Optical Sum-Frequency Spectroscopy

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Sum Frequency Generation: Basic Principle





$$P_{i}^{(2)}(\omega) = \chi_{ijk}^{(2)} E_{j}(\omega_{1}) E_{k}(\omega_{2})$$
$$S \propto |P_{i}^{(2)}|^{2}$$

From structure symmetry, some $\chi_{ijk}^{(2)}$ elements vanish, and others do not but may depend on one another.

Measurements with selected input/output polarization combinations allow deduction of nonvanishing $\chi^{(2)}_{ijk}$

Special Case:

 $\chi_{ijk}^{(2)} = 0$ in media with inversion symmetry

$$\vec{P}_{S}^{(2)}(\omega = \omega_{1} + \omega_{2}) = \vec{\chi} : \vec{E}(\omega_{1})\vec{E}(\omega_{2})$$
$$\vec{\chi}^{(2)} = (\chi_{S}^{(2)} + \frac{\chi_{B}^{(2)}}{i\Delta k})\vec{E}(\omega_{1})\vec{E}(\omega_{2})$$
$$\vec{\chi}_{B}^{(2)} = 0 \quad \text{in media with inversion symmetry}$$
$$\vec{\chi}_{S}^{(2)} \neq 0 \quad \text{at surfaces or interfaces} \quad ---$$

$$SFG \propto |\hat{\mathbf{e}} \cdot \vec{\chi}^{(2)} : \hat{e}_1 \hat{e}_2 |^2$$
$$\chi^{(2)} = \chi^{(2)}_{NR} + \sum_q \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q}$$



As $\omega_2 \rightarrow \omega_q$, or $\omega \rightarrow \omega_{el}$, SFG is resonantly enhanced, $\Rightarrow \Rightarrow$ Spectroscopic information.



Information from SFG Measurements

$$\chi_{ijk}^{(2)} = \int d\Omega f(\Omega) \alpha_{ijk}^{(2)}(\Omega)$$

$$\alpha_{ijk}^{(2)}(\Omega) = \sum_{g,n,n'} \{ \frac{\langle g \mid r_i \mid n \rangle \langle n \mid r_j \mid n' \rangle \langle n' \mid r_k \mid g \rangle}{(\omega - \omega_{ng})(\omega_2 - \omega_{n'g})} + 7 \text{ other terms } \}$$

- Structural symmetry
- Electronic and vibrational spectra
- Distribution function $f(\Omega)$
- Dynamics

Sum-Frequency Spectroscopy



Determination of Average Molecular Orientation

$$SFG \propto |\hat{\mathbf{e}} \cdot \vec{\chi}_{\mathrm{S}}^{(2)} : \hat{e}_{1}\hat{e}_{2}|^{2}$$
$$\vec{\chi}_{\mathrm{S}}^{(2)} = \vec{\chi}_{NR}^{(2)} + \sum_{q} \frac{\vec{A}_{q}}{\omega_{2} - \omega_{q} + i\Gamma_{q}}$$

 $A_{q,ijk}$ can be deduced from measurements with different input/output polarization combinations

$$A_{q,ijk} = N_s \sum_{\xi,\eta,\zeta} < (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\eta})(\hat{k} \cdot \hat{\zeta})a_{\xi\eta\zeta}^{(2)}$$

Average orientation of species can be determined knowing $A_{q,ijk}$ and $a_{\xi\eta\zeta}^{(2)}$.

Experimental Setup



Surface Sum-Frequency Spectroscopy

Basic Idea: Surface and Bulk have different structural symmetry.

