Light, Liquids & Interfaces
Micro-390

Lecture 12:
Quantifying molecular structure at 2D interfaces

Sylvie Roke

Material to study: These slides & notes

Exercises: 25,26,27

Key concepts Lecture 11

- Surface potential is the potential at the surface: more informative, but harder to measure than the zeta potential

- Poisson-Boltzmann for surfaces, linear approximation

- Models for the electrical double layer and when to apply them: Helmoltz, Gouy-Chapman, Gouy-Chapman-Stern, Grahame

- Interfaces 3D: importance of colloids in everyday life

- DLVO theory and stability of colloids

- Zeta and surface potentials for colloids

Planned Lecture Material

Main Course book:
JN Israelachvilli, Intermolecular and surface forces, Academic Press Third edition, 2009.; abbreviation JNI

Topics	Material
1. Introduction; Probability and thermodynamics	Notes, Chapter 1 Notes, Ben-Amotz, Chapter 1 + notes
2. Driving forces and interactions	Notes, Chapter 2: paragraphs: 2.1 - 2.4, 2.6, 2.7 Notes, Chapter 3: paragraphs: 3.1 – 3.8 Notes, Chapter 4: paragraphs: 4.1 – 4.7; 4.9-4.11 Notes, Chapter 5: paragraphs: 5.1 - 5.4; 5.6; Notes, Chapter 6: paragraph: 6.1; Notes, Chapter 7: paragraph: 7.1-7.3;
3. Water	Notes, Chapter 8: 8.1; 8.2; 8.5-8.7
4. Spectroscopy of liquids	Notes, Atkins 9.4 (Vibr. Motion); 13.1,13.2; 13.9; 13.13,13.14;13.15;13.16
5. Interfaces in 2D and 3D	Notes, Atkins Ch. 19.15; Ohshima, CH1:1-2;3.1.1-3.1.2.;
6. Techniques to probe interfaces	Notes **In Progress**
7. State of the art	Notes

Material so far covered

Topic 6 & 7:

Techniques to probe interfaces & state of the art.

Material to study: Slides and Notes
Exercises: 25,26,27

Dec 5: Techniques to probe interfaces

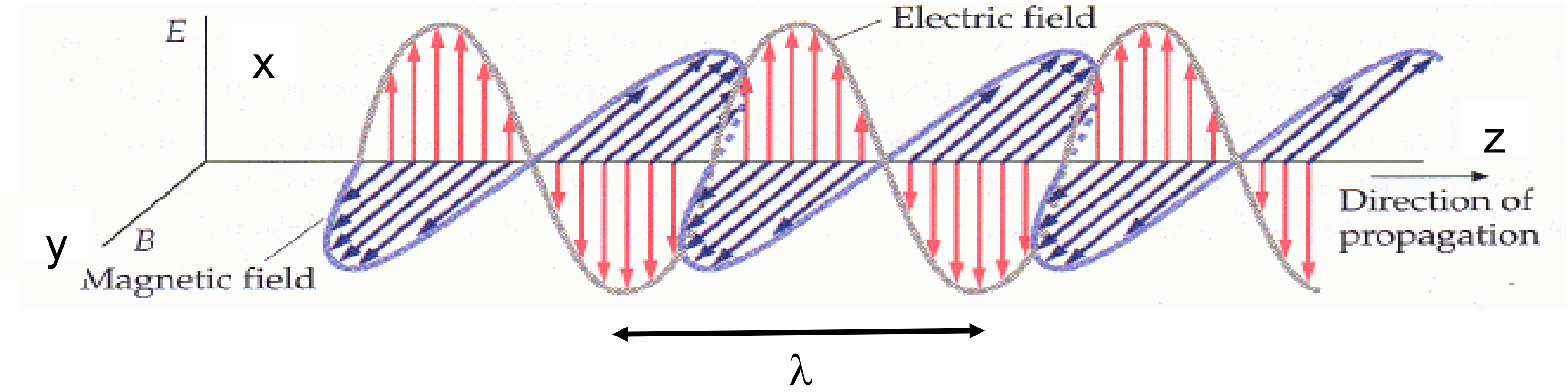
Dec 12: Techniques & state of the art

Dec 19: Q & A, finish exercises; potential lab tour (sign up)

Probing surfaces with IR radiation

Reminder of IR spectroscopy
Vibrational surface spectroscopy

Light = electro-magnetic wave



Light is an oscillating transverse electric and magnetic field:

Traveling wave: $\mathbf{E} = \mathrm{E_0 e^{-i(kr-\omega t)}}\,\mathbf{u}$ → Polarization direction, here x

Amplitude

Wave vector
(direction of propagation, here z)

Angular frequency

Energy of one photon: $h\frac{c}{\lambda} = h\upsilon = h \cdot 2\pi\omega$

Momentum of a photon: $h\boldsymbol{k}$ with $k = \frac{2\pi n}{\lambda}$

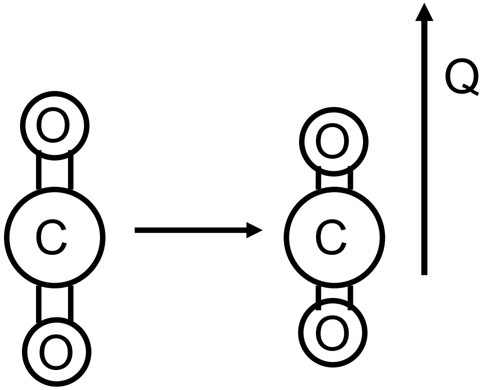
If we measure an electric field,

we measure the intensity

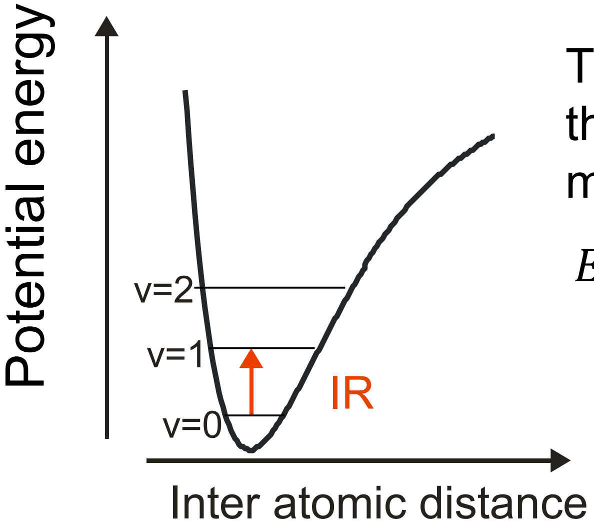
$\mathrm{I \sim |E|^2}$

Vibrational Energies and Modes

Vibrational energies report on the relative displacement of atoms within a molecule with respect to their equilibrium positions

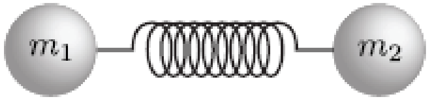


Normal modes (Q_i) are the **eigenvectors** of the equations of motion and describe the various vibrational modes with a set of orthogonal vectors as a basis



The **eigenvalues** for the equations of motion are given by the vibrational energies that correspond to each normal mode.

$$E = (v + 1)\hbar\omega$$

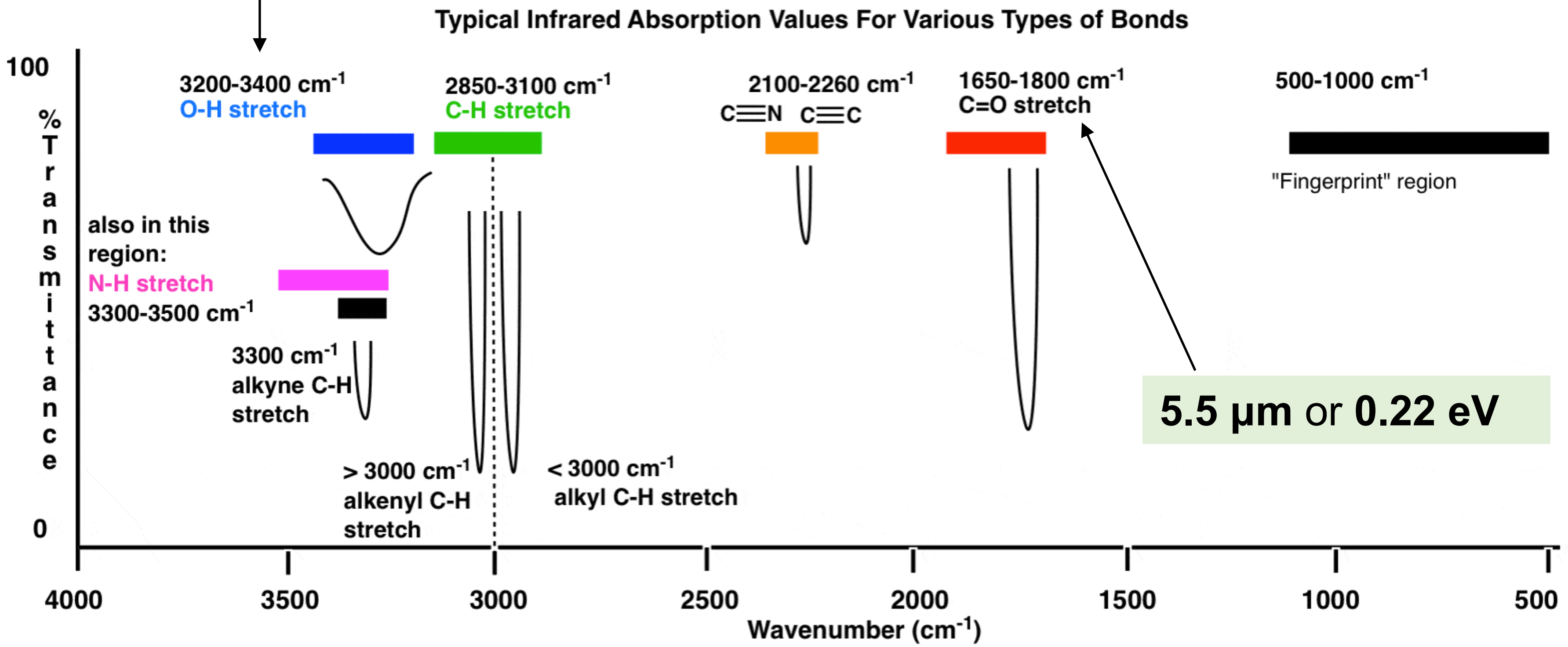


$$\omega = \sqrt{\frac{k}{m'}}$$

$$m' = \frac{m_1 m_2}{m_1 + m_2}$$

Functional Groups

3.1 µm or **0.4 eV**



5.5 µm or **0.22 eV**

Decreasing energy
Increasing λ

Source: https://www.masterorganicchemistry.com/2016/11/23/quick_analysis_of_ir_spectra/

