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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Structure of Thin Polymer Film Interfaces Using Broadband Vibrationally Resonant Sum Frequency Generation

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Structure of Thin Polymer Film Interfaces Using Broadband Vibrationally Resonant Sum Frequency Generation

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Polymer Interfaces

Bulk polymer signal completely dominates interfaces in linear spectroscopies

Molecular structure at free and buried polymer interfaces important to:

Optoelectronics, LCD's

Adhesion/Laminates

Polymer Blends/ Composite Materials

Biocompatability/ Biofouling/ Tissue Engineering

Sum Frequency Generation for the study of interfaces

2nd order nonlinear optical process:
- non-destructive
- forbidden in centrosymmetric media
- only allowed at interfaces where inversion symmetry is broken.

⇒ Interface and surface specific

$\omega_{SUM} = \omega_{VIS} + \omega_{IR}$

Vibrationally-Resonant SFG:
Alignment and orientation of molecules and functional groups at interfaces.

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Vibrationally Resolved Sum Frequency Generation

$\omega_{SUM} = \omega_{VIS} + \omega_{IR}$

Sum Frequency Response:

$$E_i(\omega_{SUM}) \sim \chi^{(2)}_{ijk}(\omega_{SUM})\, F_{il}(\omega_{SUM})\, F_{jm}(\omega_{VIS})\, F_{kn}(\omega_{IR})\, \mathbf{E}_m(\omega_{VIS})\, \mathbf{E}_n(\omega_{IR})$$

$\chi^{(2)}_{ijk}(\nu_{SUM})$ **is the 2nd order nonlinear suseptibility**

$F_{il}(\nu_{SUM})\, F_{jm}(\nu_{VIS})\, F_{kn}(\nu_{IR})$ **are Fresnel transfer matrices relating incoming and outgoing E fields to "polarized sheet"**

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Vibrationally Resolved Sum Frequency Generation

$$E_i(\omega_{SUM}) \sim \chi^{(2)}_{ijk}(\omega_{SUM})\, F_{il}(\omega_{SUM})\, F_{jm}(\omega_{VIS})\, F_{kn}(\omega_{IR})\, E_m(\omega_{VIS})\, E_n(\omega_{IR})$$

For azimuthally symmetric sample, only 4 non-vanishing $\chi^{(2)}_{ijk}$:

$$\chi_{zxx} = \chi_{zyy} \qquad \chi_{xxz} = \chi_{yyz}$$
$$\chi_{xzx} = \chi_{yzy} \qquad \chi_{zzz}$$

Experimentally, we access each of these tensor elements by using different polarization combinations of the incident and generated beams.

P	S	S	:	χ_{zxx}
S	P	S	:	χ_{xzx}
S	S	P	:	χ_{xxz}
P	P	P	:	$\chi_{zzz} + \chi_{zxx} + \chi_{xzx} + \chi_{xxz}$

Vibrationally Resolved Sum Frequency Generation

$$\omega_{SUM} = \omega_{VIS} + \omega_{IR}$$

$$\text{SFG Signal} \propto \left| \chi^{(2)}_{(Non\text{-}resonant)} + \chi^{(2)}_{(Resonant)} \right|^2$$

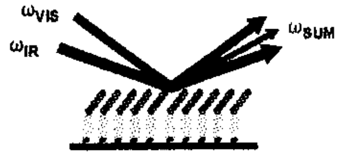
$$\chi^{(2)}_{(Non\text{-}resonant)} \sim \beta e^{i\phi}$$

$$\chi^{(2)}_{(Resonant)} \sim N \cdot \sum_j \frac{\mu_j \cdot \alpha_j}{\omega_{IR} - \omega_j + i\Gamma_j}$$

⇒ **System must be <u>both</u> IR and Raman active**

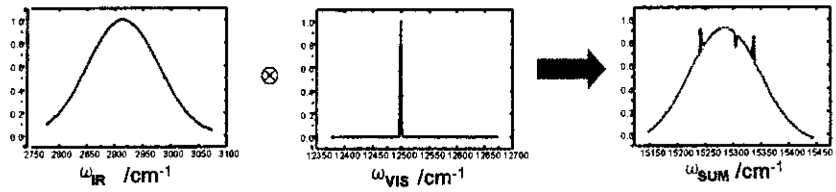
⇒ **Isotropic systems show no SFG signal**