Information from Surface SFG Measurements

- Surface structural symmetry
- Surface electronic and vibrational spectra
- Surface distribution function $f(\Omega)$
- Surface dynamics

Surface Sum-Frequency Generation



Output from a monolayer:

$$S(\omega) = \frac{8\pi^3 \omega}{\hbar c^3} |\chi_{ijk}^{(2)}|^2 I_1 I_2 AT \text{ photons/pulse}$$

$$\approx 10^4 \text{ photons/pulse}$$

for $|\chi_{ijk}^{(2)}| \square 10^{-15} esu, I_1 \sim I_2 \sim 10 \text{ GW/cm}^2$
 $A \sim 0.1 \text{ mm}^2, T \sim 10 \text{ psec.}$

Output highly directional:

$$k_{\parallel}(\omega_1) + k_{\parallel}(\omega_2) = k_{\parallel}(\omega)$$

Advantages

- Submonolayer sensitivity
- Surface specificity
- Output highly directional
- Non-detrimental, in situ, remote sensing
- High spatial, temporal, spectral resolution
- Applicable to any interfaces accessible by light

many unique applications

Surface Specificity of SFG



Unique Applications

Buried interfaces

•Surface structures of neat bulk materials: polymers, liquids, etc.

- •Molecular adsorption under ambient condition
- •Surface dynamics
- Surface microscopy

Neat Liquid Interfaces

• Molecules are randomly oriented in the bulk liquid, but could be more orderly arranged at a surface or interface.



- Surface vibrational spectrum provides information about surface structure.
- Surface structure determines surface properties.
- Surface vibrational spectrum is important, but cannot be obtained by conventional techniques.
- SFG is unique for surface vibrational spectroscopy of neat liquids.

Water Interfaces

Water:

Most abundant and important liquid on earth

Water interfaces play pivotal roles in many areas of science and technology:

Home and industrial applications: washing, cleaning, corrosion, plating Environmental problems:

pollution, nutrient circulation

Life Science:

membrane formation, protein hydration Geoscience:

soil formation and weathering

Experimental Techniques

Probing macroscopic properties:

- Surface tension
- Surface potential
- Ellipsometry (Anisotropic refractive indices)

Probing microscopic properties:

- X-ray spectroscopy
- STM & AFM
- Second harmonic generation
- Sum-frequency vibrational spectroscopy

SF Vibrational Spectra of Vapor/Water Interface

SF Spectrum (SSP) of OH Stretches at Vapor/Water Interface



Dependence on Polarization Combination

$$S \propto |\hat{e} \cdot \chi_s^{(2)} : \hat{e}_1 \hat{e}_2|^2$$



Du et al, PRL 70, 2313 (1993)

Wei, Shen, PRL 56, 4799(2001)

Hydrogen Bonding Of water Molecules

Hexagonal Ice Structure Near Surface





SIDE VIEW

Assignment of Spectral Features

- Dangling OH bond at 3700 cm⁻¹
- Weak peak at ~3600 cm⁻¹
- Water-like peak at ~3400 cm⁻¹
- Ice-like peak at ~3200 cm⁻¹



Spectra of $|\chi^{(2)}(\omega)|$, Re $\chi^{(2)}(\omega)$, and Im $\chi^{(2)}(\omega)$



Results and Interpretations

- 3700 cm⁻¹ narrow positive peak: Dangling OH with H pointing up (Antisymmetric stretch)
- ~3400 cm⁻¹ broad negative liquid-like peak: Bonded OH in local disordered Hbonding network; net orientation with H pointing down
- ~3100 cm⁻¹ weak positive ice-like peak: Bonded OH in more ordered local Hbonding network; weak net orientation with H pointing up
- ~3600 cm⁻¹ weak narrow positive peak: Symmetric OH stretch mode of water molecules with one dangling OH bond











Water Interfaces with Hydrophilic and Hydrophobic Solid Surfaces

Hydrophilic: Water/Quartz Hydrophobic: Water/OTS/Quartz

SFG Vibrational Spectra of Water at the Water/Quartz Interface





Spectra of $|\chi_s^{(2)}|$, $\text{Re}\chi_s^{(2)}$, and $\text{Im}\chi_s^{(2)}$ of Quartz/water Interfaces



Ostroverkhov et al, PRL 94, 046102 (2005)

Water at Hydrophobic Interfaces



Interfacial Water Structure

- Interfacial water molecules form an ordered/disordered hydrogen-bonding network; water surface has a more ordered structure than the bulk.
- Many other water interfaces show a similar vibrational spectrum, indicating that they have a similar interfacial structure (although the degree of ordering may be different)



Studies of Polymer Surfaces



Almost Everything Is Replaceable.

