
Second Harmonic Generation from Oxazine Dyes at the Air/Water Interface

Daniel A. Steinhurst
US Naval Research Laboratory
Washington, DC



Introduction

Why Study Interfaces?

Interfaces are involved in many physical / biological / atmospheric systems

Compared with isotropic (bulk) environments:

- Are interfaces unique? If so, how?
- Are microscopic and macroscopic properties altered similarly?

Why Study Dye Aggregates?

Industrial Applications

- Photography, photovoltaic cells, light harvesting devices

Dye Aggregates are a sensitive probe of environment

- Laser dyes are well characterized in the bulk
- Dye aggregates are more prevalent at the air/water interface than in the bulk (IR125, Levinger, 1995)

Second Harmonic Generation at the Air/Water Interface

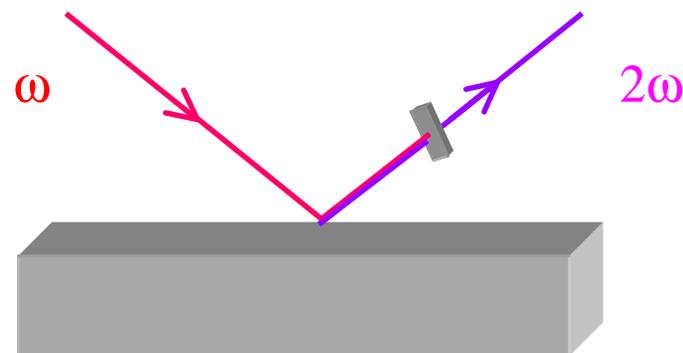
Nonlinear surface spectroscopy:

Detects molecules only at the interface

Second Harmonic Generation (SHG)

$$I(2\omega) \propto |\chi^{(2)} I(\omega)|^2$$

$$\chi^{(2)} = N_s \langle T \rangle \beta$$



Previous SHG and Sum Frequency Generation studies of air/liquid (& liquid/liquid) interfaces:

Steady state (spectra; IR & UV/VIS) > dynamics (VIS)

Steady state	Dynamics
pH, pK	rotational reorientation
adsorption free energy (ΔG_{ads})	isomerization
surface polarity	

SHG from Oxazine Dyes at the Air/Water Interface

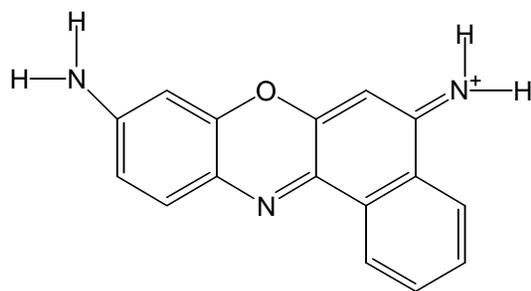
Steady-state SHG Studies - study equilibrium properties:

- Electronic Structure: I_{SHG} vs. λ spectra
- Surface K_d and ΔG_{ads} : I_{SHG} vs. bulk dye concentration
- Composition: dependence on bulk salt, surfactant, other solvents
- Aggregate orientation at interface: anisotropy (I_{SHG} vs γ)

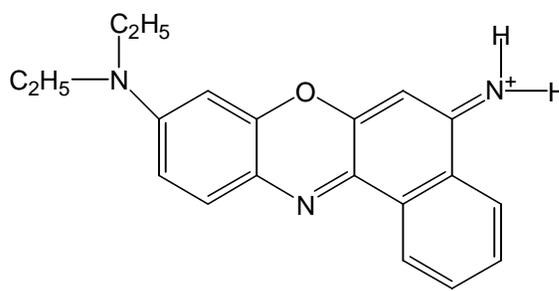
Dynamics Studies

Visible pump - probe transient absorption of bulk dye solutions

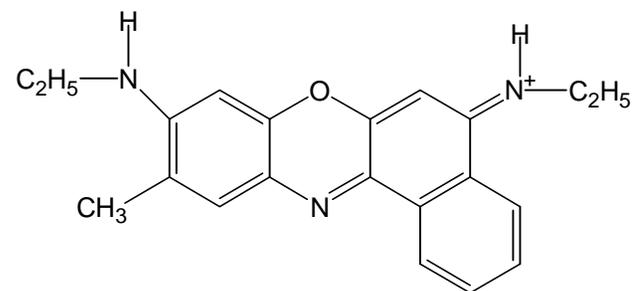
Visible pump - SHG probe of the dyes at the air / water interface



Cresyl Violet



Nile Blue



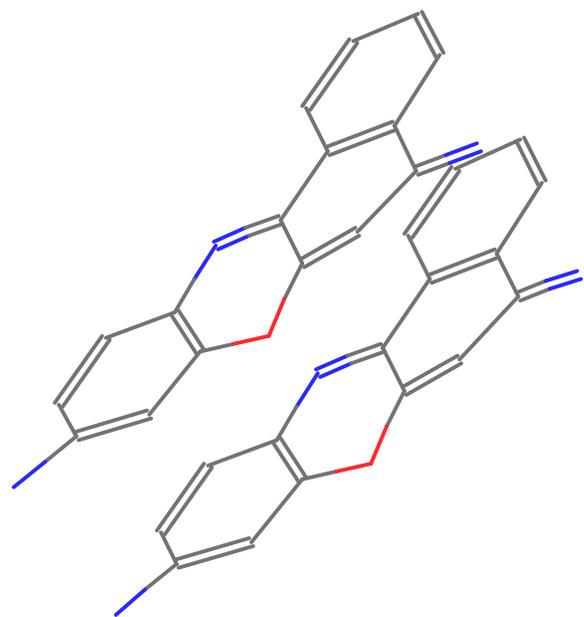
Oxazine 720

H-Aggregate Dimer Electronic Structure

Exciton theory of dipole - dipole coupling (Kasha, 1958)

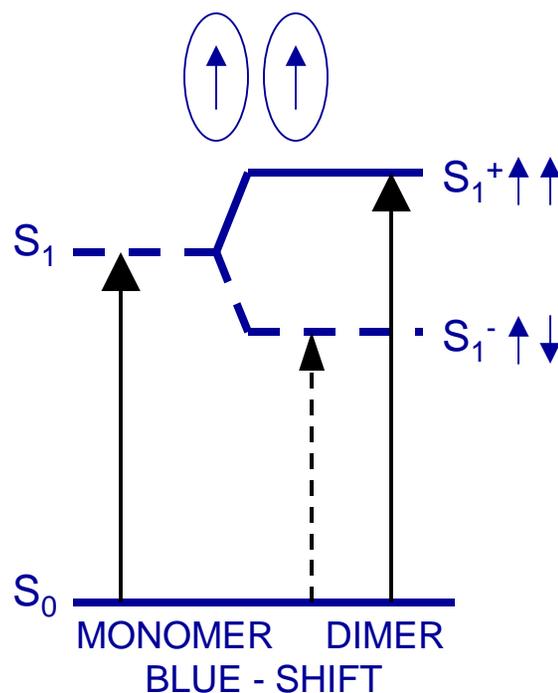
Coupling depends on distance and relative orientation of monomers

