Molecular Anisotropy at Air/Solid and Solid/Liquid Interfaces with Sum-Frequency Generation Vibrational Spectroscopy

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Outline

1. Surface Vibrational Spectroscopy with high resolution & intrinsic lineshape
2. Molecular Anisotropy at Air/Solid and Solid/Liquid Interfaces: Mica

Many Areas in SFG-VS Surface/Interface Studies

- Biological Membranes
  - Membrane proteins, lipid bilayers, drug interactions

- Industrial Processes
  - Paints, coatings, corrosion, food formulation

- Material Sciences and Devices
  - OLED, solar cell, photovoltaic devices

- Surface/Interface Properties
- Catalysis
  - Catalyst/substrate interactions, reaction mechanisms, intermediates

- Environment/Geosciences
  - Mineral/water and bacteria/mineral interactions

- Characterization Tools
  - Spectroscopy, imaging

- Fundamental Understanding
  - Structure, orientation, conformation, dynamics

- Macroscopic
- Microscopic

- Bridging the Gap with SFG-VS
  - Time-resolved dynamics, surface selectivity, sub-monolayer sensitivity

- Applications
  - Knowledge Base
Surface/Interface: One Last Frontier? with Intrinsic Broken Centrosymmetry

Surface/Interface is everywhere/ubiquitous

Asymmetric forces at the interface

Bulk           Surface

Asymmetric forces at the interface

Unique Chemistry
- Steric Effect
- Solvation, ion effects
- Self-assembly

Non-bonding Interactions Controls
Molecular Self-Assembly, and Chiral Structures

Complex Interfaces (Inhomogeneities):
- Simple composition with complicated behavior
- Composition/behavior both complicated

Surface-Selective Chemical/Structural Spectroscopic Probes
Why Vibrational Spectroscopy

Advantages
1. Label free structure and dynamics probe
2. Natural reaction coordinate
3. Sensitive to intra- and intermolecular interactions, Vibronic couplings, etc.

Difficulties
1. Spectral assignment
2. Lineshape and dynamics analysis
SFG-VS is Surface Selective Probe
Selective Interface probe with monolayer sensitivity

Molecular electronic and vibrational resonances

a. Normal SFG (IR + Visible)
b. Double resonance SFG (IR + UV/Visible)
c. Double resonance SFG (UV/Visible + IR)
d. Electronic SFG/SHG (UV/Visible + Visible)

Key Information

- Surface Density: Ns
- Molecular Orientation
- Molecular Spectroscopy
- Kinetic & Dynamics, etc…

SFG-VS is both IR and Raman Spectroscopy

\[
\beta_{ijk}^{(2)} \propto \alpha_{ij} \mu_k
\]

\[
\beta_{ijklm}^{(4)} \propto \alpha_{ij} \mu_k \mu_l \mu_m
\]

\[
\beta_i^{(1)} \propto \mu_i
\]

\[
\beta_{ijkl}^{(3)} \propto \mu_i \mu_j \mu_k \mu_l
\]
- **Aqueous interfaces:** water hydrogen bonding
- **Buried interfaces:** binding and interactions
- **Metal surfaces:** coupling, electron transfer
- **Biomolecules/membrane:** lipid, protein, DNAs, sugar
- **Polymer and material surfaces:** functional groups
- **Crystalline materials:** cellulose, collagen, explosives

**Limit of detection by SFG:** ~20 ng of particle mass

**Atmospheric Aerosol**  
**Living Cells**  

**Reaction and dynamics**  
**Heter/homoogeneous catalysis**  
**Mineral/water**  
**Mineral/bacteria**

*Nature* 474, 192 (2011)  
*Biointerphases* 6, 171 (2011)
Water Molecules at Air/Water Interface and Electrolyte Solution Surface

Free O-H reorientation at the top-most layer

• Wang et al., J. Chem. Phys., 141, 18C507, 2014
Surface of Nano- and Micro-Particles in Aqueous Solution

2nd Order Mie Scattering is Surface Selective


Figure 1. Chiral SFG spectra of the model peptides and protein. (A) Schematics of secondary structures of the hIAPP aggregate, LKα14, rhodopsin, pHLIP, and rIAPP. The chiral SFG spectra at the air—water interface in the (B) amide I region and (C) N—H stretch region.


