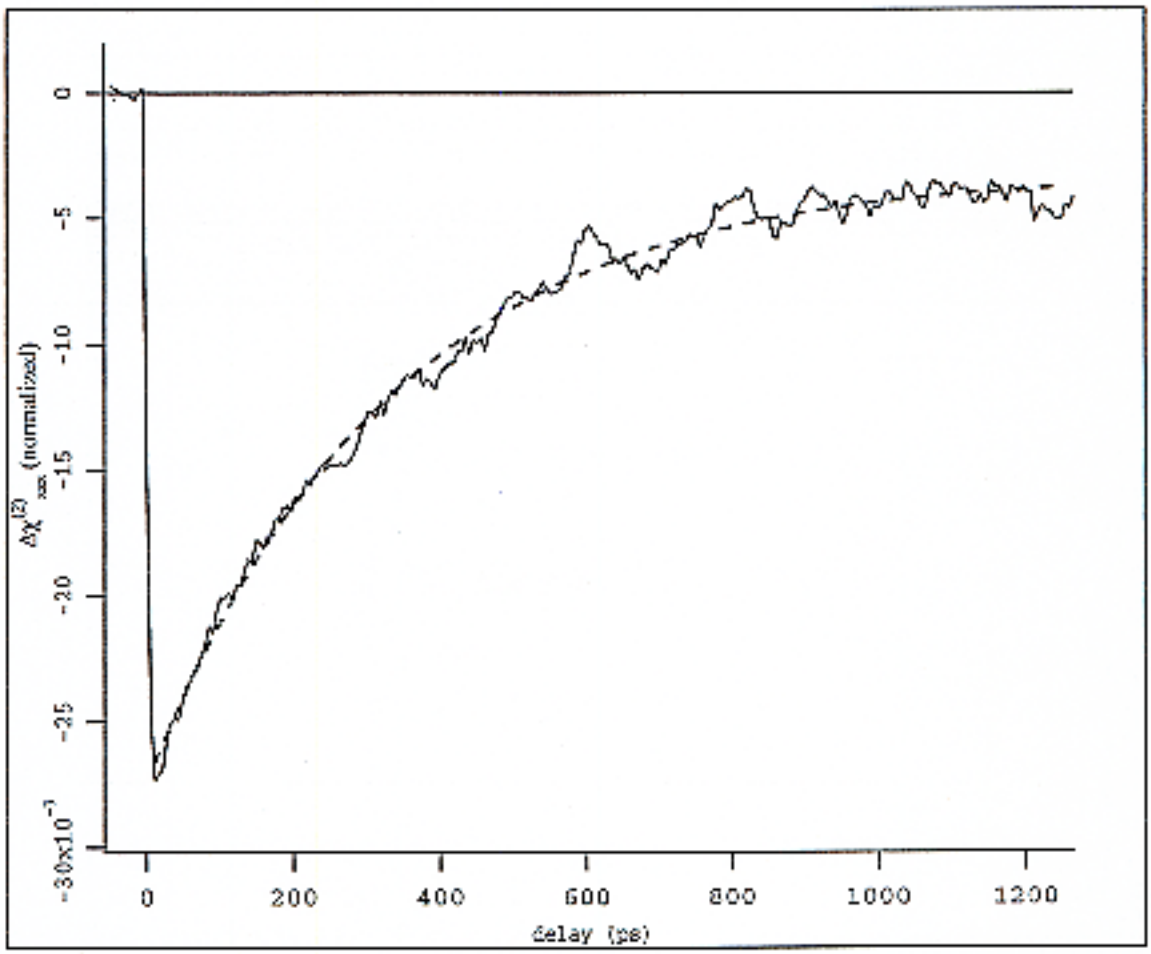
$\Downarrow$

USE CIRCULARLY POLARIZED PUMP LIGHT TO ACHIEVE ISOTROPIC IN-PLANE ORIENTATIONAL DISTRIBUTION