Electronic level splitting - spectral shift of aggregate absorption



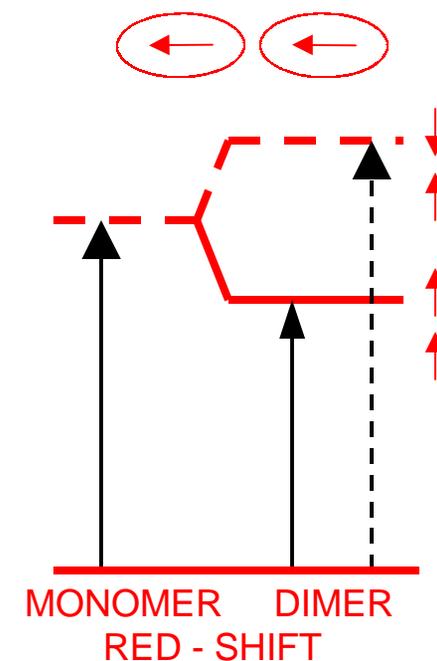
Cresyl violet
H-Aggregate

H-Aggregate
PARALLEL



From Kasha, 1976

J-Aggregate
HEAD-TO-TAIL



Bulk Solution Absorption and K_d

Dimer Equilibrium: for initial $[M]_0$ and fraction x that remains as monomer



$$K_d = \frac{[M]^2}{[D]} = \frac{2[M]_0 x^2}{(1-x)}$$

$$[D] = \frac{(1-x)[M]_0}{2} \quad [M] = x[M]_0$$

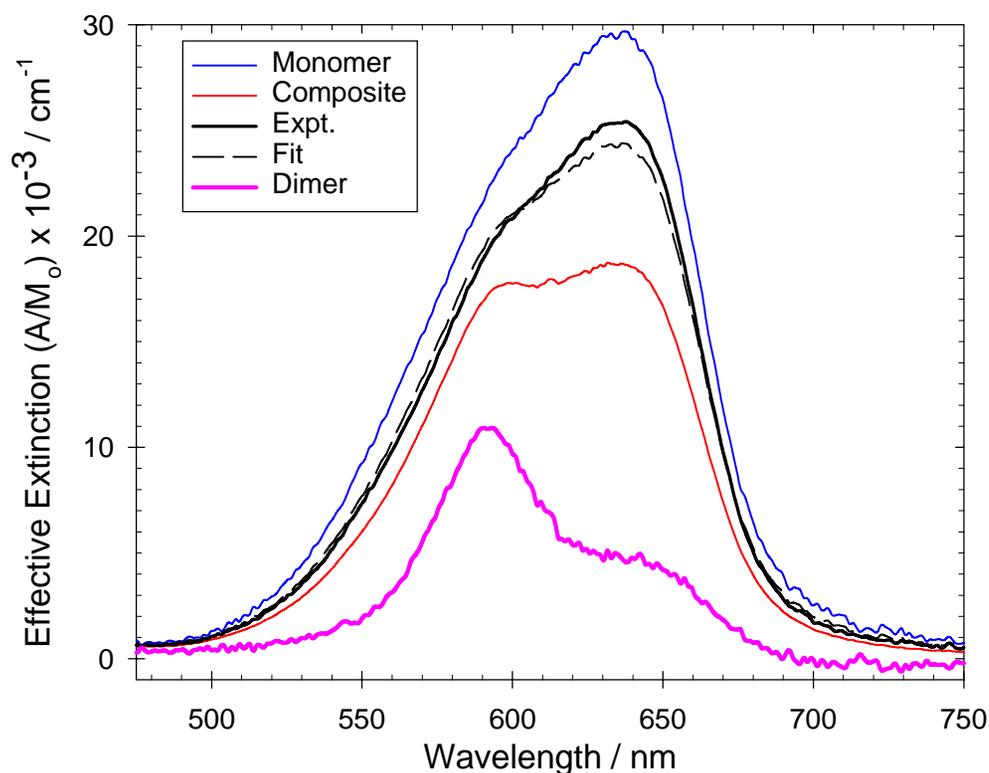
Determine K_d from
UV/vis absorption spectra
($M_0 < 10^{-4}$ M)

Spectral dependence on M_0

$$\epsilon_{\text{eff}}(\lambda) = A/M_0$$

$$\epsilon_{\text{eff}}(\lambda) = \epsilon_M(\lambda)x + \epsilon_D(\lambda)(1-x)/2$$

$$\epsilon_M(\lambda) \text{ from low } M_0$$



Fit x to $\epsilon_{\text{eff}}(\lambda, M_0)$ to get K_d

Results from Bulk Solution Absorption Spectra

Agreement with previous results for K_d :