### Table 1. List of systems investigated by SFG. Experiments of dynamics and those at the electrochemical interface are denoted by (d) and (ec), respectively, and sol=solid, liq=liquid, vac=vacuum, and vap=vapor.

<table>
<thead>
<tr>
<th>Species/spectral range (cm(^{-1}))</th>
<th>System/substrate</th>
<th>Type of interface</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH stretch, 3000–3900</td>
<td>H(_2)O</td>
<td>liq/vap</td>
<td>32, 160, 161</td>
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<td></td>
<td>Hexane</td>
<td>liq/liq</td>
<td>152, 153</td>
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<tr>
<td></td>
<td>Pt(111)</td>
<td>sol/vac</td>
<td>46, 164</td>
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<td></td>
<td>Quartz</td>
<td>sol/liq</td>
<td>162</td>
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<tr>
<td></td>
<td>Surfactant, CCl(_4)</td>
<td>liq/liq, vap</td>
<td>8, 161, 163, 165–169</td>
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<tr>
<td>Acids and salts</td>
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<td>Alcohol</td>
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<td>Alkyl isocyanate</td>
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<td>Polymer film</td>
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<tr>
<td></td>
<td>H(_2)O</td>
<td>liq/vap</td>
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<td>CH stretch, 2700–3100</td>
<td>CH(_2)OH</td>
<td>liq/vap</td>
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<tr>
<td></td>
<td>Polymers</td>
<td>sol/air</td>
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<td>Water</td>
<td>sol/liq</td>
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<tr>
<td></td>
<td>Sapphire</td>
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<td>Self-assembled monolayers</td>
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<tr>
<td>Thiol</td>
<td>Metal</td>
<td>sol/air, liq</td>
<td>40, 41, 55, 80, 193–195, 90(ec), 3, 31, 85, 196–199</td>
</tr>
<tr>
<td>Siloxane</td>
<td>Silica, CaF(_2), glass</td>
<td>sol/air, liq, sol</td>
<td>141, 200–203(d), 204(d)</td>
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<tr>
<td>Amphiphiles</td>
<td>Water, glass, quartz, sapphire,</td>
<td>sol/air, sol</td>
<td>39, 54, 205(d), 37, 82, 141, 142, 145, 147</td>
</tr>
</tbody>
</table>

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SFG-VS as *in-situ* Surface Analytical Tool

**Advantages and challenges**

**Challenges**

**Fundamental understanding:**
- How to analysis and assign spectra?
- How to accurately determine *orientation* of molecular group?
- How to study *dynamic processes* of molecules at interfaces?

**Applications:**
- How to measure various interfaces: solid/liquid interface, powder and amorphous surfaces, etc.
- How accurate can we measure

---

**Are there additional information from IR and Raman of the surface?**

*Limited conditions apply*
Towards *in-situ* SFG Spectral Assignment

- **Polarization selection rules:** Symmetric and asymmetric modes peak at different polarization
- **Polarization spectra:** Symmetry of the transition

### Air/Ethylene Glycol (HOCH$_2$CH$_2$OH) Interface

![Ethylene Glycol SFG IR Spectra](image)

**SFG Intensity (Normalized)**

**Wavenumber (cm$^{-1}$)**


### Air/Heptanol (HOC$_7$H$_{15}$) Interface

![Air/Heptanol SFG IR Spectra](image)

**SFG Intensity (a.u.)**

**Wavenumber (cm$^{-1}$)**

- $\chi^{(2)}_{ijk}$
- SFG
- Vis
- IR

**HR-BB-SFG-VS**

-Recent Development at EMSL/PNNL

Sub $1\text{-cm}^{-1}$ **High-Resolution Broadband Sum-Frequency Generation Vibrational Spectroscopy**