- DYNAMICS DUE TO OUT OF PLANE MOTION θ

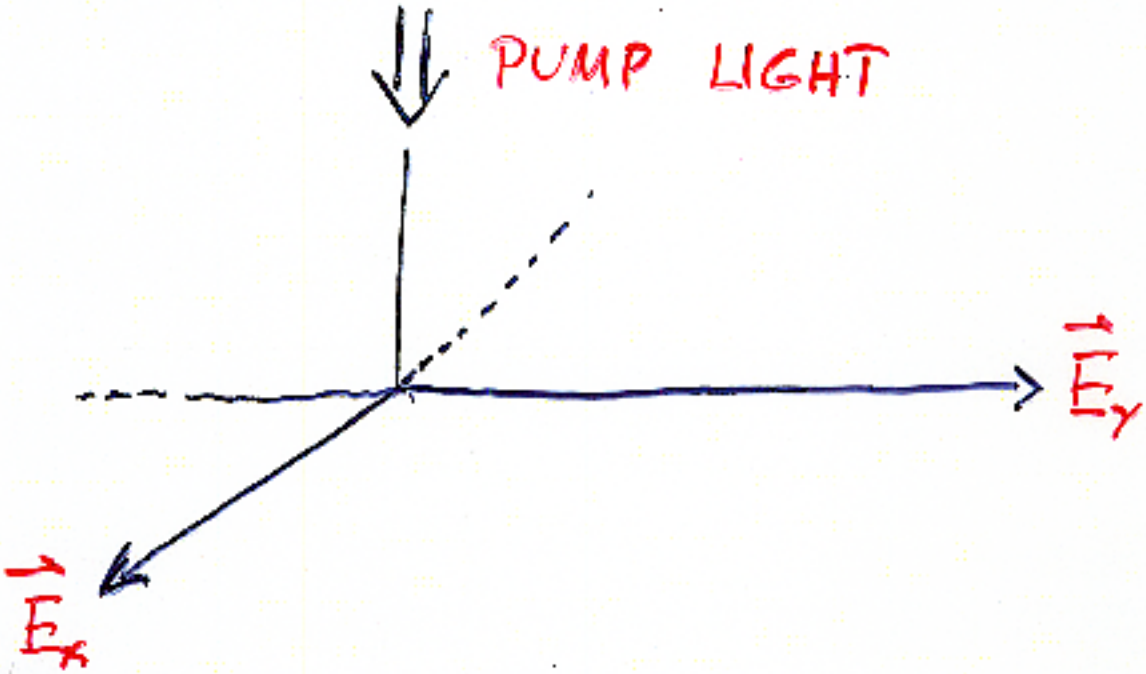
Circularly polarized pumping showing only the out-of-plane orientational motion