- For Ox720 with literature^{a,b}
- Relative scaling^c: Ox720 > NB > CV

Adding salt increases dimer concentration ($1/K_d$) by factor of 2 - 3

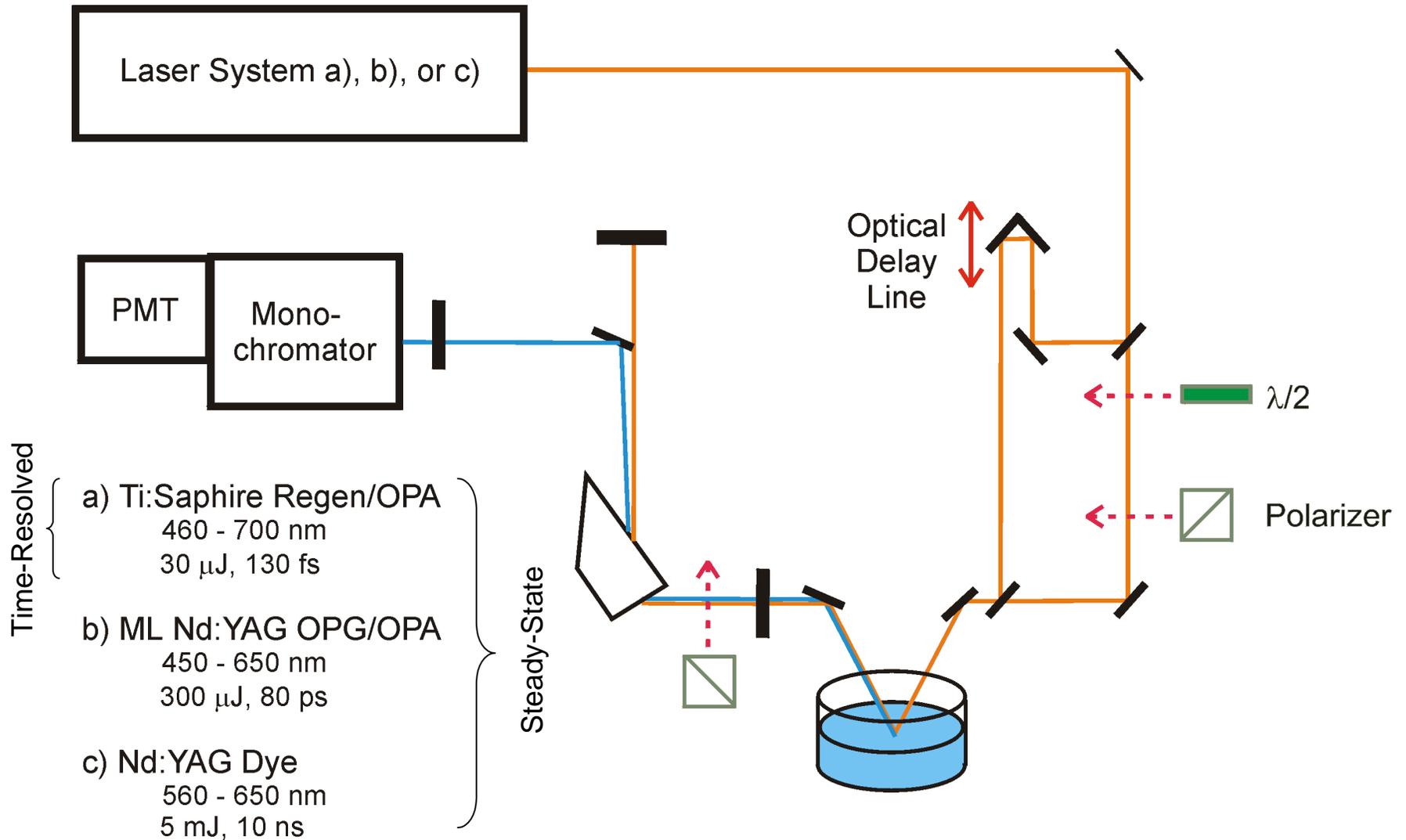
Oxazine dyes in water: Peak positions and K_d			
Dye	λ_{\max} (monomer) (nm)	λ_{\max} (dimer) (nm)	$1/K_d$ (M^{-1}) ($\pm 30\%$)
oxazine 720	620	570	50,000 50,000 ^a 10,000-100,000 ^b
Nile blue	630	590	10,000
cresyl violet	580	550	3200

^a Gvishi & Reisfeld, 1989

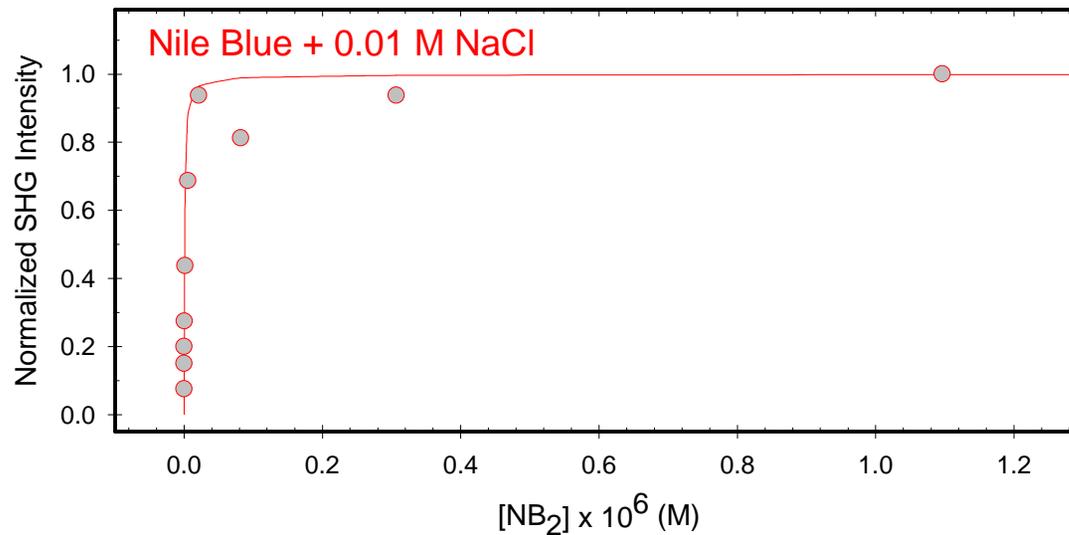
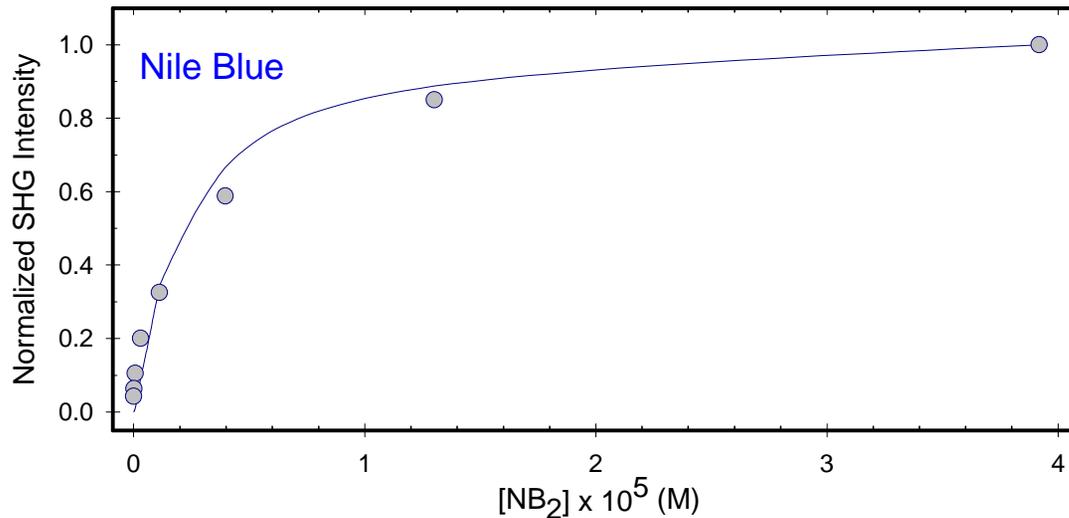
^b Herkstroeter et al., 1990