**Push Limit of Resolution and SNR**

**Key:** How accurate spectra and lineshape can be measured?

How Much Resolution is Needed?

\[ f_V \approx 0.5346 f_L + \sqrt{0.2166 f_L^2 + f_G^2 + f_I^2} \]

*The approximation with only 0.02% error for Voigt line width

- \( f_V \): Voigt width (Spectral)
- \( f_L \): Lorentzian width (Homogeneous)
- \( f_G \): Gaussian width (Inhomogeneous)
- \( f_I \): Gaussian width (Laser/Instrument)

<table>
<thead>
<tr>
<th>( \Delta \nu_G (cm^{-1}) )</th>
<th>( \Delta \nu_L = 5 , cm^{-1} )</th>
<th>( \Delta \nu_L = 10 , cm^{-1} )</th>
<th>( \Delta \nu )</th>
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<tr>
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<td>0.74</td>
<td>0.41</td>
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<td>4</td>
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</tr>
<tr>
<td>6</td>
<td>4.11</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6.00</td>
<td>4.60</td>
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</tr>
<tr>
<td>10</td>
<td>7.94</td>
<td>6.38</td>
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</tr>
<tr>
<td>15</td>
<td>12.85</td>
<td>11.05</td>
<td></td>
</tr>
</tbody>
</table>


High Resolution Broadband SFG-VS

Spectral Resolution ~ 0.6cm⁻¹, Time resolution ~ 35fs

Electronic Synchronization Units for both Oscillator and Amplifier Lasers

Source selection by flipper mirror
SFG-VS Measurement in a Nutshell

Key: Complicated convolution to simple product

**Time-domain SFG polarization**

\[
P^{(2)}(t; \tau) = \int_0^\infty dt_2 \int_0^\infty \chi^{(2)}(t_2, t_1; \tau) E_{\text{vis}}(t - t_2) E_{\text{IR}}(t - t_2 - t_1) dt_1
\]

**FID-SFG**

\[
P^{(2)}(t; \tau) = E_{\text{vis}}(t; \tau) \left[ \chi^{(2)}(t) \otimes E_{\text{IR}}(t) \right]
\]

**Frequency-domain SFG polarization**

\[
\tilde{P}^{(2)}(\omega_{SF}; \tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\tau \omega} P^{(2)}(t; \tau) dt
\]

\[
= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\tau \omega} E_{\text{vis}}(t; \tau) \left[ \chi^{(2)}(t) \otimes E_{\text{IR}}(t) \right] dt
\]

\[
= \tilde{E}_{\text{vis}}(\omega_{vis}; \tau) \otimes \left[ \chi^{(2)}(\omega_{SF}) E_{\text{IR}}(\omega_{IR}) \right]
\]

Spectrally narrow visible probe

\[
\tilde{E}_{\text{vis}}(\omega_{vis}; \tau) = E_{\text{vis}}(\omega_{vis}; \tau) \delta(\omega)
\]

\[
\tilde{E}_{\text{vis}}(\omega_{vis}; \tau) \otimes \left[ \chi^{(2)}(\omega_{SF}) E_{\text{IR}}(\omega_{IR}) \right] = \chi^{(2)}(\omega_{SF}) E_{\text{vis}}(\omega_{vis}) E_{\text{IR}}(\omega_{IR})
\]

\[
\left| \tilde{E}_{\text{vis}}(\omega_{vis}; \tau) \otimes \left[ \chi^{(2)}(\omega_{SF}) E_{\text{IR}}(\omega_{IR}) \right] \right|^2 = \left| \chi^{(2)}(\omega_{SF}) \right|^2 \left| E_{\text{vis}}(\omega_{vis}; \tau) E_{\text{IR}}(\omega_{IR}) \right|^2 = \left| \chi^{(2)}(\omega_{SF}) \right|^2 I(\omega_{vis}) \tilde{I}(\omega_{IR})
\]

\[
\chi^{(2)}(\omega_{SF}) \quad \text{Accurate measurement only}
\]

\[
\left| \chi^{(2)}(\omega_{SF}) \right|^2 \quad \text{possible in frequency domain!!!}
\]
HR-BB-SFG-VS: Accurate Measurement of Intrinsic SFG Response