Coumarin 314, 26 μM, at the water/air interface

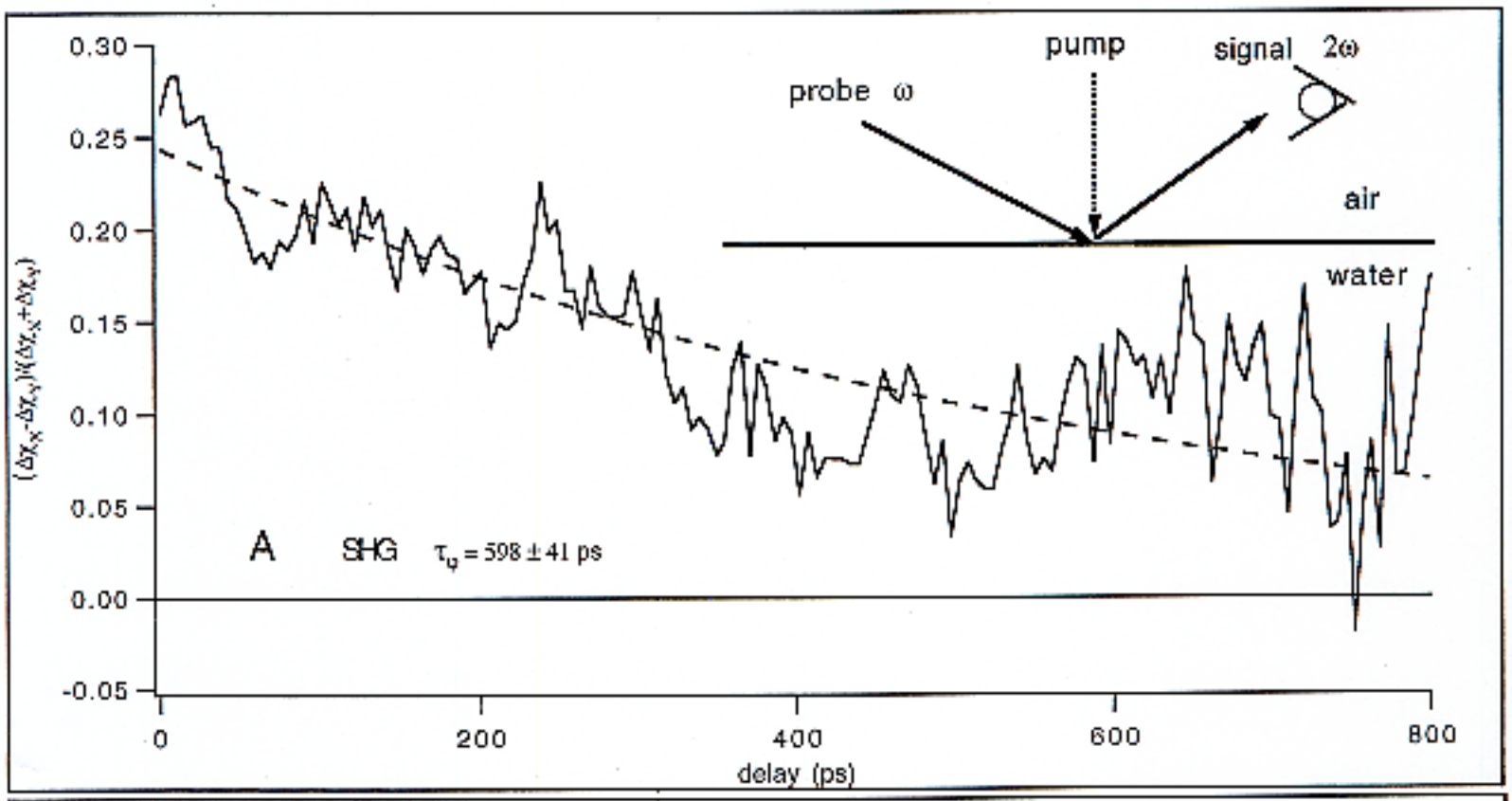
- Fit to a single exponential ; ***out-of-plane*** **decay time = 350 ± 18 ps.**
- The remaining ~15% bleach after 1000 ps is the electronic ground state recovery.

