Development of Sum Frequency Generation Imaging Microscopy

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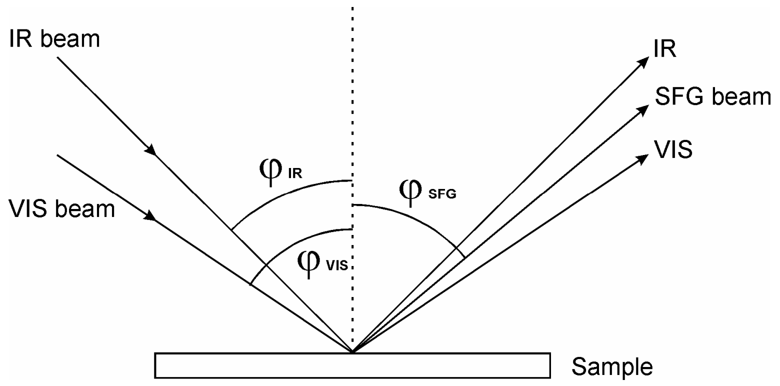
Outline

- Basic principles of SFG spectroscopy
- Features of SFG
- SFG spectrometer
- Challenges of SFG imaging
- Possible solutions
- EKSPLA SFG microscope

Basic principles of Vibrational SFG Spectroscopy

- Sum Frequency Generation (SFG) is a second-order nonlinear optical process, which is used to generate **a vibrational spectrum of molecules at an interface**.
- SFG is generated trough overlapping of infrared (ω_{IR}) and visible (ω_{VIS}) laser beams to produce an output at the sum frequency ($\omega_{SFG} = \omega_{IR} + \omega_{VIS}$).
- SFG allowed in media without inversion symmetry. At surfaces and interfaces inversion symmetry is necessary broken, so SFG can be used as an effective surface probe.
- Different polarization combinations of pump beams and analysis of SFG beam polarization provides information about orientation of adsorbate vibrational modes.



$$I(\omega_{SFG}) \sim \left|\chi^{(2)}\right|^2 I(\omega_{VIS})\, I(\omega_{IR})$$

$$\chi^{(2)} = \chi^{(2)}_{NR} + \chi^{(2)}_{R}$$

$$\chi^{(2)}_{R} \sim A_{\upsilon} M_{\upsilon,g} / (\omega_{IR} - \omega_0 - i\gamma)$$

SFG as an Analytical Technique

Method	Surface/Interface Monolayer Specificity	Good Spatial and Spectral Resolution	Structural Information	Functional Group Orientation	Suitable for Liquid/Solid, Gas/Solid, Liquid/Gas, Liquid/Liquid Interfaces	*In situ* Measurement	Effective at Polymer-Liquid Interface	Non-destructive
SFG	●	●	●	●	●	●	●	●
Reflection Infrared Spectroscopy		●	●	●*	●	●*		●
Attenuated Total Reflection Infrared Spectroscopy		●	●	●*	●	●*	●*	●
Raman Spectroscopy		●	●	●*		●*		
Contact Angle Measurement							●	●
Neutron Reflection	●	●	●					
X-Ray Photoelectron Spectroscopy (XPS)	●	●	●					
Surface Light Scattering	●	●				●	●	●
Secondary Ion Mass Spectroscopy (SIMS)	●	●	●					