Vibrational mode frequencies

- Heavier atoms vibrate at lower frequencies (m' ↑):

  υ(stretch H_2) > υ(stretch N_2) > υ(stretch O_2)
  υ(F-H stretch) > υ(Cl-H stretch) > υ(I-H stretch)
  υ(C-H stretch) > υ(N-H stretch) > υ(O-H stretch)

in this case binding geometry changes k

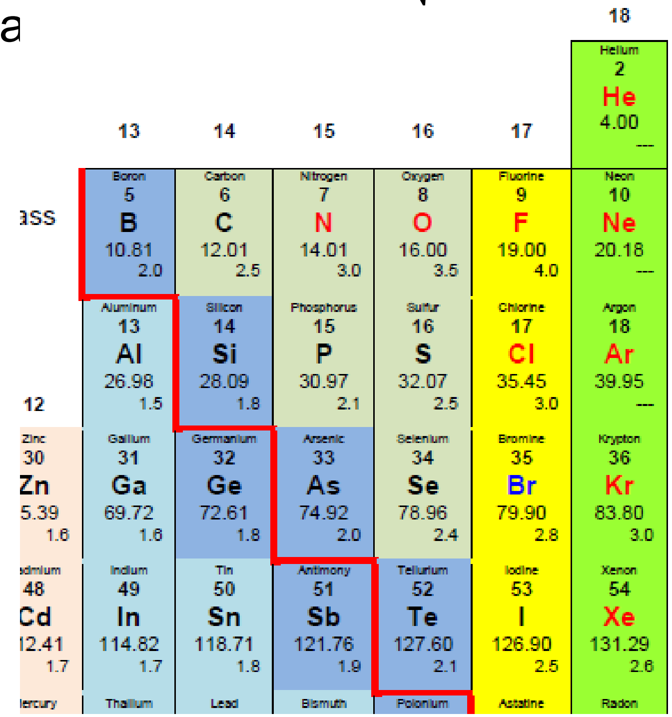
- Stronger bonds have higher frequencies (k ↑):

  υ(stretch C≡ C) > υ(stretch C= C) > υ(stretch C-C)
  Stretch > Bend > Libration

$$\omega_0 = \sqrt{\frac{k}{m'}}$$

- Interactions between molecules are visible as spectra

  Removing electron density lowers k
  Adding electron density increases k

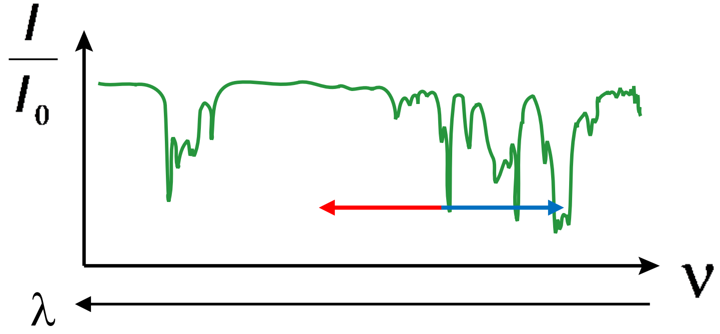


ass

12	13	14	15	16	17	18
						Helium 2 He 4.00 ---
	Boron 5 B 10.81 2.0	Carbon 6 C 12.01 2.5	Nitrogen 7 N 14.01 3.0	Oxygen 8 O 16.00 3.5	Fluorine 9 F 19.00 4.0	Neon 10 Ne 20.18 ---
	Aluminum 13 Al 26.98 1.5	Silicon 14 Si 28.09 1.8	Phosphorus 15 P 30.97 2.1	Sulfur 16 S 32.07 2.5	Chlorine 17 Cl 35.45 3.0	Argon 18 Ar 39.95 ---
Zinc 30 Zn 5.39 1.6	Gallium 31 Ga 69.72 1.6	Germanium 32 Ge 72.61 1.8	Arsenic 33 As 74.92 2.0	Selenium 34 Se 78.96 2.4	Bromine 35 Br 79.90 2.8	Krypton 36 Kr 83.80 3.0
dmium 48 Cd 12.41 1.7	Indium 49 In 114.82 1.7	Tin 50 Sn 118.71 1.8	Antimony 51 Sb 121.76 1.9	Tellurium 52 Te 127.60 2.1	Iodine 53 I 126.90 2.5	Xenon 54 Xe 131.29 2.6
lercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon

Shift to lower frequency: Red shift, λ ↑

Shift to higher frequency: Blue shift, λ ↓



Selection Rule & Allowed Transitions

In order to have a transition the expectation value for the dipole transition needs to be non-zero.

Expectation value for dipole moment in polarization direction k:
The total dipole moment in direction k (μ_k) is determined by the sum of dipole moments for each normal mode

$$\boxed{\mu_k \sim \sum_{i=1}^{3N-6} \left(\frac{\partial \mu_k}{\partial Q_i}\right)_{Qi=0} \langle \psi_n | Q_i | \psi_g \rangle}$$

Sum of dipole moments created in each normal mode

Change in dipole moment at equilibrium position of normal mode Q_i

Overlap of orbitals when the vibrational mode i is excited ?

Computing the expectation value (=dipole transition moment) we find that:
1 – Only vibrational modes that have **a changing dipole moment at the position of equilibrium** are allowed. This is the <u>selection rule for infrared spectroscopy</u>
2 – Transitions only happen with $\upsilon \pm 1$ (thanks to properties of the Hermite polynomials)

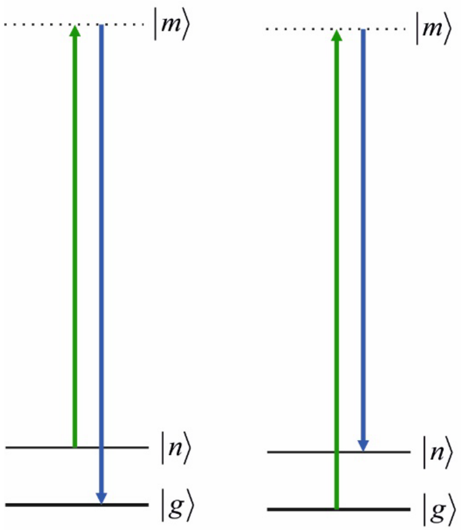
Raman Spectroscopy

For a Raman transition we have the expectation value:

$$\langle \alpha_{pq} \rangle = \left| \langle \psi_{final} | \hat{\alpha}_{pq} | \psi_{init} \rangle \right|$$

$$\mathrm{I} \sim \left| \langle \alpha_{pq} \rangle \right|^2$$

Anti Stokes Stokes



For vibrational transitions with a non-resonant visible interaction we can make the following approximation:

$$\boxed{\alpha_{pq} \sim \sum_{i=1}^{3N-6} \left(\frac{\partial \alpha_{pg}}{\partial Q_i} \right)_{Qi=0} \langle \psi_n | Q_i | \psi_g \rangle}$$

Selection rule: Change in polarizability at equilibrium position of normal mode Q_i