Surface properties of polymers are controlled by surface composition, structure, and molecular orientations. Molecular-level information is needed.

Techniques Available for Probing

- Infrared spectroscopy
- Atomic force microscopy
- Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy
- Sum-frequency vibrational spectroscopy

Probing Surface Modification of Polymers

- Surface has composition and structure generally different from bulk.
- Precipitation of certain molecular groups or components dominates the surface properties without changing the bulk properties.
- Adjusting bulk composition, doping with impurities, or changing end groups of main and side chains can modify surface structure and properties.
- Surface-specific probe at the molecular level is needed ⇒ SFVS.



SME = H

ÇH₃

ÇH3

End Groups:

Name of the End Groups Name of the Whole Polymer BioSpan (BN)

$$SME = -O-R-Si-O+Si-O+Si-CH_3$$

$$-OCH_2CH_2(OCH_2CH_2)_nOH$$

$$PDMS$$

$$BioSpan S (BS)$$

$$BioSpan P (BP)$$

Infrared Spectra of BN, BS, and BP


SF Vibrational Spectra





Other Means of Modifying Polymer Surfaces

For patterned templates,

- Etching
- Photo-induced reactions
- Mechanical rubbing

Surface-Induced Liquid Alignment

- Rubbed polymer films (e.g. polyimide, polyvinyl alcohol, etc)
 - \Rightarrow Surface structual change



- \Rightarrow Surface induced bulk alignment of liquid crystals
- \Rightarrow Liquid crystal display (LCD)





Example

Polyvinyl Alcohol (PVA)

100% hydrolyzed Molecular weight: 14,000



Spin-coated on fused quartz Film thickness : ~30 nm Rubbed with velvet cloth



SF Vibrational Spectra of Rubbed PVA



Qualitative Understanding



Determination of Average Molecular Orientation

$$SFG \propto |\hat{\mathbf{e}} \cdot \vec{\chi}_{\mathrm{S}}^{(2)} : \hat{e}_{1}\hat{e}_{2}|^{2}$$
$$\vec{\chi}_{\mathrm{S}}^{(2)} = \vec{\chi}_{NR}^{(2)} + \sum_{q} \frac{\vec{A}_{q}}{\omega_{2} - \omega_{q} + i\Gamma_{q}}$$

 $A_{q,ijk}$ can be deduced from measurements with different input/output polarization combinations

$$A_{q,ijk} = N_s \sum_{\xi,\eta,\zeta} < (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\eta})(\hat{k} \cdot \hat{\zeta})a_{\xi\eta\zeta}^{(2)}$$

Average orientation of species can be determined knowing $A_{q,ijk}$ and $a_{\xi\eta\zeta}^{(2)}$.

Quantitative Analysis

Conclusion

- CH₂ groups on PVA surface point outward in air.
- After rubbing, PVA chains are well aligned along the rubbing direction and tilted by ~3° in the anti-rubbing direction.



In Situ Studies of Surface Chemical Reactions

Motivations

- Industrial catalysis processes proceed under high ambient pressure.
- Academic studies of surface catalysis are often conducted in UHV.
- In situ surface probes of real catalytical processes are desired.