* Limited conditions apply

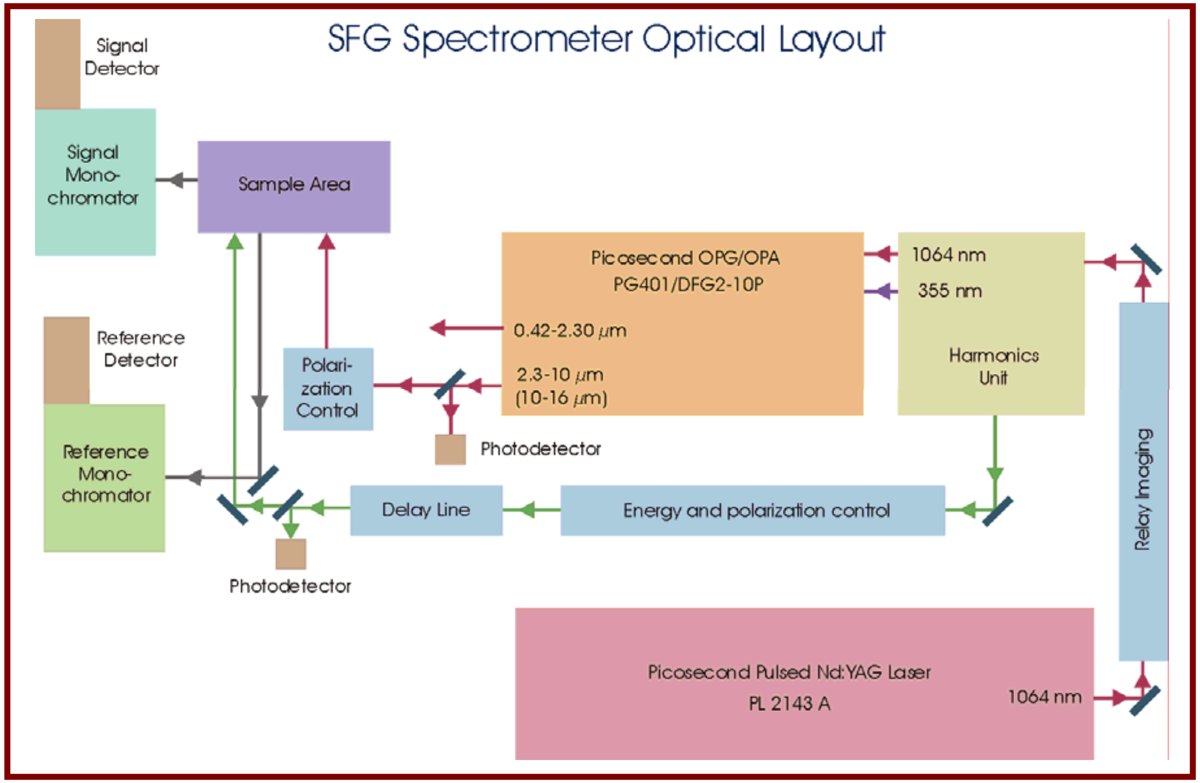
Table 1. Comparison of SFG to other conventional surface analysis techniques

(Polymer Technology Group, Inc.)

Powerful tool for *in-situ* investigation of surfaces and interfaces:

- Highly surface-specific
- Sensitive to sub-monolayers
- Applicable to all interfaces accessible by light
- Molecular selectivity
- Remote sensing in hostile environment
- Surface dynamics investigation

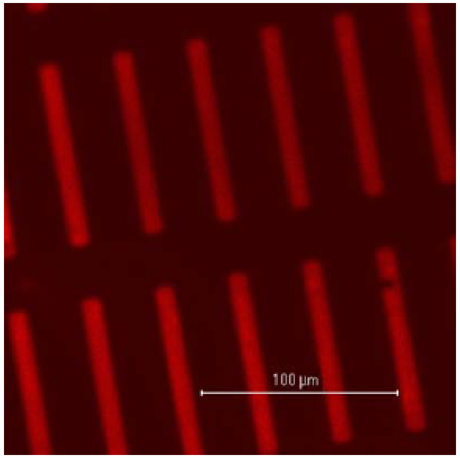
Vibrational Sum Frequency Generation Spectrometer



- Picosecond Nd:YAG laser
- Harmonics generation unit
- Optical parametric generator
- Monochromator
- Signal detectors
- Data acquisition system
- Controlling software
- Beam delivery optics
- Guiding beam for system alignment

SFG imaging advantages

- High interface specificity
- Monolayer sensitivity
- Chemical contrast
- Structural information
- Spatial distribution
- Answering questions of sample inhomogeneity