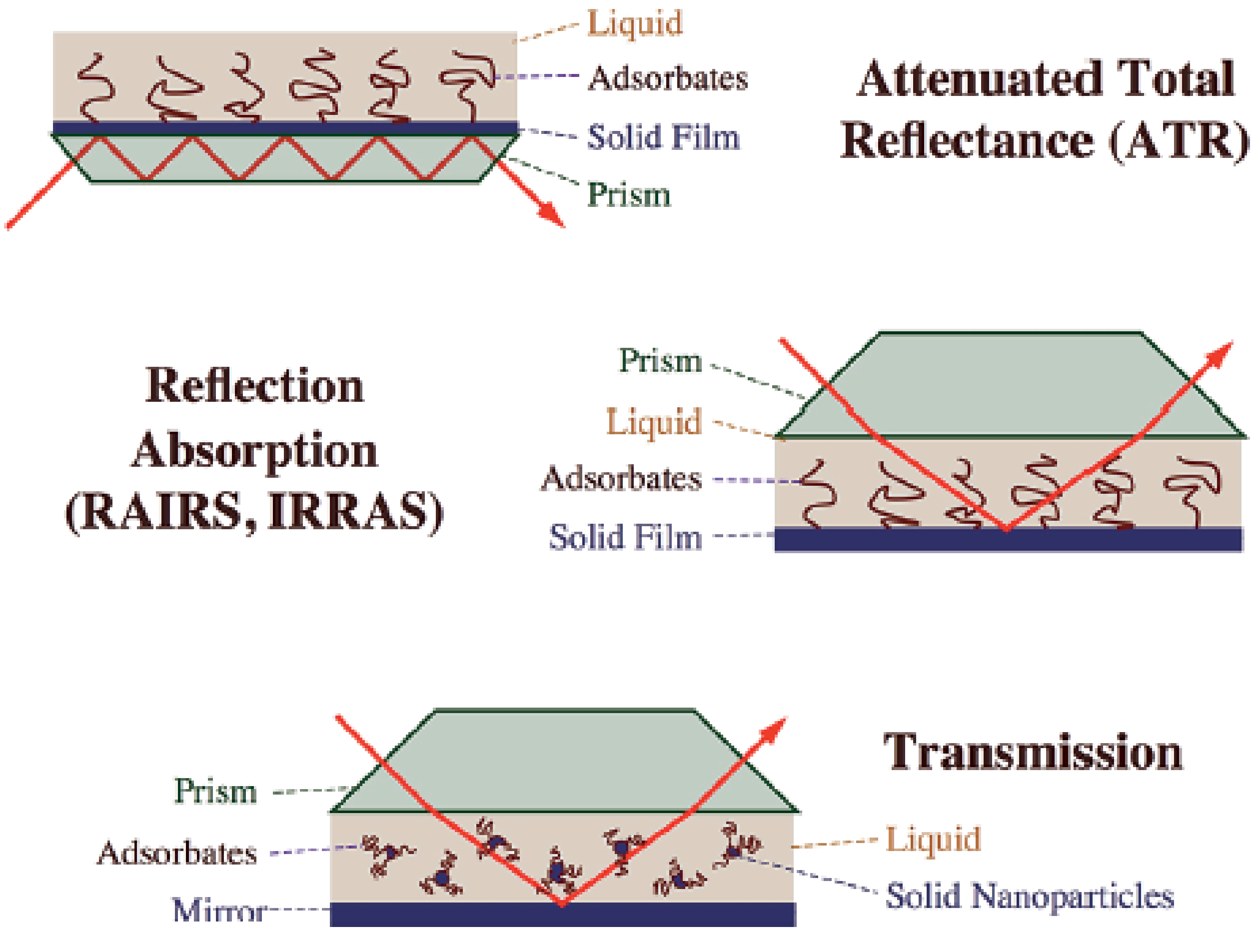
Probing Interfaces

Approaches to measure interfaces:

Build structures that can provide monolayer information:

- Langmuir-Blodgett films
- Supported lipid bilayers
- UHV metal surfaces with monolayers of molecules
- Exploit total internal reflection
- Exploit optical properties of metals

Vibrational surface spectroscopy



Various optical geometries enable the probing of interfacial structure

Probing depth is determined by penetration of field (evanescent wave)

For IR the evanescent wave is a few microns deep

Metals: virtually no bulk contribution

Chem. Rev. 2012, 112, 2920–2986

Reflection from a surface

All light-matter interactions are dictated by the Maxwell Equations and the continuity relation (charge in = charge out).

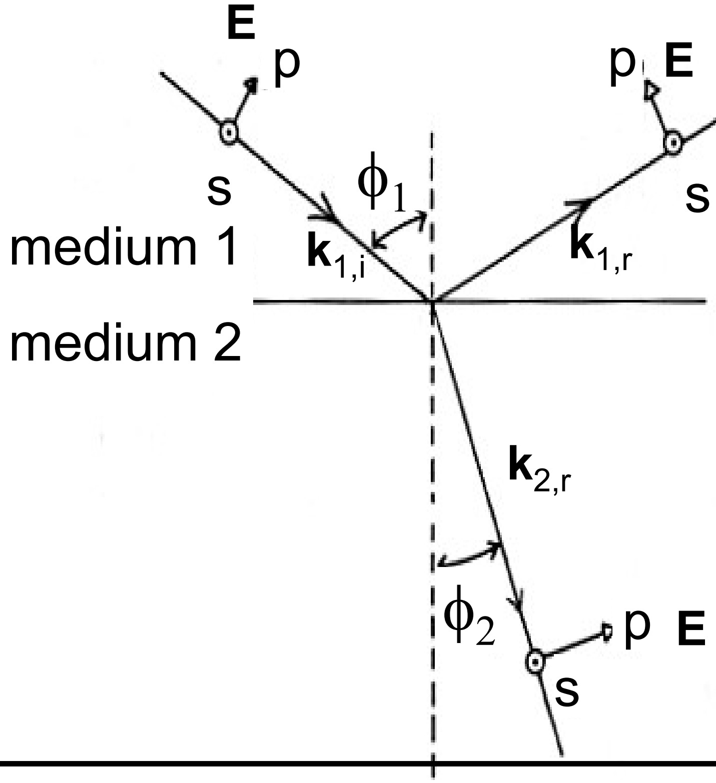
Requirement: **E, B** fields are continuous across interface

Transmission: Snell's law: $n_1 \sin \phi_1 = n_2 \sin \phi_2$

Reflection: Fresnel coefficients

$$r^p_{12} = (E_r/E_i)_p = \frac{n_2\cos\phi_1 - n_1\cos\phi_2}{n_2\cos\phi_1 + n_1\cos\phi_2}$$

$$r^s_{12} = (E_r/E_i)_s = \frac{n_1\cos\phi_1 - n_2\cos\phi_2}{n_1\cos\phi_1 + n_2\cos\phi_2}$$

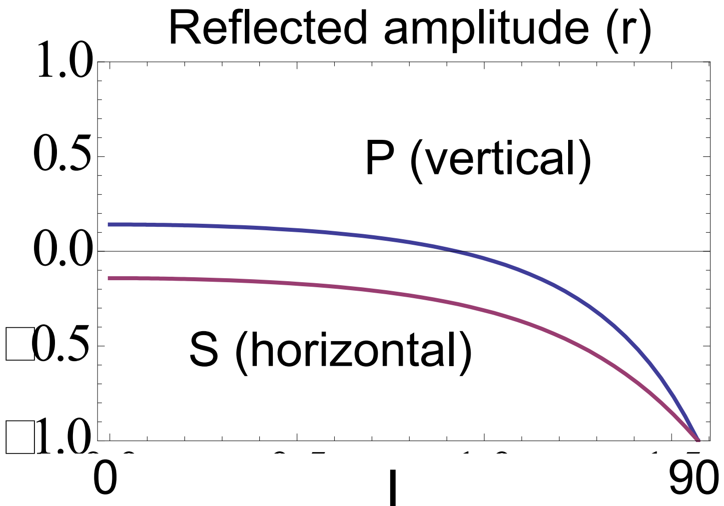


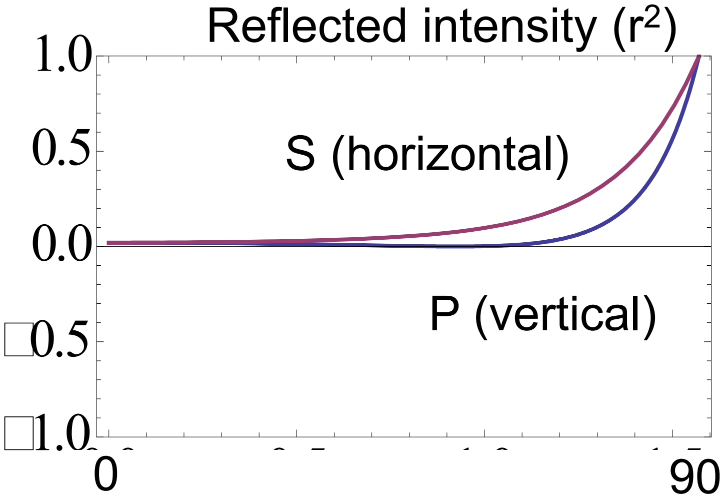
Different reflection coefficients for parallel* (P) and perpendicular* (S) polarizations

