united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

SMR/1238-27

ADRIATICO RESEARCH CONFERENCE on

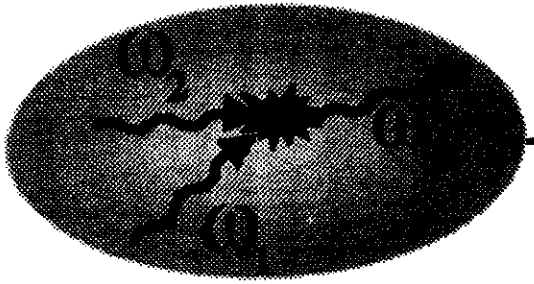
LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Application of Sum-Frequency Generation Spectroscopy to Interfaces

M. S. Yeganeh
Exxon Research & Engineering Co.,
Annandale - NJ, United States of America



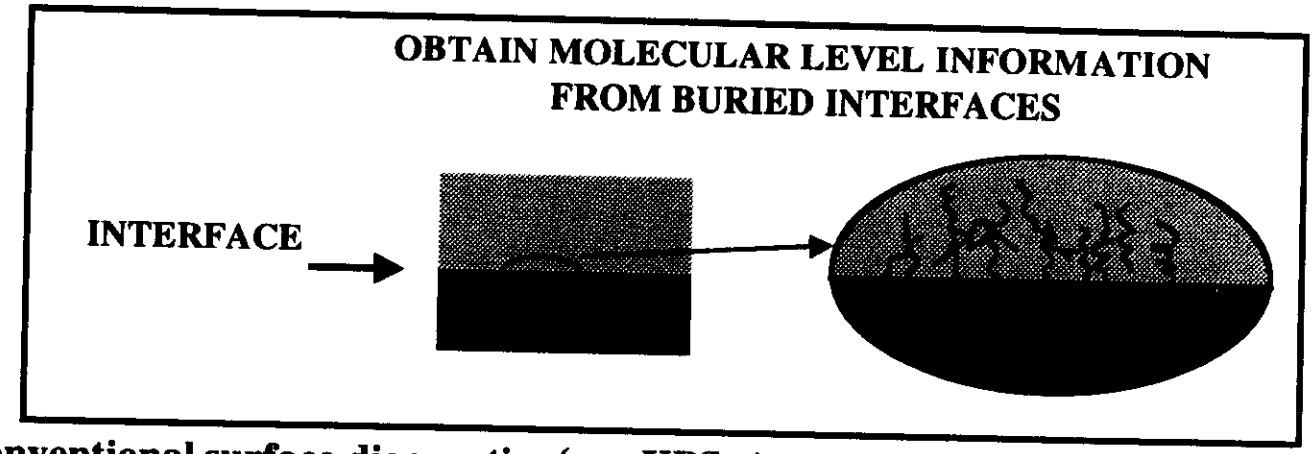
Application of Sum-Frequency Generation Spectroscopy to Interfaces

M. S. Yeganeh, S. D. Dougal, D. Zhang, H. Pink, and C. Zhang
ExxonMobil Corporate Strategic Research, Annandale New Jersey, 08801

ICTP-Lasers in Surface Science Conference
Sept. 2000

Interfacial Studies

- **Interfaces play a critical role in commercially important areas such as corrosion control, composite material strength, lubrication, oil recovery, fuel cells, polymers and catalysis.**



- **Conventional surface diagnostics (e.g. XPS, Auger, SEM, etc.) have limited penetration depth.**

  -UHV is not suited for the study of liquid/solid, liquid/liquid and high pressure gas/solid interfaces.

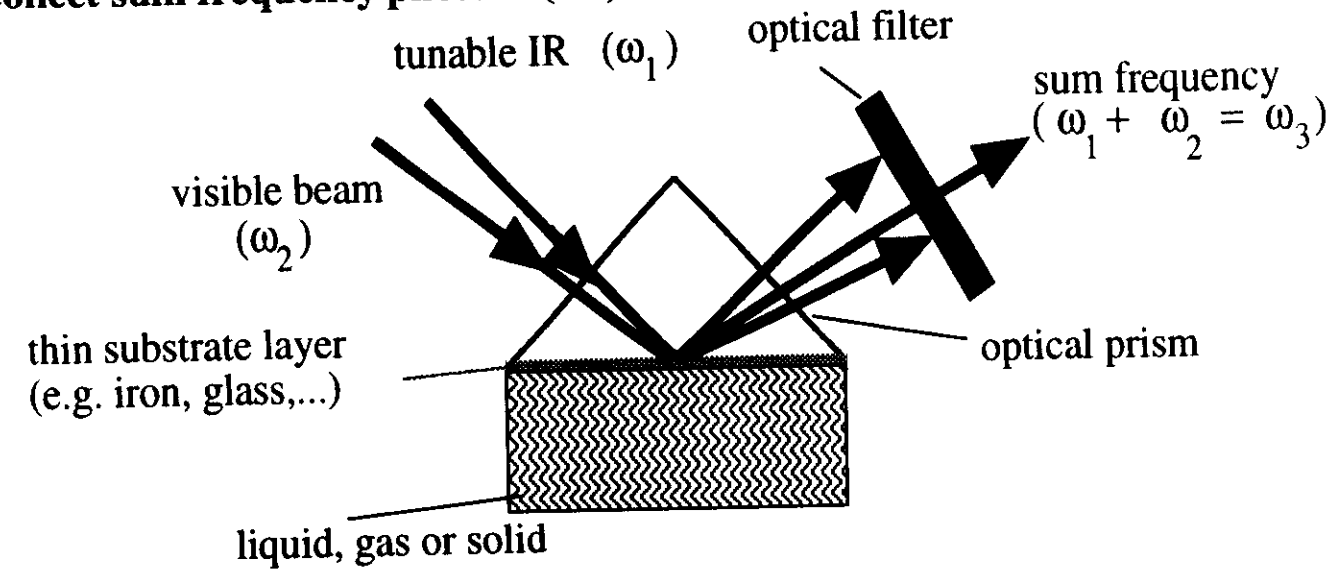
- **Conventional optical spectroscopies (e.g. FTIR, ATR, etc.) lack ability to differentiate interface from bulk.**

- **Second-order nonlinear optical (e.g. Sum-frequency generation) spectroscopy, as a new and unique tool, possesses long penetration depths and intrinsic interface specificity.**

Sum Frequency Generation Spectroscopy

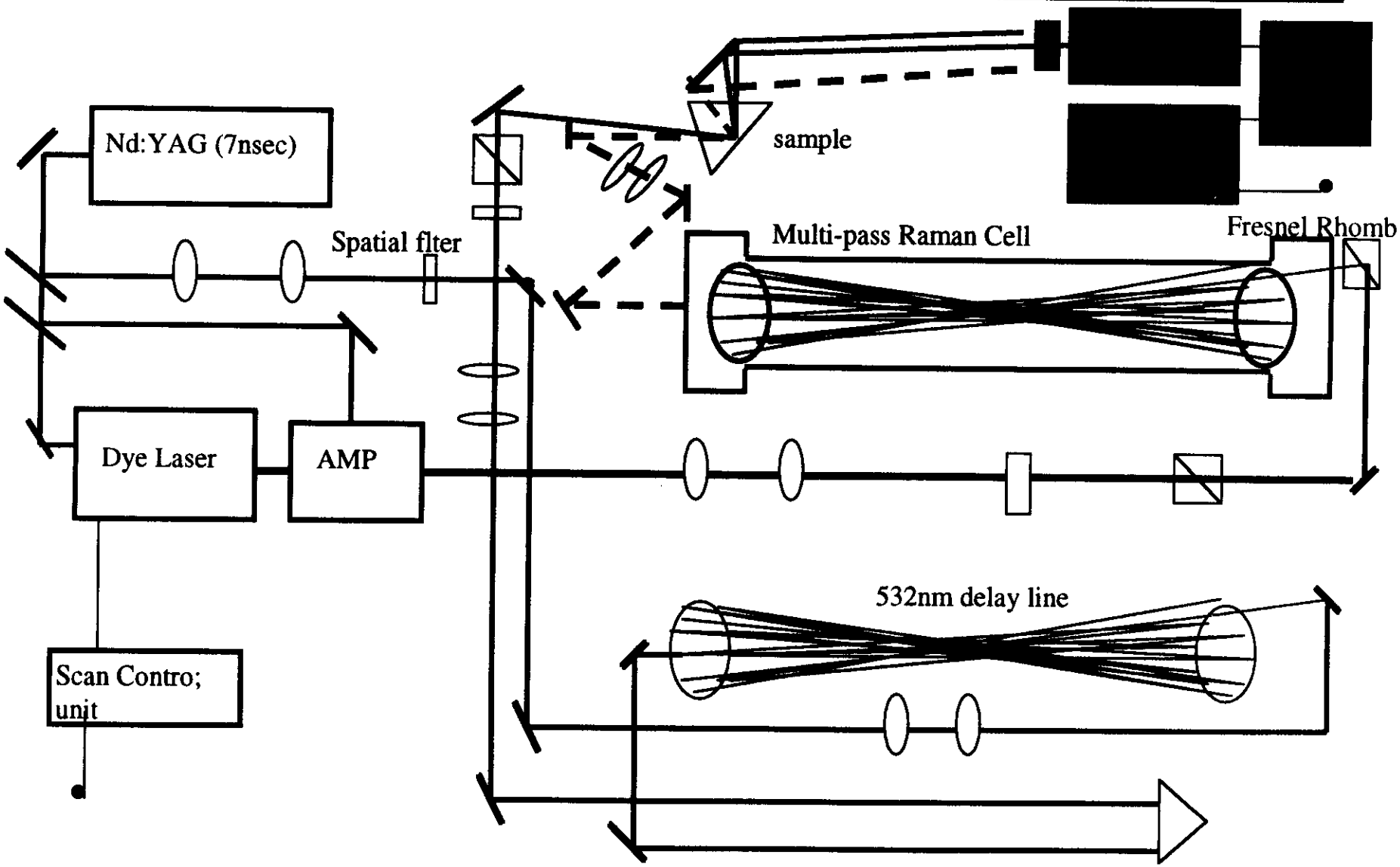
$$P = \chi^{(1)} E + \chi^{(2)} : E\,E + \chi^{(3)} : E\,E\,E + \ldots$$

- **Illuminate sample with laser beams having photon frequency w1 and w2.**
- **Photons with frequencies w1 and w2 interact with materials at the interface and produce new photons with frequency w3.**
- **Collect sum frequency photons (w3) as a function of input photon frequency (w1).**



- **Sum frequency generation is only allowed at the interface.**
- **IR-visible sum-frequency generation enables one to identify species and their structures at interfaces.**

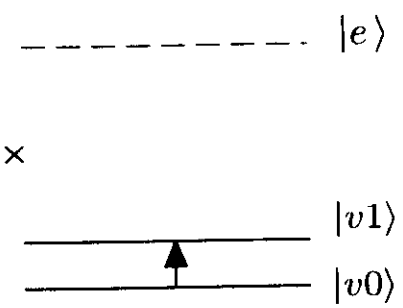
The SFG Optical Set-up at ExxonMobil



BRIEF THEORETICAL BACKGROUND

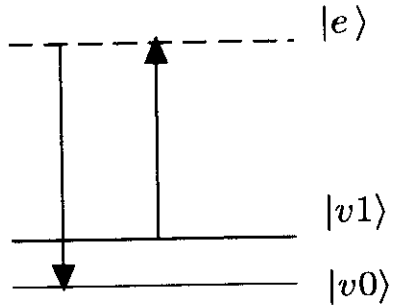
Absorbtion of IR photon

$$\chi_R = \Sigma_{v1} \frac{\langle v0|\mu_k|v1\rangle}{\hbar(\omega_{ir}-\omega_{v1v0}+i\Gamma_{v1v0})} \times$$



Raman adsorbtion of green photon and emission of blue photon

$$\Sigma_m \left[\frac{\langle v1|\mu_i|e\rangle\langle e|\mu_j|v0\rangle}{\hbar(\omega_{vis}-\omega_{ev0})} + \frac{\langle v0|\mu_i|e\rangle\langle e|\mu_j|v1\rangle}{\hbar(\omega_{vis}+\omega_{evo})}\right]$$



$$\chi_R \propto \frac{\partial\mu}{\partial Q} \times \frac{\partial\alpha}{\partial Q}$$

IR dipole moment derivitive **Raman polarizability**

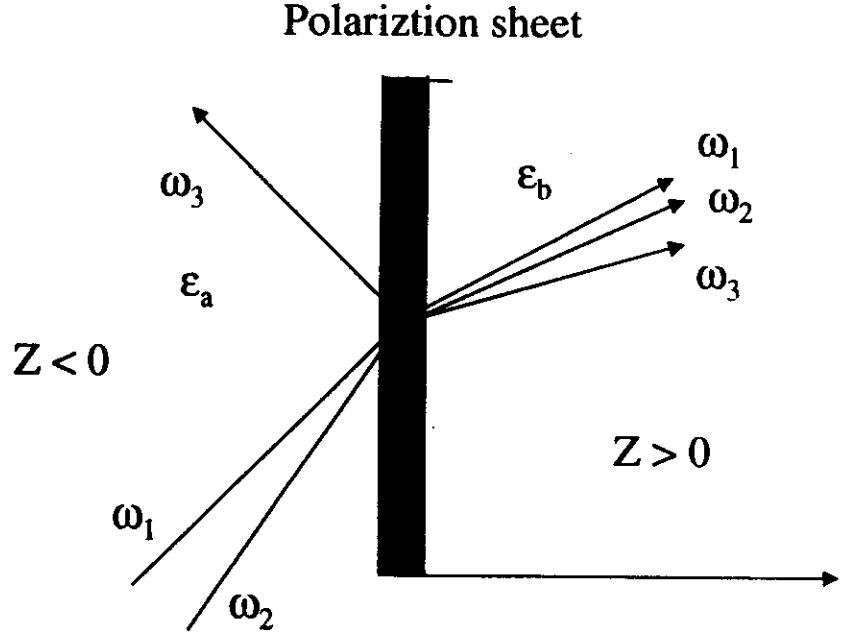
SFG in Total Internal Reflection Geometry

Three layer geometry
Example: ssp polarization configuration

$$L_{xx}(\Omega) = \frac{2\epsilon_a k_{bz}}{\epsilon_b k_{az} + \epsilon_a k_{bz}},$$

$$L_{yy}(\Omega) = \frac{2k_{az}}{k_{az} + k_{bz}},$$

$$L_{zz}(\Omega) = \frac{2\epsilon_a k_{az}(\epsilon_b/\epsilon')}{\epsilon_b k_{az} + \epsilon_a k_{bz}}.$$