-Key idea: long visible and short IR

Time-domain description:

\[ R^{(2)}(t_1) = |A_{NR}| e^{i\psi_{NR}} \delta(t_1) - i\theta(t_1) \sum A_q e^{-i\omega_q t_1} e^{-\frac{t_1^2}{\tau_q}} e^{-\frac{\Delta \omega_q^2}{2}} \]

\[ P^{(2)}(t; \tau) = E_{vis}(t; \tau) [R^{(2)}(t) \otimes E_{IR}(t)] \]

\[ I_{SFG-FID}(\tau) \propto \int_{-\infty}^{\infty} |P^{(2)}(t; \tau)|^2 dt \]

Frequency-domain description:

\[ \tilde{E}_{SFG}(\omega_{SF}) \propto \tilde{P}^{(2)}(\omega_{SF}; \tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P^{(2)}(t) dt \]

\[ = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{vis}(t; \tau) [R^{(2)}(t) \otimes E_{IR}(t)] dt \]

\[ = \tilde{E}_{vis}(\omega_{vis}; \tau) \otimes [\tilde{R}^{(2)}(\omega_{SF}) \tilde{E}_{IR}(\omega_{IR})] \]

\[ I_{SFG}(\omega_{SF}) \propto |\tilde{E}_{SFG}(\omega_{SF})|^2 \]

\[ \tilde{R}^{(2)}(\omega_{IR}) = |A_{NR}| e^{i\psi_{NR}} + \sum A_q \frac{A_q}{\omega_q - \omega_{IR} - i\Gamma_q} \otimes e^{-\frac{\omega_{IR}^2}{2\Delta \omega_q^2}} \]

\[ = |A_{NR}| e^{i\psi_{NR}} + \sum \int_{0}^{\infty} \frac{A_q}{(\omega_q - \omega') - i\Gamma_q} e^{-\frac{\omega_{IR}^2 - \omega'^2}{2\Delta \omega_q^2}} d\omega' \]

Unified treatment on the spectral resolution and temporal effects of the frequency-resolved sum-frequency generation vibrational spectroscopy (SFG-VS),

*PCCP*, 2013, 15, 19970-19984
Our First Sub-Wavenumber Resolution Spectrum of Air/DMSO Interface

\[ f_V \approx 0.5346 f_L + \sqrt{0.2166 f_L^2 + f_G^2 + f_I^2} \]

Estimate broadening with \( f_G = 0 \)

1. High resolution broadband SFG (HR-BB-SFG):
   When: \( f_I = 0.7 \text{ cm}^{-1} \)
   \( f_L = 8.6 \text{ cm}^{-1} \)
   Then: \( f_V = 8.66 \text{ cm}^{-1} \)

2. Normal broadband SFG (BB-SFG)
   When: \( f_I = 15.7 \text{ cm}^{-1} \)
   \( f_L = 8.6 \text{ cm}^{-1} \)
   Then: \( f_V = 20.8 \text{ cm}^{-1} \)

Resolution (0.6-0.7 cm\(^{-1}\)) limited by Spectrograph (750 mm, 1800 l/mm), not Laser (0.2 cm\(^{-1}\))
Resolving Chemical Shift of “Identical” Groups

- ssp and ppp spectra have completely different line shape
- ssp spectra contains two peaks with the same phase (2:1)
- ppp spectral contains two peaks with opposite phase (1:1)
- The two peaks are separated by ~ 2.7 cm⁻¹


Why Sub-wavemunber HR-BB-SFG-VS?