Surface Reaction Studies under High Gas Pressure

- In situ identification of surface species.
- Correlation of surface species with reaction products.
- Example: CO oxidation on Pt(111)

Oxidation of CO on Pt(111): $2CO + O_2 \Rightarrow 2CO_2$

- An important catalytical process (first studied by I. Langmuir, 1922)
- Rare in situ surface studies under real atmosphere

(plenty UHV results available) (IR spectroscopy on supported catalyst: Lindstrom and Tsotsis, 1985)

Pressure gap rpoblem

(Catalytical results under real atmosphere and under UHV may be different.)

Experimental Arrangement



CO on Pt(111)



Stretch Vibrations of CO on Pt(111)



(100 torr CO + 40 torr O₂)/Pt(111)



TOR = **Turn-Over Rate** = $\#CO_2$ produced per surface Pt atom per sec.

 $T_{I} = Ignition temperature$ = 760K Reaction is self-sustained for T > T_{I}



CO coverage varied by CO/O₂ relative partial pressure.





Results (with Excess CO)

• Below Ignition Temperature (TI):

Low reaction rate Surface dominated by atop CO Number of atop CO decreases as TOR increases

• Above Ignition Temperature (TI):

High reaction rate Surface dominated by incommensurate CO Number of incommensurate CO increases as TOR increases

Incommensurate CO species are responsible for surface catalytical reaction $(2CO + O_2 \Rightarrow 2CO_2)$

Surface Melting of Ice

Surface Melting of Ice (Proposed by Faraday in 1850)



A quasi-liquid layer exists on ice at $T_S < T < T_{melt}$

Relevance: skating, skiing, atmospheric pollution, glacier gliding, etc.

Phenomenological Theory



Experimental Proofs

Photoemission: (Nason and Fletcher, 1975)	T _s ≈ - 160°C
Proton backscattering:	$T_S \approx -50^{\circ}C$
(Golecki and Jaccard, 1978)	$L \approx 80 \text{ nm} @ -2^{\circ}C$
Ellipsometry:	$T_S \approx -10^{\circ}C \text{ (prism)}$
(Beaglehole and Nason, 1980) (Furukawa et al, 1987)	$\begin{array}{l} L \approx 10 \ nm @ \ -2^{\circ}C \\ T_{S} \approx - \ 2^{\circ}C (\text{basal}) \end{array}$
	$\begin{array}{l} T_{S} \approx \text{-} \ 4^{\circ}C (\text{prism}) \\ L \ \approx 30 \ nm @\text{-}2^{\circ}C \ (\text{prism}) \end{array}$

Optical reflectometry andNo surfaceinterference microscopy:Incomplete(Elbaum, Lipson and Dash, 1993)point (pure

No surface melting below -2°C Incomplete wetting near triple point (pure vapor / ice)

$$\begin{split} T_S &\approx -13.5 \pm 2.6^\circ C ~\text{(basal)} \\ L &\approx 15 ~nm ~@\text{-2°C (basal)} \\ T_S &\approx -12.8 \pm 1.9^\circ C ~\text{(prism)} \\ L &\approx 7 ~nm ~@\text{-2°C (prism)} \end{split}$$



Vapor/Ice SF Vibrational Spectrum





Temperature Dependence of Free OH Mode



 $T_s \sim 200 K$





Orientational order parameter:

$$S = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle_{f(\theta)} = \frac{\cos\theta_{\max} + \cos^2\theta_{\max}}{2}$$

Ice Surface $\Leftrightarrow \theta_{\max} \approx 0 \Leftrightarrow S \approx 1$



Water Surface \Leftrightarrow Large $\theta_{\max} \Leftrightarrow$ Small S



Results

- Surface melting of ice (*libration of dangling OH*) begins at ~200K.
- Disordering of the quasi-liquid layer increases with temperature.