^c Morozova and Zhigalova, 1982

SHG Interface Studies



SHG Concentration Dependence - Adsorption Isotherm



Surface Adsorption:
Langmuir adsorption kinetics:
measure ΔG_{ads}

$$I \propto \theta^2$$

$$\theta = \frac{CkD}{(1+kD)}$$

θ = coverage

D = bulk conc. of dimer (K_d)

$$\Delta G_{\text{ads}} = -RT \ln(55.5 \cdot k)$$

Aggregates Prefer the Interface

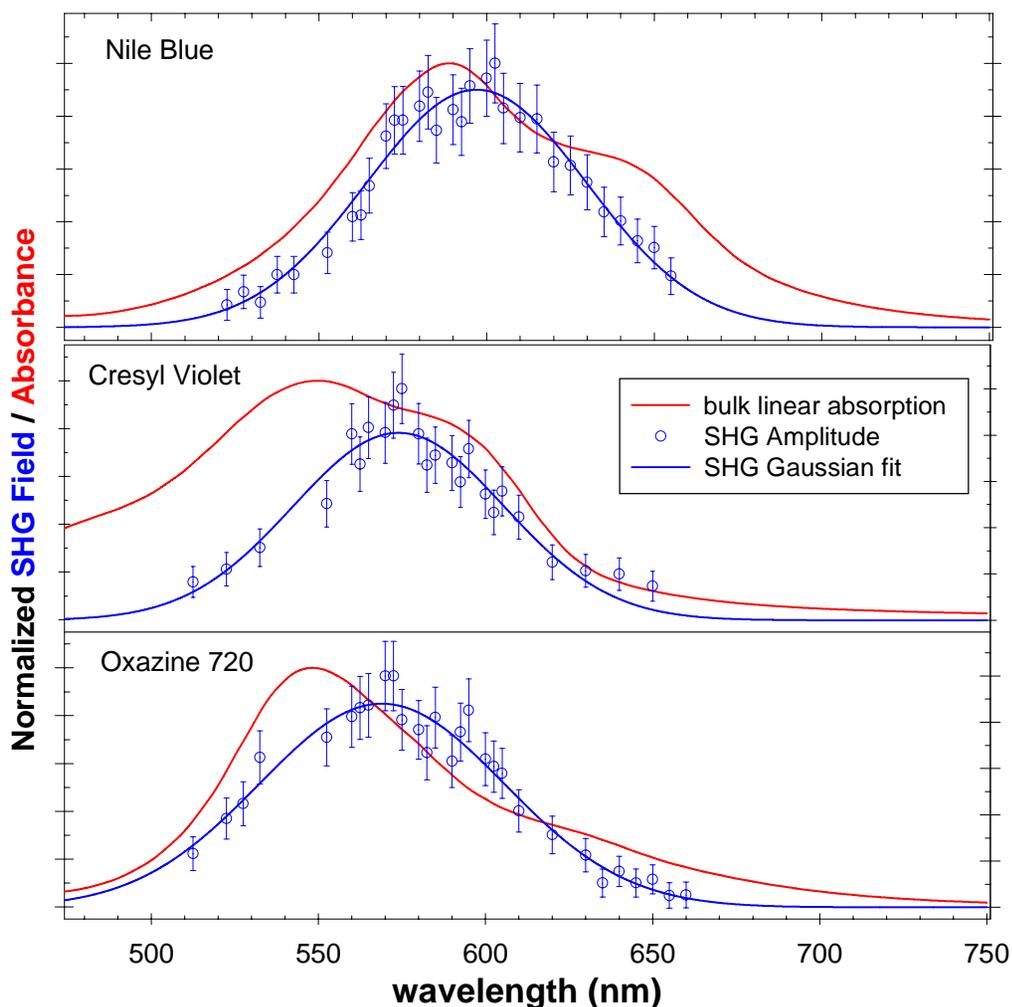
Surface Free Energies: ΔG_{ad} for oxazine dyes

Dye	ΔG_{ad} (kcal/mole, ± 1)	
	w/o salt	w/ salt
oxazine 720	-10.4	- 14.6
Nile blue	- 9.7	- 14.1
cresyl violet		- 9.6

- Large ΔG_{ad} - strong preference for dimer formation at surface
 ΔG_{ad} (p-nitrophenol) \approx -6 kcal/mole
- Dimer excess at surface - seen for IR125 (Levinger, 1995)
- Consistent with SHG for variations of solution composition
 - Salt increases SHG signal more than expected from bulk K_d
 - No SHG observed in non-aggregating conditions
 - ◆ Methanolic and surfactant solutions
 - ◆ Non-aggregating oxazines

SHG is from aggregates only!

SHG Spectra of Oxazines at Air/Water Interface

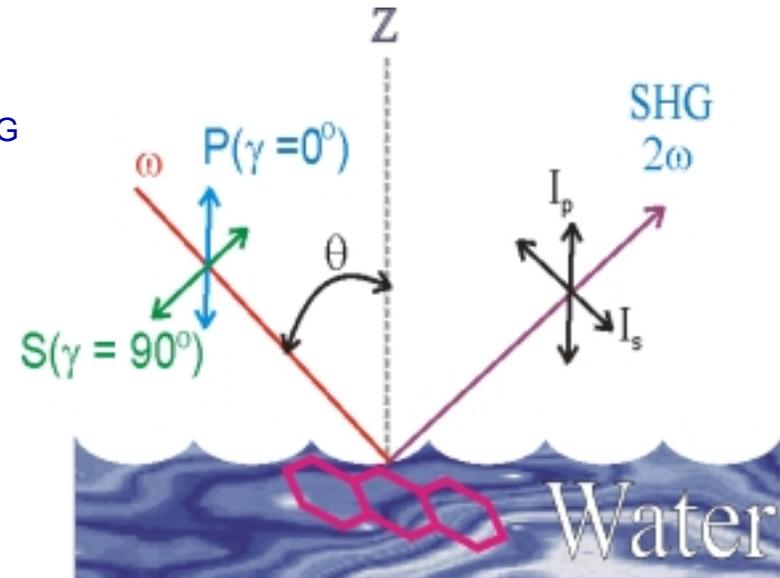


- One band in SHG spectra **single species**
- SHG(ω): resembles input resonance (at ω) more than output (at 2ω)
- SHG peaks are slightly red-shifted
- Red-shift previously reported for dye dimers at air / solid interface (Kemnitz & Leach): intermolecular interactions rather than a more polar interface
- Interface polarity has been found to be average of two bulk phases (Eisenthal)