Accurate width + Accurate line shape

- ssp FWHM ≈ 8.8 cm⁻¹
- ppp FWHM ≈ 4.7 cm⁻¹
Understanding structural phase and spectral interference


Prof. Wei Gan
Lineshape of A Complex Spectrum

HR-BB-SFG-VS & BB-SFG-VS

Conventional BB-SFG-VS:
1 ps probe: Strong delay effects
HR-BB-SFG-VS:
90 ps probe: No delay effects

Cholesterol Monolayer @ air/water interface
Simulate Time-Dependent BB-SFG-VS with HR-BB-SFG-VS Parameters

- Quantitative reproduced temporal effects
- Intrinsic spectral lineshape and coherent dynamics

1. Accuracy in spectral lineshape is essential in complex spectral analysis
2. HR-BB-SFG spectral lineshape is delay independent

Unified treatment on the spectral resolution and temporal effects of the frequency-resolved sum-frequency generation vibrational spectroscopy (SFG-VS), PCCP, 2013, 15, 19970-19984
Cholesterol and derivatives in the C-H stretching region

Unpublished data
SFG-VS: Beyond the Technique for Surface/Interface Studies

IR & Raman: 100mM in CCl₄
SFG: 35 Å²/molecule air/water

SFG-VS: A Unique Technique for Spectroscopy and Dynamics Studies

\[ \alpha_{quffer}^{i',j',k'} = \frac{1}{2\varepsilon_0 \omega_q} \frac{\partial \alpha_{i,j}^{(1)}}{\partial Q_{q'} \partial Q_q} \]

Unified treatment on the spectral resolution and temporal effects of the frequency-resolved sum-frequency generation vibrational spectroscopy (SFG-VS), *PCCP*, 2013, 15, 19970-19984
Towards User Friendly Analytical Instrument
-Promises with New Laser Technology & Engineering

Fiber laser based 100kHz system

APL Photonics 2, 066102 (2017); doi: 10.1063/1.4983691

EKSPLA’s new custom made/commercial 1kHz system

FIG. 1. Schematic layout of the triple-beam setup for the generation of narrowband VIS and broadband IR pulses. BS: beam sampler, PR: partial reflector, WP: half-wave plate, PB: Brewster-type thin film polarizing beam splitter, D: delay stage, FS: fused silica window, Si: silicon window, LPF: long-pass filter, B: beam dump. DM1: dichroic mirror, highly reflective (HR) at 1.03 μm/2.6–3.6 μm, highly transmitting (HT) at 1.4–1.7 μm, DM2: dichroic mirror, HR at 2.7–3.6 μm, HT at 1.03 μm/1.3–1.7 μm. All lenses, wave plates, crystals, and filters are AR-coated.

06/11-16/2017, ICAVS9, Victoria, Canada
Technical Base: Short fs + Long ps Laser System
New Capability: Multi-Modal Nonlinear Spectroscopy Platform

Chemical, Steric and Environmental Effects, Vibronic Coupling, etc. in Energy and Electron Transfer Processes
1. Surface Vibrational Spectroscopy with high resolution & intrinsic lineshape

2. Molecular Anisotropy at Air/Solid and Solid/Liquid Interfaces: Mica

Broad Applications of SFG-VS: Fundamental and Applied

- **Aqueous interfaces:** water hydrogen bonding
- **Buried interfaces:** binding and interactions
- **Metal surfaces:** coupling, electron transfer
- **Biomolecules/membrane surfaces:** lipid, protein, DNAs, sugar
- **Polymer and material surfaces:** functional groups
- **Crystalline materials:** cellulose, collagen, explosives

Atmospheric Aerosol   Living Cells

- **Reaction and dynamics**
  - Heter/homoogeneous catalysis
- **Mineral/water**
- **Mineral/bacteria**

Limit of detection by SFG: ~20 ng of particle mass

**Nature** 474, 192 (2011)
**Biointerphases** 6, 171 (2011)
SFG-VS of Crystalline Cellulose

Starch: α-glucose with α-1,4-glycosidic bonds
Not-SFG active

Cellulose: β-glucose with β-1,4-glycosidic bonds
SFG Active

Biomass degradation

Polymorphism of Crystalline Cellulose

Seong Kim
(Penn State)