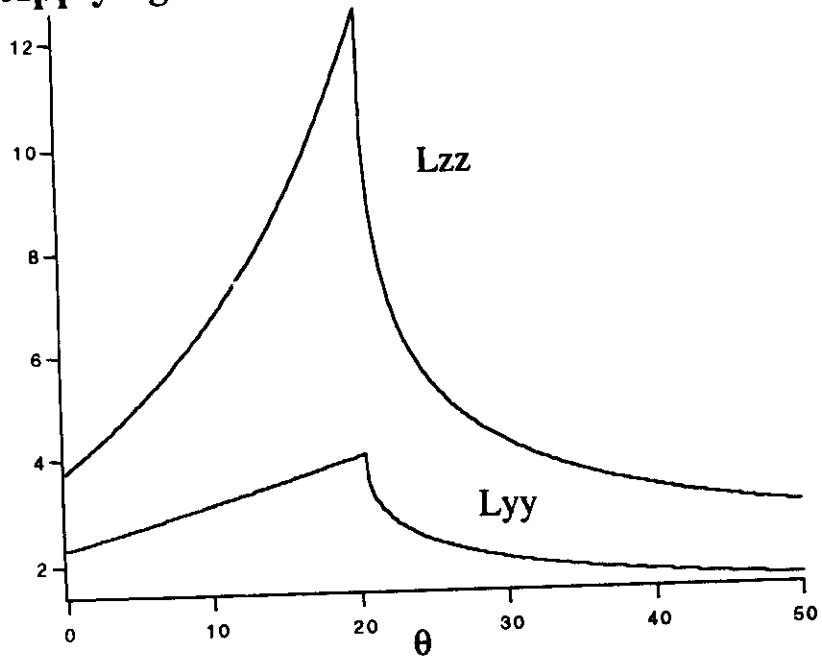


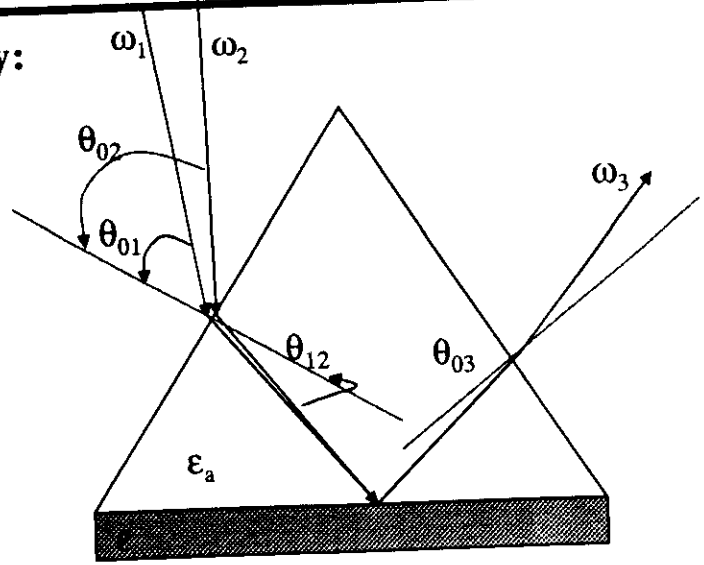
zx is the plane of the incidence

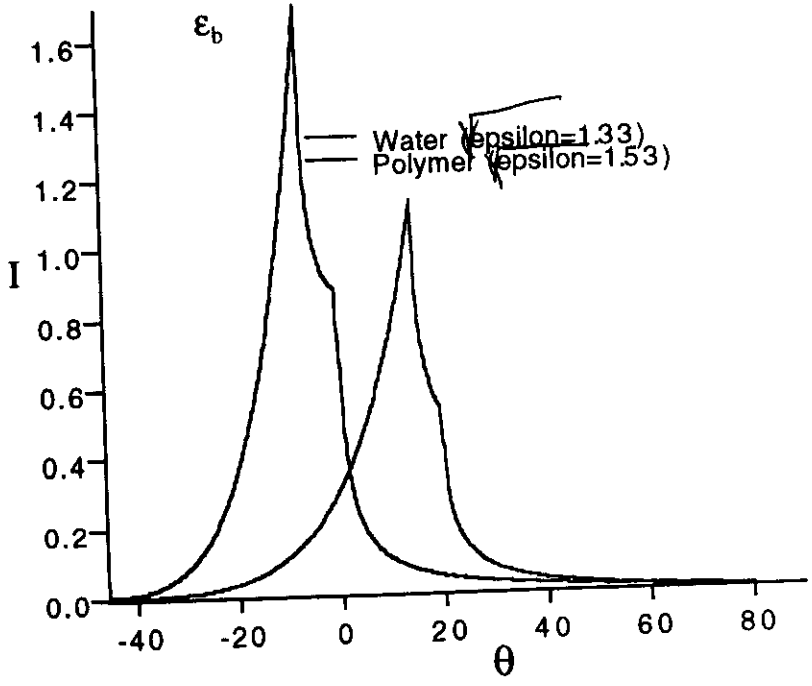
$$E_s(\omega_3) = i\left(\frac{2\pi k_1^2(\omega_3)}{k_{1z}(\omega_3)\epsilon_1(\omega_3)}\right) L_{yy}(\omega_3)\chi_{yyz}L_{yy}(\omega_{vis})L_{zz}(\omega_{ir})E_y(\omega_{vis})E_z(\omega_{ir})$$

SFG in Total Internal Reflection Geometry (Continued)

Applying the above relationships to a prism geometry:

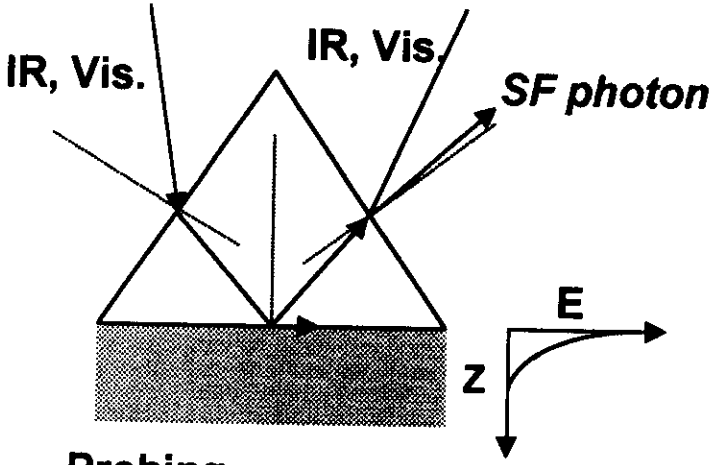




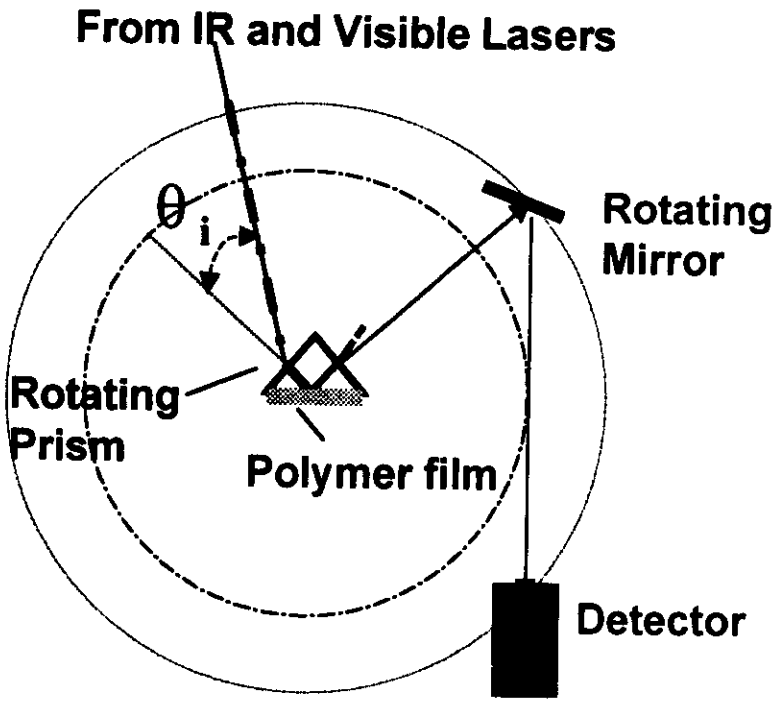


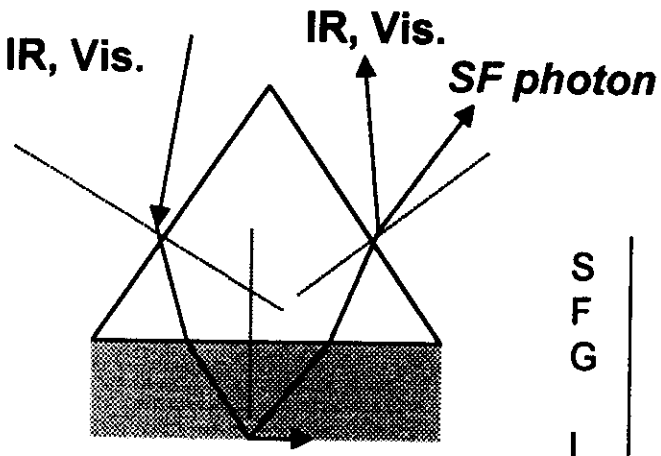
SFG signal is enhanced by 2-3 order of magnitudes at the critical angle.

Probing Two Interfaces in One Material

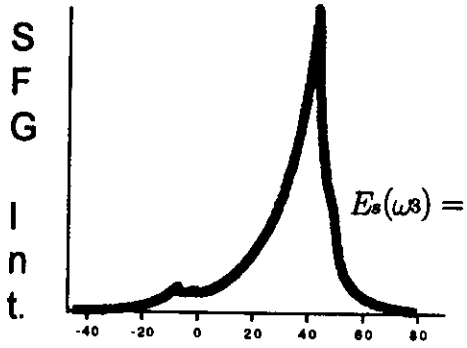


Probing Polymer/Solid Interface





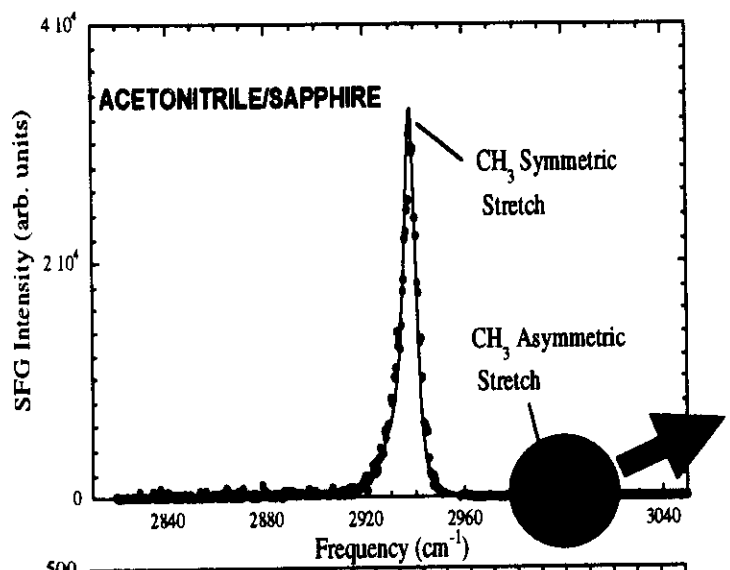
Probing Polymer/Air Interface

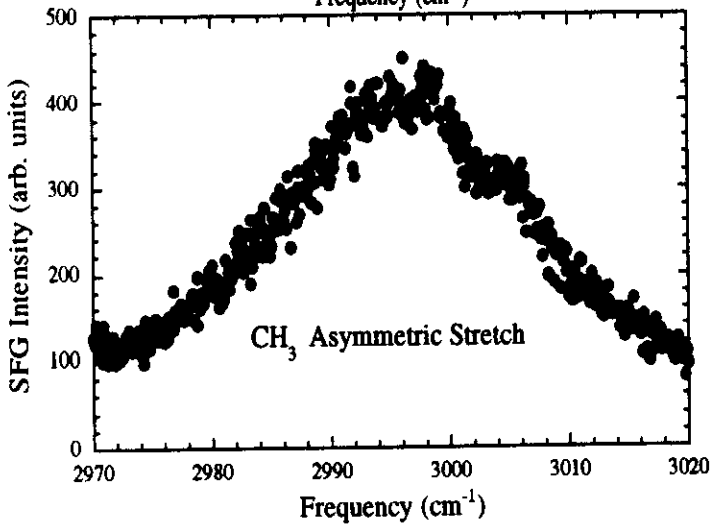


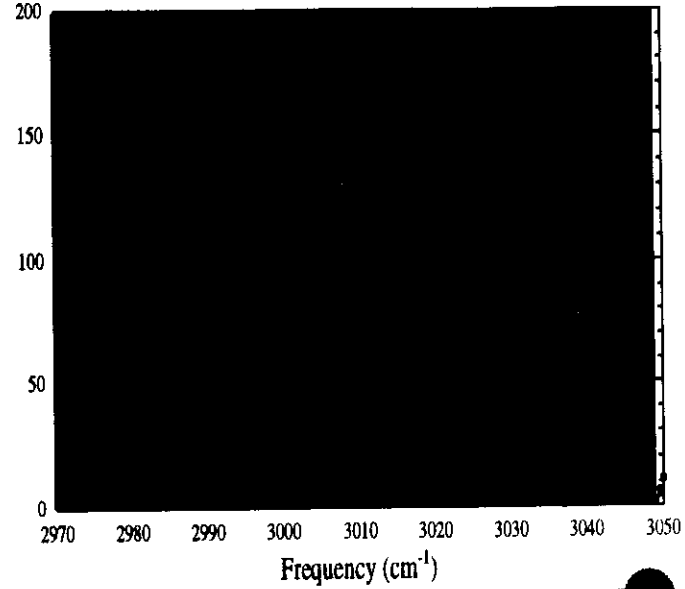
$$E_s(\omega 3) = i\left(\frac{2\pi k_1^2(\omega 3)}{k1z(\omega 3)\epsilon 1(\omega 3)}\right) L_{yy}(\omega 3)\chi_{yyz} L_{yy}(\omega vis) L_{zz}(\omega ir) E_y(\omega vis) E_z(\omega ir)$$

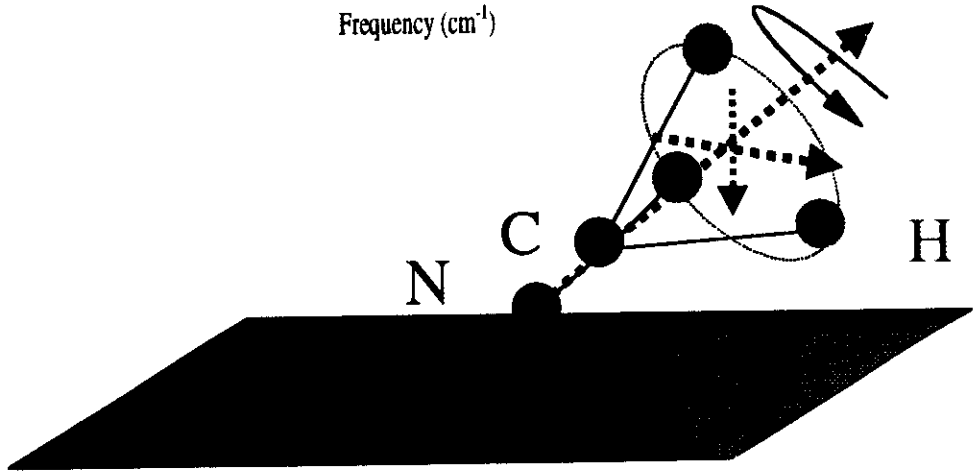
Provide Index of Reflection of Polymer at two interfaces:
Index of Reflection ⟶ Density

Improved Sensitivity and Resolution

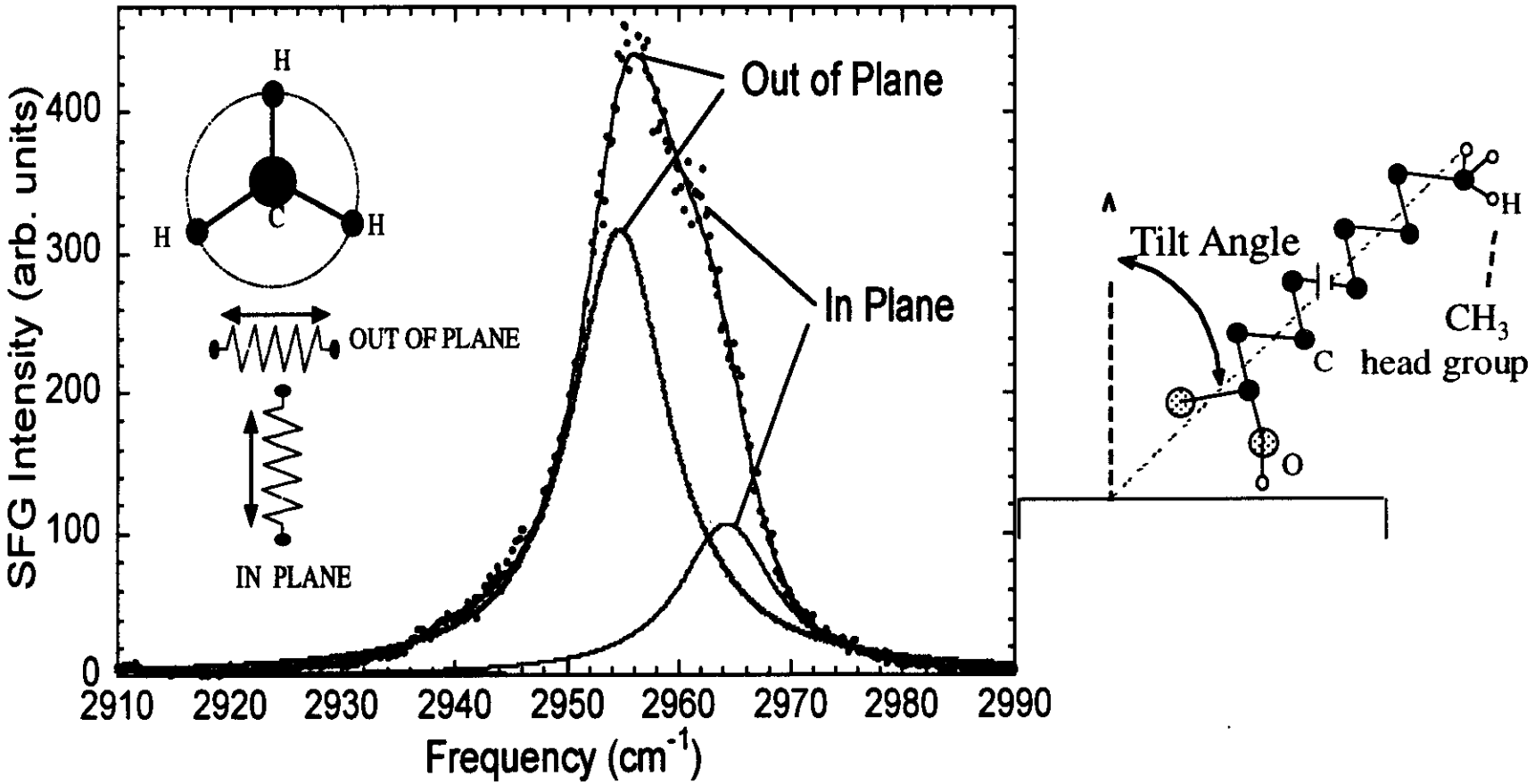








Improved Sensitivity and Resolution: Interfacial Molecular Orientation of a Self Assembled Layer



- **The Splitting Between the In-Plane and Out-of-Plane Stretch of the CH3 Moiety was Detected.**
- **Using this Single Spectrum the Tilt Angle Can be Accurately (<10%) Determined.**