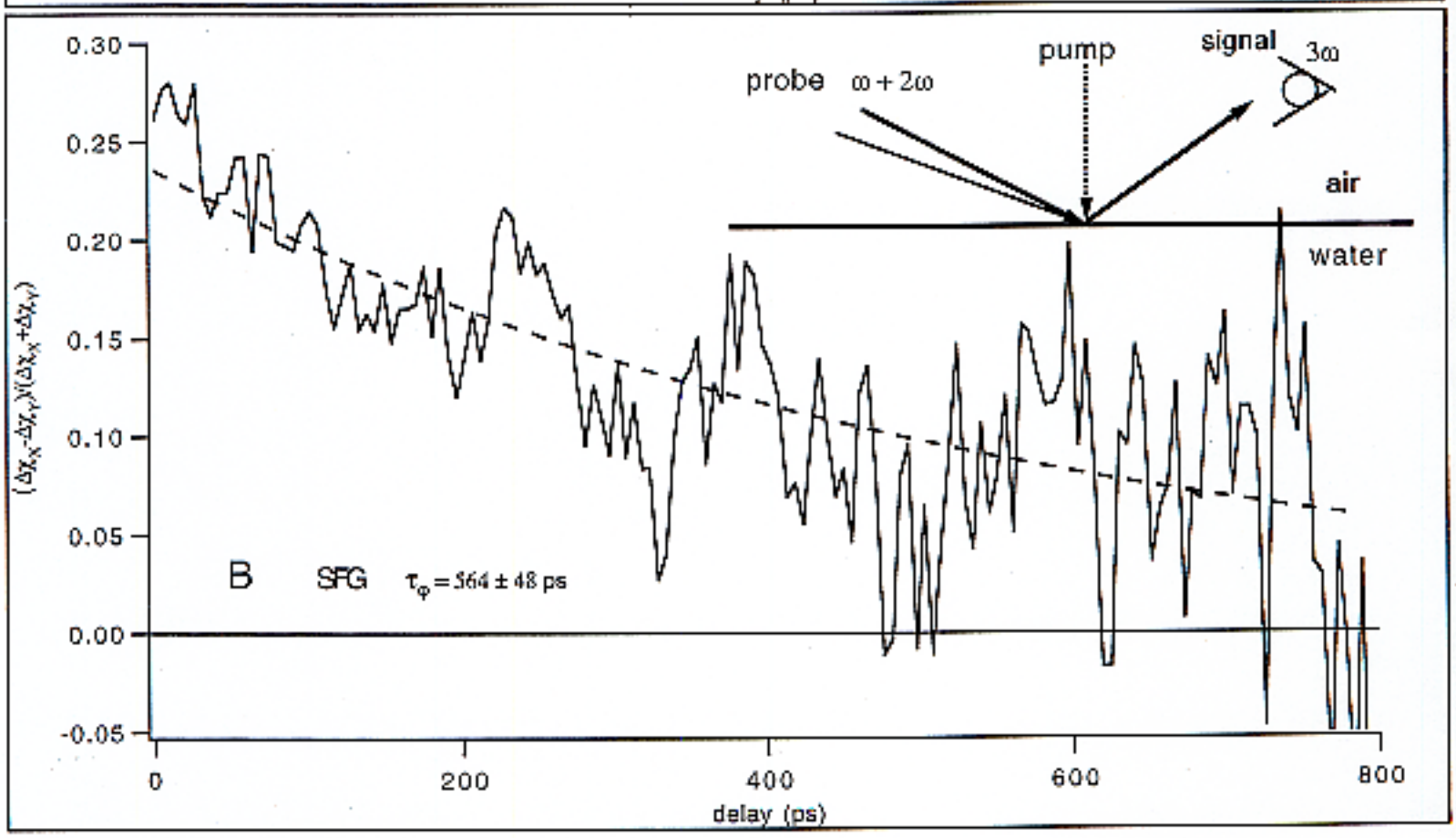
HOW TO ELIMINATE OUT OF PLANE ROTATION, Θ, FROM DYNAMICS

- USE X-POLARIZED PUMP TO PHOTOSELECT MOLECULES NEAR $\phi = 0°$.
- USE Y-POLARIZED PUMP TO PHOTOSELECT MOLECULES NEAR $\phi = 90°$
- 

- BOTH X AND Y PUMP PHOTOSELECTION ALONG Θ IS THE SAME
- $$\frac{I_{2\omega}^{X} - I_{2\omega}^{Y}}{I_{2\omega}^{X} + I_{2\omega}^{Y}}$$ DEPENDS ONLY ON ϕ

Relative Decay of Anisotropy from X vs Y Pump (X-Y)/(X+Y)
In-Plane Rotation of C314 at Air-Water Interface





Second Harmonic and Sum Frequency Dectection Yield Identical Results

Summary of Orientational Relaxation Study

- Orientational relaxation slower at air/H_2O interface than in bulk H_2O

	Air/H_2O	Bulk H_2O
Coumarin	$\tau_\theta = 350ps$	$\tau = 100ps$
	$\tau_\phi = 560ps$	
Rhodamine 6G	$\tau_\theta = 450ps$	$\tau = 200ps$