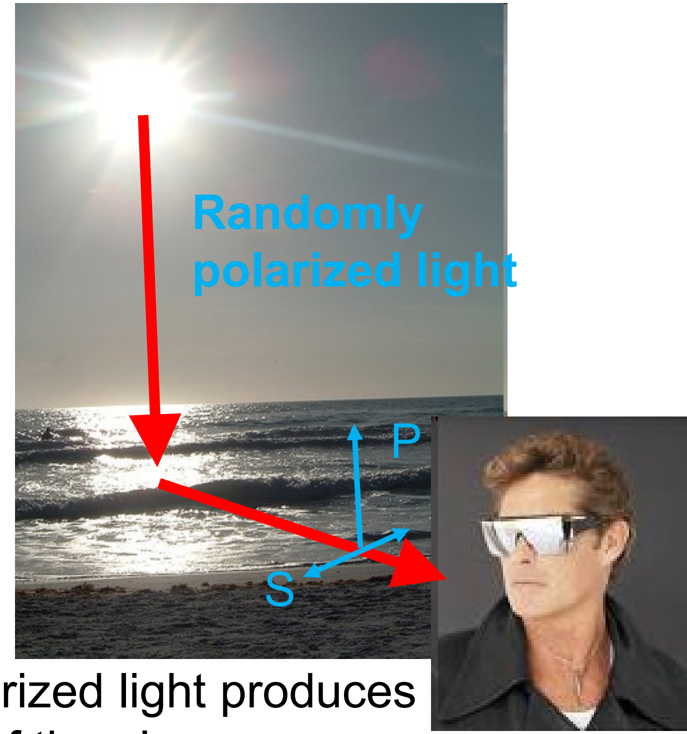
*w.r.t. to **k**-vector plane

Reflection from a surface

Reflection of light from an air/water interface



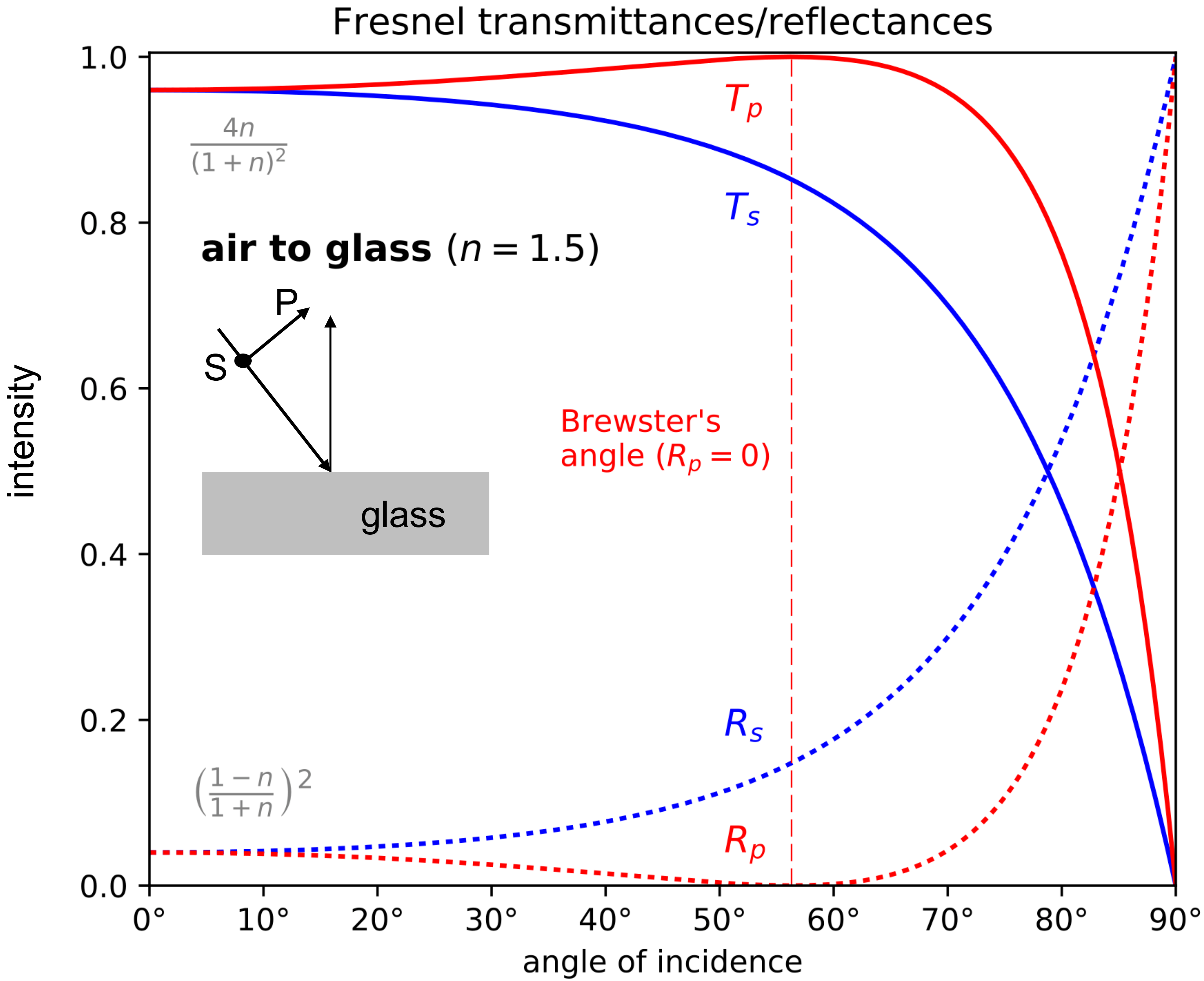




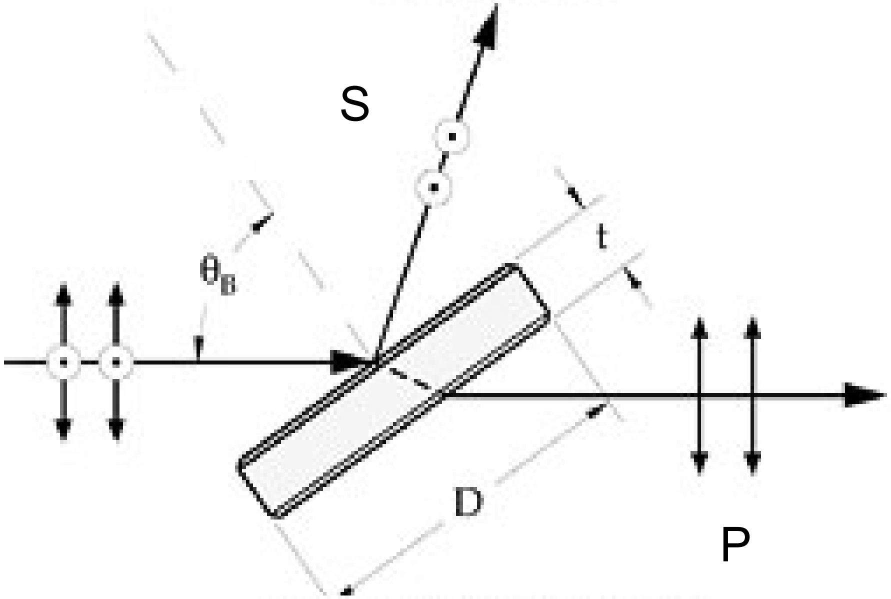
S-polarized light produces most of the glare

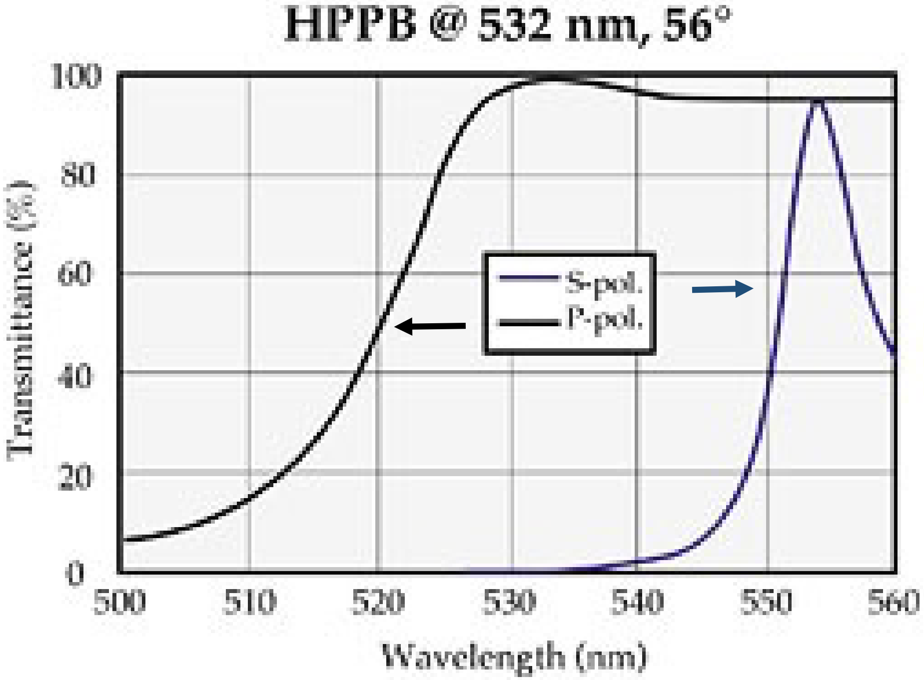
Sunglasses transmit only P

Polarized sunglasses improve contrast by eliminating unwanted sun light reflections


Fresnel transmittances/reflectances
1.0
0.8
0.6
0.4
0.2
0.0
intensity
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
angle of incidence
$\frac{4n}{(1+n)^2}$
$\left(\frac{1-n}{1+n}\right)^2$
air to glass ($n = 1.5$)
P
S
glass
T_p
T_s
R_s
R_p
Brewster's
angle ($R_p = 0$)

Use of Brewster Angle: Thin Film Polarizer

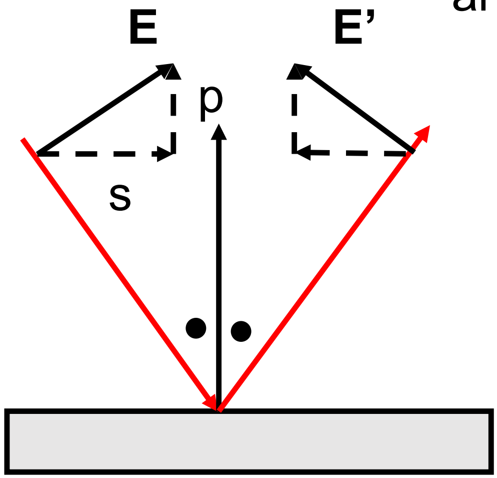




TFP's make use of the Brewster angle to separate linear polarized light components, used as seperation elements in optical systems

TFP's work only over a narrow spectral range; material is fused silica (UV), BK7 glass (VIS) or CaF_2 (IR) with a specific coating (example from lambda.cc)