Sum-Frequency Spectroscopy for Bulk Studies

Surface-Induced Pyroelectric Ice

(Ice Film with a Net Electric Polarization)

Ice Structure

• Ice Rules (Bernal-Fowler-Pauling)

Tetrahedral H-bonding One and only one proton between two oxygen atoms

- Residual Entropy (Pauling, 1935)
- Ferroelectric Transition $T_c = 0 K$
- Dipole-Dipole Interaction Energy (Onsager, 1936; Slater, 1941)



Pauling's Calculation on Residual Entropy

- Number of vertices (oxygen atoms) = n
- Total number of H-bonds = 4n/2 = 2n
- Each bond has 2 possible configurations: *Proton residing at one or the other end*
- Number of ways arranging the bonds = 2²ⁿ Not all of them are allowed by ice rules
- Around each vertex, number of bonds = 4
 # bond configurations = 2⁴
 # bond configurations allowed by ice rules = 6
 Fraction of allowed configurations = 6/2⁴
- Total number of lattice configurations = $2^{2n}(6/16)^n$
- Residual entropy = k $\ln[2^{2n}(6/16)^n]$ = nk $\ln(3/2) = 0.4055$ nk (Nagle: 1.5065 < w < 1.5068)




Hexagonal Ice on Pt(111)



H₂O adsorbs with O bonded to Pt.

First monolayer of H₂O forms a surface dipole layer.

Surface-Induced Ordering



Surface dipole layer could induce ferroelectric ordering in neighboring layers following the ice rules.

Experimental Arrangement



Sum Frequency Vibrational Spectroscopy As An Effective Probe for Surface-Induced Polar Ordering

$$SFG \propto |\chi_{S,eff}^{(2)}|^2$$
$$\chi_{S,eff}^{(2)} \cong \int_{Int} \chi_D^{(2)} dz$$





Thermal Desorption Spectra of Ice on Pt(111)



Sum Frequency Vibrational Spectra of Ice on Pt(111)



Dependence of Polarization on Film Thickness



Summary

SF vibrational spectroscopy on Ice/Pt(111) shows:

existence of surface-induced polar ordering (pyroelectricity) in ice films grown on Pt(111) with a decaying length of 30 ML at 120K Sum-Frequency Spectroscopy as a Novel Probe for Molecular Chirality

Chiral Molecules



Characteristics

- Cannot be brought to coincidence with its mirror image by translation and rotation.
- Have no inversion symmetry.
- Chiral coefficients for the two enantiomers have opposite signs.

Importances of Molecular Chirality

- Origin of life: more than 90% of natural biological molecules are homo-chiral. Why?
- Same molecules with different chiralities can have very different properties.
- Molecular chirality is most important for biology: secondary structural changes, complexation, drug quality control, etc.

Conventional Optical Probes for Molecular Chrality

Circular Dichroism (CD)

Optical Rotatory Dispersion (ORD)

$$(n+i\beta)_{+} - (n+i\beta)_{-} = \Delta n + i\Delta\beta$$

Limited Sensitivity of CD and ORD

Electronic Transitions: $\frac{\Delta n}{n} \sim \frac{\Delta \beta}{\beta} \sim 10^{-3} - 10^{-4}$ Vibrational Transitions: $\frac{\Delta n}{n} \sim \frac{\Delta \beta}{\beta} \sim 10^{-4} - 10^{-5}$

Detection Limit:

 $(\Delta\beta)l_{\rm lim}\sim 10^{-4}$

For electronic transitions, $\beta \sim 10^3$ / cm; $l_{\rm lim} \sim 1 \ \mu {\rm m}$

Why is the sensitivity limited?

CD is electric-dipole forbidden

Chiral response is characterized by rank-3 tensor coefficients

 μ_{lmn} with $l \neq m \neq n$

Linear optical response is characterized by rank-2 tensor(\mathcal{E}_{ij}) under electric-dipole approximation. For rank-3 chiral response, we must involve higher-order magnetic-dipole contribution.

$$\varepsilon_{lm}(k) = \varepsilon_{lm}(0) + G_{lmn}k_n$$

with $|G_{lmn}k_n| \square |\varepsilon_{lm}|$

Shortcomings of CD and ORD

- Difficult to probe chirality of thin films and monolayers.
- Difficult for *in situ* probing of chirality.
- Difficult to study chiral functions and dynamics of practical systems.