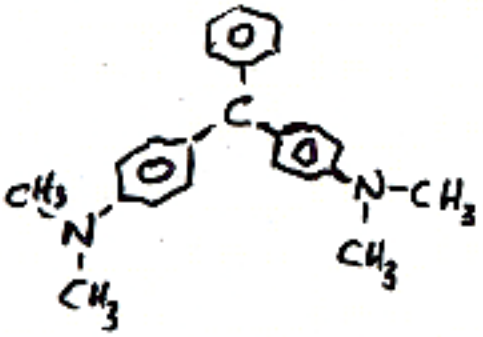
- First measurement of anisotropy in molecular rotational dynamics at an interface

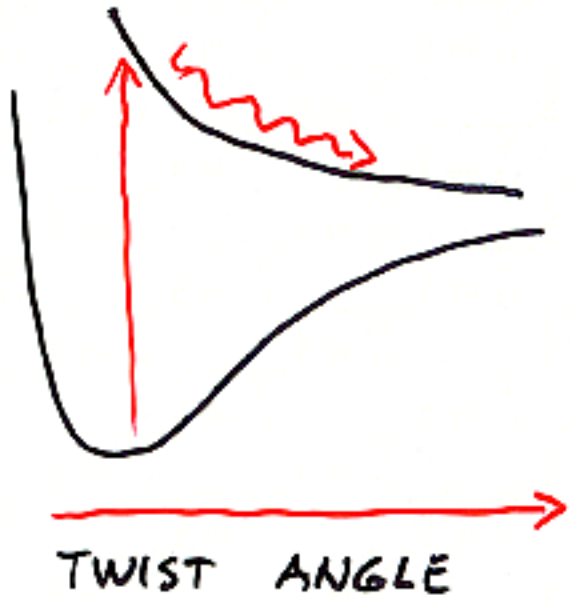
- "Out of plane" motion faster than "in plane" motion attributed to dependence of potential energy on θ and not ϕ

  At equilibrium all forces are isotropic in the surface plane, thus independent of ϕ.

FRICTION DEPENDENT REACTIONS AND ORIENTATIONAL RELAXATION MEASUREMENTS OF FRICTION

ISOMERIZATION





ISOMERIZATION DYNAMICS :

$$\frac{1.9\,ps\,(air/H_2O)}{0.7\,ps\,(bulk\ H_2O)} = 2.7$$

ORIENTATIONAL DYNAMICS :