SHG Polarization Dependence and Orientation

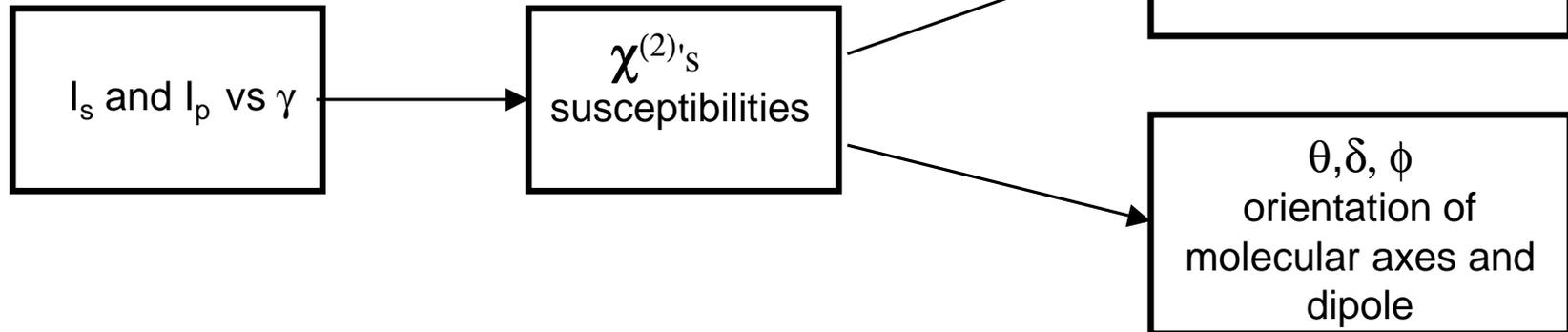
Input (γ) and output polarization resolved I_{SHG}

- Orientational information
- SHG dependence:
concentration or orientation?



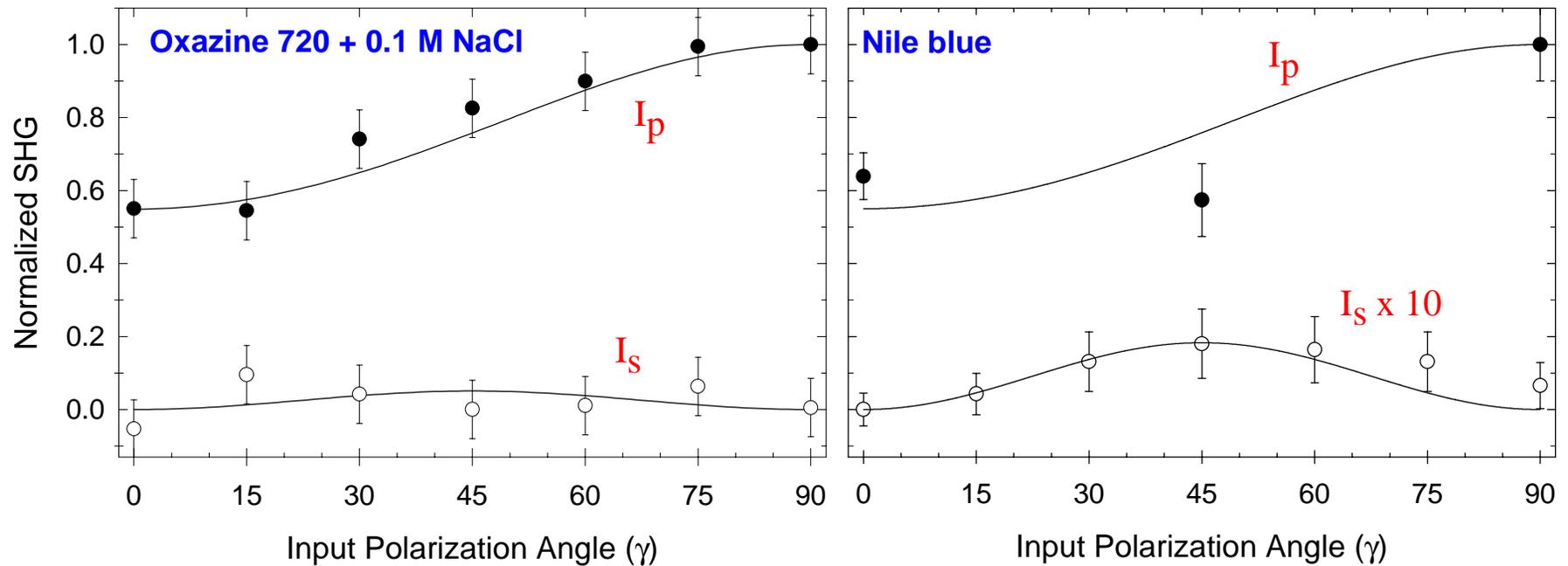
Methods extensively developed and used

$$\chi_{\text{IJK}} = N_s \Sigma \langle T_{\text{IJKijk}}(\theta, \delta, \phi) \rangle \beta_{\text{ijk}}$$



SHG Polarization Dependence

Measurements can be reproduced within model

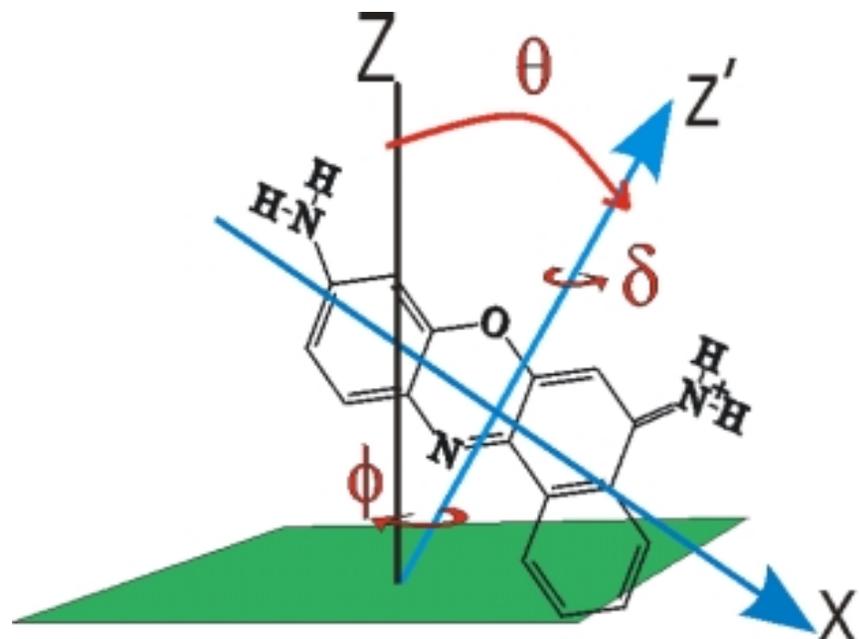


- Relationships observed and related to parameters:

- $I_{ps} > I_{pp}$
- $I_p > I_s$
- $I_{s,45^\circ} > I_{ss}$ or I_{sp}

Results from SHG Polarization Dependence/Anisotropy

	[NaCl] (M)	$\delta = 45^\circ$, random
		θ ($^\circ$)
Nile blue	0	17.2
	0.01	20.3
oxazine 720	0	23.4
	0.1	22.5
cresyl violet	0	26.0
	0.1	24.5



Similar results for all dye samples:

- Little or no detectable orientation variation
- I_{SHG} vs. solution composition: [Dimer] not orientation!!!