Spectral Differences Between Surface Region and Crystalline Core

- Red-TIR Geometry
- Blue-Non-TIR Geometry

- For surface, TIR >> Non-TIR
- For Bulk Crystalline material: TIR <= Non-TIR

Spectral Resolved Polarization Dependent Azimuthal Angle Patterns For Molecular Crystalline Structure Determination

Experimental and Theoretical Study of Azimuth Angle and Polarization Dependences of Sum-Frequency-Generation Vibrational Spectral Features of Uniaxially Aligned Cellulose Crystals

Xing Chen, Christopher M. Lee, Hong-Fei Wang, Lasse Jensen, and Seong H. Kim

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3Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, 220 Handan Road, Yangpu District, Shanghai 200433, China

ABSTRACT: Comprehensive interpretation of vibrational sum-frequency-generation (SFG) spectroscopic features of SFG-active nanodomains interspersed in amorphous bulk requires the knowledge of nonlinear susceptibility, \( \chi^{(2)} \), of the SFG-active phase as a function of its spatial arrangement in the bulk as well as the polarizations of the probe lights. This study reports the full analysis of the azimuth angle and polarization dependence of SFG signals from a control sample consisting of uniaxially aligned cellulose \( \beta \) crystals. The \( \chi^{(2)} \) terms of cellulose were estimated from quantum mechanics calculations using time-dependent density functional theory (TD-DFT), and a simple structural model was built with truncated glucose dimers. The theoretical azimuth angle and polarization dependences of characteristic CH/CH\(_2\) and OH stretch modes of cellulose were compared with the experimentally observed trends. These comparisons revealed that the relative polarity of crystallites within the SFG coherence length, the random quasi-phase-matching of polycrystalline domains, and the preferential packing of crystallites in the bulk play important roles governing the spectral features. Compared to that of small molecules, the difference between chiral and achiral responses in SFG spectra is more difficult to observe because of the inhomogeneous distribution of crystallites in the bulk sample.
**Model System: Muscovite Mica**

Structure and distribution of ions at solid/solution interface?

[E.T. Herruzo et al., *Nanoscale*, 5 (2013)]

How does interface structure impact nucleation and molecular assembly?

2D epitaxy of Al(OH)₃ on Mica [Legg et al., (In prep)]

How does interface structure evolve and impact particle attachment?

[D. Li et al. *Science*, 336 (2012)]

Collagen assembly on Mica

Structure of Muscovite Mica

- T-O-T layer of $\text{KA}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$
- Highly oriented hydroxyl groups inside mica lattice (not exposed)
- Common stacking $\rightarrow 2M_1$ (stacking alternates $120^\circ$ and $240^\circ$)
- 3 identical lattice directions
- Easy to prepare clean surface via peeling
- Monoclinic $2/m=C_{2h}$, No bulk SHG signal

-OH group of mica is IR & Raman active
- Bulk -OH groups lies ~16° away from (001) mica face
- 4 directions of OH transition moments, rotated by 60° (or 120°)

Polarized IR of Mica

Raman of Mica
SFG Study of Air-Mica Interface

- Highest quality grade mica purchased from Ted Pella
- Mica surface was ozone (30 mins) + plasma (15 mins) cleaned
- External geometry
  (Scanning setup $\rightarrow$ Vis 65° & IR 55°)
  (High Res. setup $\rightarrow$ Vis 45° & IR 55°)

Mica absorbs in the OH region, SFG signal is from top surface
Reproducibility of the SFG Spectra

• **3600-3680 cm\(^{-1}\)** due to \(-\text{OH}\) groups inside mica lattice
• SFG spectra from mica surface is **not always reproducible**!!
• Does it matter how we put mica on the sample holder?
Azimuthally-Resolved SFG Spectra of Air-Mica Interface