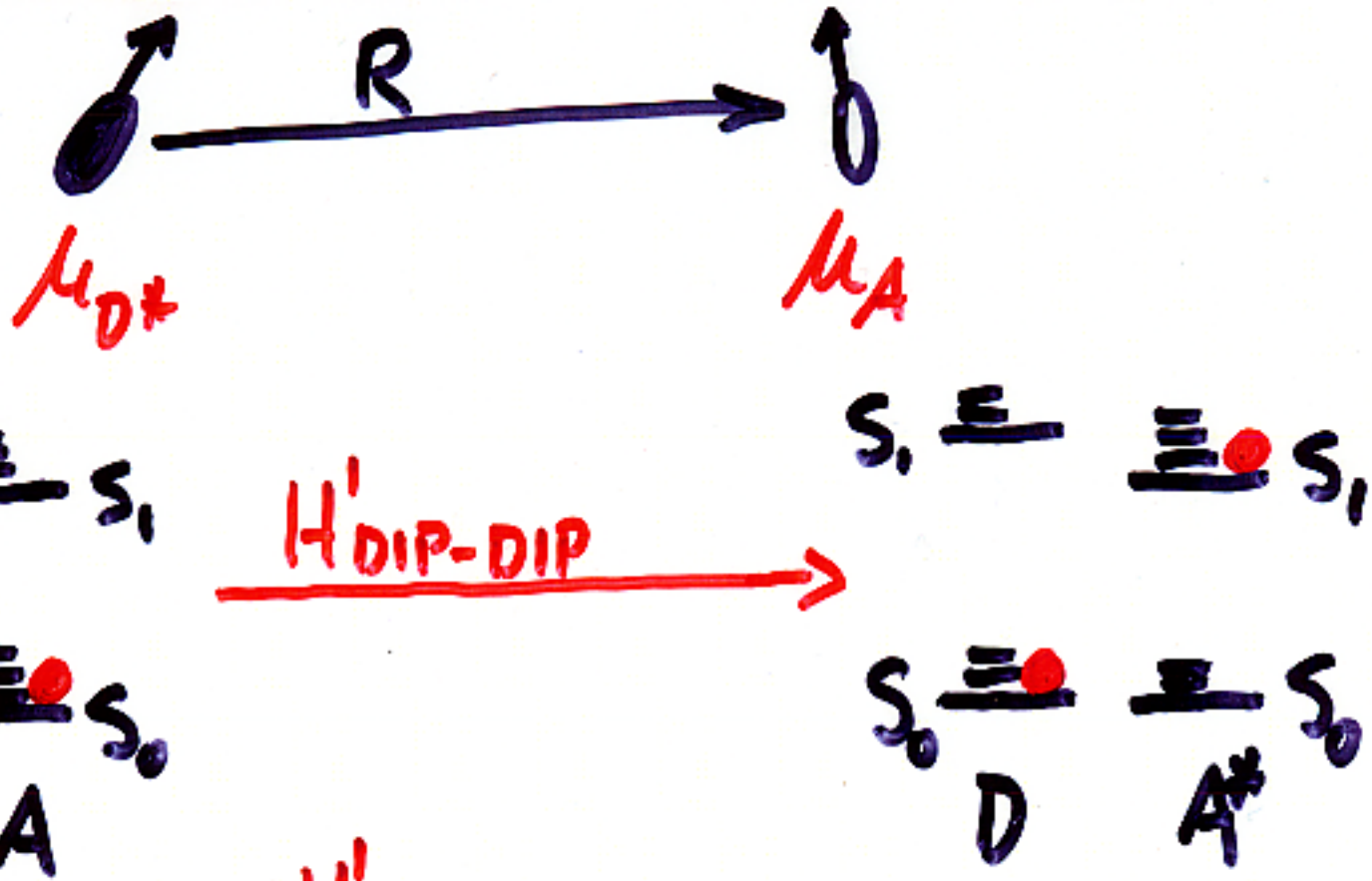
RHODAMINE 6G :