Yeganeh et. al. Vacuum Society, 1995, Technical Digest

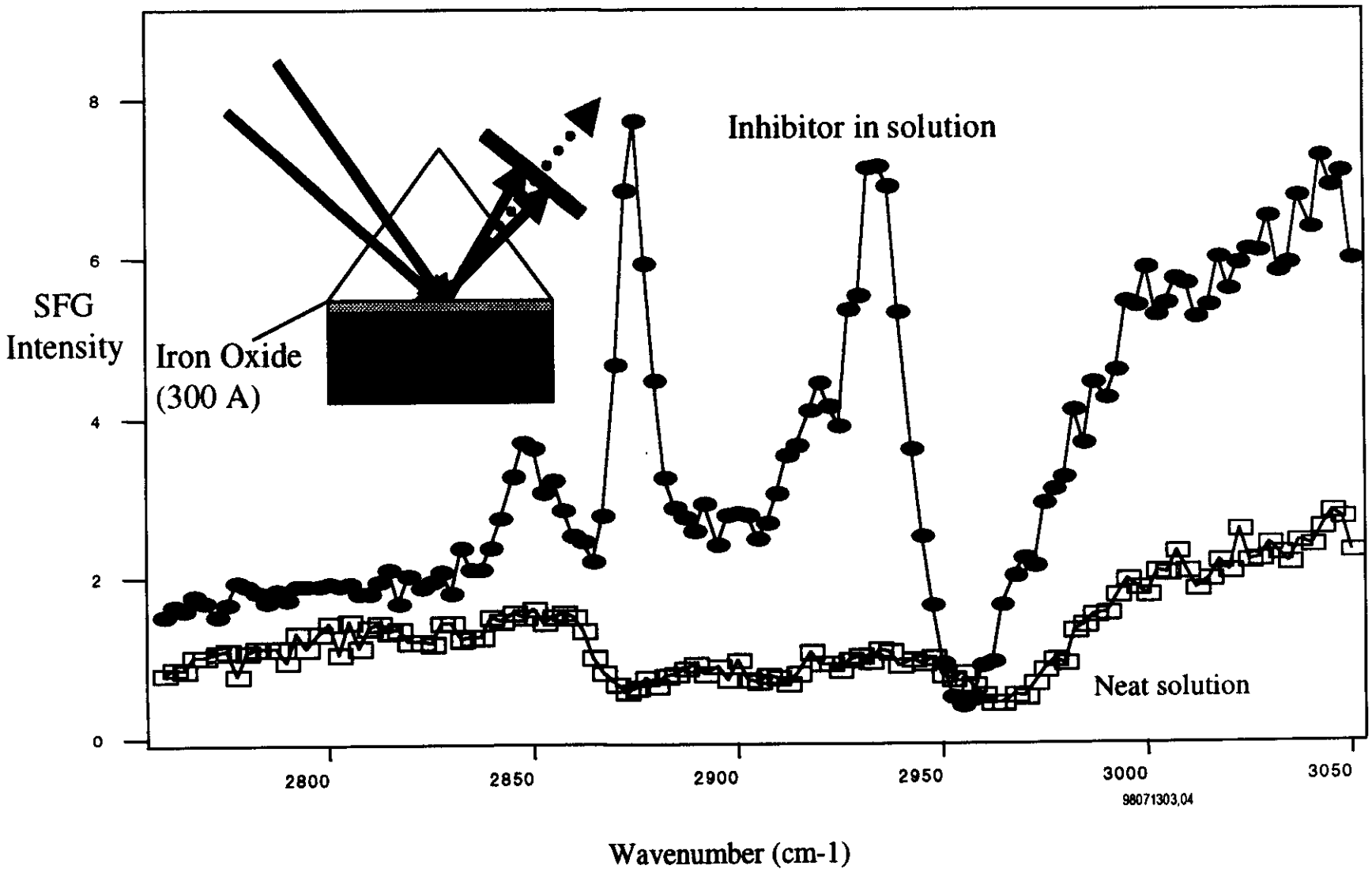
Application of SFG to Lubrication

- Obtaining a better understanding of how the adsorption of lubricity additives determines lubricity in fuels.

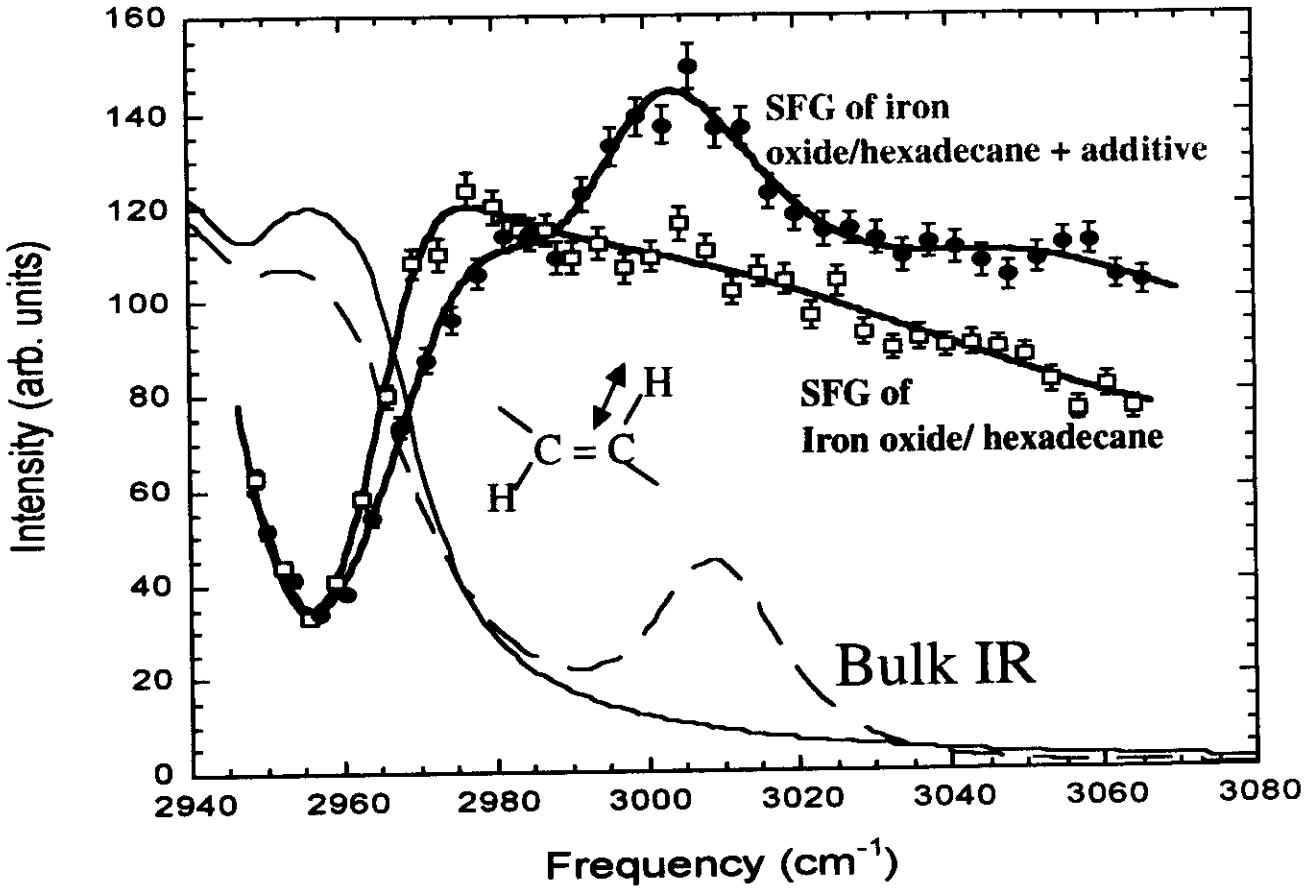
  - Does a particular additive adsorb onto the surface?
  - What is the relationship between surface coverage and friction coefficient?

It is essential to study the adsorption of friction modifiers <u>in-situ</u> at liquid/solid interfaces.

In-situ Adsorption of an Additive from Solution onto an Iron Oxide Surface



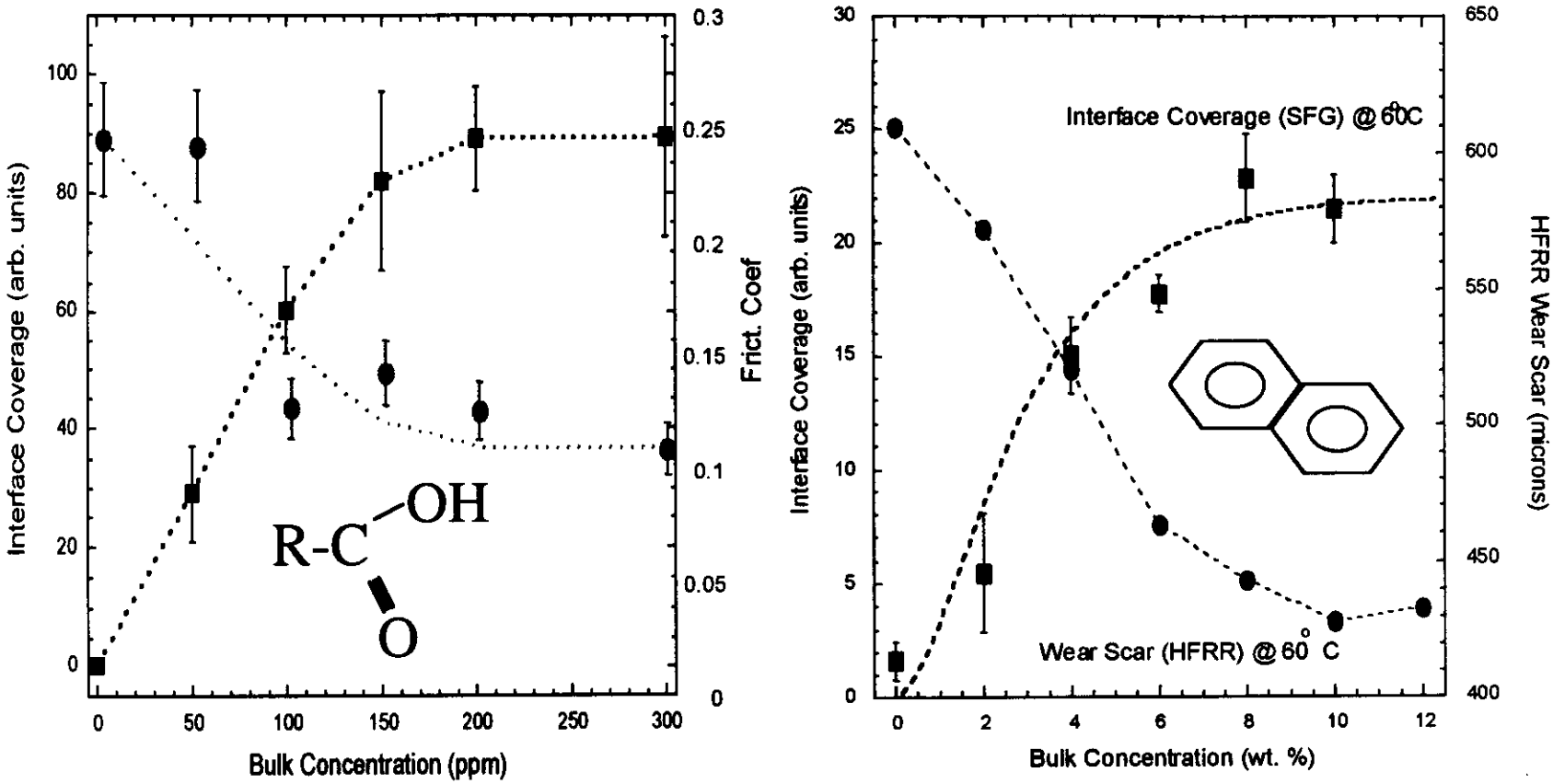
Adsorption of a Friction Modifier on an Iron Oxide



- **Adsorption onto iron oxide was observed in-situ.**
- **The structure at ~3005 cm^{-1} is assigned to an olefinic -CH in the molecular backbone of the additive .**

Yeganeh et. al. QELS, 1999, Technical Digest

Adsorption Isotherm of a Friction Modifier and Its Friction Coefficient



- **In boundary lubrication, performance of a lubricity additive (i.e. friction coefficient and the wear) depends on its adsorption process.**

High Frequency Reciprocating Rig (HFRR)*

High Frequency Friction Machine

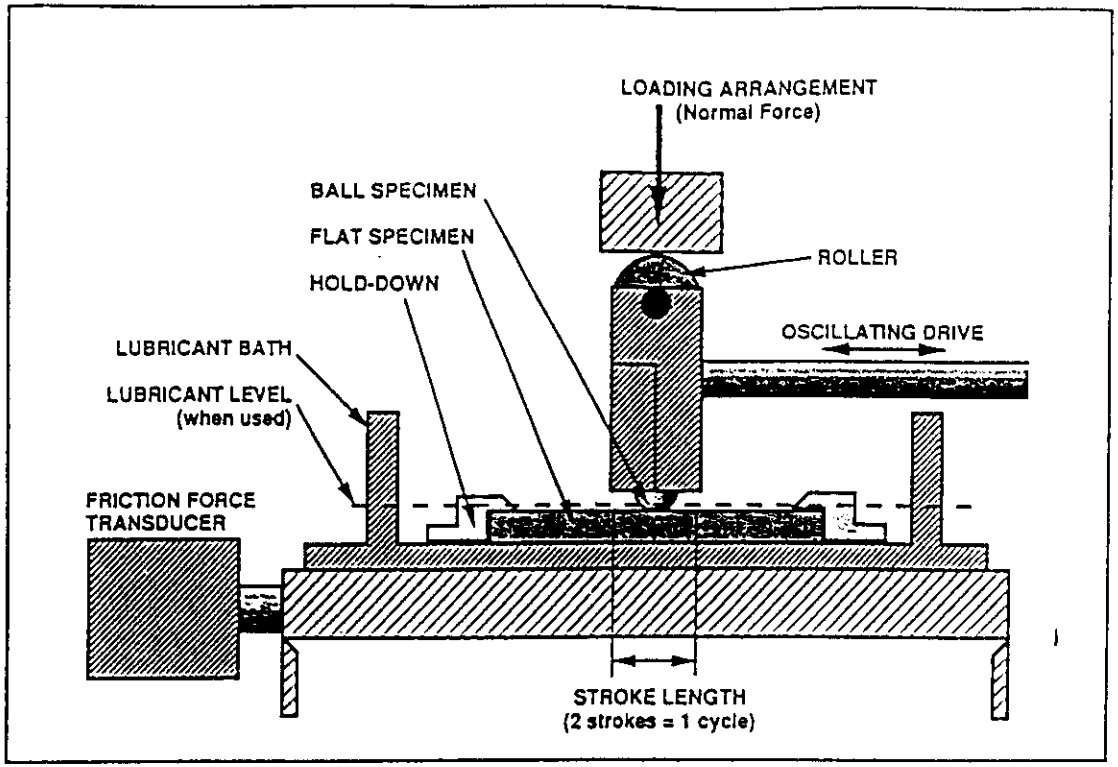


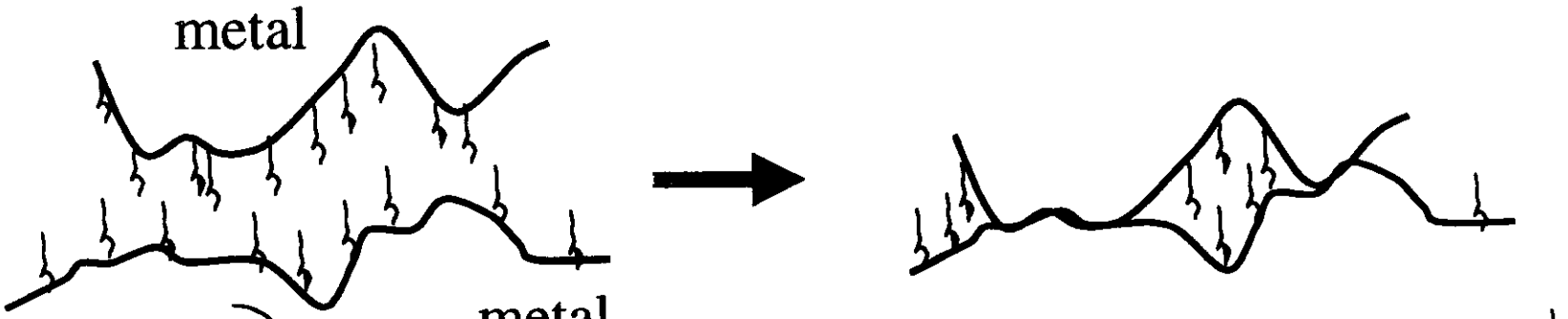
FIG. 1 Reciprocating Test—Schematic Diagram

* ISO, *Determination of Lubricity of Diesel Fuel by High Frequency Reciprocating Rig (HFRR) Test,* ISO Provisional Standard, TC22/SC7N595, 1995.