- Three peaks centered at 3622 cm\textsuperscript{-1}, 3651 cm\textsuperscript{-1}, & 3672 cm\textsuperscript{-1}
- 3672 cm\textsuperscript{-1} peak has opposite phase compared to the previous two peaks.
- Bulk studies say that Si/Al substitution causes O-H stretching frequency to shift

\[ b_{NR} = 0.025 \pm 0.02 \]
\[ \phi_{NR} = 0 \pm 0 \]

\begin{align*}
\begin{array}{ccc}
\text{w (cm}^{-1}) & 3621.9 \pm 0.3 & 3651.1 \pm 1.2 & 3671.6 \pm 3.4 \\
\text{b} & 2.89 \pm 0.07 & 0.66 \pm 0.40 & -3.52 \pm 0.65 \\
\text{G (cm}^{-1}) & 9.57 \pm 0.42 & 9.14 \pm 2.65 & 20.00 \pm 2.10
\end{array}
\end{align*}
• Al substitution causes frequency shift
• \(-\text{OH}\) in hexagonal cavity with 2 Al substitution is more red-shifted than with 1 Al substitution
• Blue \(-\text{OH}\) group has an average orientation of 16° from [001] surface, which corresponds to \(q = 74°\)
Orientation of –OH Groups

- Modes almost parallel to surface should have largest SSP signal.
- Significant SPP, PSP, and PPS signal. This probes chirality.
- But –OH groups, in general, are achiral!!!
- -OH groups in anisotropic orientation produces chiral signature → Prochirality
• We can tell where the –OH groups in the topmost T-O-T layer is pointing
• Azimuthal dependence for 3626, 3655 and 3672 cm\(^{-1}\) peaks are similar.
What Different Polarization Probes

SSP $\rightarrow$ yyx
  yyz

PPP $\rightarrow$ xxx
  xxz
  xzx
  zxx
  zzz

SSS $\rightarrow$ yyy

SPS $\rightarrow$ yxy
  yzy

SPP $\rightarrow$ yxx
  yxz
  yzx
  yzz

PSS $\rightarrow$ xyy
  zyy
-OH direction lies along one of the mica lattice
Protein nanorods breaks 3 fold symmetry of mica surface and dominantly align along the same direction as the underlying –OH groups
Up vs. Down: Azimuthal Dependence

- "Top" & "Bot" identical in most imaging and spectroscopy techniques
- Only makes sense if we assume "top" & "bot" face is terminated by identical T-O-T layer
- But peeling experiment suggested even layer peeling!!!
  - Maybe some kind of fault in stacking or cleaving bias my the manufacturer??
Effect of Peeling/Cleaving

- The dominant O-H direction usually remains the same after peeling.
- Mica has preference to peel in even layers??
- Sometimes –OH direction changes. Maybe due to odd layer peeling?
TOP 1 and TOP 2 shows same azimuthal pattern → Even layer cleave
Then BOT 1 should be terminated by Green –OH groups, which is rotated by 60° from Blue –OH groups
Also suggests even layer peeling
Mica-D$_2$O Interface

- External geometry
  (Scanning setup $\Rightarrow$ Vis $\sim$35° & IR 30°)
• Redshift evidence for “ice-like” water?
Literature: Water on Mica

SPFM showing epitaxial water on mica

MD simulation showing 2D H-bond network water on mica

AFM showing epitaxial water film on mica

- Evidence for epitaxial “ice-like” water?
D$_2$O Water Spectra on Mica Surface

- At least 3 types of water (2350, 2480, & 2633 cm$^{-1}$).
- PPP intensity of 2633 cm$^{-1}$ peak is larger than SSP. That means 2633 cm$^{-1}$ water has different configuration.
- Polarization analysis tells us that 2350 and 2480 cm$^{-1}$ is coming from config 1 water, whereas 2633 cm$^{-1}$ is coming from config 2 water.
- For H$_3$O$^+$ covered mica, there are more water molecules with config 1.