Steady-State SHG of Oxazine Dyes

Results from several measurements:

SHG Only from Dimers at Surface

- Single band in spectra
- Orientation independent of coverage
- I_{SHG} consistent with bulk aggregate behavior
 - Increases with salt concentration
 - No SHG from
 - ◆ Methanolic and surfactant solutions
 - ◆ Non-aggregating oxazines

Interface effects vary with property:

- Dimer preference at water surface
 - Surface less polar than bulk - average of bulk phases (Eisenthal)
 - Our measurement of ΔG_{ads} also consistent with lower polarity
- Red-shifted spectra
 - Could be intermolecular interactions of dyes

Aggregates at the interface are a sensitive probe of surface effects!

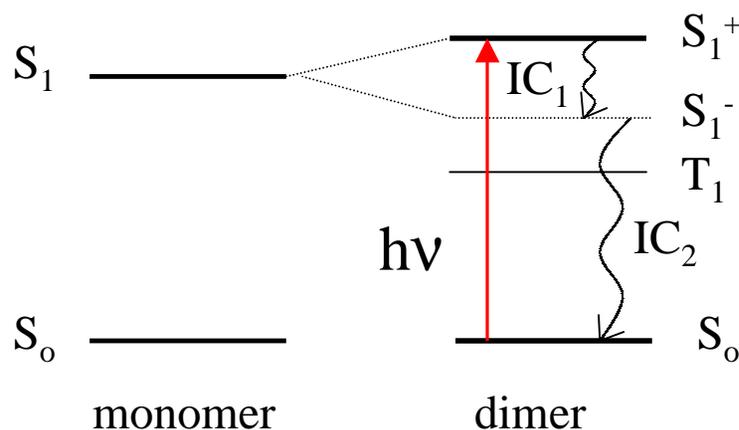
Ultrafast Studies of Oxazines at Air/Water

Previous ultrafast work on:

- **Dyes in solution** Solvation dynamics - mature field
- **Aggregates** Mostly thin film / monolayer and J-aggregates
- **Liquid interfaces** Rotational dynamics & isomerization
- **Oxazines** CV, NB on SiO₂ and SnO₂ nanoparticles (Kamat)

of decay times: One for insulators

Two for semiconductors (back ET)



Initial internal conversion -
 $S_1^+ \rightarrow S_1^-$ (IC_1): <100 fs
Fluorescence not observed

Resolved time:

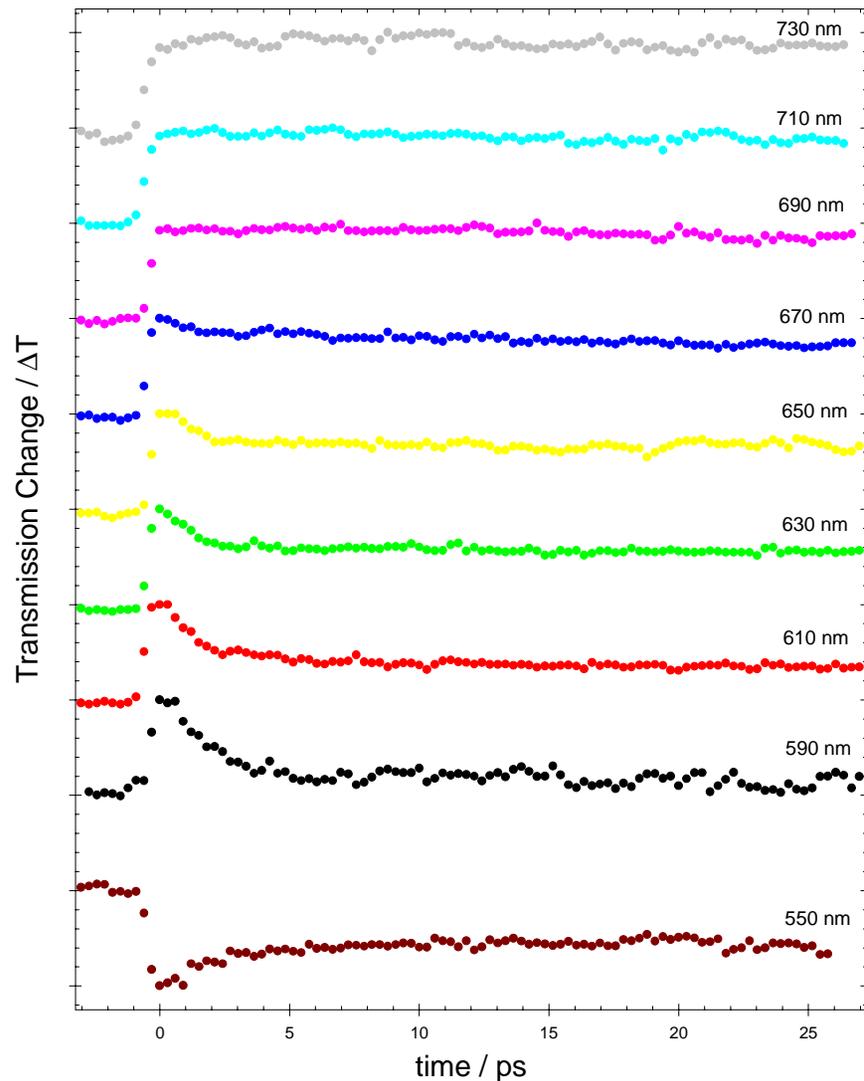
$S_1^- \rightarrow S_0$ (IC_2 or k_{nr})