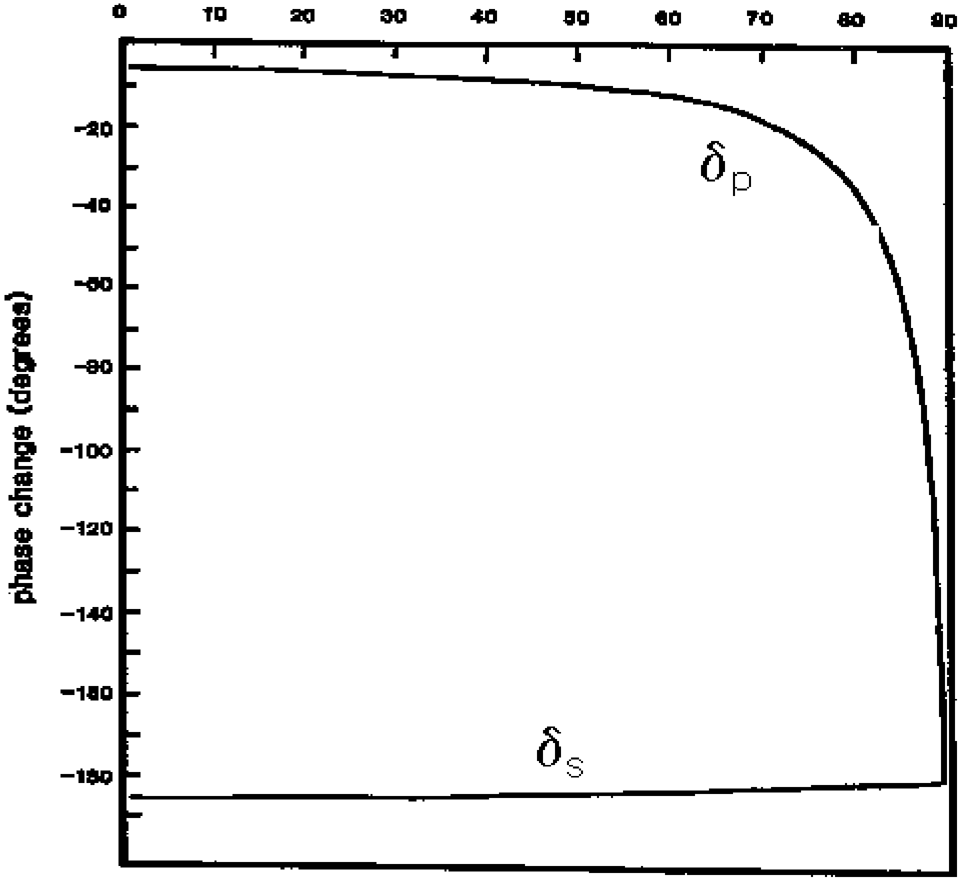
Reflection from a metal surface



No electric field parallel to interface: only P present

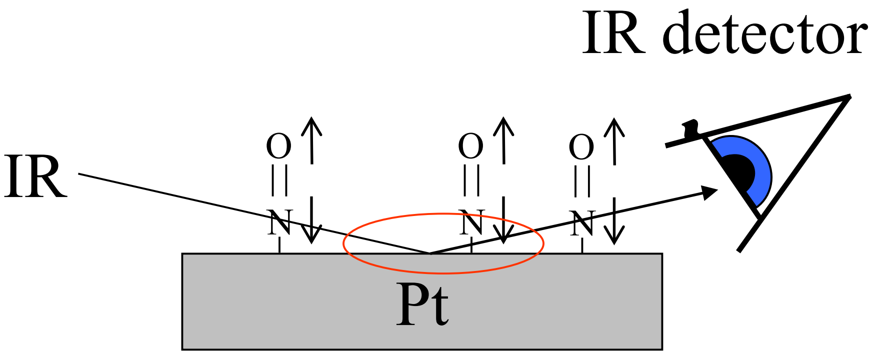
Reason, there cannot be a charge distribution upon reflection (continuity relation)

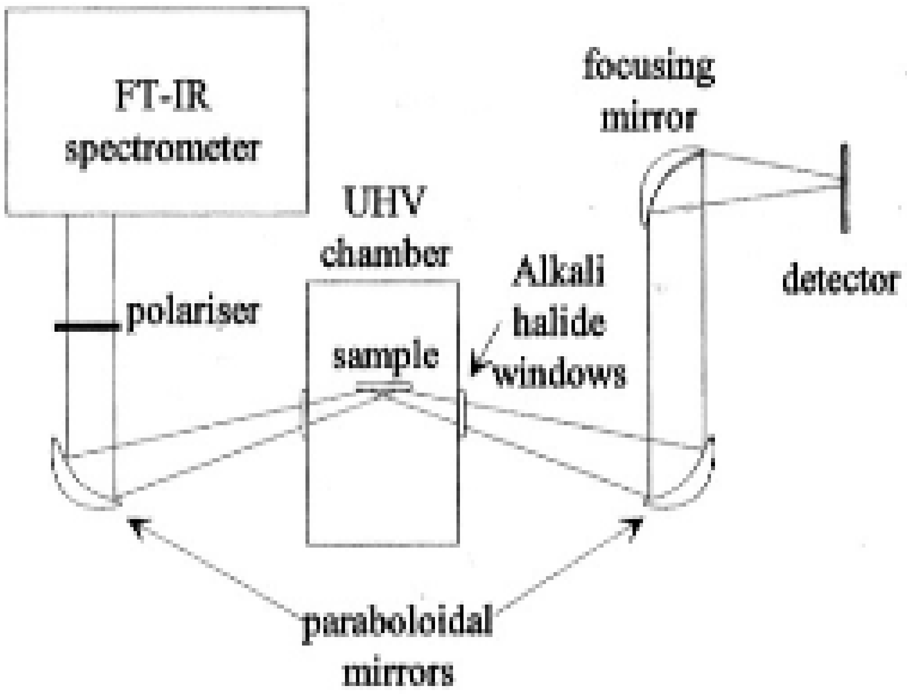
Phase (δ) of reflected components as function of input angle:



RAIRS: probing molecules on metals

RAIRS = reflection absorption infrared spectroscopy





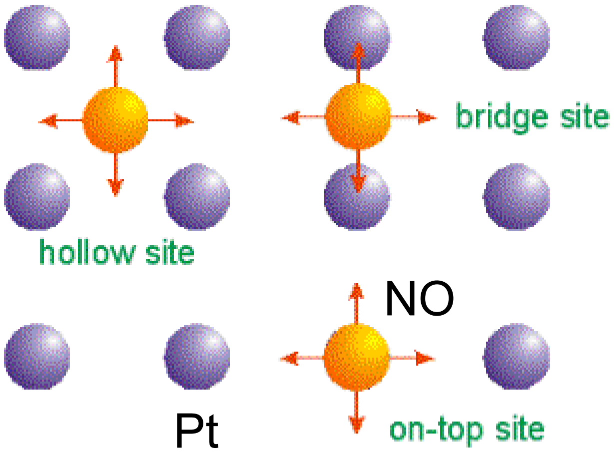
Combine features of infrared spectroscopy (chemical specificity) with conditions imposed by reflection:

Determine bonding strength of molecules, and sometimes orientation of the molecules

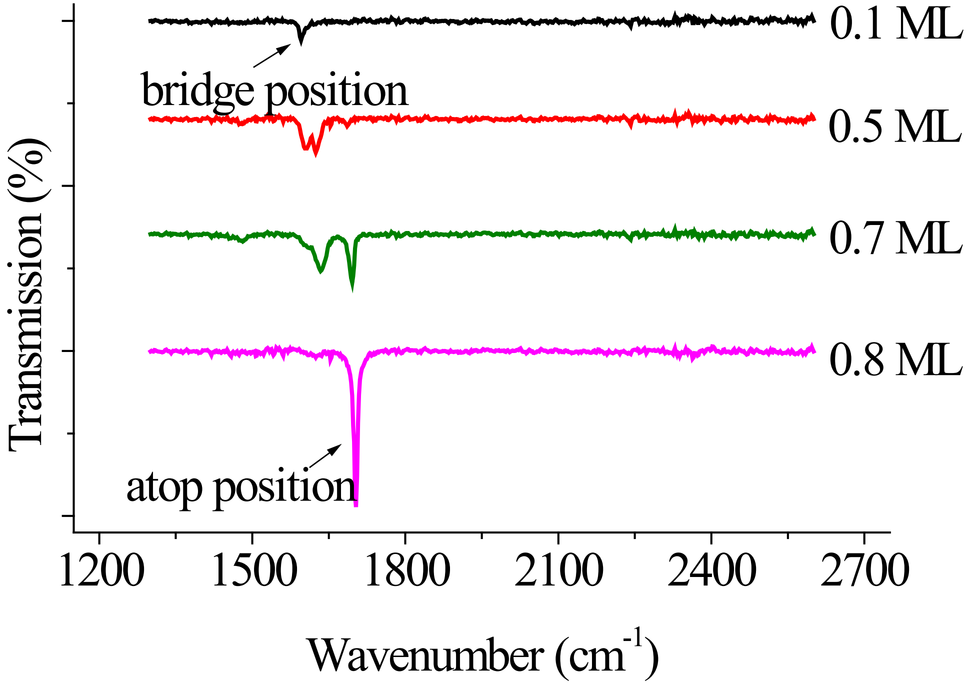
Because only P component survives: average tilt angle can be retrieved

RAIRS

Example: determining the bonding sites of N=O on Pt using RAIRS



Top view of surface in UHV



Determine kinetics of N=O (nitrous oxide) adsorption on a Pt surface

Frequency: binding site

Width and Intensity: chemical environment & vibrational coupling

Probing Interfaces

Approaches to measure interfaces:

Build structures that are monolayer in size:

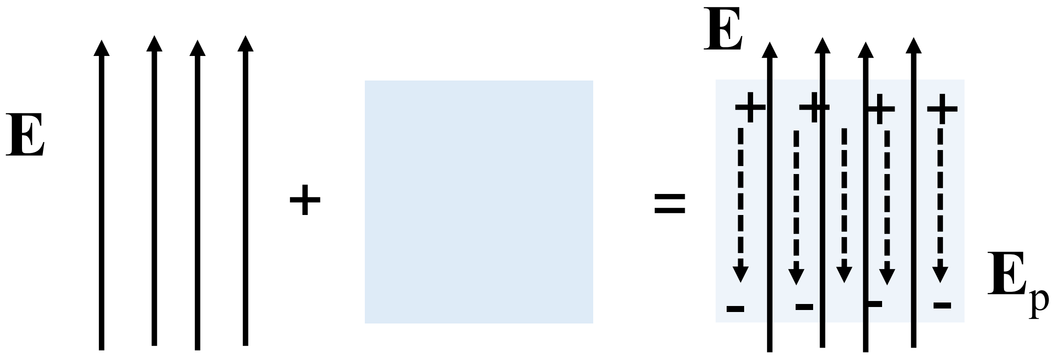
- Langmuir-Blodgett films
- Supported lipid bilayers
- UHV metal surfaces with monolayers of molecules
- Exploit total internal reflection
- Exploit optical properties of metals

Reflection Second Harmonic & Sum Frequency Generation

Fields in a medium

Macroscopic polarizability is the ability of a medium to respond to and reduce the magnitude of an external electromagnetic field (**E**).