Fractional Film Defects Model (background) :

In the classical theory of boundary lubrication:

- A friction modifier reduces wear and friction by generating layers adsorbed on a solid surface that reduce the total area of solid-to-solid contact **(Hardy, 1920)**
- Friction modifier performance improves with increasing bulk concentration. **(Bircumshaw, 1925)**
- **Kingsbury (1958)** and **Rowe (1966)** introduced the concept of residence time of an adsorbed molecule on solid surfaces
- **Jahanmir** and **Beltzer (1986)** extended this concept to the fractional film defects model



$$f = \frac{\tau_m}{P_m}\frac{A_m}{A_r}$$

$$A_r = A_a + A_b$$

$$A_m = A_{ma} + A_{mb}$$

$$\theta = \frac{A_a}{A_r}$$

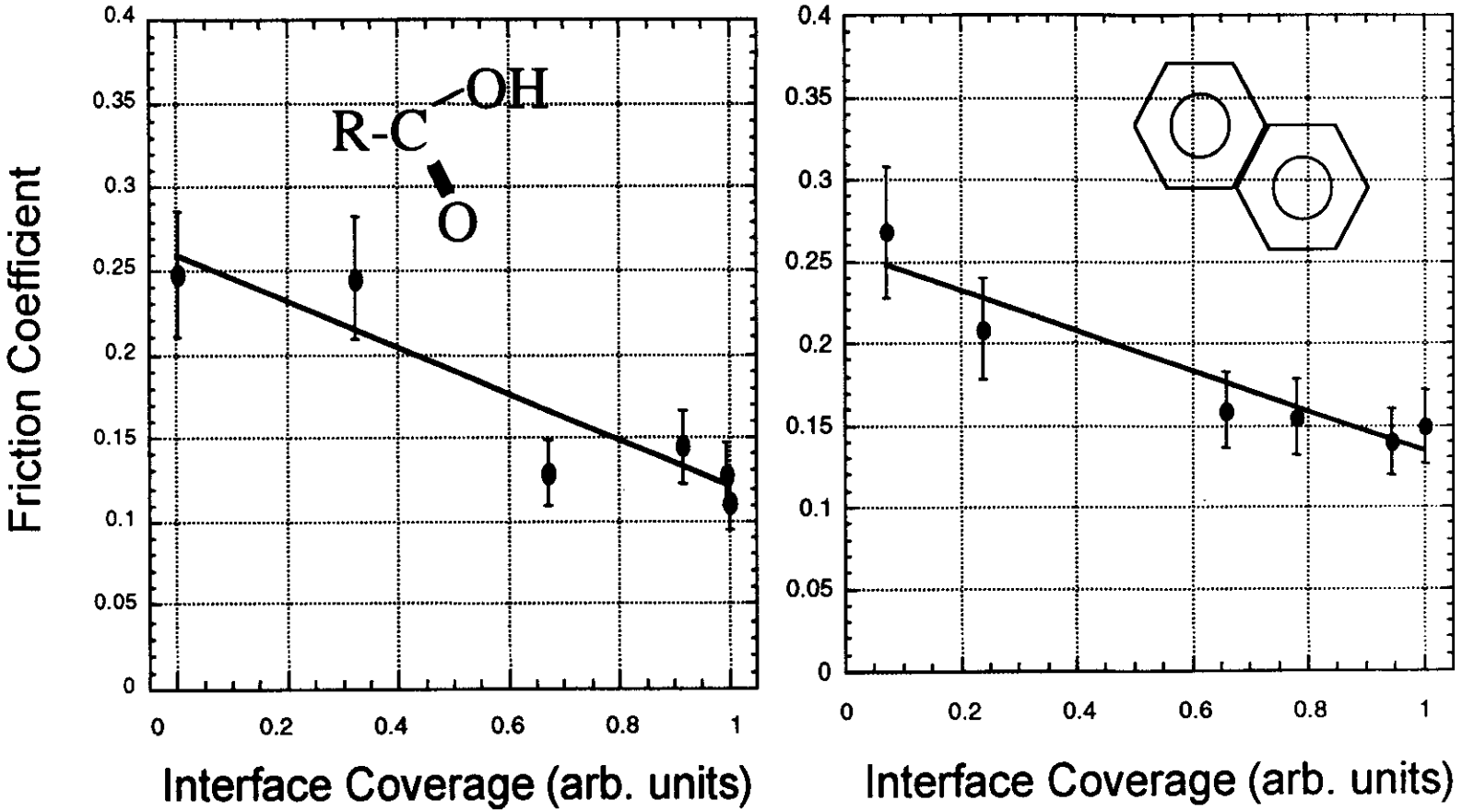
f_b is the base lubricant (solvent) friction coefficient (i.e., at $\theta = 0$)

and f_a is the additive friction coefficient (i.e., at $\theta = 1$).

*S. Jahanmir and M. Beltzer, *Journal of Tribology*, **108**, 109 (1986).

Fractional Film Defect Model

$$f = (f_a - f_b)\,\theta + f_b$$



Summary

- We have used sum-frequency generation (SFG) spectroscopy with High Frequency Reciprocating Rig (HFRR) to investigate the adsorption of a friction modifier to an iron oxide substrate and its relationship to friction reduction.

- Our results demonstrate a strong correlation between the adsorption of friction modifier and the reduction in friction coefficient.

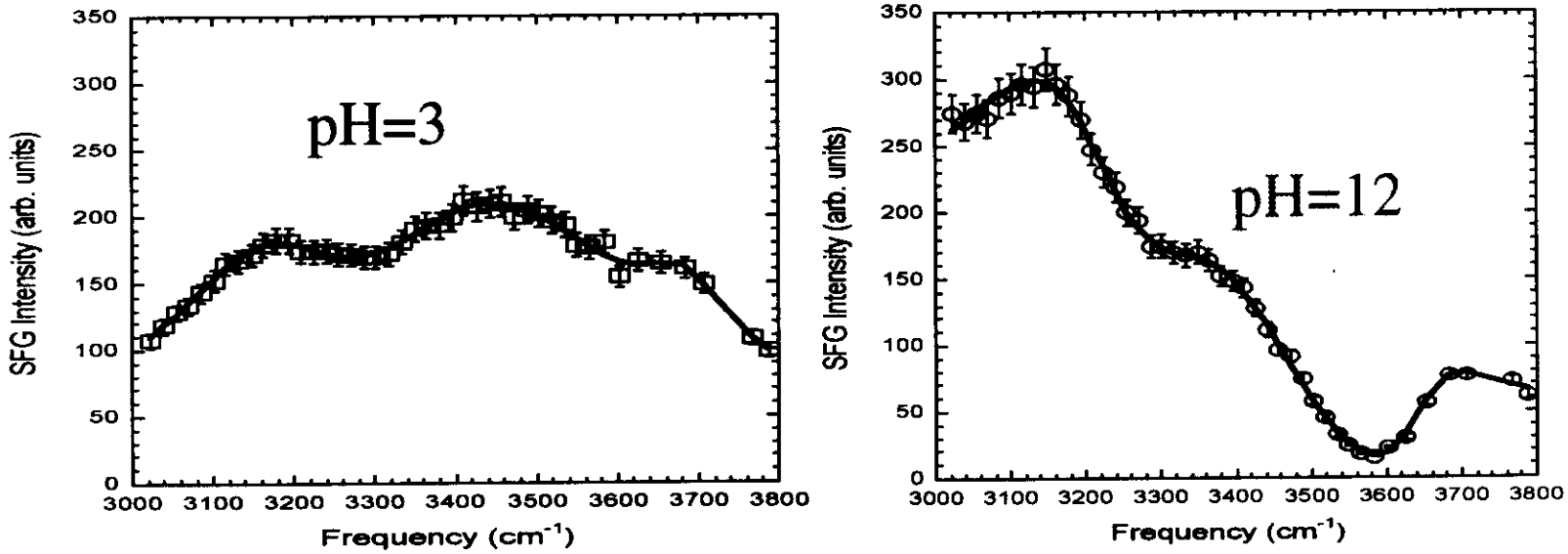
Application of SFG to Aqueous/Solid Oxide

- Many important applications and processes are linked to aqueous solution/ solid oxide interfaces:

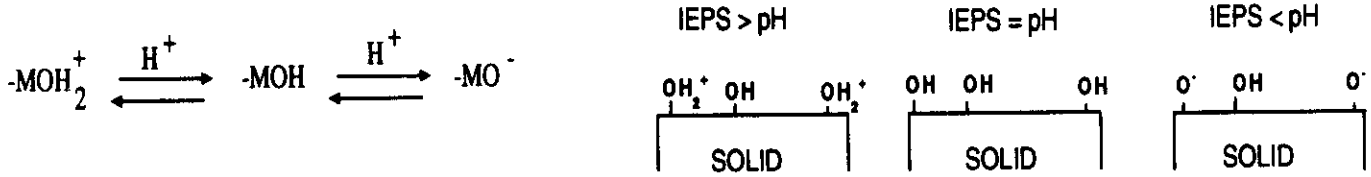
  - Adsorption from an aqueous solution
  - Aqueous Corrosion

Understand the interaction between water and a solid at the interface

Surface-Induced Ordering or Disordering of Interfacial Water Molecules

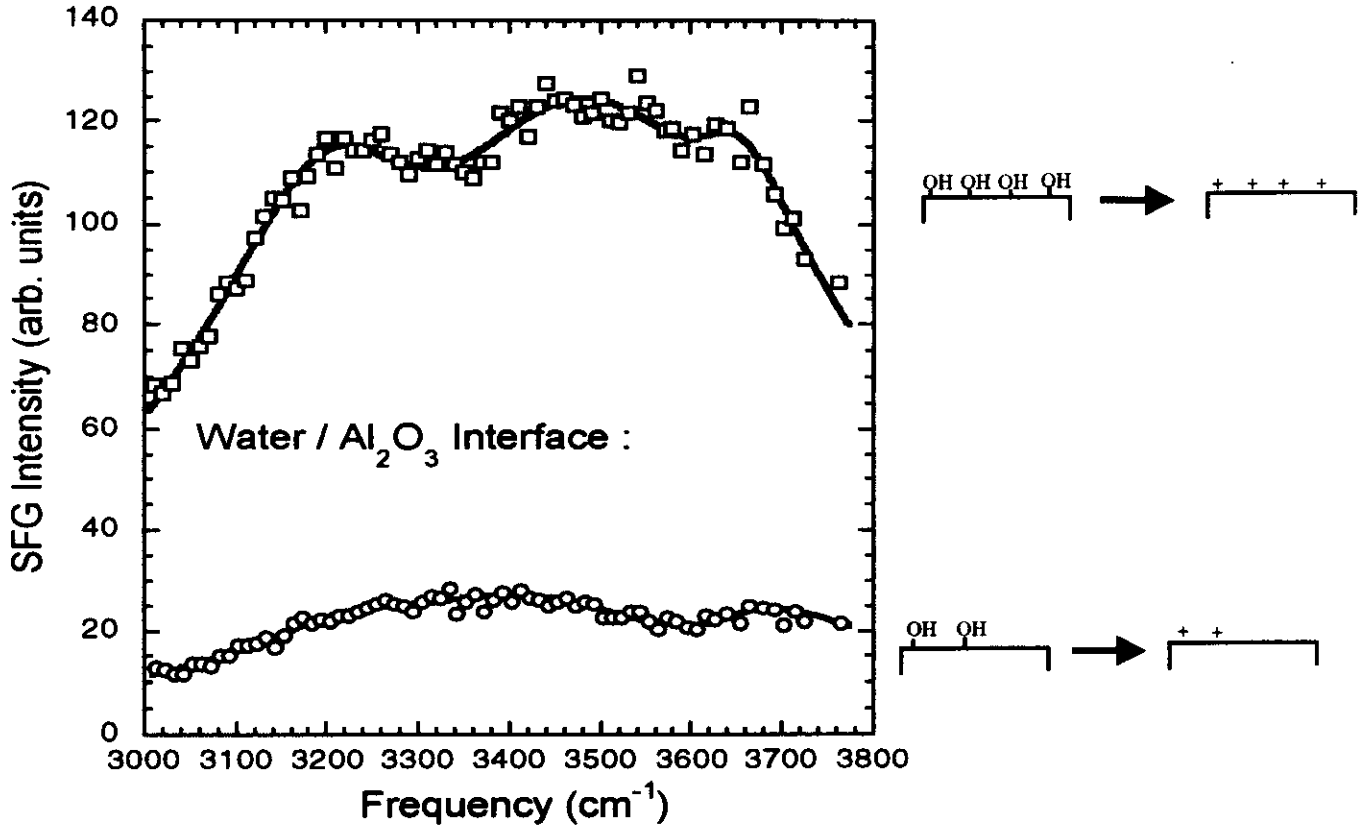


The variation of the signal intensity with pH of the solution is related to the interfacial charge density.



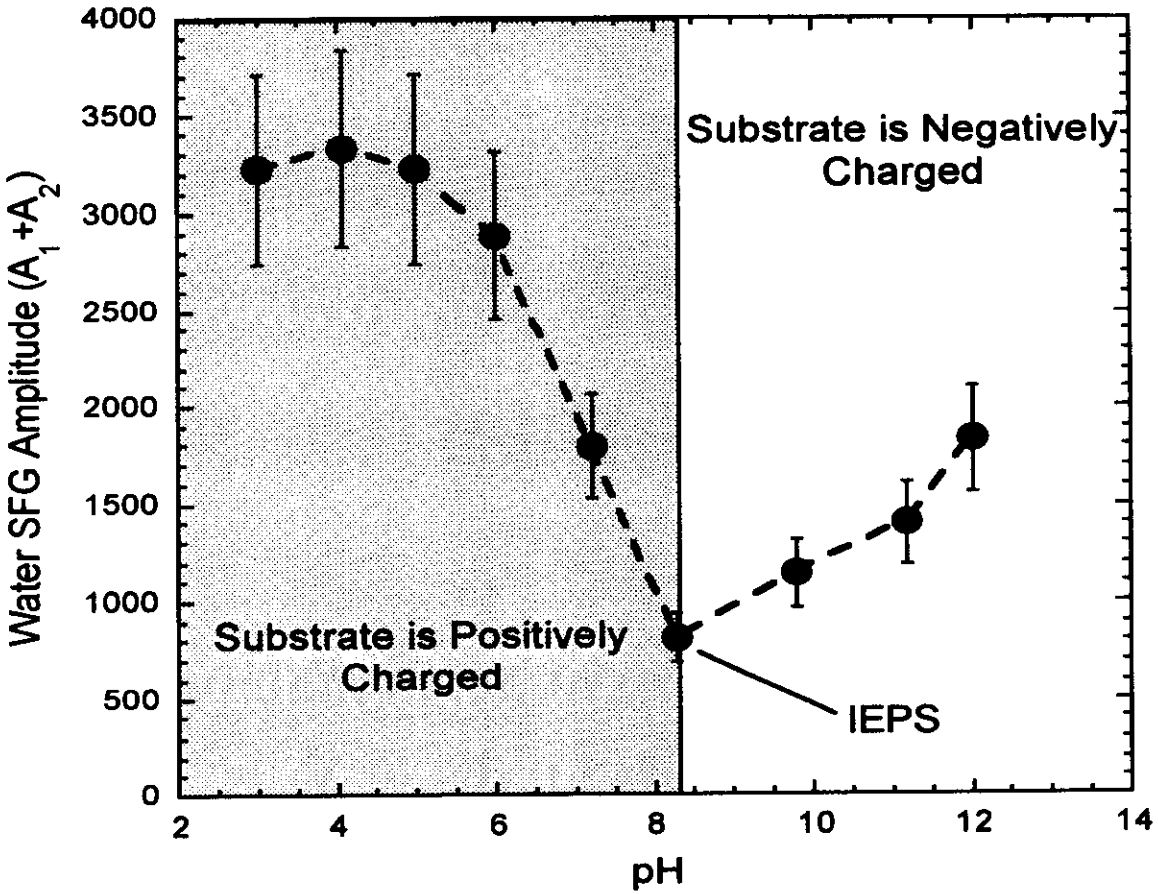
If the pH of an aqueous solution exceeds the IEPS, the surface is negatively charged and if it is below the IEPS it is positively charged.