CV: 2.5 ps

NB: <20 ps

Transient Absorption in Solution

Nile blue 580 nm pump / continuum probe

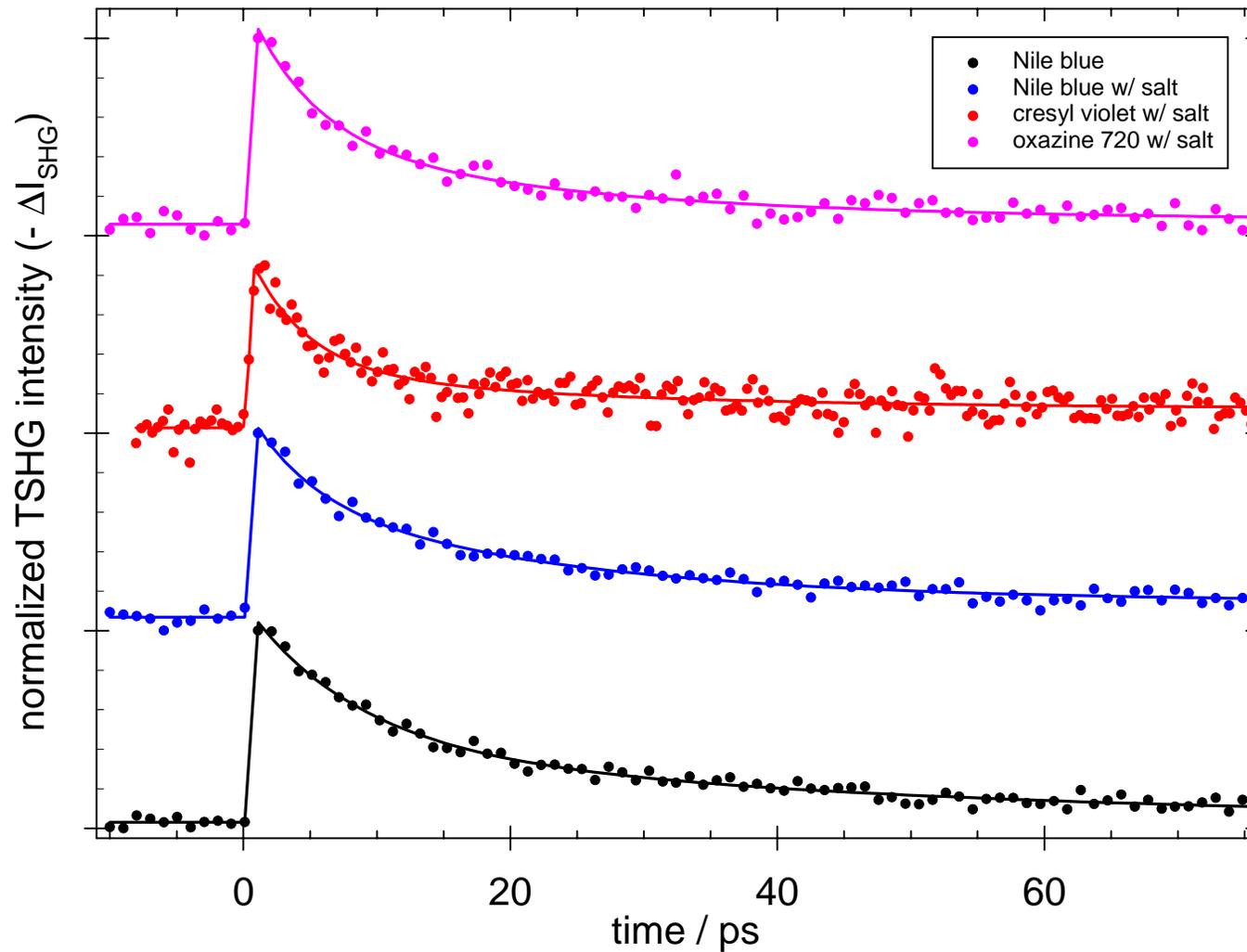


Results can be described in terms of well-known mechanisms:

- Time-Resolved Stokes shift due to solvation dynamics, delayed red shift
- Excited-state lifetimes in water (τ_f), (literature)
 - NB: 420 ps
 - Ox720: 1.8 ns
 - CV: 3.3 ns
- No evidence of signals from bulk dimers

Ultrafast TSHG at the Air/Water Interface

580 nm pump - SHG (290 nm) probe



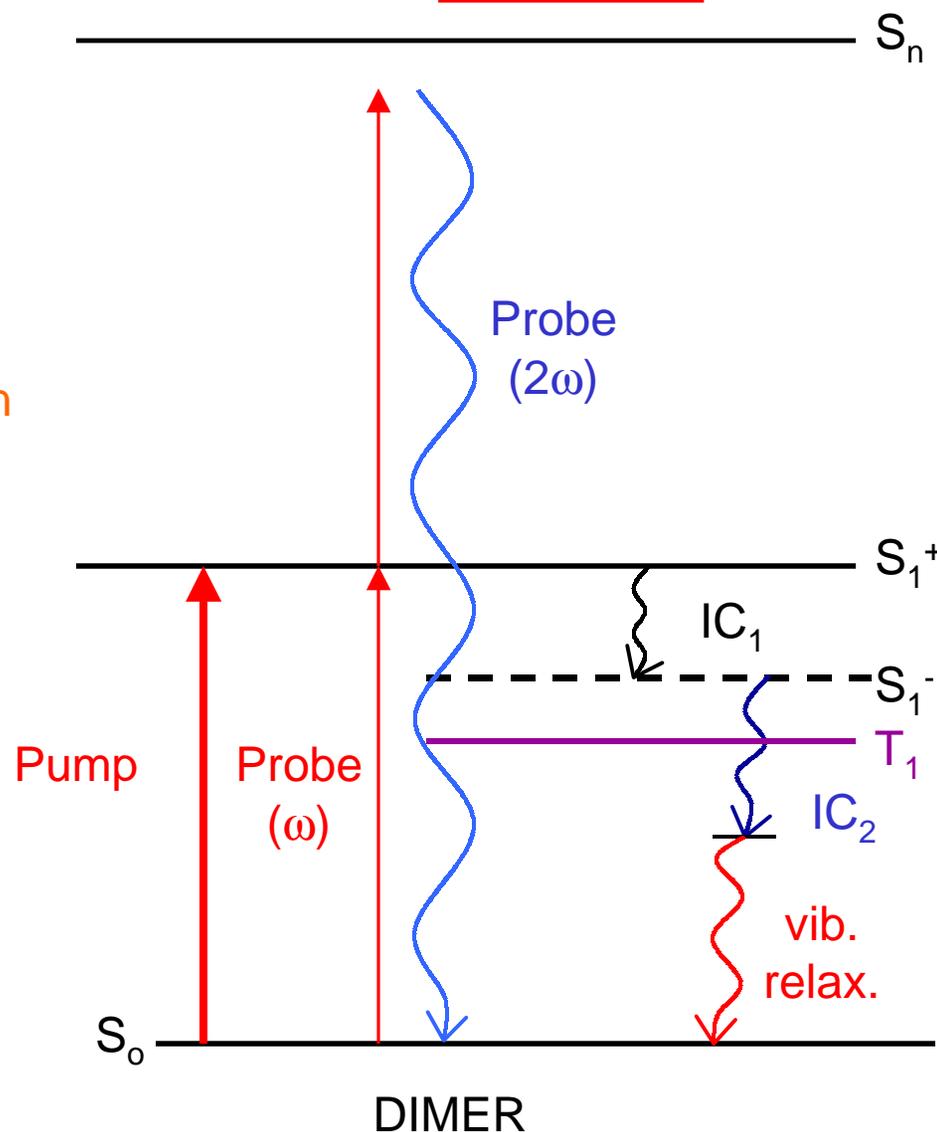
Ultrafast TSHG at the Air/Water Interface

580 nm pump - SHG (290 nm) probe

- Single-photon resonant SHG
- Two parallel GSR mechanisms
 - Ground state solvent relaxation
 - Vibrational relaxation of hot ground state aggregates

TSHG decay times for aqueous oxazine dye solutions.

dye	τ_1 ($\pm 15\%$) ps	τ_2 ($\pm 15\%$) ps
OX720	5	23
CV	4	23
NB	5	22
NB w/o LiCl	8	44



Conclusions

Are interfacial properties consistent with the idea of averaging bulk values?