$$\frac{450\,ps\,(air/H_2O)}{200\,ps\,(bulk\ H_2O)} = 2.3$$

COUMARIN 314

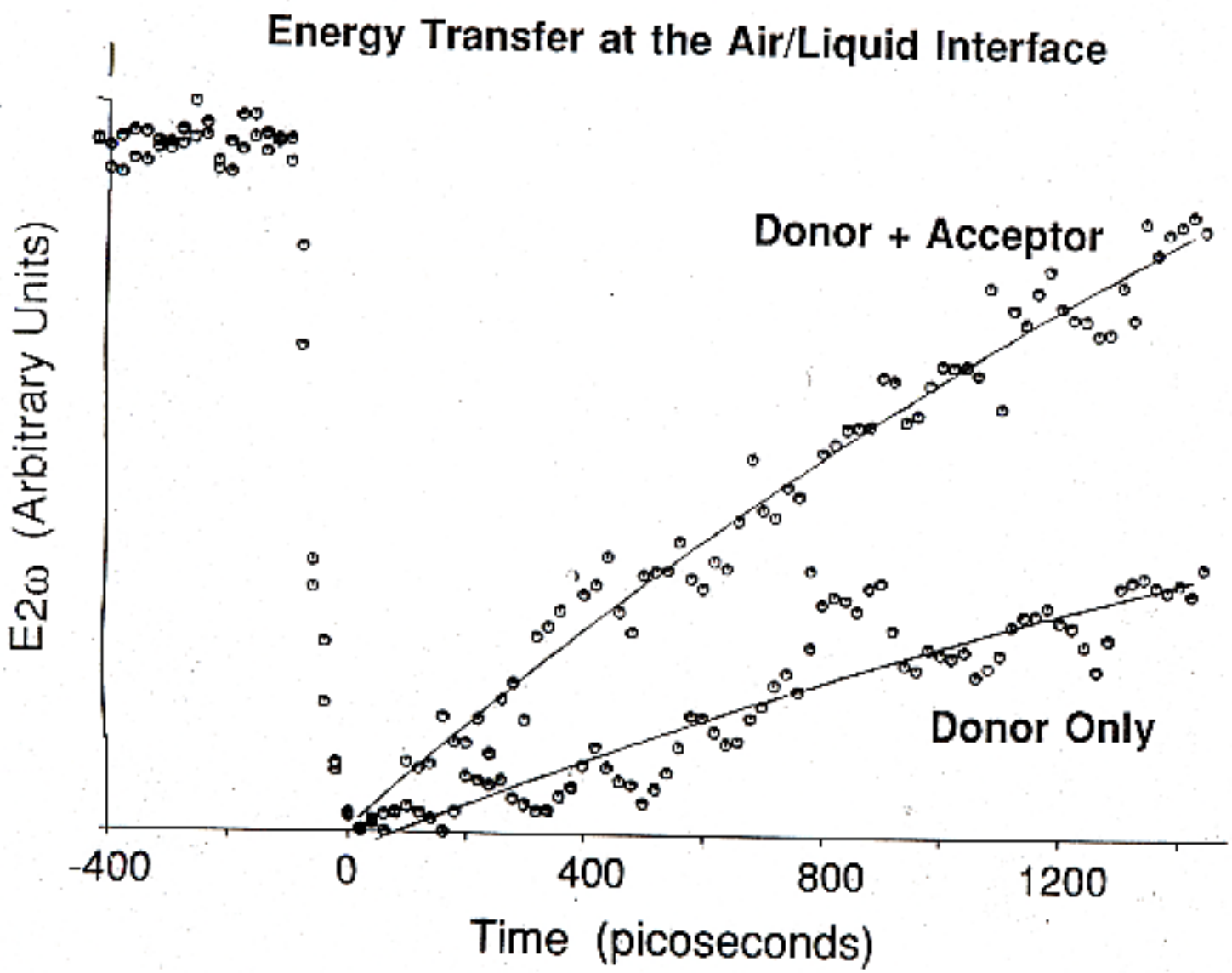
$$\frac{350\,ps\,(air/H_2O)}{100\,ps\,(bulk\ H_2O)} = 3.5$$

INTERMOLECULAR ENERGY TRANSFER



$$\Psi_i = \psi_{D^*}\,\psi_A \xrightarrow{H'_{DIP-DIP}} \Psi_f = \psi_D\,\psi_{A^*}$$

3-DIMENS.-IONAL: $$D^*(t) = D^*(0)\exp\left[-\frac{t}{\tau_0} - a\left(\frac{t}{\tau_0}\right)^{1/2}\right]$$


Energy Transfer at the Air/Liquid Interface
Donor + Acceptor
Donor Only
E2ω (Arbitrary Units)
-400
0
400
800
1200
Time (picoseconds)

EFFECT OF DIMENSIONALITY ON ENERGY TRANSFER

IF MECHANISM IS DIPOLE-DIPOLE COUPLING

$$\Downarrow$$

$$H'_{DIP-DIP} = \frac{\vec{\mu}_D \cdot \vec{\mu}_A}{R^3} - \frac{3\,\vec{\mu}_D \cdot \vec{R}\;\vec{\mu}_A}{R^5}$$