Surface With Higher OH Number Density Generates Stronger E-Filed in an Aqueous Solution



- **SFG Was Used to Determine the Relative Surface Hydroxyl Number Density**

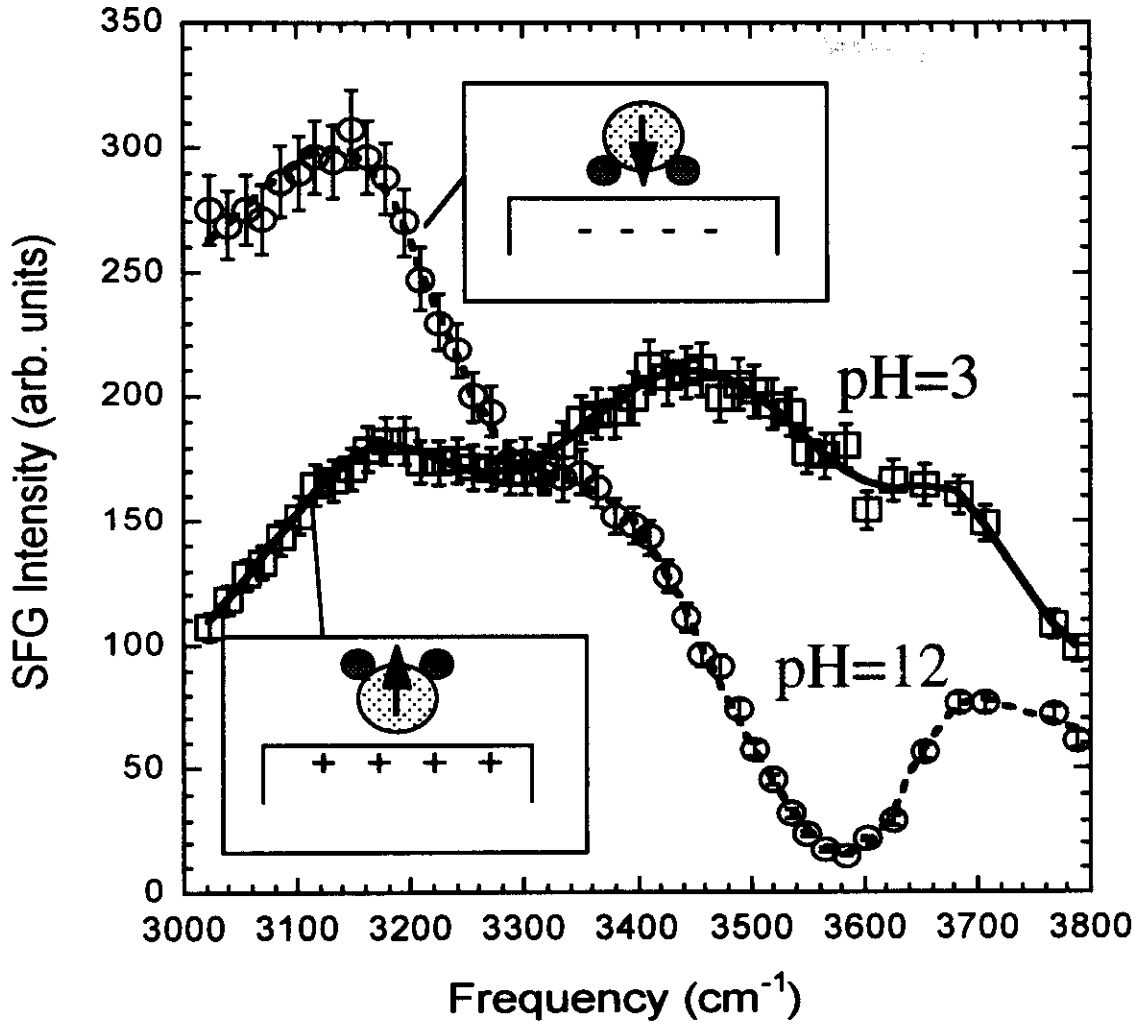
SFG Was Used to Determine the IEPS



- **The marked minimum in the water signal strengths at pH of ~8 is assigned to a surface charge density of zero.**
- **This result indicates that the IEPS of our surface is ~8.**

Yeganeh et. al. PRL, 83, 1179 (1999)

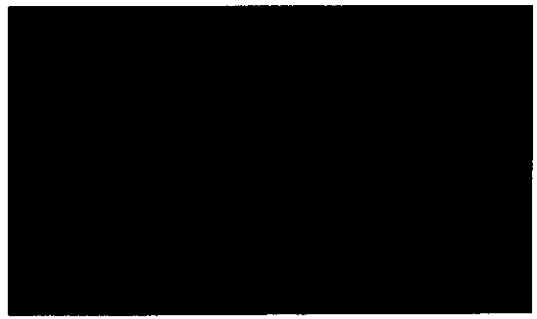
Orientation of Water dipoles at a Liquid/Oxide Interface



$$I_{SFG} = \left| A_{NR} + \sum_{\alpha=1}^{\alpha=3} \frac{A_\alpha e^{i\varphi_\alpha}}{(\omega - \omega_\alpha) + i\Gamma_\alpha} \right|^2,$$

$\Delta\varphi_{3200}=(0.99 \pm .09)\pi$

$\Delta\varphi_{3450}=(0.97 \pm .04)\pi$



Water dipoles at a liquid/solid interface flip by 180° when the pH of the aqueous solution crosses the isoelectric point of the surface (IEPS).

Summary

- We have demonstrated that the interfacial water SFG signal intensities depend strongly on the total hydroxyl number density at the interface.

- We have shown that the water dipole flips by 180° when the pH of the solution crosses the IEPS of the substrate.

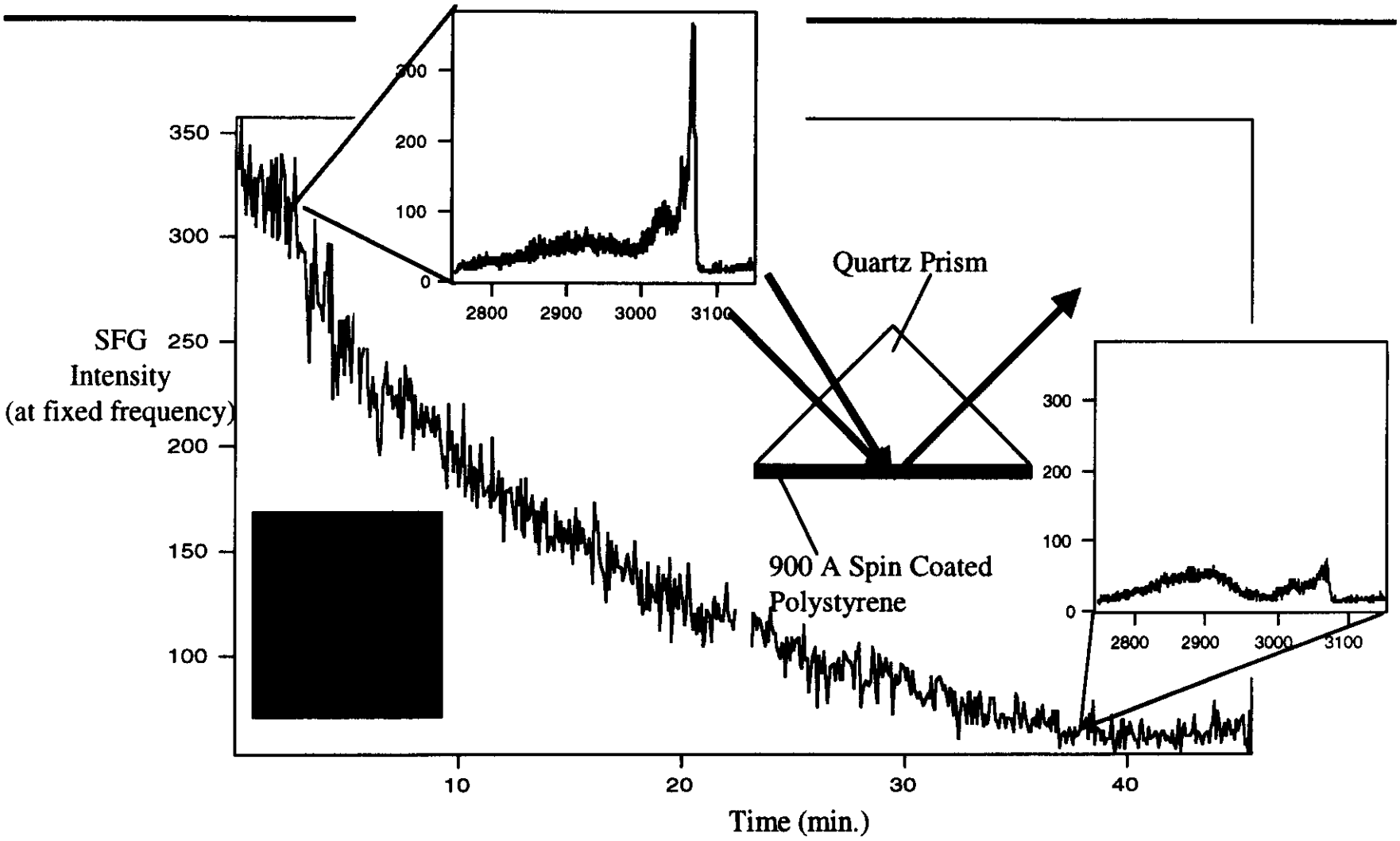
- The dependence of the SFG signal intensities on total charge density was used to determine the IEPS of non-conductive, low surface area materials.

Application of SFG to Polymer Surfaces and Interfaces

- Many polymer properties and applications are closely related to the interfacial composition and structure:
  - Adhesion
  - Lubrication

- Molecular level information about the chemical composition and the structure of polymer is essential
  - -polymer surfaces
  - -solid/polymer and liquid/polymer interfaces

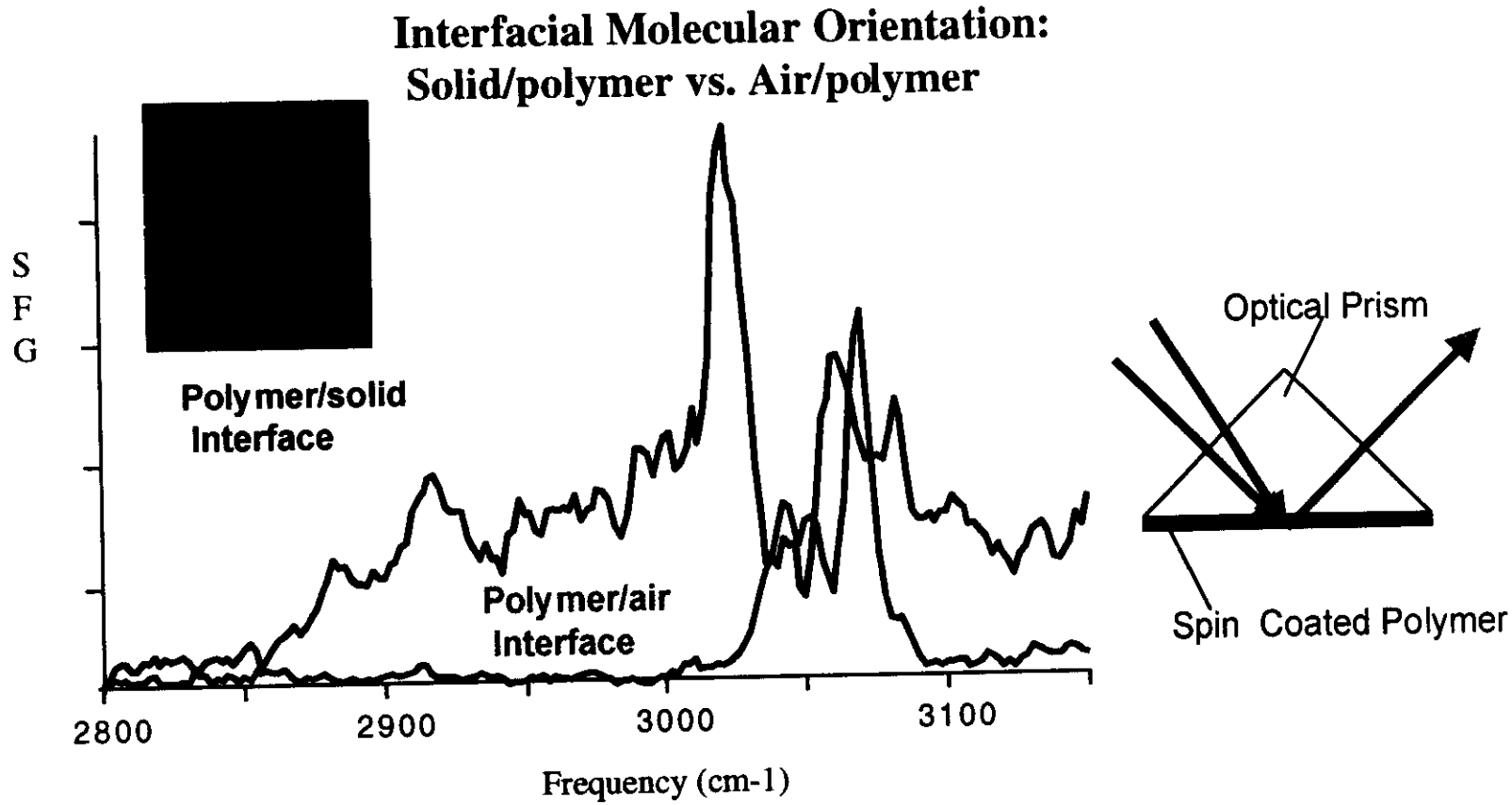
Kinetic of Photo-degradation of Polystyrene Surface



The surface of polystyrene degrades within ~40 minutes.

(Zhang et. al. Langmuir, 16, 4528 (2000))

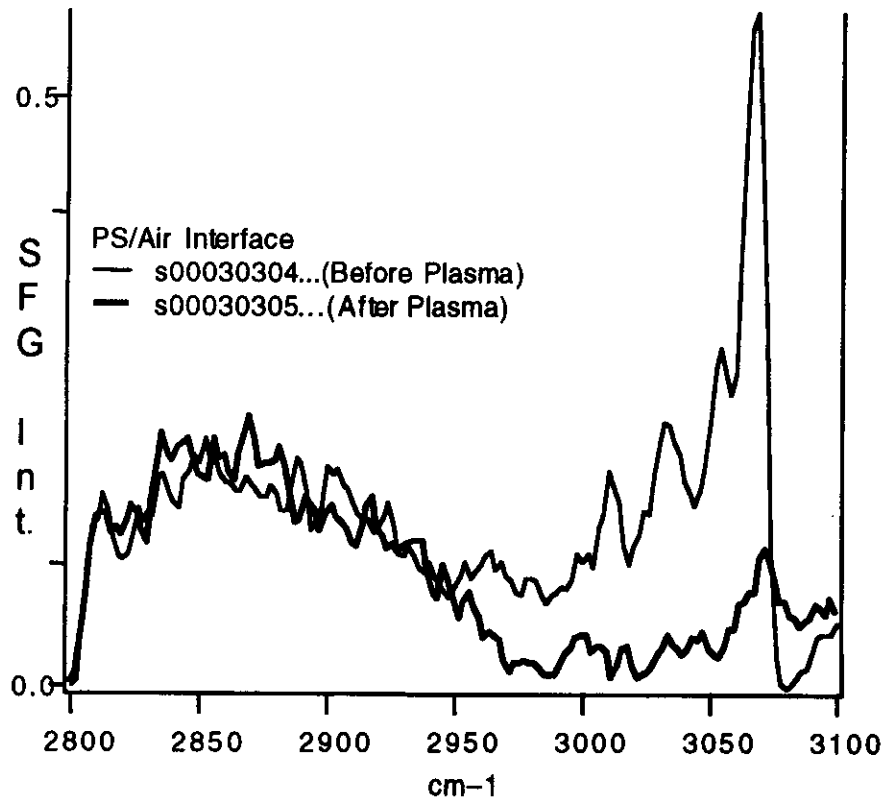
Probing Two Interfaces : Polystyrene as a Model System

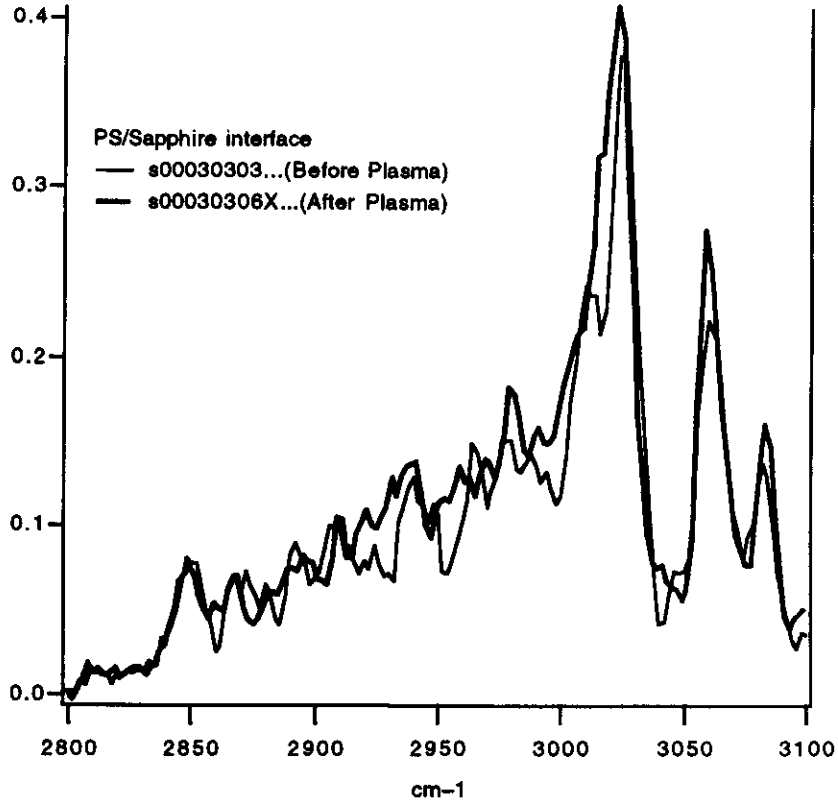


- **The surface structure of polymer (e.g. polystyrene) at the polymer/air interface is drastically different than that at the polymer/solid interface.**
  K. Gautam et. al., PRL *in press*