Broadband Vibrationally Resolved Sum Frequency Generation



Spatial Resolution:
~laser spot size (100μm)

Mix broad bandwidth infrared laser (ω_{IR}) **with** **narrow bandwidth visible laser (ω_{VIS})** **to get** **broad bandwidth sum frequency (ω_{SUM})**



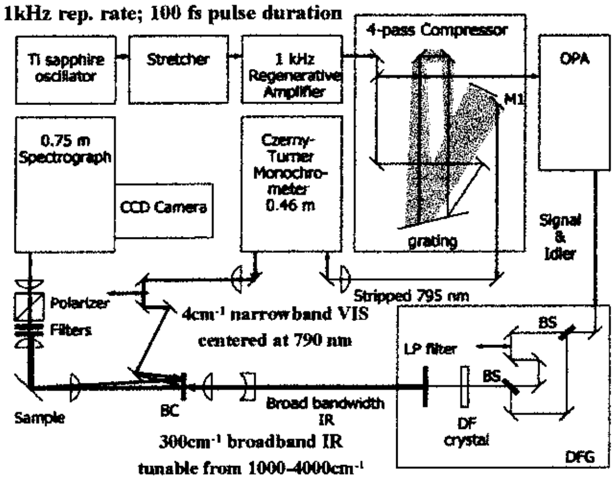
100 fs laser pulse

Multichannel detector

Novel broadband approach to SFG developed at NIST.

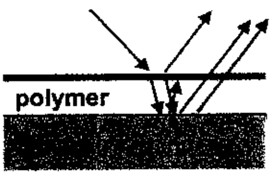
Actual Implementation

1kHz rep. rate; 100 fs pulse duration



Optics Letters **23**, 1594 (1998).

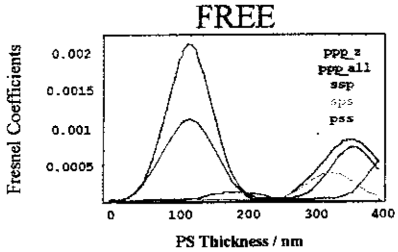
Polystyrene Films on Si(100)



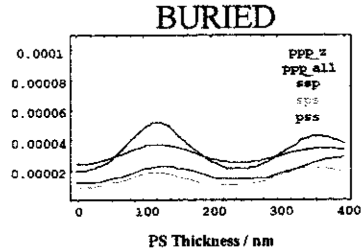
Interference of both the incident ($\mathbf{E}_{VIS}$ and $\mathbf{E}_{IR}$) and generated ($\mathbf{E}_{SUM}$) electric fields cause oscillations as a function of film thickness.

Calculated signal from each interface:

FREE



BURIED



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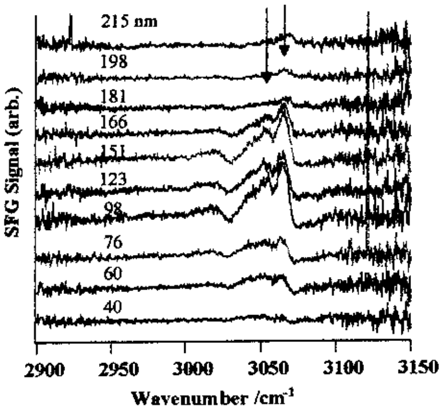
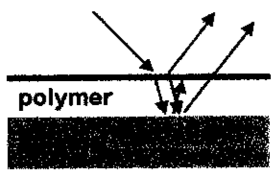
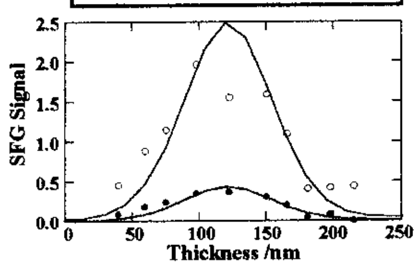
Polystyrene Films on Si(100)

SFG signal from "SSP" polarization:





Comparison of measured and calculated SFG signal:



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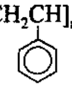
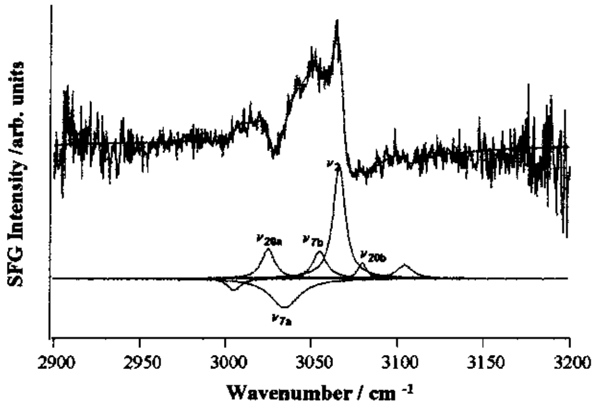
"SSP" SFG Spectra of 93 nm PS on Si(100)

Atactic Polystyrene
-[$CH_2CH]_n$-



Spectra are fit:

$$\text{SFG Signal} = \left| \beta e^{i\phi} + \sum_j \frac{\mu_j \cdot \alpha_j}{\omega_{IR} - \omega_j + i\Gamma_j} \right|^2$$



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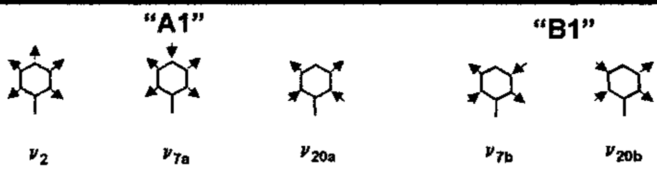
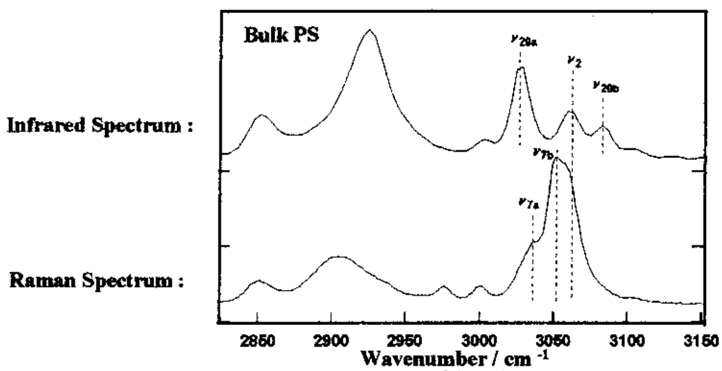
Normal Modes of Mono-Substituted Benzene





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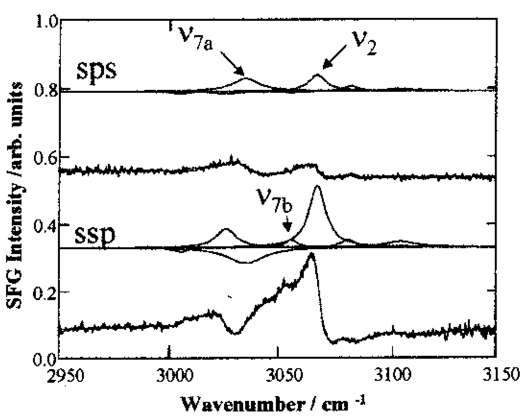
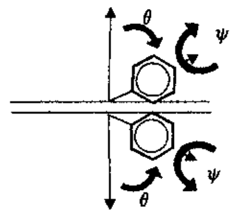
Orientation of Phenyl Groups at Free PS Surface



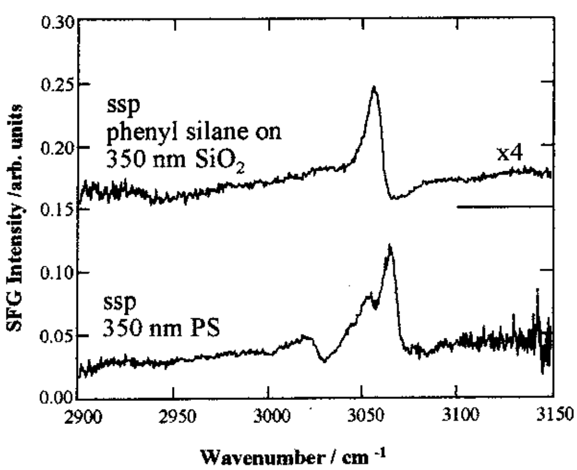
Analysis of ν_{7b} (B_1), ν_{7a} (A_1) and ν_2(A_1), assuming a narrow distribution in θ and ψ indicates:

θ~60-70° ψ~45-50°

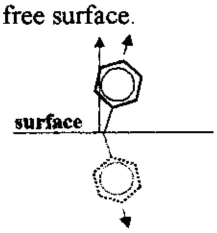


Note: Analysis cannot distinguish between ψ near 45° and a very broad distribution about ψ~0°

Orientation of Phenyl Groups at Free PS Surface



Comparison to phenyl silane establishes that the phenyl groups point away from the bulk polymer at the free surface.

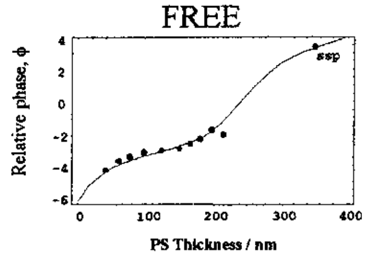


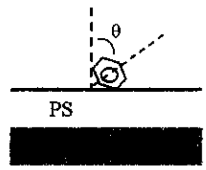
Phenyl silane:

θ~39-44° ψ~29-35°

Orientation of Phenyl Groups at Free PS Surface

FREE





Comparison of relative phases with calculated Fresnel factor weights

⇒ Indicates phenyl ring orientation is away from the bulk polystyrene film at the free surface.

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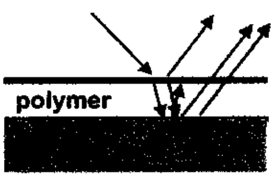
Polystyrene Films on Si(100)

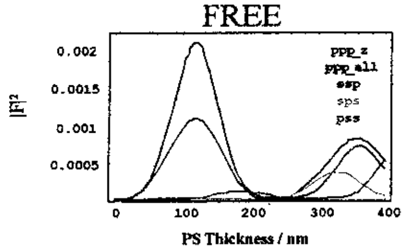
Optimization of SFG Signal from the Interface



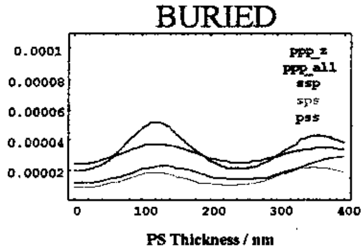
Interference of both the incident ($\mathbf{E}_{VIS}$ and $\mathbf{E}_{IR}$) and generated ($\mathbf{E}_{SUM}$) electric fields cause oscillations as a function of film thickness.

Calculated signal from each interface:

FREE



BURIED



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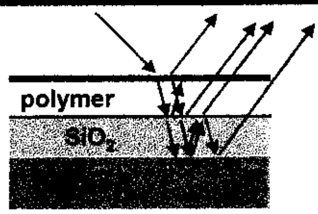
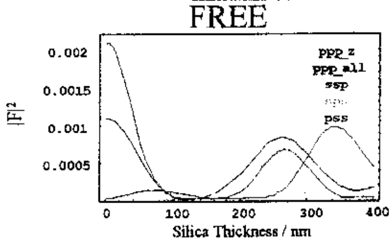
Polystyrene Films on SiO_2 on Si [illegible]

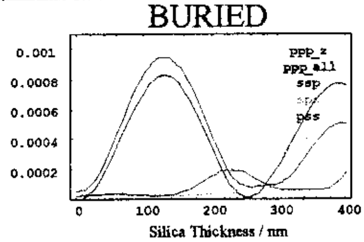
Optimization of SFG Signal from the [illegible] Interface



Optimization of a two-layer system consisting of a 120nm PS film over variable thickness SiO_2 films can enhance SFG signal from the buried interface.