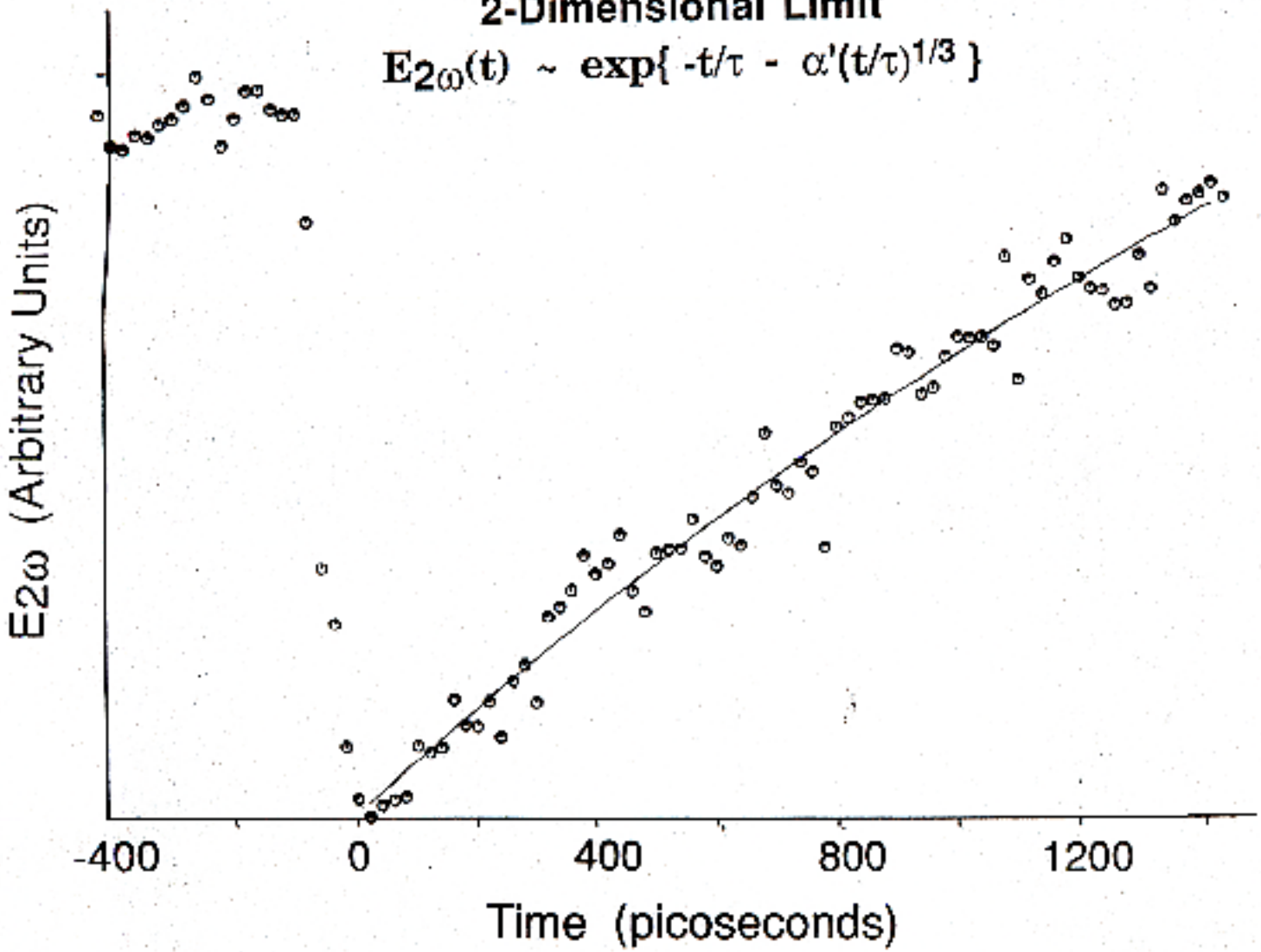
$$\Downarrow$$

DECAY LAWS

3-D : $D^*(t) = D^*(0)\exp\left[-t/\tau_0 - a\left(t/\tau_0\right)^{1/2}\right]$

2-D : $D^*(t) = D^*(0)\exp\left[-t/\tau_0 - b\left(t/\tau_0\right)^{1/3}\right]$

Energy Transfer at the Air/Liquid Interface

2-Dimensional Limit

$$E_{2\omega}(t) \sim \exp\{ -t/\tau - \alpha'(t/\tau)^{1/3} \}$$