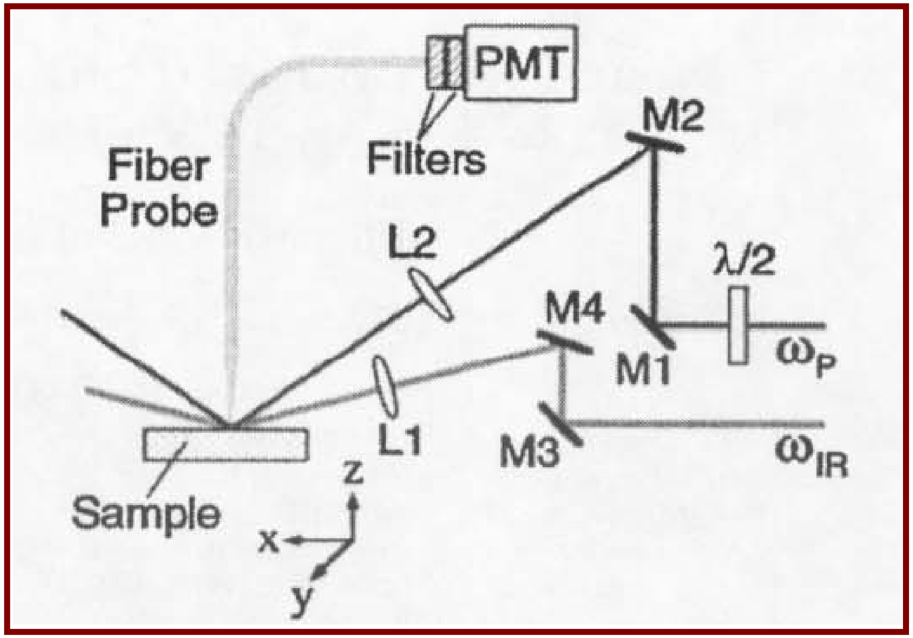
Difficulties:
- Low efficiency
- Sensitivity of samples to damage
- Oblique incidence of pump beams

Possible solutions of SFG imaging

- Raster scanning
- Near-field microscopy
- Far-field imaging

Near-field microscopy

- High resolution (200 nm)
- Low coupling efficiency to fiber
- No results with vibrational resonances



Richard D. Schaller and Richard J. Saykally
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Samples of near-field microscopy

Langmuir **2001**, *17*, 2055–2058

Near-Field Infrared Sum-Frequency Generation Imaging of Chemical Vapor Deposited Zinc Selenide

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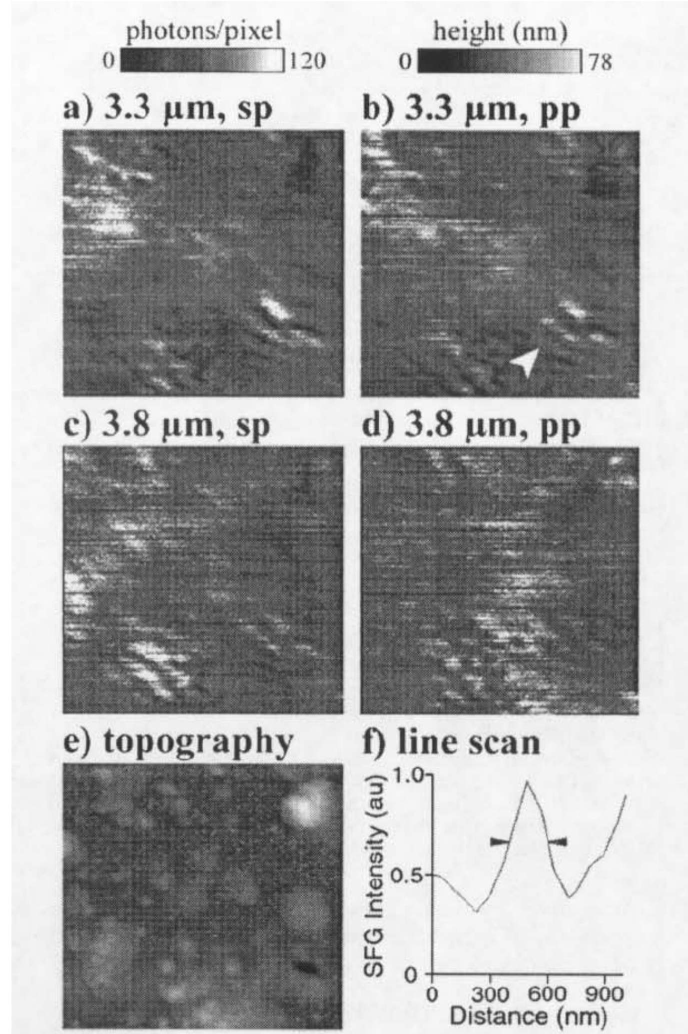