Calculated signal from each interface:





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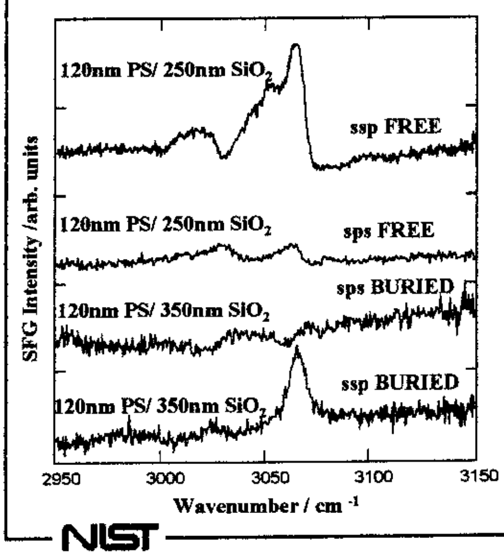
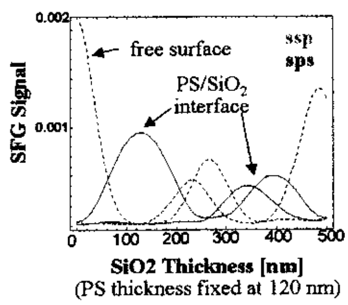
Orientation of Phenyl Groups at the Buried PS Interface





At first glance, a dramatic spectral change between free surface and buried interface optimized systems

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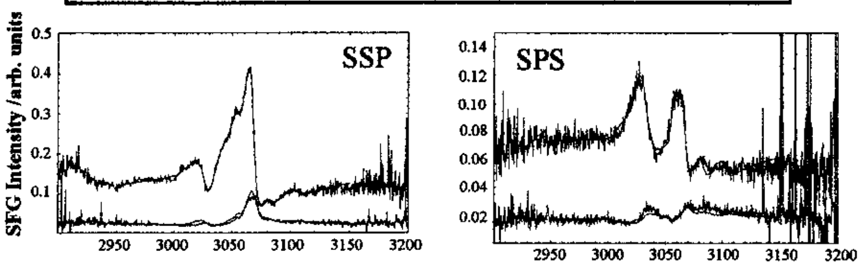
Order of Phenyl Groups at the Buried PS Interface

Amplitudes and phase changes of the SFG signal from the "buried interface" system can be explained by contribution solely from "free surface".



Upper limit of order at buried interface < $\frac{1}{6}$ order at free surface.

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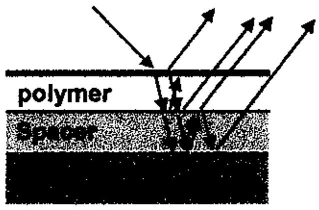
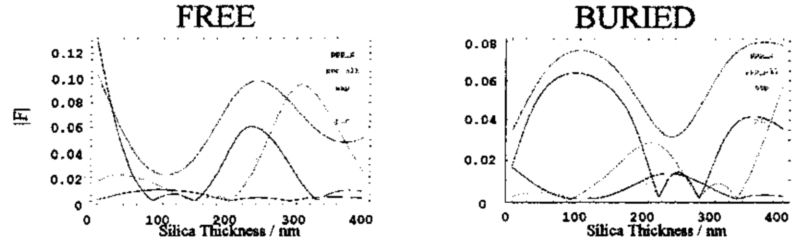
Polystyrene Films on Au



Re-design of a two-layer system consisting of a polymer film over a variable thickness SiO_2 over Au offers better extinction between free vs. buried interface signals.

Calculated signal from each interface:



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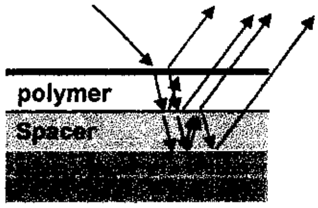
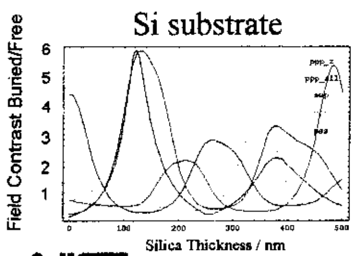
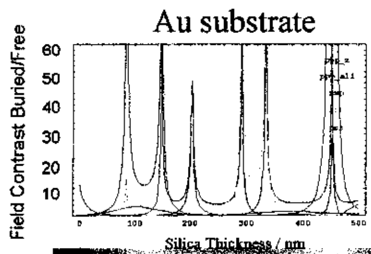
Polystyrene Films on Au



Re-design of a two-layer system on Au offers better contrast between free vs. buried interfaces; i.e. allows detection of weaker signals and better S/N from buried interface