Can we find a more sensitive chiral probe?

Sum-Frequency Spectroscopy for Probing Molecular Chirality (Development of a Novel Powerful Tool)

Sum-Frequency Spectroscopy



$$S_{SF} \propto |P_i^{(2)}(\omega)|^2$$
$$P_i^{(2)}(\omega = \omega_1 + \omega_2) = \chi_{ijk}^{(2)} E_j(\omega_1) E_k(\omega_2)$$



$$\begin{split} S_{SF} &\propto |P_i^{(2)}(\omega)|^2 \\ P_i^{(2)}(\omega = \omega_1 + \omega_2) &= \chi_{ijk}^{(2)} E_j(\omega_1) E_k(\omega_2) \\ \text{In isotropic chiral media,} \\ \chi_{achiral}^{(2)} &\approx 0 \\ \chi_{chiral}^{(2)} &= \chi_{ijk}^{(2)} (i \neq j \neq k) \neq 0 \quad (\text{electric-dipole allowed} \\ \chi_{chiral}^{(2)} / \chi_{achiral}^{(2)} >> 1 \quad \text{as compared to} \quad \Delta n/n << 1 \end{split}$$

SF spectroscopy also has submonolayer sensitivity.

Better Sensitivity Expected from Using SF Spectroscopy to Probe Chirality

Bulk Nonlinear Susceptibilities of Chiral Liquids

$$P_{B,l}^{(2)}(\omega = \omega_1 + \omega_2) = (\chi_B^{(2)})_{lmn} E_m(\omega_1) E_n(\omega_2)$$

$$(\chi_B^{(2)})_{lmn} = \chi_{chiral}^D \mathcal{E}_{lmn} \qquad \begin{array}{l} \mathcal{E}_{lmn} = \pm l & \text{for } l \neq m \neq n \\ + \chi_{lmpn}^Q k_{2p}^2 + \chi_{lpmn}^Q k_{1p}^2 + \chi_{plmn}^Q k_p \end{array}$$

Nonvanishing Independent Elements: Chiral elements (electric-dipole allowed)

$\chi^{D}_{chiral} arepsilon_{lmn}$

Achiral elements (electric-dipole forbidden)

$$\begin{split} \chi^{Q}_{llmm}, & \chi^{Q}_{lmml}, & \chi^{Q}_{lmlm}, \\ \chi^{Q}_{llll} &= \chi^{Q}_{llmm} + \chi^{Q}_{lmml} + \chi^{Q}_{lmlm} \end{split}$$



Chiral Elements can be deduced from:

$$SPP \rightarrow \chi^{(2)}_{zxy}$$
$$PSP \rightarrow \chi^{(2)}_{yzx}$$
$$PPS \rightarrow \chi^{(2)}_{zyx}$$

$$SFG \propto |\chi_{
m ijk}^{(2)}|^2$$

Experimental Setup



Probing Molecular Chirality of Electronic Transitions

Binaphthol as an Example (Twisted Dimer with coupled excitons)



Chiral Spectra of Excitonic Transitions of BN

BN in THF solution

BN monolayer on water



M.Belkin et al, PRL (2001)

S.H. Han et al, Phys. Rev.(2002)

Probing Molecular Chirality of Vibrational Transitions

Chiral SF Spectrum of BN in Solution



M.A. Belkin et al, PRL (2003)

Chiral Vibrational Spectra of a BN Monolayer on Water



M.A. Belkin et al, PRL (2003)

SF Chiral Responses of Amino Acids (Molecules with a Chiral Center)



N. Ji, Y.R. Shen, JACS **126**, 15008(2004) **127**, 12933(2005)

Chiral SFG Microscopy

Chiral Optical Microscopy is useful to track biological molecules and their chiral structures and conformations relevant to their functions in biological systems.