SFG NSNOM images of MCD ZnSe

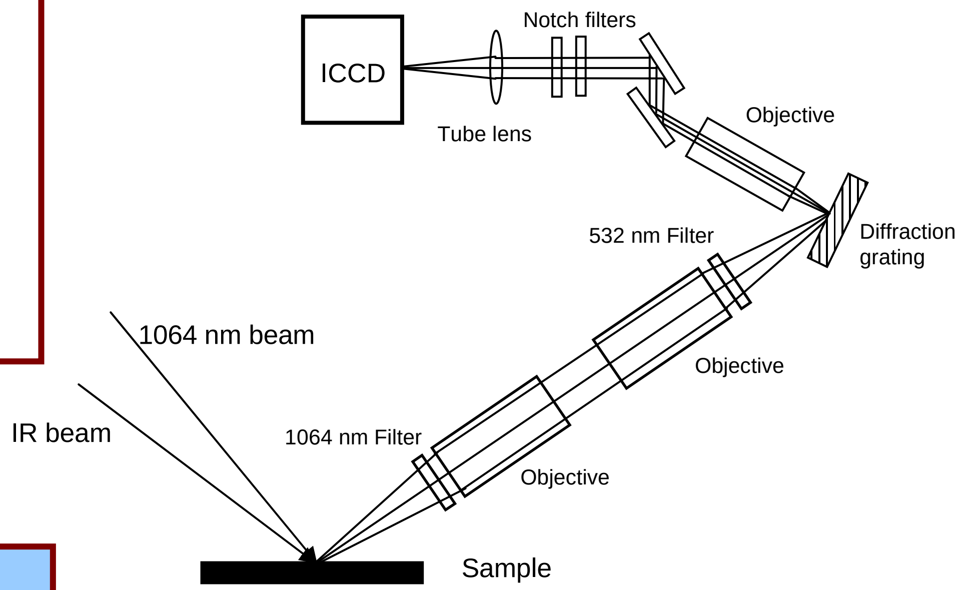
White features are interpreted as strain patterns within ZnSe crystal lattice.

Far-field imaging

Problem of SFG geometry:

Optimal pump beams incidence angles 50 – 60 deg

Undistorted oblique imaging?



Solution:

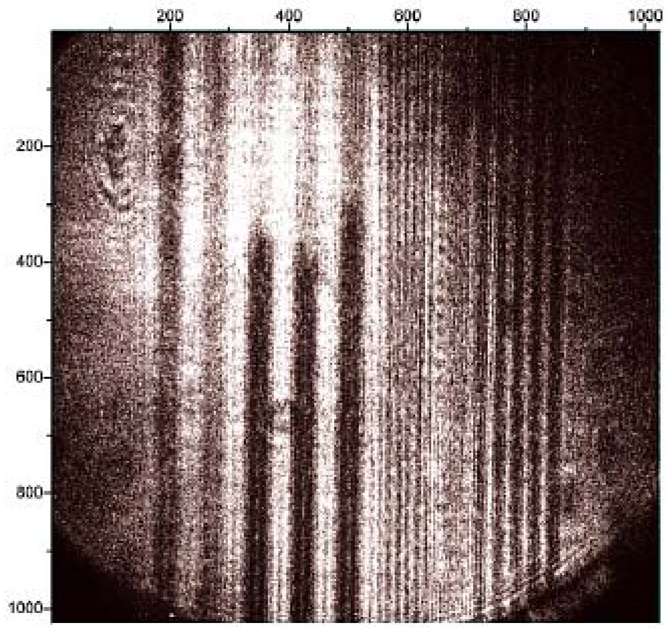
Detection via an intermediate image on the surface of a blazed grating