Possible Assignments of Mica-D$_2$O Interface

According to Aashish Tuladhar?
D$_2$O on mica surface is rotationally anisotropic (for both 2350 and 2480 cm$^{-1}$)

Four lobes probably represents 2 types of oriented water on mica surface

1$^{st}$ lobe lies along the mica –OH direction, whereas the 2$^{nd}$ lobe does not match perfectly

Evidence for epitaxial water arrangement on mica surface?
• 3705 cm$^{-1}$ peak is rotationally isotropic.
Rotationally Isotropic SiO$_2$/H$_2$O Interface

- Water next to silica surface is rotationally isotropic.
Effect of Peeling on D$_2$O Orientation

- Anisotropic pattern is maintained on peeling/cleaving
- No dependence of thickness
D$_2$O Orientation

**Air/Mica, 3622 cm$^{-1}$**

**Mica/D$_2$O, 2400 cm$^{-1}$**

**Mica/D$_2$O, 2550 cm$^{-1}$**

**Mica/D$_2$O, 2650 cm$^{-1}$**

**Mica/D$_2$O (50mM CsI), 2550 cm$^{-1}$**
Water is epitaxially arranged on mica surface!!

But not exactly the configuration proposed

Water in “locked” configuration \( \Rightarrow \) Is this “real” evidence for “ice-like” water?
Non H-Bonded O-D on Mica Surface

- Mica/D$_2$O interface vSFG spectral shape is dependent on azimuthal rotation
  *Azimuthal degree is arbitrary here*

- At 195°, there are 3 water peaks (2350, 2480, & 2633 cm$^{-1}$) like discussed earlier. No sharp feature at 2680 cm$^{-1}$ observed.

- At 0° and 120°, you observe an additional peak at 2680 cm$^{-1}$

- At 135°, H-bonded features are suppressed and 2680 cm$^{-1}$ becomes dominant.

- 2680 cm$^{-1}$ O-D stretch ($\times$ 1.36) $\approx$ 3645 cm$^{-1}$ O-H stretch

- Is 2680 cm$^{-1}$ due to H/D exchange?
Azimuthal dependence

• 1 lobe of the 2550 cm\(^{-1}\) O-D stretch lies perfectly along the underlying –OH group

• 2550 cm\(^{-1}\) and 2680 cm\(^{-1}\) O-D stretches have different azimuthal pattern

• 2680 cm\(^{-1}\) does not lie along the O-H group of mica
  \[\rightarrow\] 2680 cm\(^{-1}\) cannot be due to O-D exchange

• Contrary to previous reports, non H-bonded water exist at muscovite surface!
Cyclohexanol (Vapor) on CaF$_2$

- Cyclohexanol next to CaF$_2$ surface is also rotationally isotropic.
Cyclohexanol (Vapor) on Mica

Mica/Cyclohexanol

Air-Mica, 3626 cm\(^{-1}\)
Arrangement of Water on Mica Surface?

Air/Mica 3626 cm$^{-1}$

Mica/D$_2$O 2400 cm$^{-1}$

Oriented water arrangement in surface ice
Summary: Mica

- SFG is a powerful tool in interfacial science
- The topmost –OH group is oriented
- Even layer peeling? Theoretical investigation required
- Water (and also organic molecules) next to mica surface is anisotropic
  → Epitaxial growth of water next to mica surface using SFG
  → Water in “locked” configuration. True evidence for “ice-like” water?

Water plays role in molecular assembly?

Other Works

Water confined between two surfaces

Correlation between water structure and ion occupancy

Water next to Graphene Oxide

Collagen on mica pH 4.0 (Jinhui); in prep.
“In many cases, SFG is shown to be the only technique available that can provide detailed information about a liquid interface at the molecular level.”

1. Liquid Interfaces: A Study by Sum-Frequency Vibrational Spectroscopy
   P. B. Miranda and Y. R. Shen, JPCB, 1999, 103, 3292-3307

2. Probing Liquid/Solid Interfaces at the Molecular Level

Buried Solid/liquid interfaces
Questions?

Unless our knowledge is measured and expressed in numbers, it does not amount to much. —Lord Kelvin