Interaction of electric field (**E** [V/m]) with medium:



Medium consist of charged electrons and nuclei which will be displaced by external **E** field

E field distorts atoms & molecules: separates/displaces charges & induce dipoles

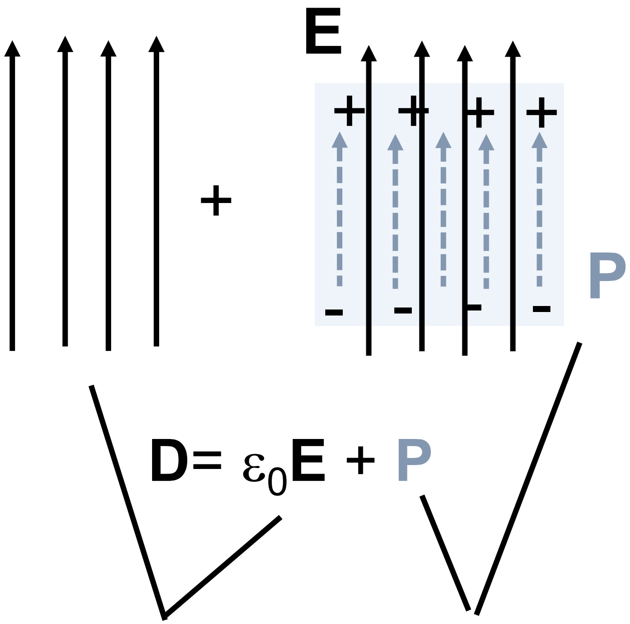
These charge displacements create a response field ($\mathbf{E}_p$)

These two field interfere: $\mathbf{E}_{eff}=\mathbf{E}+\mathbf{E}_p$

Macroscopic Polarizability (**P**)

Polarizability (**P**) is the field that is present in the medium

Displacement field (**D**) in a medium =



$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P}$

Displacement field in vacuum

Polarization

D is a field, but it is *not* an electric field. Unit: [C/m^2]. It is a <u>density of dipoles</u> [(Cm)/m^3]

$\mathbf{P} = \varepsilon_0\,\chi^{(1)}\mathbf{E}$ is material contribution to **D** in medium:

$\varepsilon = 1 + \chi^{(1)}$, ε is the dielectric permittivity, frequency dependent

$n^2 = 1 + \chi^{(1)}$, n is the refractive index

Macroscopic Polarizability (**P**)

Polarizability (**P**) is the field that is present in the medium

P = $\varepsilon_0 \chi^{(1)}$**E** is material contribution to **D** in medium

But at high electromagnetic field strength there can also be higher order terms in E:

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

With terms:

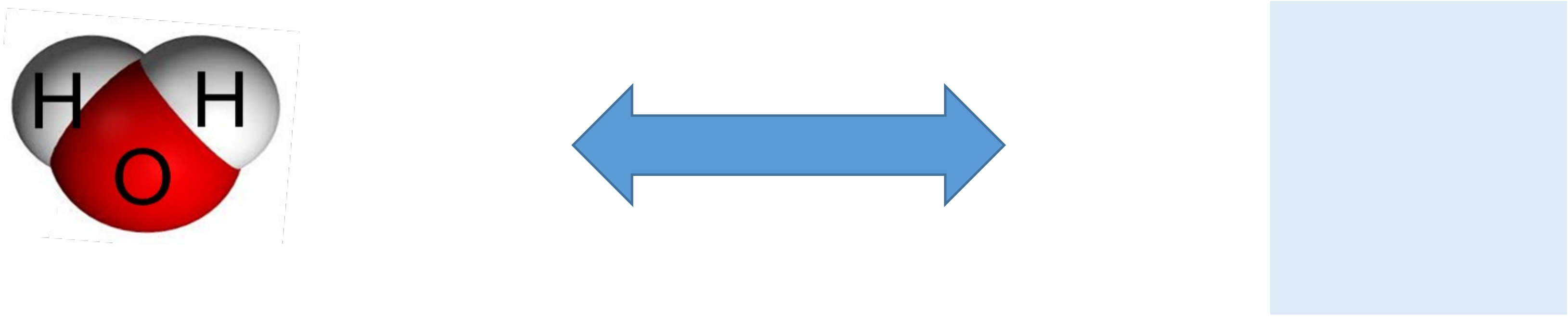
$$P_i^{(1)}(\omega) = \epsilon_0 \sum_j \chi_{ij}^{(1)}(\omega;\omega) E_j(\omega)$$

$$P_i^{(2)}(2\omega) = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)}(2\omega;\omega,\omega) E_j(\omega) E_k(\omega) \qquad 2\omega = \omega + \omega$$

$$P_i^{(3)}(3\omega) = \epsilon_0 \sum_{j,k,l} \chi_{ijkl}^{(3)}(\underset{\substack{\uparrow \\ \text{photons out}}}{3\omega}; \underset{\substack{\uparrow \\ \text{photons in}}}{\omega,\omega,\omega}) E_j(\omega) E_k(\omega) E_l(\omega) \qquad 3\omega = \omega + \omega + \omega$$

These are examples of different frequencies that can be generated; these are called second harmonic and third harmonic generation.
Any other combination is also possible (sum frequency generation)

Molecular vs Macroscopic polarization (Lecture 5)



Molecular polarization:
u or **p*** [Cm] (permanent dipole)

Molecular induced dipole:
$\mathbf{u}_{\text{ind}}$ or $\mathbf{p}_{\text{ind}}$

*u: used by Israelachvilli;
p: used for optics/spectroscopy

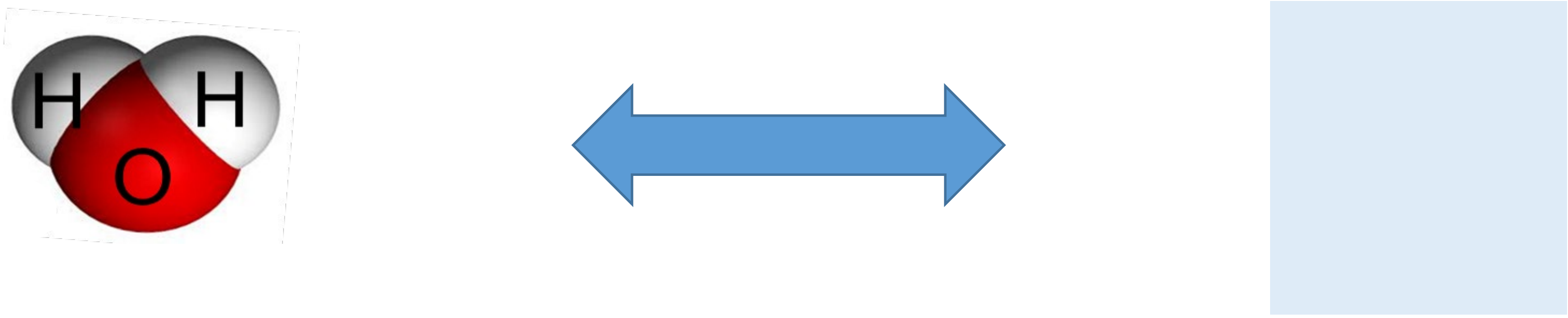
Macroscopic polarization **P**

$$\boldsymbol{P} = \sum_{all\ molecules} \boldsymbol{p}_i = N\langle \boldsymbol{p} \rangle$$

Number of molecules per unit volume contributing to the polarization

$$\chi^{(1)} = \frac{N}{\varepsilon_0} \langle \alpha \rangle_{orientations}$$

Molecular vs Macroscopic polarization



Molecular polarization:
μ or **p** [Cm] (permanent dipole)

μ: used quantum mechanically;
p: used for optics/spectroscopy

Macroscopic polarization **P**

$$\boldsymbol{P} = \sum_{all\ molecules} \boldsymbol{p}_i = N\langle \boldsymbol{p} \rangle$$