EKSPLA

EKSMA group

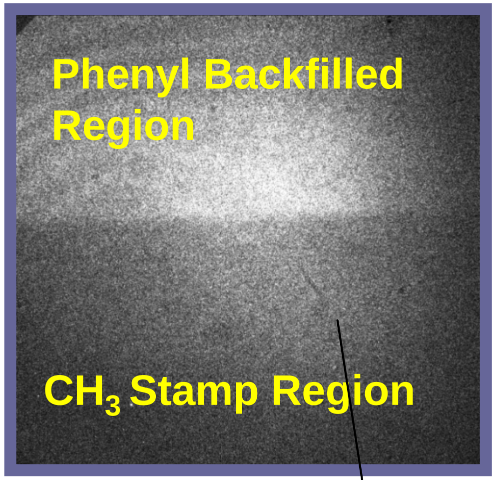
EKSPLA SFG imaging microscope (joint project with Steven Baldelli group, HU)

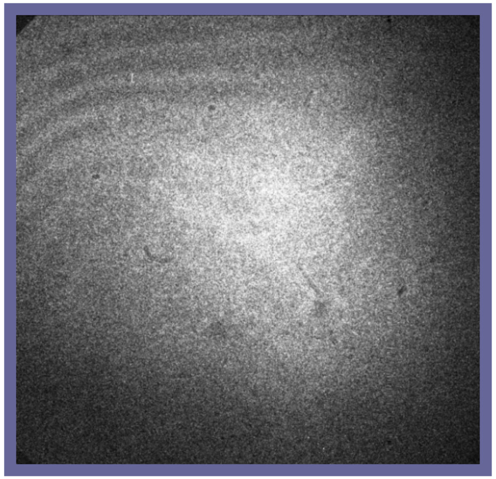
Specifications	
Resolution	<5 µm
Field of view	300 µm
Magnification	20, 10
Wavelength range	2000 – 3800 cm^{-1}

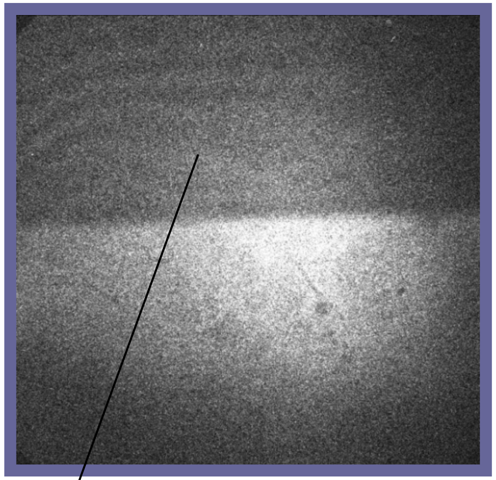


An image of ODT covered etched gold sample.
The first lines are spaced, in order left -right 20, 5, 1, 2, and 8 micrometers.
Image taken at ω_{IR}=2875 cm^{-1} and acquired for 5000 laser shots.

Origin of chemical contrast



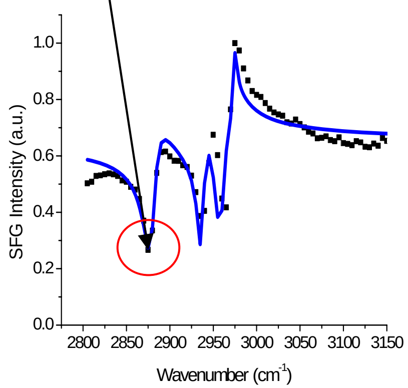


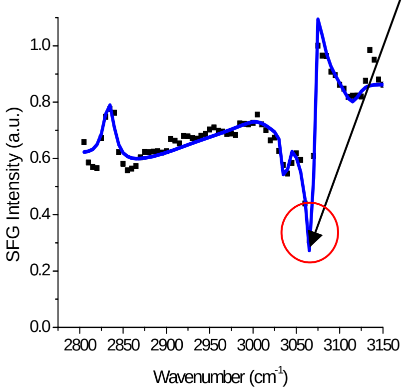


2875 cm^{-1} - represent resonant CH_3

2955 cm^{-1} - represent non-resonant

3060 cm^{-1} - represent resonant phenyl





hexadecane-1-thiol

16-phenylhexadecane-1-thiol

Conclusions

- **SFG imaging microscope with few µm resolution was developed and tested**
- **Microscope was succesfully used for imaging of:**

✓ Microcontact-printed mixed self-assembled monolayers

✓ CO deposition on PT

✓ Polymer blends