In collaboration with K. Gautam, D. Schwab and A. Dhinojawala

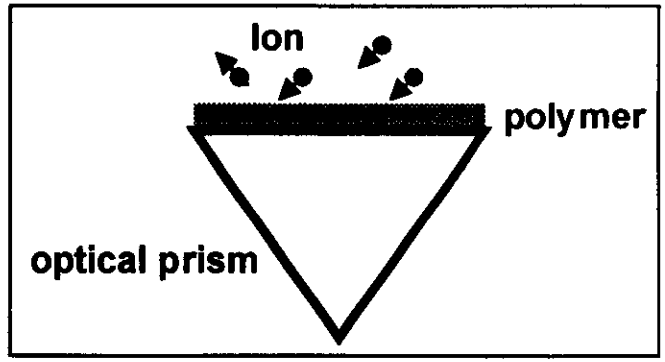
Polymer/Air and Polymer/Solid Interfaces Can Be Detected and Studied With the Same Film



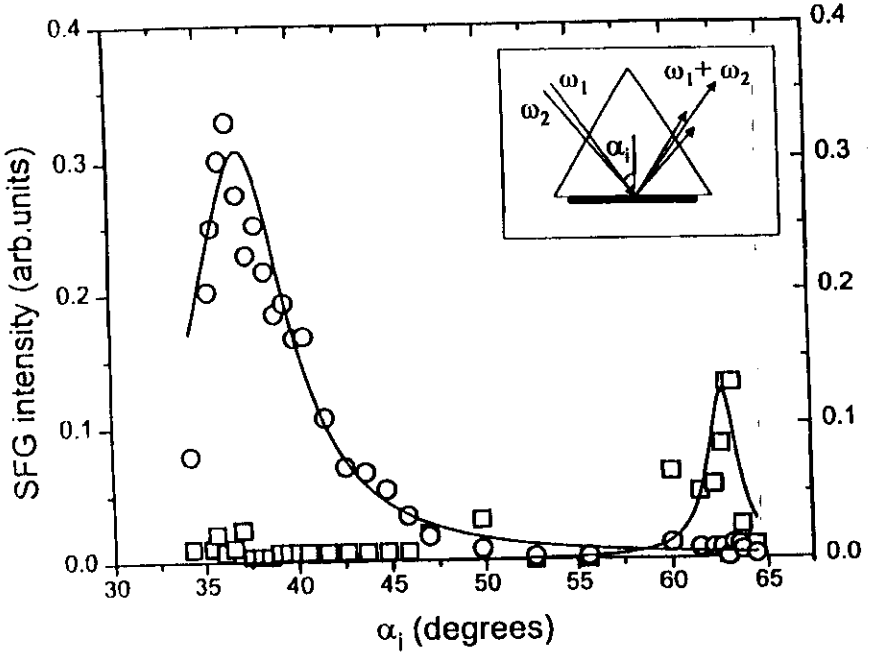


- **SFG is capable of detecting and examining TWO interfaces on a single film**
- **Plasma alters the molecular structure of the polymer/ air interface** (Zhang et. al. Langmuir, 16, 4528 (2000)).

In collaboration with K. Gautam, D. Schwab and A. Dhinojawala



Polymer/Air and Polymer/Solid Interfaces: Packing Density



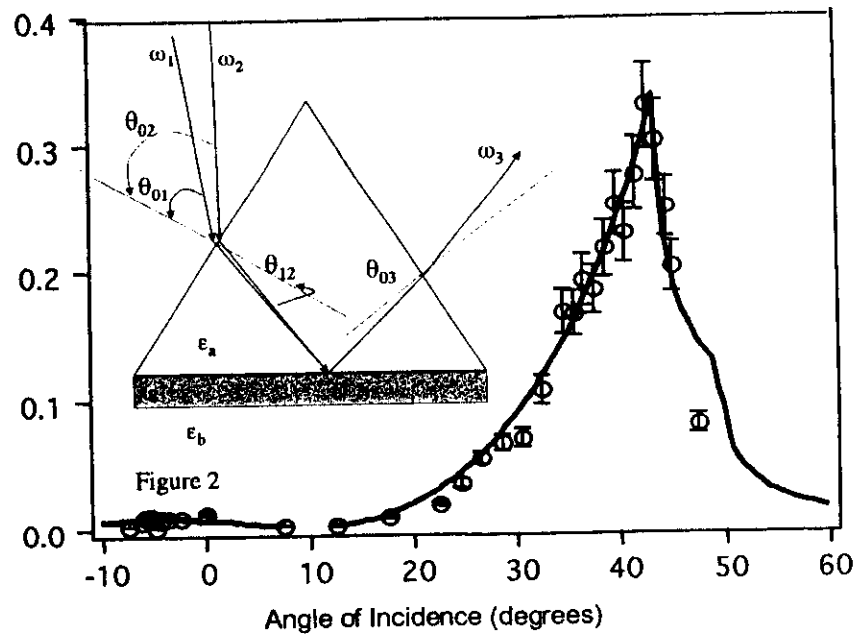
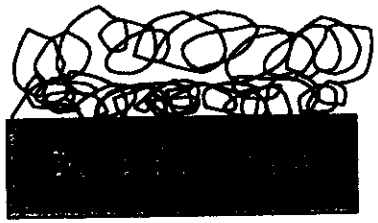


Figure 2



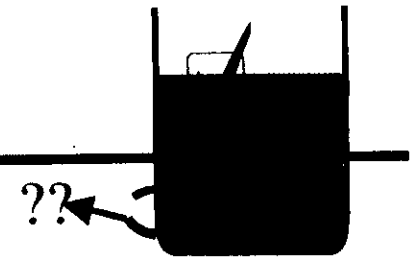
- **The index of reflection of polymer film is higher at the solid/polymer than at the polymer/air interface.**
  - **Molecules are closer packed at a solid/polymer interface**
    - **+ Confirmed by neutron reflectometry**

In collaboration with K. Gautam, D. Schwab and A. Dhinojawala

Summary

- Polymer surfaces and interfaces can be inspected using SFG Spectroscopy
- Surface Photo-degradation of PS is completed within 40 minutes
- Molecular arrangement of PS at the air/polymer interfaces is drastically different than the polymer/solid interface.

Normal Alkane: Bulk, Surface and Interface



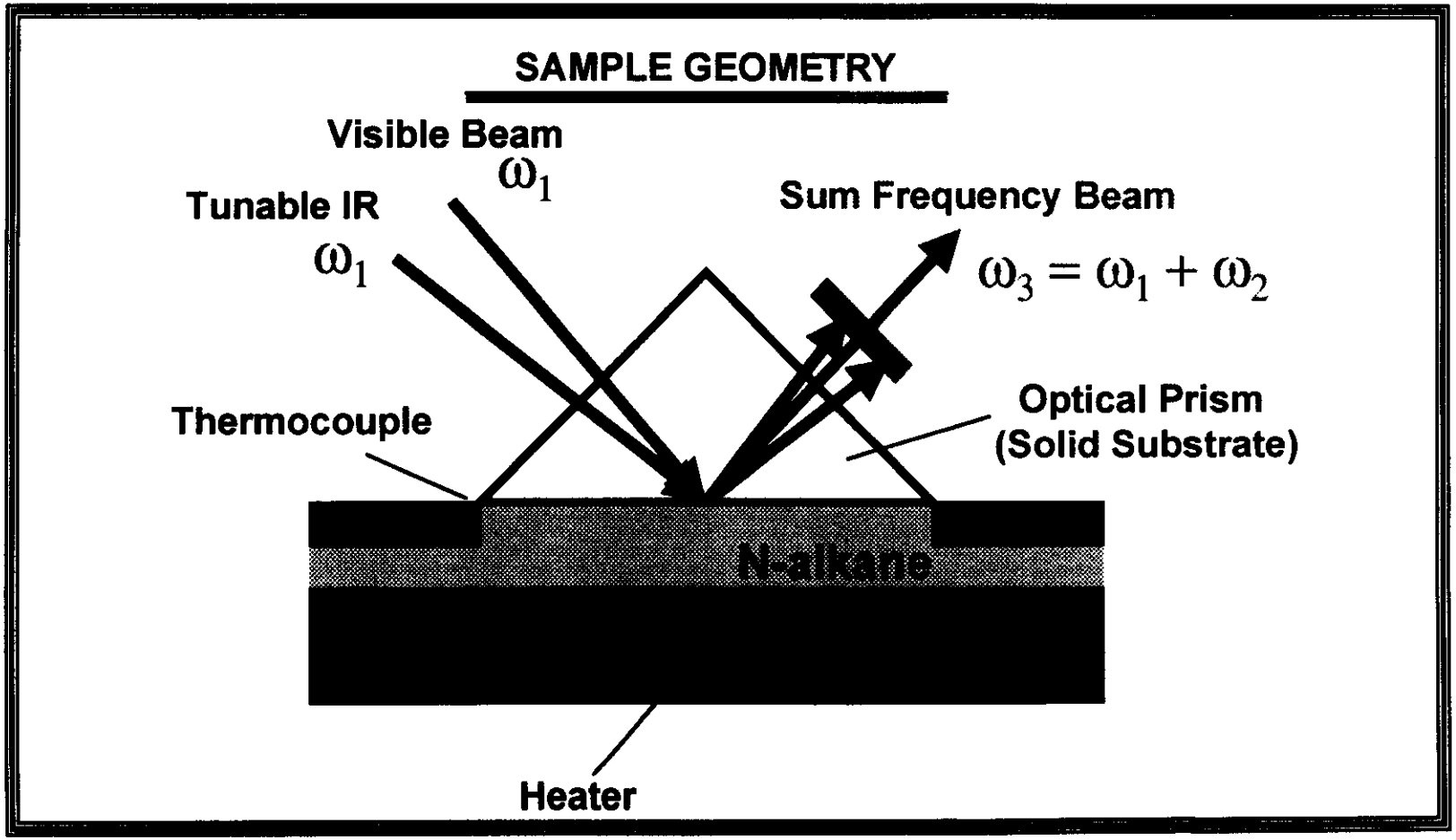
- **N-alkanes are one the most fundamental building blocks of lipids, surfactants, liquid crystals, polymers and fuels.**

- **N-alkanes have shown rich physical properties:**
  - **+ BULK**
    Rotator Phase: Some n-alkanes exhibit an intermediate phase between crystalline and isotropic liquid. (Muller R. Soc. 1932, Sirota, JCP, 1993)

  - **+ SURFACE**
    Surface Freezing: The surface of liquid n-alkane freezes at about 3 degrees above the bulk solidification temperature. (Wu PRL, 199X)

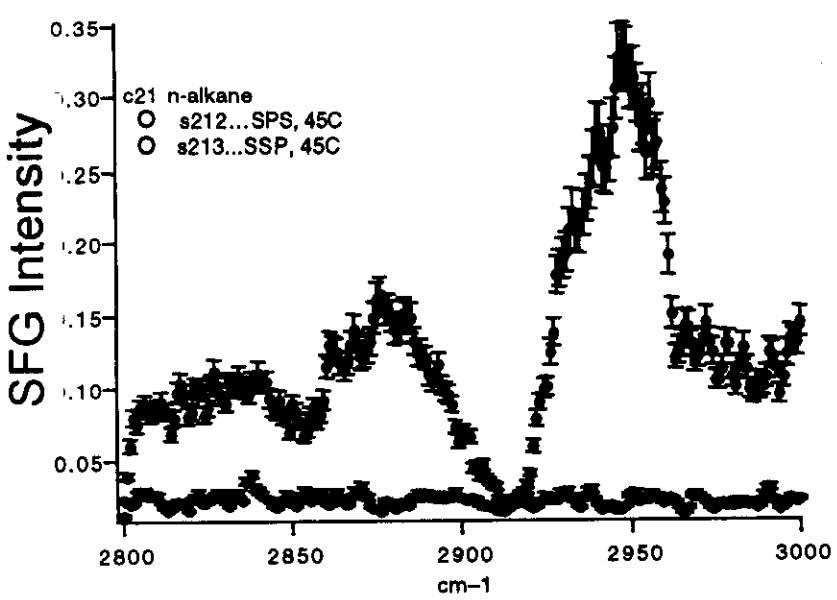
  - **+ INTERFACE:**
    The behavior of n-alkane at solid/alkane interfaces is relatively unexplored.
    - **Monolayer alkane on substrates** (Fuhrmann; Surface Science 1999)
    - **MD calculations** (Xie, PRB 1993)

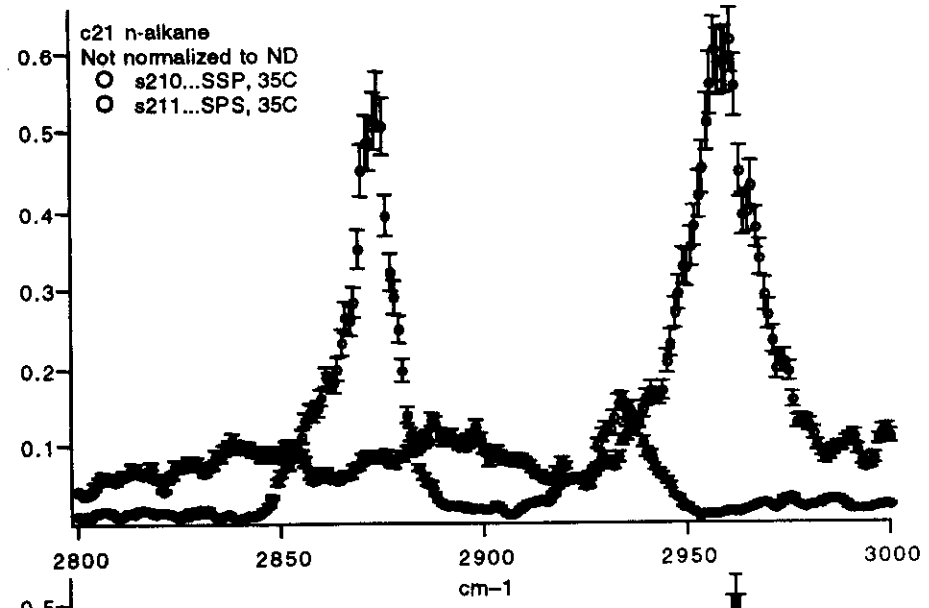
Sum Frequency Generation (SFG) Probes Solid/Solid and Solid/Liquid Interfaces



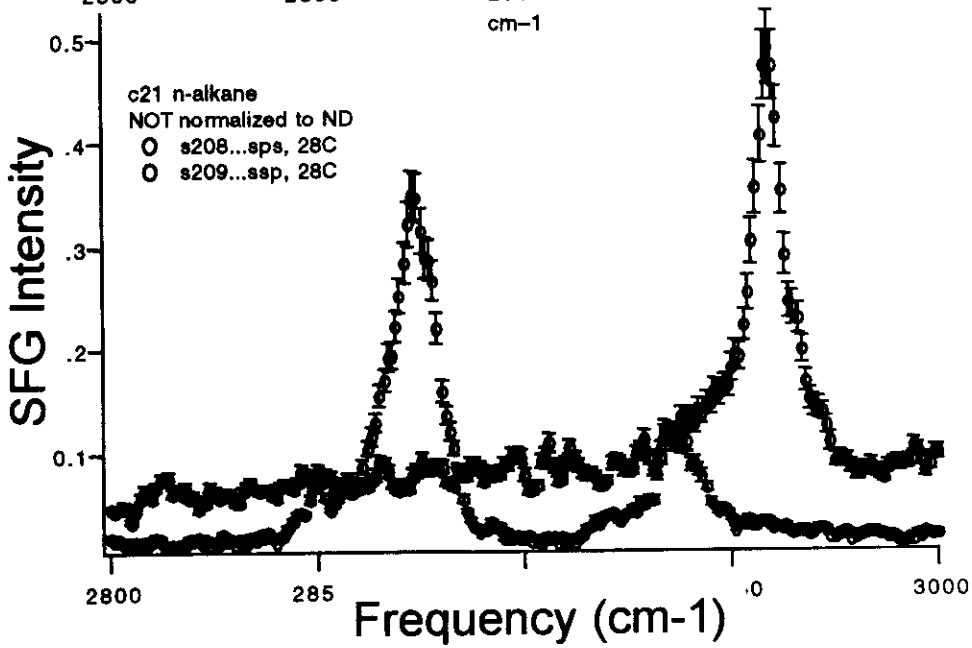
IR-vis. SFG is a vibration probe sensitive to molecular compositions and structure at interfaces.