Number of molecules per unit surface contributing to the polarization

For second order processes:

$$p_a^{(2)} = \sum_{b,c} \beta_{abc}^{(2)} E_b E_c$$

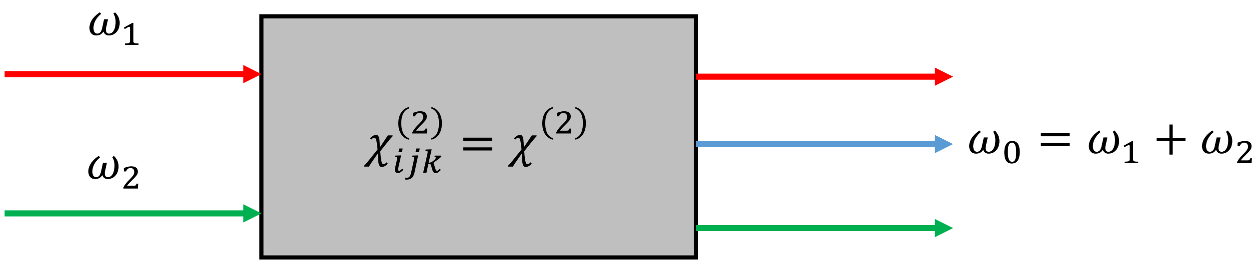
$$P_i^{(2)}(2\omega) = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega)$$

$$\boldsymbol{\chi}_s^{(2)} = \frac{N}{\epsilon_0} \langle \boldsymbol{\beta}^{(2)} \rangle \longleftarrow$$

All molecular orientations

SFG and SHG

Sum Frequency Generation:

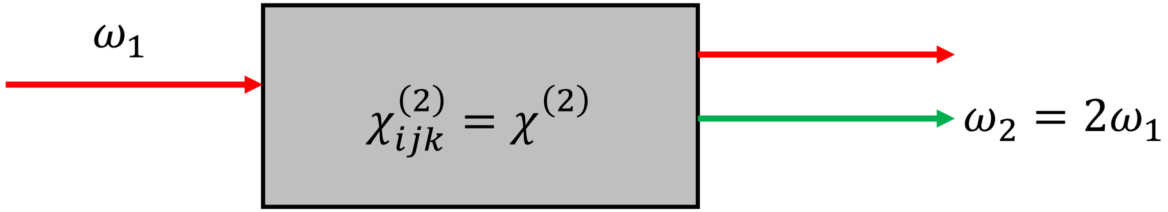


$$P_i^{(2)}(\omega_0) = \epsilon_0 \sum_{j,k} \chi^{(2)}_{ijk}(\omega_0; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)$$

$$I_i(\omega_0) \sim \left| P_i^{(2)}(\omega_0) \right|^2$$

Direction of E-field (polarization: x,y,z direction)

Second Harmonic Generation:



$$P_i^{(2)}(2\omega) = \epsilon_0 \sum_{j,k} \chi^{(2)}_{ijk}(2\omega; \omega, \omega) E_j(\omega) E_k(\omega)$$

$$I_i(2\omega) \sim \left| P_i^{(2)}(2\omega) \right|^2$$

SHG and SFG experiments, like any optical experiment can be performed in

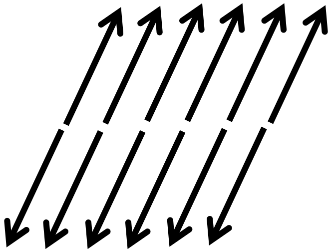
Transmission
Reflection
Scattering
Imaging geometry

The geometry of the experiment determines the relationship between the E-fields and the molecular properties

Intrinsic spatial symmetry selection rules

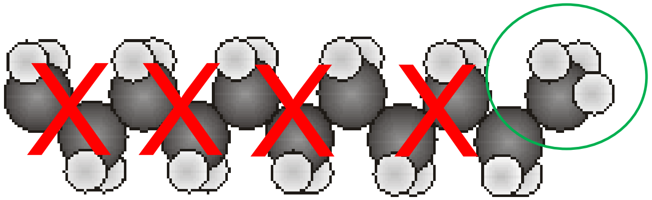
Sources for SHG and SFG

SHG / SFG is **forbidden** In centrosymmetric or isotropic media



Centrosymmetric crystal

Isotropic medium (= the same in every direction)



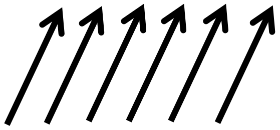
Symmetric arrangement of molecular groups

Sources for SHG and SFG

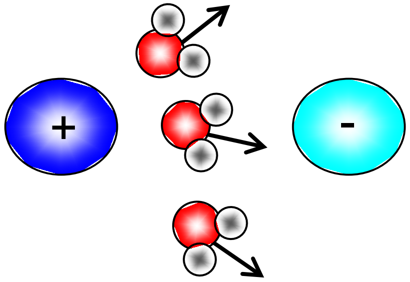
SHG / SFG is **allowed** in non-centrosymmetric environments

- Non-centrosymmetric crystals

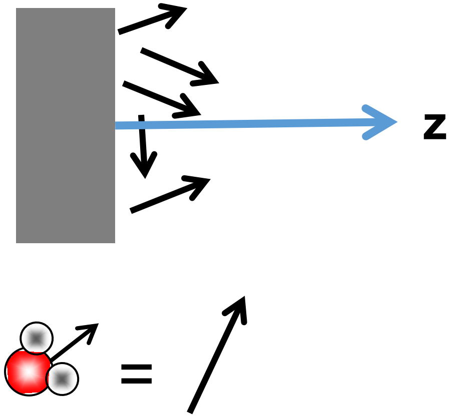
(collagen, microtubules, nanoparticles of BBO, $LiNbO_3$,….)



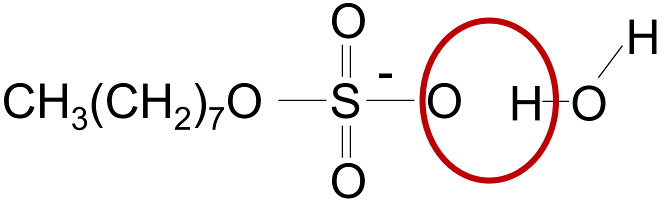
- Electric field oriented water



- Interface (along normal)



- H-bonding / chemical

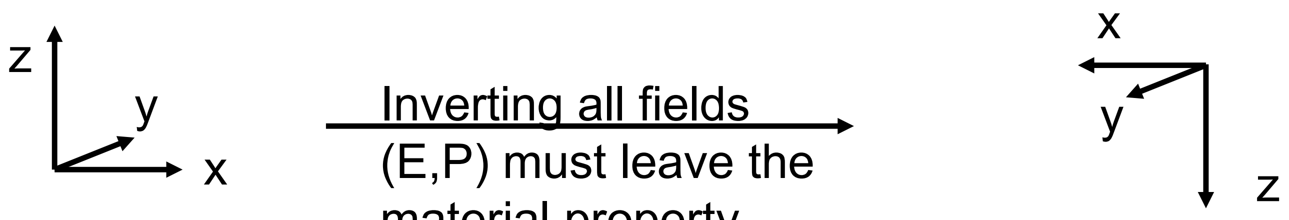


$$CH_3(CH_2)_7O - \overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}} - \overset{-}{O} \quad H - O \diagup H$$

SHG / SFG & inversion symmetry

Neumann's principle: The physical properties of a material must have the same symmetry as the spatial symmetry of the material itself

Isotropic or centrosymmetric material



Inverting all fields (E,P) must leave the material property $\chi^{(2)}_{ijk}$ unchanged

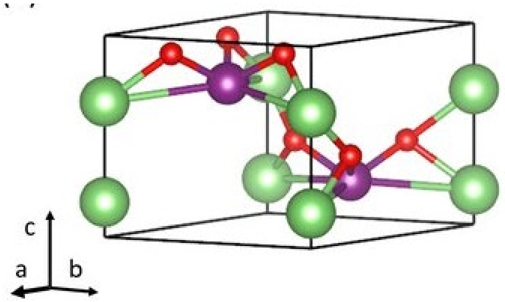
$P_i^{(2)}(\omega_0) \sim \chi^{(2)}_{ijk} E_j(\omega_1) E_k(\omega_2)$

$-P_i^{(2)}(\omega_0) \sim \chi^{(2)}_{ijk} - E_j(\omega_1) - E_k(\omega_2)$

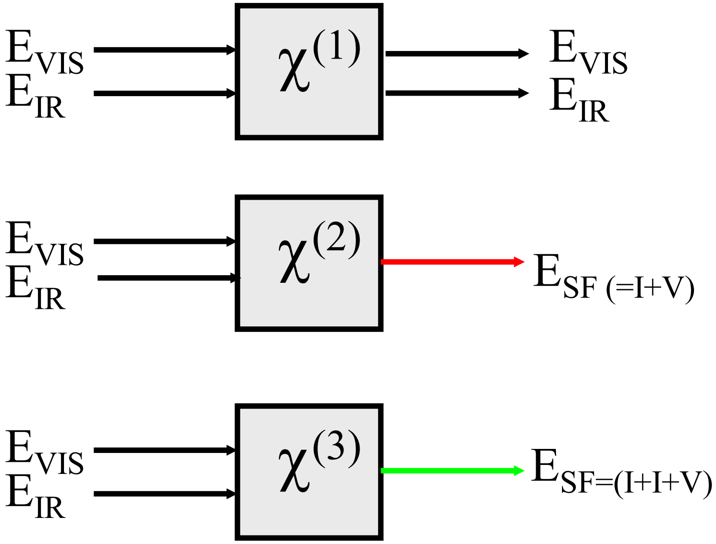
For isotropic or centrosymmetric media: $\chi^{(2)}_{ijk} = -\chi^{(2)}_{ijk} = 0$ $I_i(\omega_0) \sim \left|P_i^{(2)}(\omega_0)\right|^2 = 0$

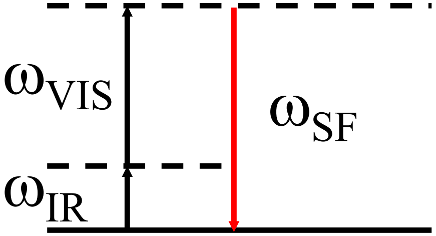
Holds for *all* even-order nonlinear interactions (SHG, SFG, FHG, etc.)