- **Some are:**
 - Dominance of dimer at surface due to
 - ◆ Dyes driven to lower polarity (hydrophobicity)
 - ◆ Interface polarity is the average of the values for water and air
- **Others are not:**
 - Red-shifted dimer SHG spectrum
 - Relative I_{SHG} and K_d vs. bulk salt concentration

Oxazine TSHG dynamics at the interface are:

- **Different** than the bulk
- New intermediate decay times are similar to previous aggregate results
 - Transient due to ground state recovery
 - ◆ Single-photon resonant SHG signal
 - ◆ Biexponential recovery
- Observed additional recovery compared to colloidal SiO_2 / water interface

Future Directions

- For Oxazines
 - Two-photon resonant studies
 - ◆ $S_1^+ \rightarrow S_1^-$ IC
 - Other interfacial environments
 - ◆ Inverse micelles
- Small molecules
 - Metal carbonyls ($Mn_2(CO)_{10}$, $Cr(CO)_6$)
 - Deep UV pump - mid-infrared probe ($\sim 7 \mu m$)
 - Colloids in organic solvents

Acknowledgements

Jeff Owrutsky

Andy Baronavski

This work was supported by the Office of Naval Research through the Naval Research Laboratory.

This work was performed while DAS held a Naval Research Laboratory / National Research Council Research Associateship.

Molecular Orientation from SHG Polarization Dependence

For isotropic molecular orientation about surface normal,

3 nonzero 2nd order susceptibilities: $\chi_{zzz}, \chi_{zxx}, \chi_{xxz}$ ($\chi_{xzx} = \chi_{xxz}$)

SHG Polarization Dependence ($\gamma = 0$ is p)

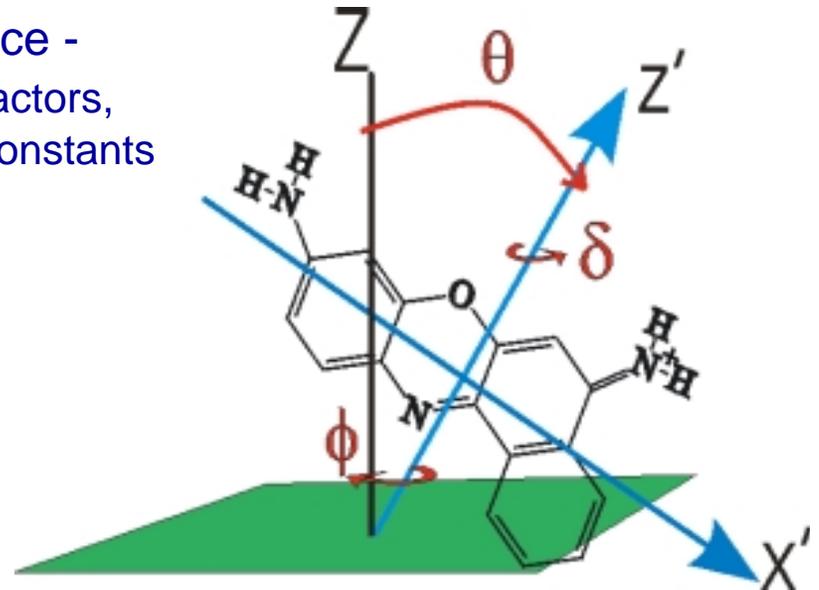
$$I_s(\gamma) = C \left| s_1 \sin 2\gamma \chi_{xxz} \right|^2 (I_\omega)^2$$

$$I_p(\gamma) = C \left| (s_2 \chi_{xxz} + s_3 \chi_{zxx} + s_4 \chi_{zzz}) \cos^2 \gamma + s_5 \chi_{zxx} \sin^2 \gamma \right|^2 (I_\omega)^2$$

$s_1 - s_5$: Coefficients for electric field at surface -
linear & nonlinear Fresnel, geometric factors,
including bulk and interface dielectric constants

χ 's (lab frame **[XYZ]** susceptibilities) related to
 β 's (molecular **[x'y'z']** hyperpolarizabilities)
and orientation (θ, δ, ϕ)

$$\chi_{IJK} = N_s \sum_{ijk} \langle T_{IJKijk}(\theta, \delta, \phi) \rangle \beta_{ijk}$$



Dye Orientation at Interface

Orientation parameter $D(\theta)$: in terms of χ 's using $T_{IJKijk}(\theta, \delta, \phi)$

$$D(\theta) = \frac{\langle \cos^3 \theta \rangle}{\langle \cos \theta \rangle} = \frac{Y \chi_{zzz} + 4\chi_{xxz} + 2\chi_{zxx}}{3\chi_{zzz} + 4\chi_{xxz} + 2\chi_{zxx}}$$

$Y = 3 - \langle \cos^2 \delta \rangle^{-1}$
 $Y = 1$ for random δ
 $Y = 2$ for $\delta = 0^\circ$

RHS: assume dominant β '(s) and δ distribution

β_{zxx} and β_{xxz} dominant (based on Heinz, similar to Dick for $D(\chi$'s))

Nile Blue:	δ ($^\circ$)	0°	45° (random)
	$D(\theta, \delta)$	0.96	0.91
	θ ($^\circ$)	12.1	17.2

Average θ also depends on distribution for θ, δ - assumed narrow so far

Other derived quantities: $\beta_r = \beta_{xxz} / \beta_{zxx} = (\chi_{zzz} + 2\chi_{xxz}) / (\chi_{zzz} + 2\chi_{zxx}) = 0.49$

Angle of **x axis**, ξ : $\cos^2(\xi) = (1 + 2\beta_r)^{-1} (\chi_{zzz} / (\chi_{zzz} + 2\chi_{zxx}))$
 $\xi = 78^\circ$

SHG Polarization Dependence: Results and Interpretation

- Results for χ 's - **more than one β significant**
- Assume β_{zxx} and β_{xxz} dominant:
 - Analogous to other planar aromatic dyes (e.g., Rhodamines)
 - Same for sandwich-type dimers (H-aggregates) as monomer
- **NO differences** in polarization dependence of SHG for:
 - Oxazine 720, Nile blue and cresyl violet, all with salt
 - Nile blue: wide concentration range & with and without salt
 - Several wavelengths (590 nm and 532 nm)
- **SHG intensity changes (with concentration & salt)**
 - **NOT due to orientation effects**
 - **Due to surface dimer population**