Variation of SFG Spectra of C21/Al2O3 Interface With Temperature

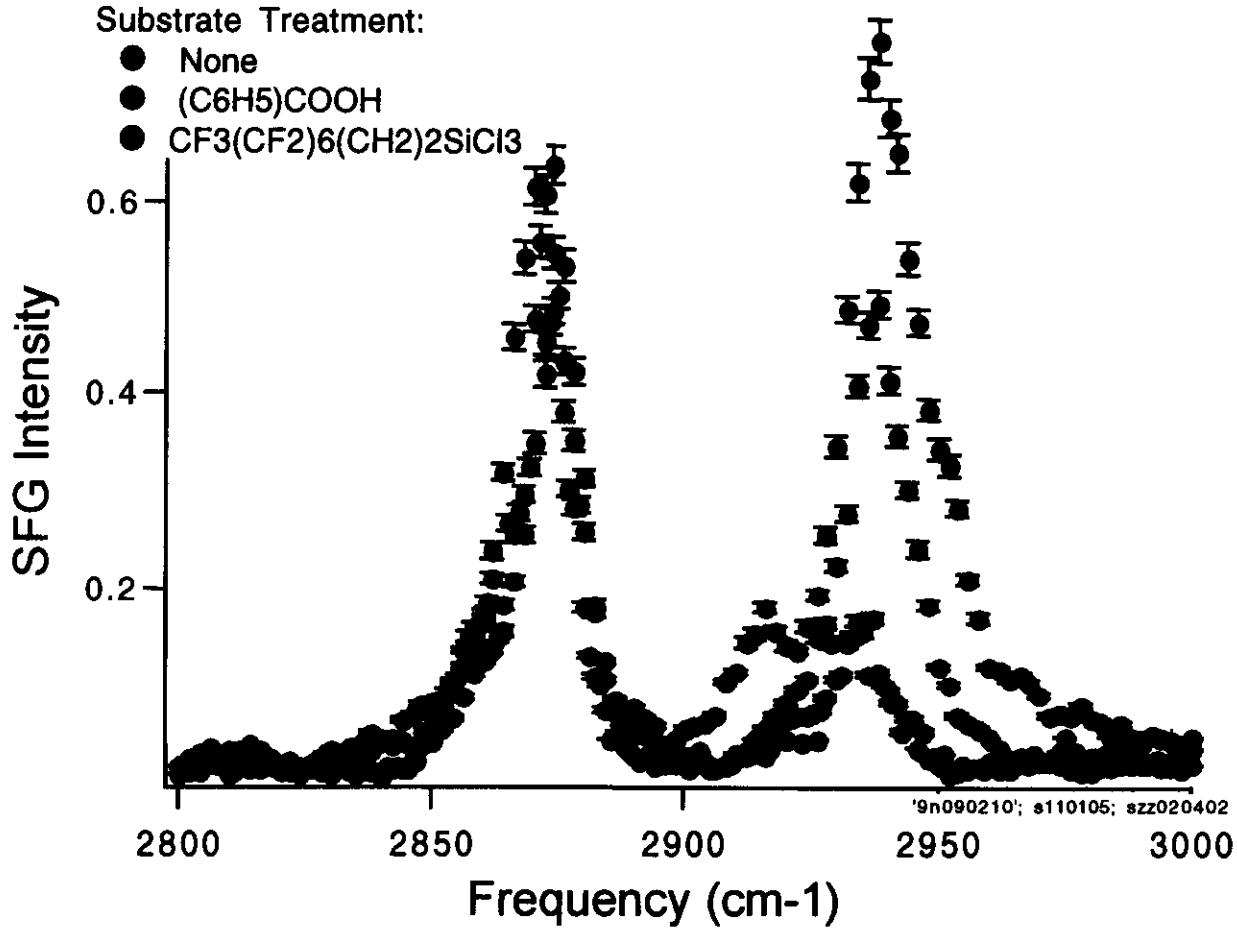




Dramatic changes in molecular structure/arrangement of n-alkane at the organic/Al2O3 interface occurs with temperature.

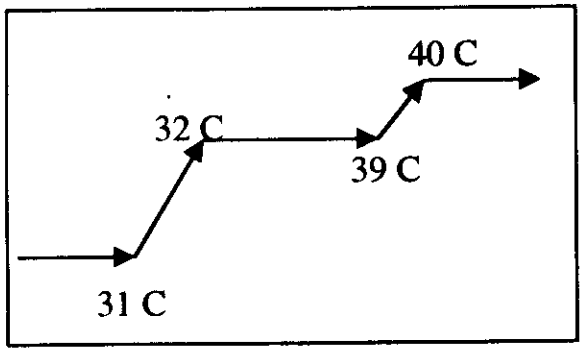


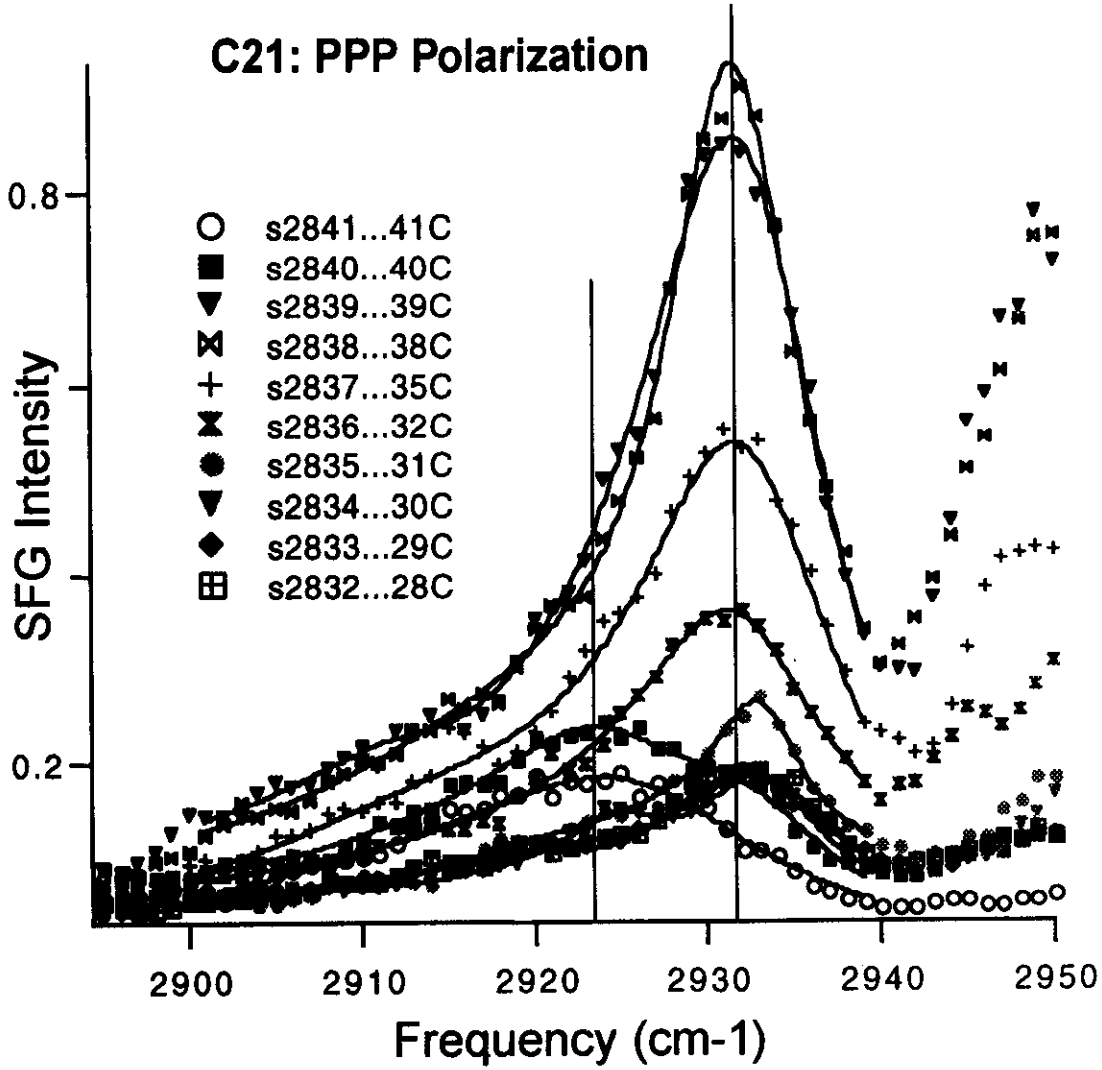
Spectral Sensitivity to Substrate Treatment



Similar variations were observed with water and OTS treatments.

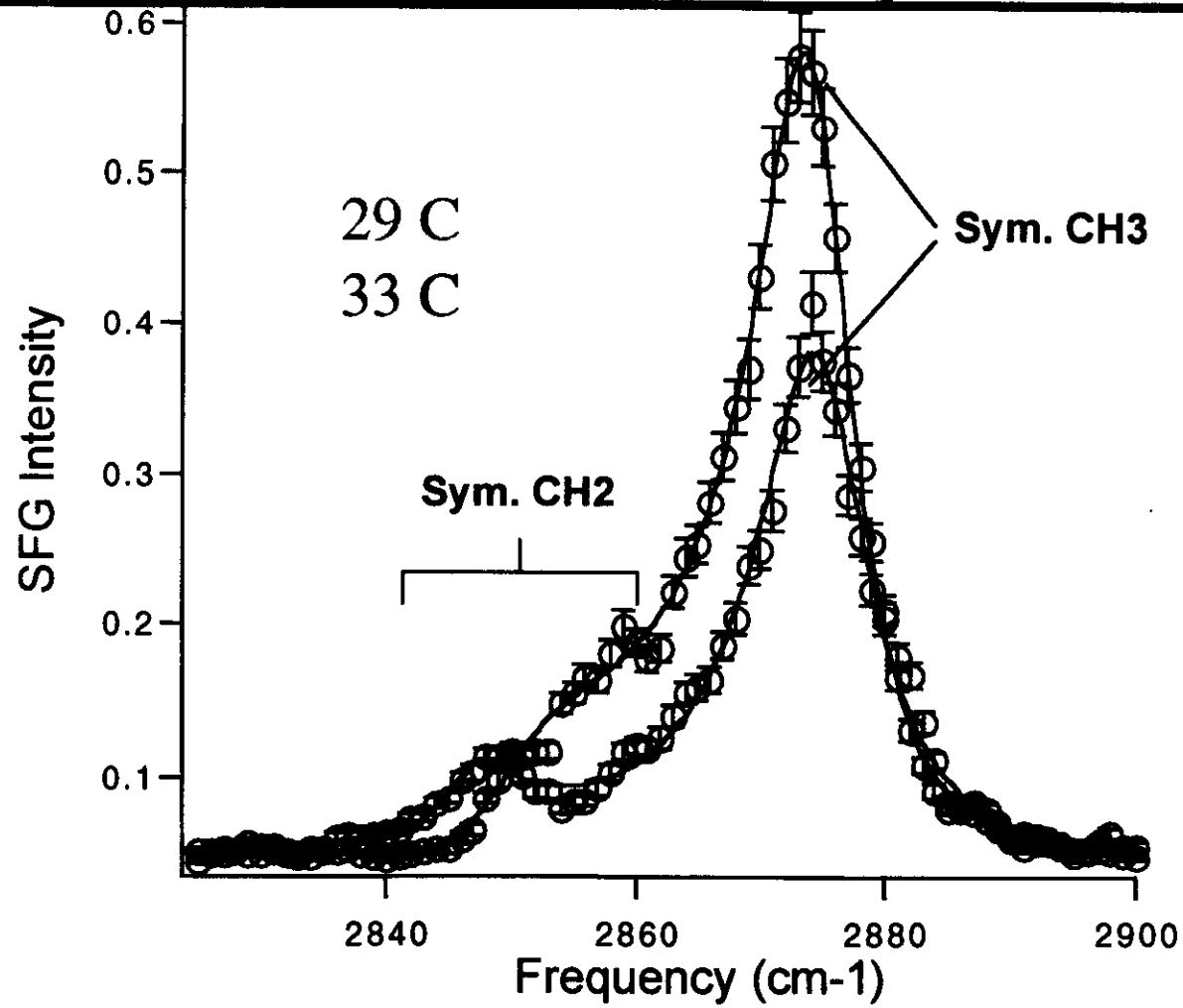
Spectral Change Was Observed in All Polarization and Resonance Features: Shift in Fermi Resonance Freq.





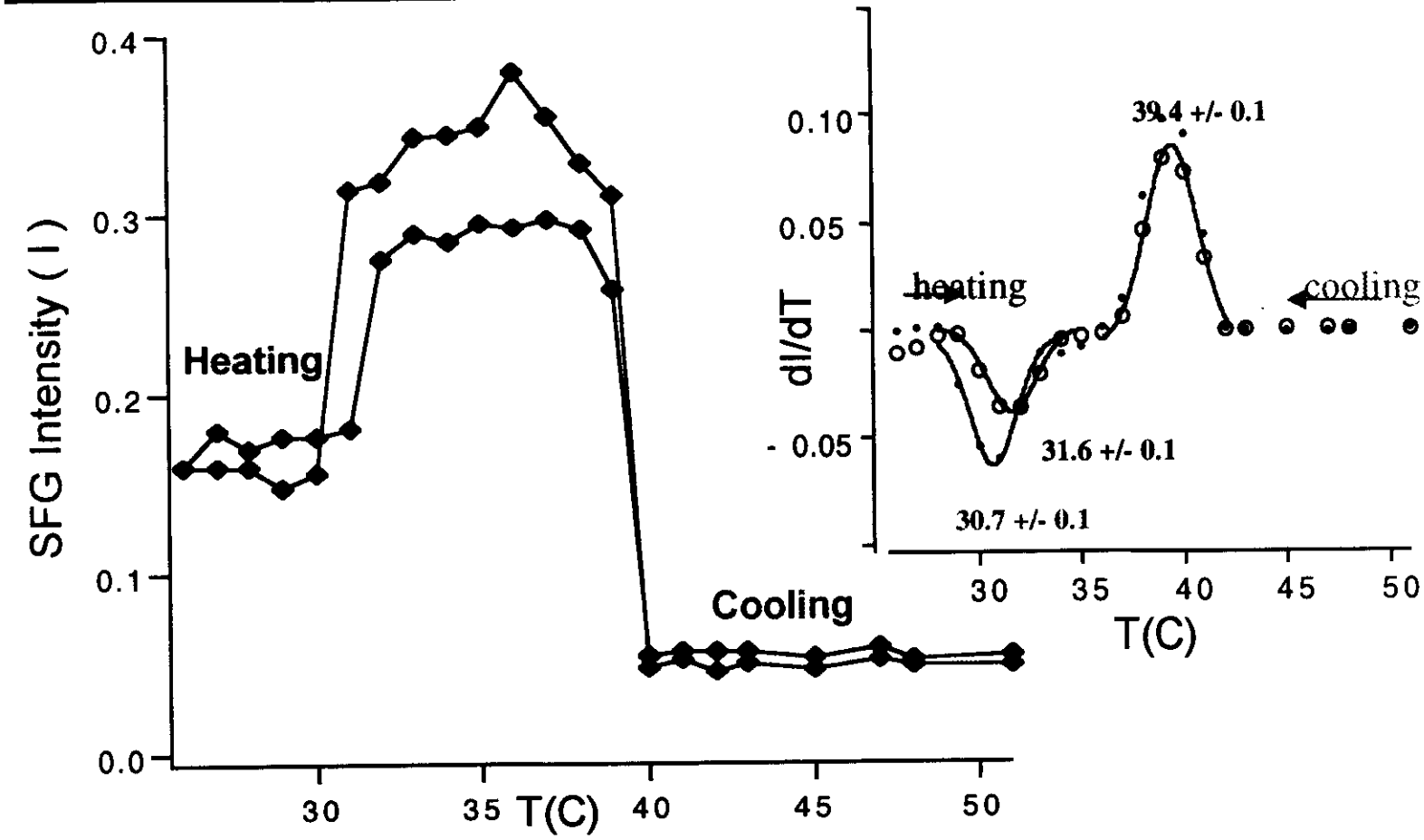
Similar Changes were observed for C23, C22, C25 and a (1:1) mixture of C23 and C25 alkanes.