Calculated signal from each interface:





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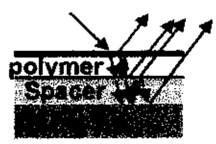
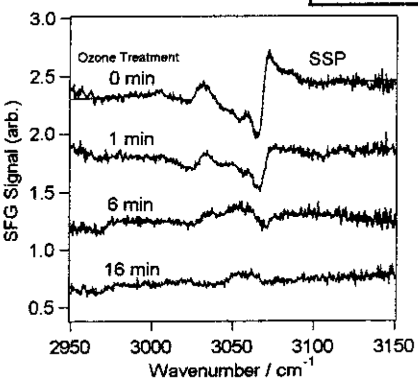
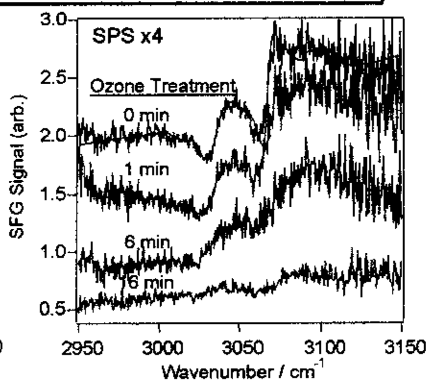
Polystyrene Films on Au



Optimization to enhance SFG from the FREE surface:

Exposure of the free surface to O_3 disrupts order of phenyl rings.





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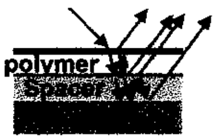
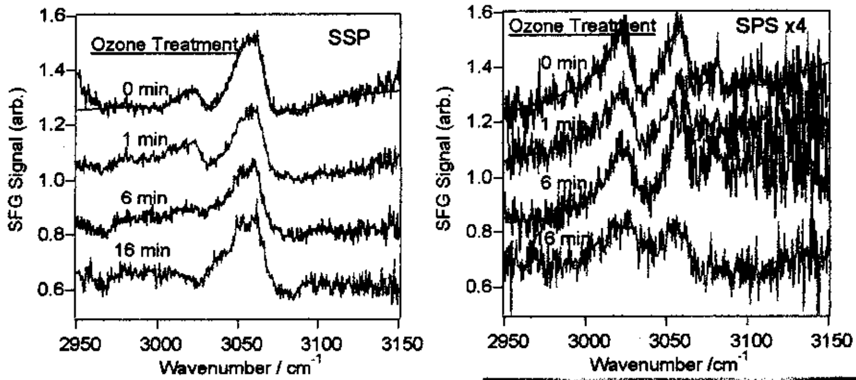
Polystyrene Films on Au



Optimization to enhance SFG from the BURIED surface:

Exposure to O_3 has no effect on phenyl rings at buried interface.



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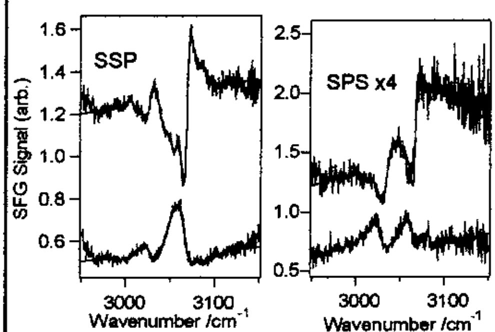
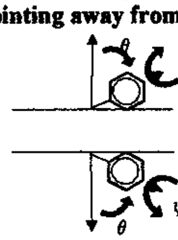
Polystyrene Films on Au



At the FREE surface: phenyl ring orientation is similar to PS/Si FREE surface:

θ~60° ψ~45°

and pointing away from substrate:



At the BURIED interface:

Phenyl rings are pointing away from the PS layer and toward the substrate.

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Summary and Future Directions

- Polymer structure at the free and buried interfaces can be separately determined.
- Possible to greatly enhance weak signals by local field effects.

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Summary and Future Directions

Experiments underway to study:

- interfaces of different polymers
- environmental effects on interfacial ordering/bonding
  influence of coupling agents on buried interface order;
  solvent and impurity effects at both interfaces
- polymer/polymer interfaces
  reactions, interdiffusion, liquid crystal interactions

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