- Absence of achiral background, e.g., water
- Selective detection of chiral molecules
- No need of fluorescence labeling

Chiral Microscopy (Collaboration with Hao Yang's Group)



Images of Silica Beads (2.5 µm) in R-BN Solution



Microscopic Images of a Cell



Ordinary

SFG

Fluorescencelabelled

Future Plan

(Collaboration with Haw Yang's group)

- •Measure chiral spectra of DNA, proteins, and other biological molecules in bulk and at surfaces
- Apply chiral microscopy to biological systems
- Study chiral molecular adsorption on chiral surfaces (understanding chiral molecular separation)
- Probe *in situ* change of molecular chirality such as protein folding, induced chirality and chiral dynamics

Microscopic Images of a Cell



Ordinary

SFG

Fluorescencelabelled

Ultrafast Surface Dynamics of Neat Materials
Ultrafast Dynamics of OH Stretch Vibrations at Water Interfaces

Ultrafast Dynamics of OH Stretches of Water

Intensively studied in bulk

Woutersen et al., PRL **81**, 1106 (1998). Lock and Bakker, JCP **117**, 1708 (2002). Cowan et al., Nature **434**, 199 (2005).

Dynamics occurring on hundreds of femtosecond timescale in the H-bonding network

Vibrational excitation Spectral diffusion Vibrational relaxation Thermalization

Surface Dynamics of OH Stretches at Water Interfaces

- Has hardly been investigated. (*Needs a surface-specific probe---- SFVS*)
- Different from the bulk because of different structures?
- Similar to the bulk as dominated by H-bonding network?
- Slower than in the bulk because of surface termination of the H-bonding network?
- Faster than in the bulk because of the more ordered structure of water interface?
- Probing methods:Free induction decay (Alex Benderskii)Spectral hole burning with SFG

Pump-Probe SFG Experimental Layout



SFG Free Induction Decay: H₂O Free-OH Stretch at Vapor/water Interface



Spectral Hole Burning

- hole width ~ homogeneous linewidth
 = 1/dephasing time
- hole recovery time
 ~ population relaxation time
- hole broadening with time
 ~ excitation transfer to neighbors
 (spectral diffusion)





Spectral Hole-Burning at Water/Silica Interface



Pump-Probe Spectroscopy of Bonded OH Stretch Modes at the Fused-silica/Water Interface



Time-Resolved SF Probing of Spectral Hole Recovery



OH Vibrational Relaxation

- Excitations of H-bonded OH stretches
- $t \le 100 \text{ fs:}$ Spectral diffusion of excitations to available OH stretches in the H-bonding network is over. (Spectral hole governed by reduced absorption from v = 0 to v = 1 and enhanced absorption from v = 1 to v = 2.
- $t \sim 400 \, fs$: Vibrational relaxation from $v = 1 \, states$.
- *t* ≥ 800 *fs*: Thermalization of deposited energy. *Temperature increase red-shifts the OH vibrational spectrum.*

$$S(t) = 1 - (1 - S_0)e^{-(t - 100)/T_v} + \Delta S[1 - e^{-(t - 100)/T_t}]$$

with $T_v = 300 \, fs$ and $T_t = 700 \, fs$

SFVS of Fused-silica/OTS/Water Interface



Pump-Probe Spectroscopy of Dangling-OH Stretch Modes at the Fused-silica/OTS/Water Interface



Results

Bonded OH stretches

- Spectral diffusion time ≤ 100 fs
- Vibrational relaxation time ~ 300 fs
- Thermalization time ~ 700 fs
- Dephasing time: ≤ 100 fs

Free OH Stretch

- Hole recovery time: 1.3 ps
- Dephasing time: 1/linewidth ~ 330 fs

Sum frequency spectroscopy is a powerful, versatile tool that allows many unique applications

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