Spectral Change Was Observed in All Polarization and Resonance Features: CH2 and CH3 Symmetric Stretches



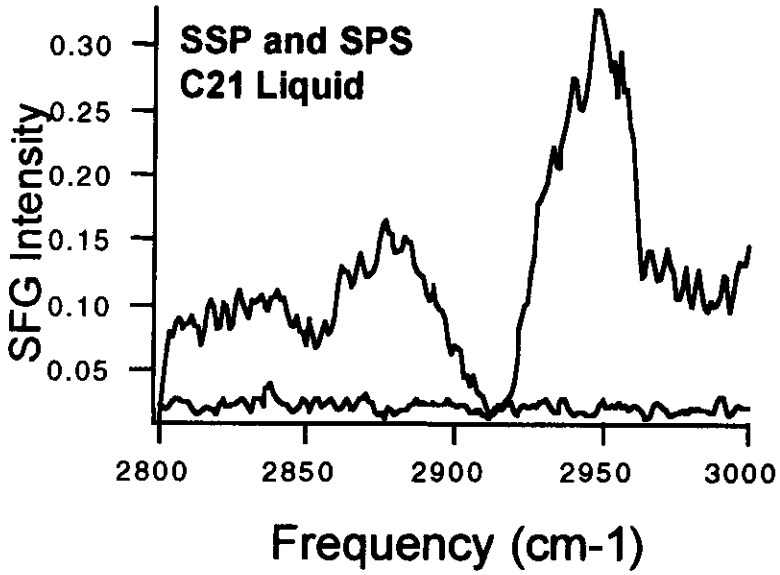
- **Position of the symmetric CH2 resonance (or its relative phase) dramatically varies with temperature.**
- **Amplitude of the CH3 symmetric stretch reduces at the R-X bulk transition temperature.**

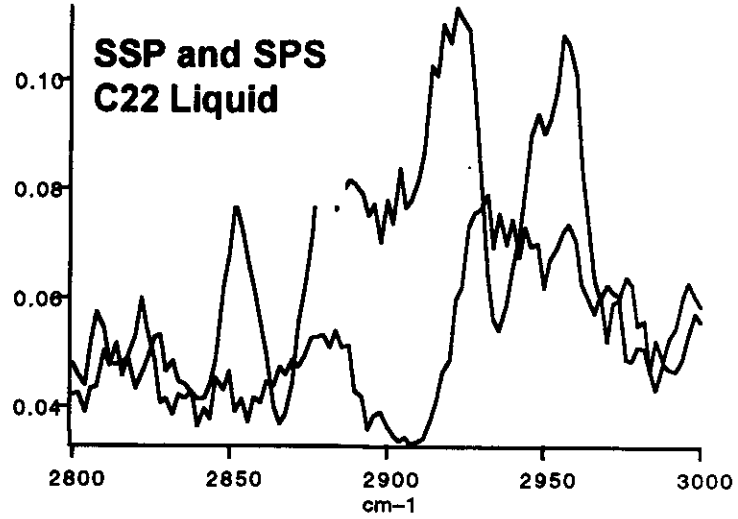
Variation of SFG Intensity of C21/Al2O3 Interface With Temperature



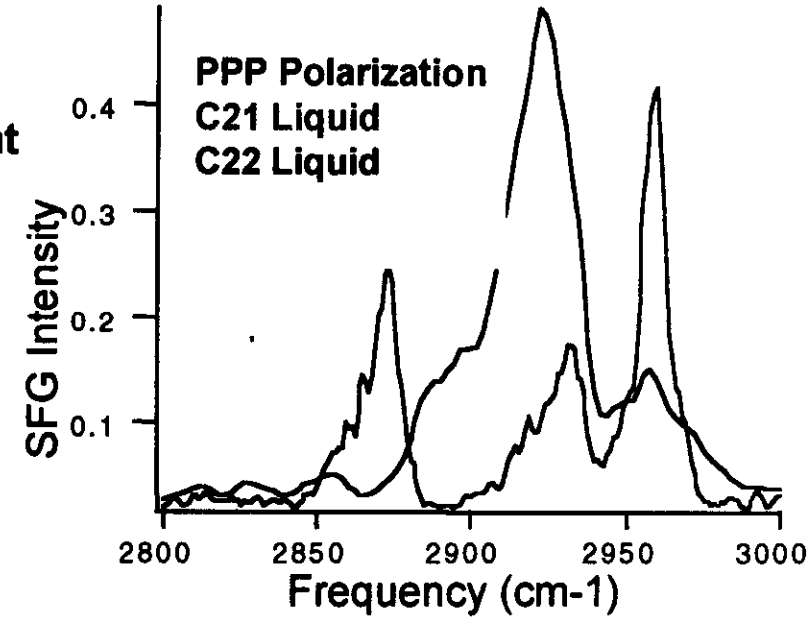
- No hysteresis at solid-liquid transitions (40 C) was observed.
- One degree of super cooling was detected at 32 C.
- The sudden changes in the interfacial SFG intensities at 32 C and 40C represent changes in molecular structure/arrangement.

Molecular Arrangement: Above Melting Point





- **N-alkane molecule possesses a significant amount of trans-gauche defects.**
- **Position of defects is not random.**



Molecular Arrangement: Below Melting Point

- Distinct spectral features:
  - -The symmetric stretch of the CH3 group is only detectable in ssp polarization.
  - -The asymmetric stretch of the CH3 group is only detectable in sps polarization.
  - -The intensity of the CH3 symmetric stretch is greater than the asymmetric stretch.

- For a hydrocarbon molecule with ONLY one CH3, these structural features strongly suggest that the methyl group is perpendicular to the interface.

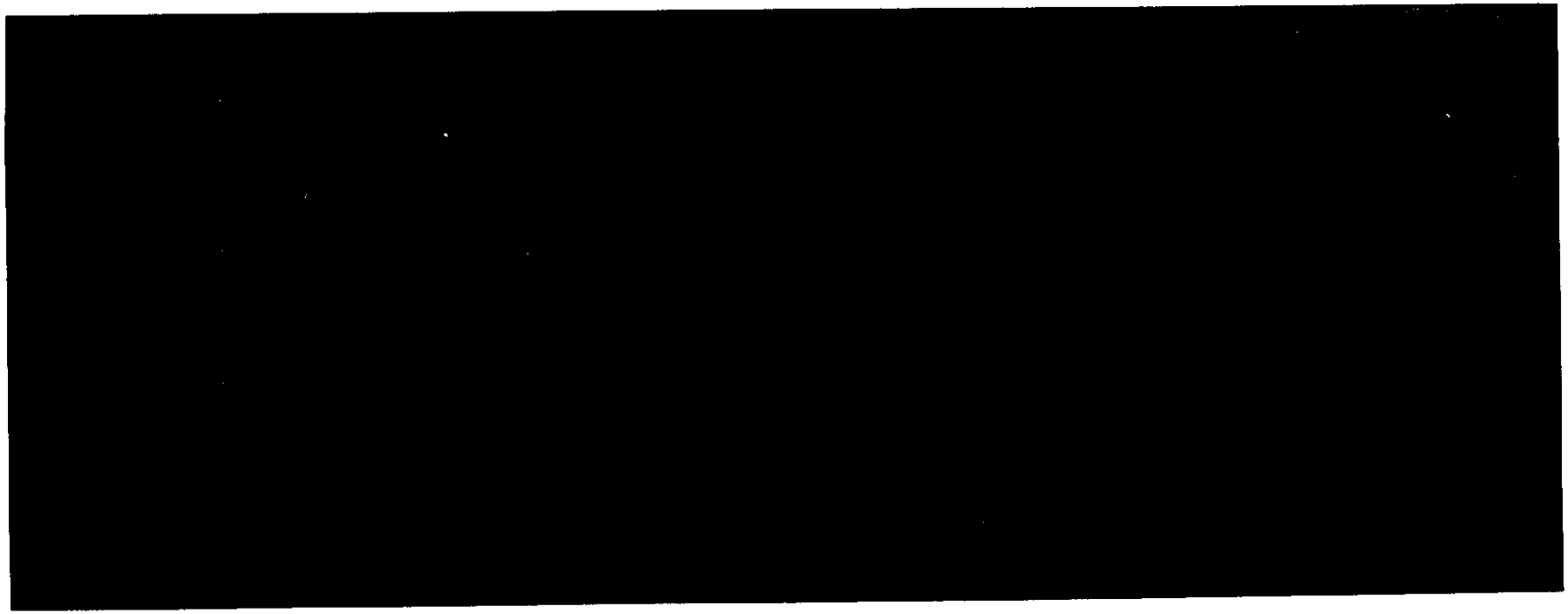
An n-alkane molecule possesses two CH3 groups, thus, a more complex model must be adopted.

Molecular Arrangement Below m.p.: The Model for Macroscopic Second Order Susceptibility, Xijk

- SFG signal intensity is proportional to $|Xijk|^2$.
- How to calculate Xijk of an n-alkane?
  - Start with a single C-H hyperpolarizability (β_{ijk}) and calculate the CH3 hyperpolarizability (α_{ijk}) using:

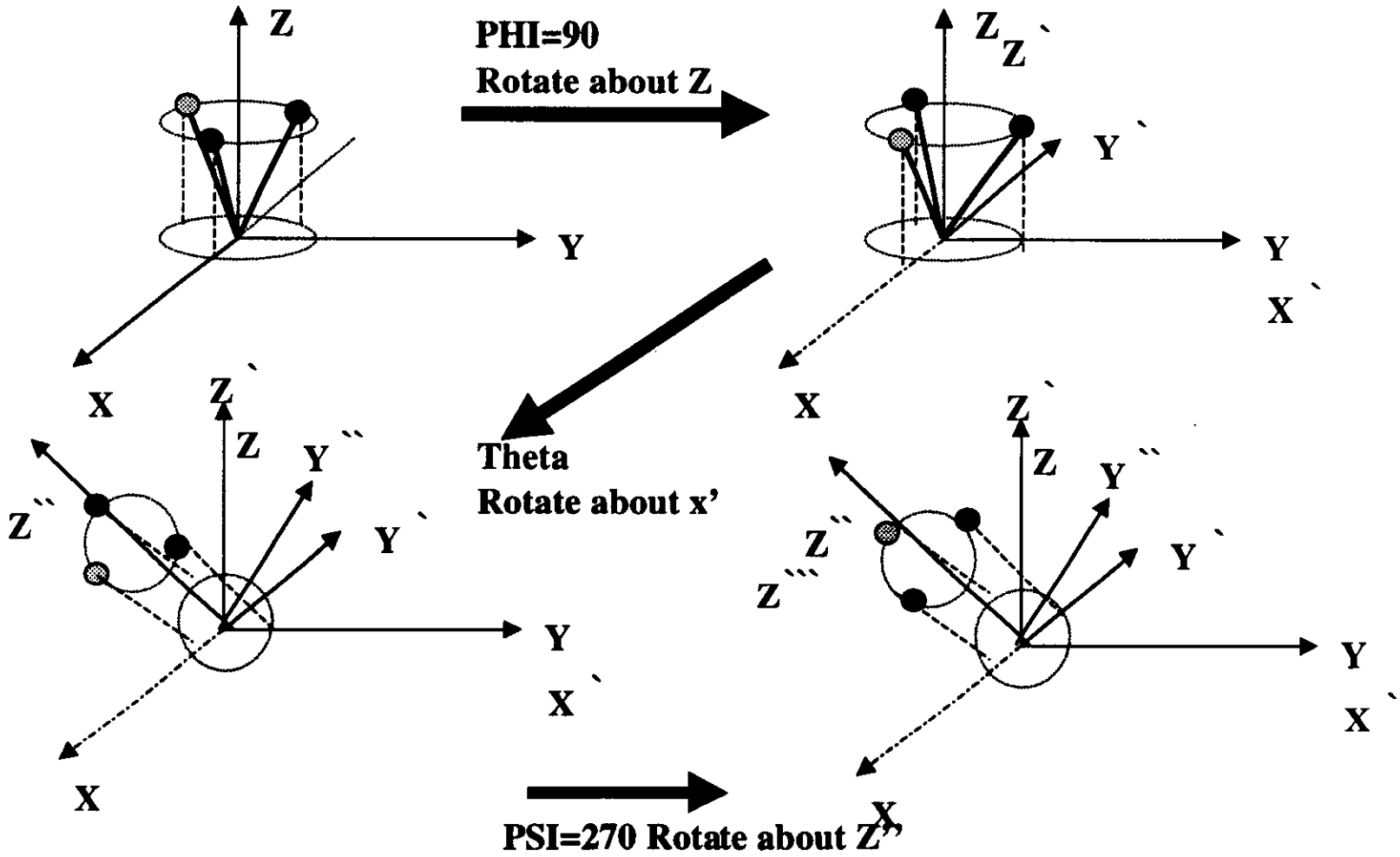
$$\alpha_{ijk} = \sum_{n,m,p} \langle i.n \rangle \langle j.m \rangle \langle k.p \rangle \beta_{nmp}$$

  + $C_{1\infty}$ symmetry : (β_{zzz} , $\beta_{xxz} = \beta_{yyz}$ are non zero elements)
  + Additive hyperpolarizability model
  + Euler transformation coordinates



Molecular Arrangement Below m.p.: The Model for Macroscopic Susceptibility, Xijk (Continued)

Calculate α_{ijk} for each CH3 in n-alkane frame using following Euler parameters



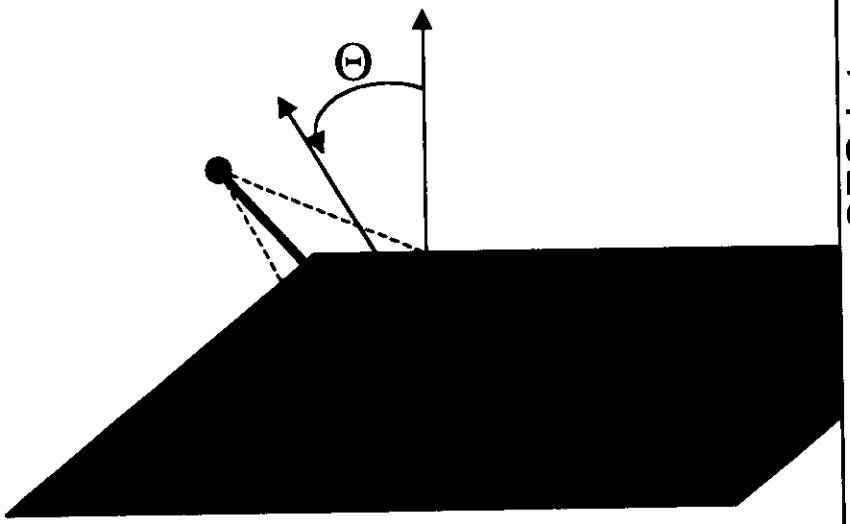
Molecular Arrangement Below m.p.: The Model for Macroscopic Susceptibility, Xijk (Continued)

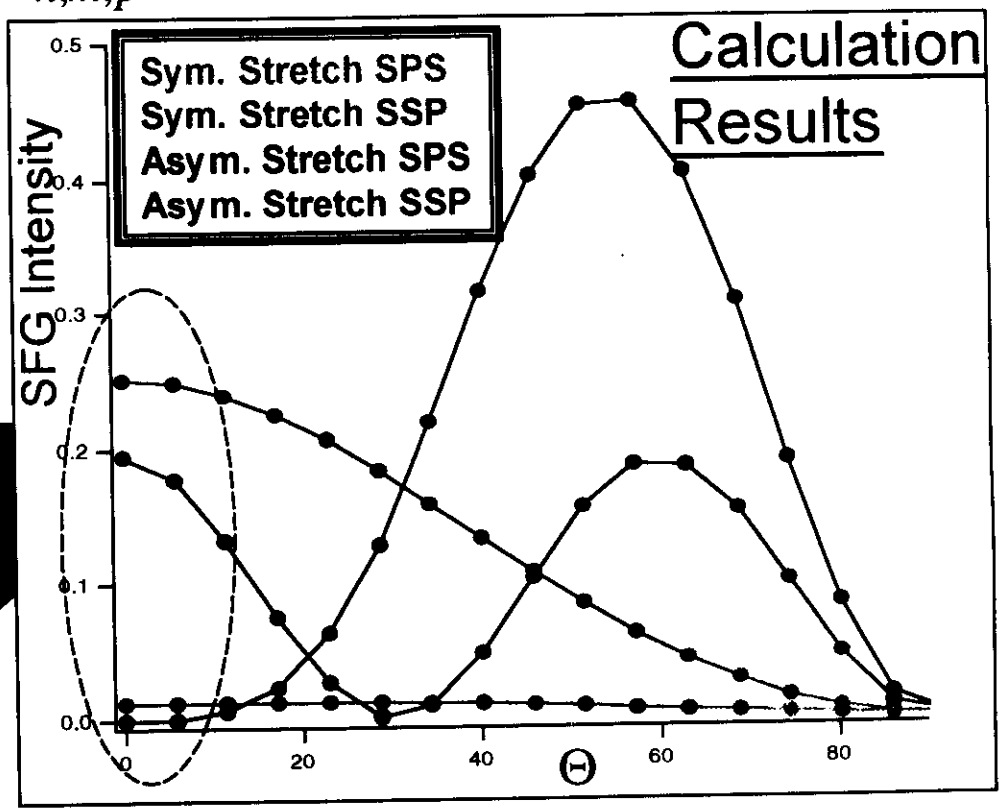
Define : $\alpha^{eff}_{ikj} = \alpha^{1}_{ikj} + \alpha^{2}_{ikj}$ **for the molecule.**

Calculate X_{ikj} **from** α^{eff}_{ikj} **using:**

$$\chi_{ijk} = \sum_{n,m,p} \langle i.n \rangle \langle j.m \rangle \langle k.p \rangle \alpha^{eff}_{nmp}$$

$$Intensity = |\chi|^2$$





For Θ close to zero (when the c-c plane is perpendicular to the surface) all experimentally observed conditions are satisfied.

Several Models Were Tested

- Other tested models:
  - The n-alkane molecule was allowed to stand vertically at various tilt angles.
  - A unit cell with two n-alkanes at various orientations

<u>None of the above models could explain the experimental observations</u>

- Comparison with previous studies:
  - MD calculations: Four layers of n-alkane molecules oriented parallel to the substrate (Xia et. al. PRB, 48, 11313 (1993))
  - Monolayer on graphite: n-alkane molecules organize in lamella with the chains oriented parallel to the lattice axis within the basal plane of graphite (Hansen et. al. PRL 83, 2362 (1999))
  - Monolayer on SiO2: Monolayer consists of densely "frozen" alkanes oriented normal to the interfaces. (Merkl et. al., 79, 4625 (1997))
  - Liquid n-alkane on quartz and ZrO2: n-alkane lies flat with a significant amount of trans-gauche defects. (quartz:Sefler et. al. CP Lett. 235, (347) (1995); ZrO2: Hatch et. al. unpublished results)

Summary

- We have used IR-visible sum frequency generation spectroscopy to examine the structural behavior of n-alkanes at n-alkane/Al_2O_3 interfaces.

- We have observed two phase transitions:
  - The first transition occurs at the bulk solidification temperature with no detectable super cooling or heating;
  - The second transition occurs at the bulk crystalline-rotator transition temperature with super cooling.

- Our polarization dependence measurements reveal that in both the crystalline and rotator phases, the n-alkane molecule lies down on the substrate with its C-C plane perpendicular to the substrate plane.