generating SF light in non-centrosymmetric crystal

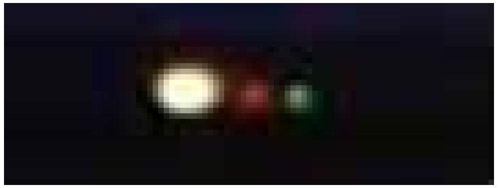


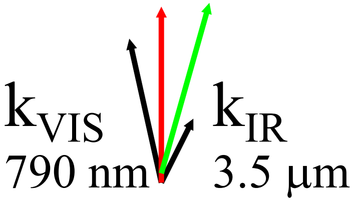
LiIO$_3$, a non-centrosymmetric crystal: SFG generated from the bulk





Non-resonant interaction

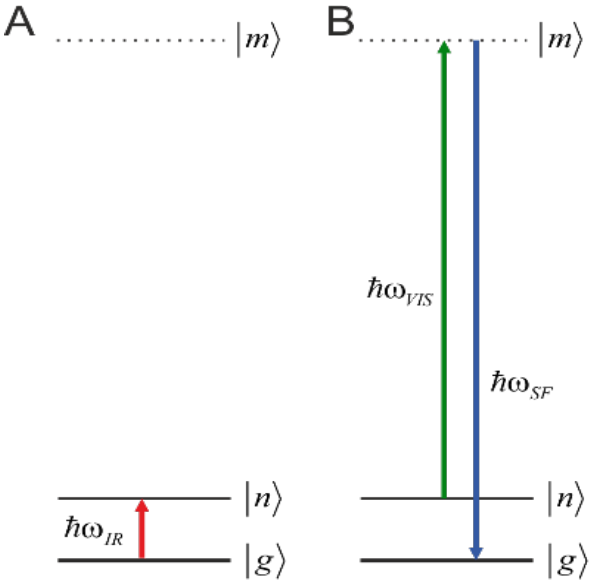




A nonlinear polarization is created in materials at high field strength (e.g. ns, ps, fs laser pulses). Emission depends on:

- The energy levels with respect to the incoming photons (on or off-resonance)
- The spatial symmetry of the material

Vibrational SFG from a liquid



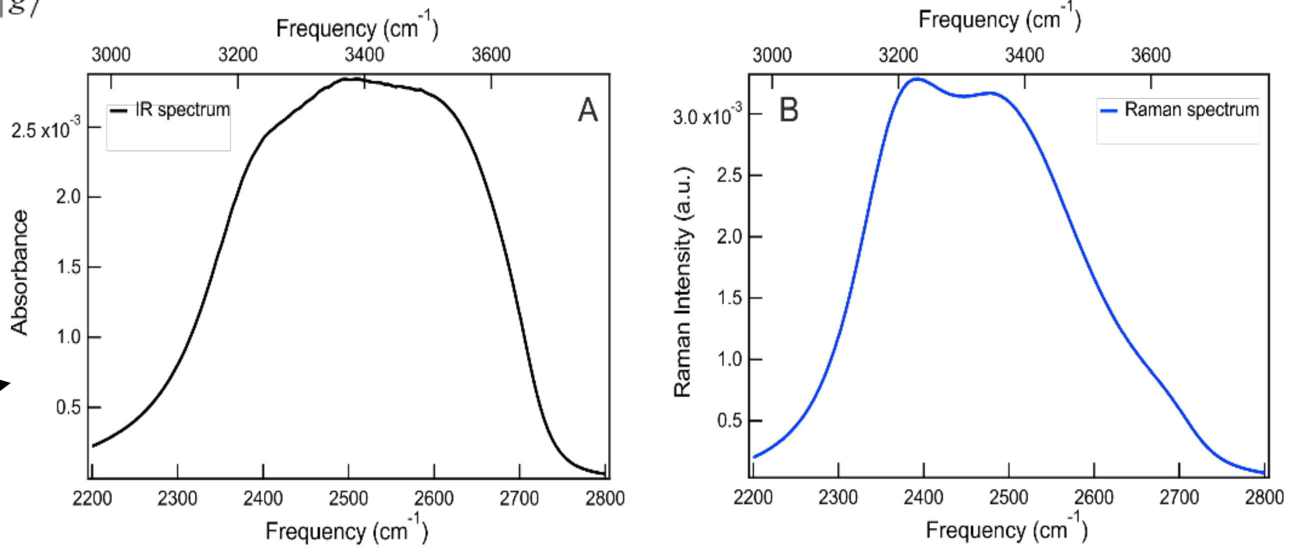
Combine SFG with a vibrational excitation:

Simultaneously excite IR and probe with Raman

Molecules must be both IR and Raman active

Combined IR/Raman selection rules:

Centrosymmetric molecules do not have modes that are both IR and Raman active

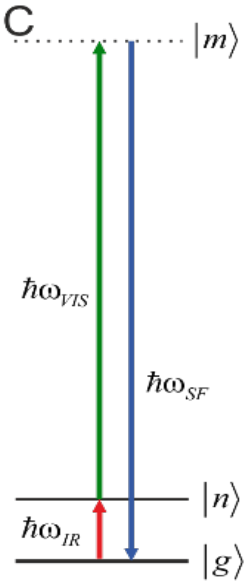


IR and Raman spectra of bulk (heavy) water

No bulk SFG spectrum is detected – liquids are generally isotropic

Raman: Ben-Amotz; IR: S. Pullancherry

Vibrational Sum-Frequency Generation



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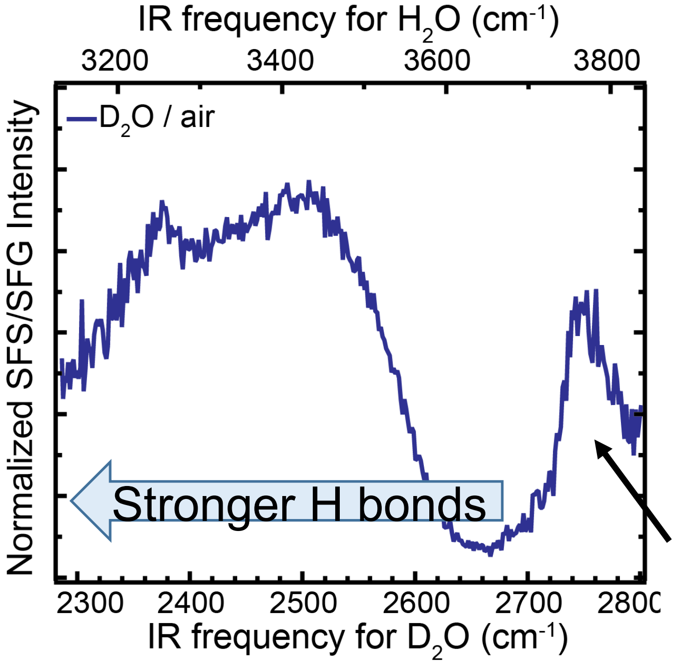


Vibrational SFG spectrum from air / water interface

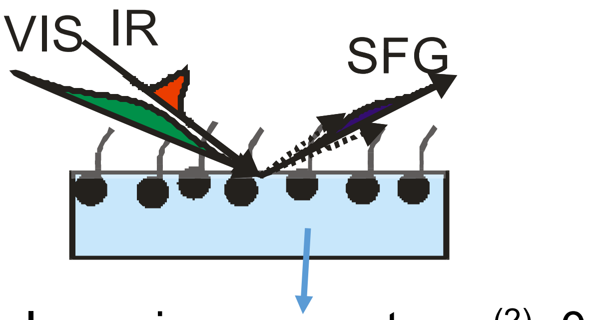
Probing depth: determined by *spatial symmetry* (Gibbs dividing surface)

Free OD/OH

Raman: Ben-Amotz; IR: S. Pullancherry

What we can learn form SFG spectra

Vibrational Sum Frequency Generation (SFG)



Inversion symmetry; $\chi^{(2)}=0$

$$I_i(\omega_0) \sim \left|P_i^{(2)}(\omega_0)\right|^2$$

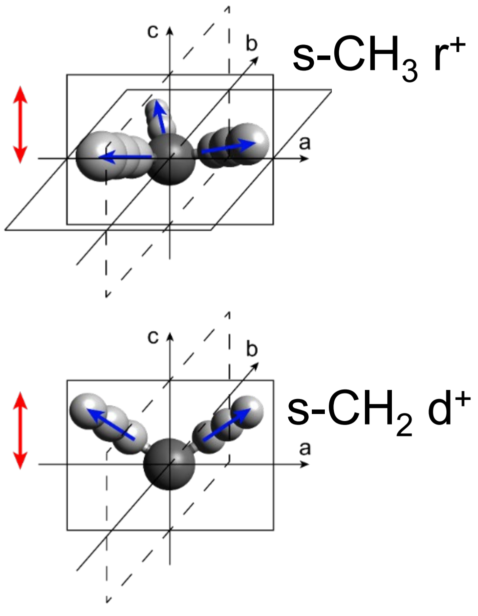
$$P_i^{(2)}(\omega_0) = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)}(\omega_0;\omega_1,\omega_2)\, E_j(\omega_1)E_k(\omega_2)$$

$$\chi_{ijk}^{(2)}(\omega) \sim \frac{\boxed{N}}{\epsilon_0} \sum_n \frac{\boxed{\langle \alpha_{ab}\mu_c \rangle_{mol.orient}}}{(\omega - \boxed{\omega_{0n}}) - i\boxed{\gamma_{0n}}}$$

Note: $\omega_0 - \omega_1 \rightarrow \omega$

Coherent vibrational spectrum

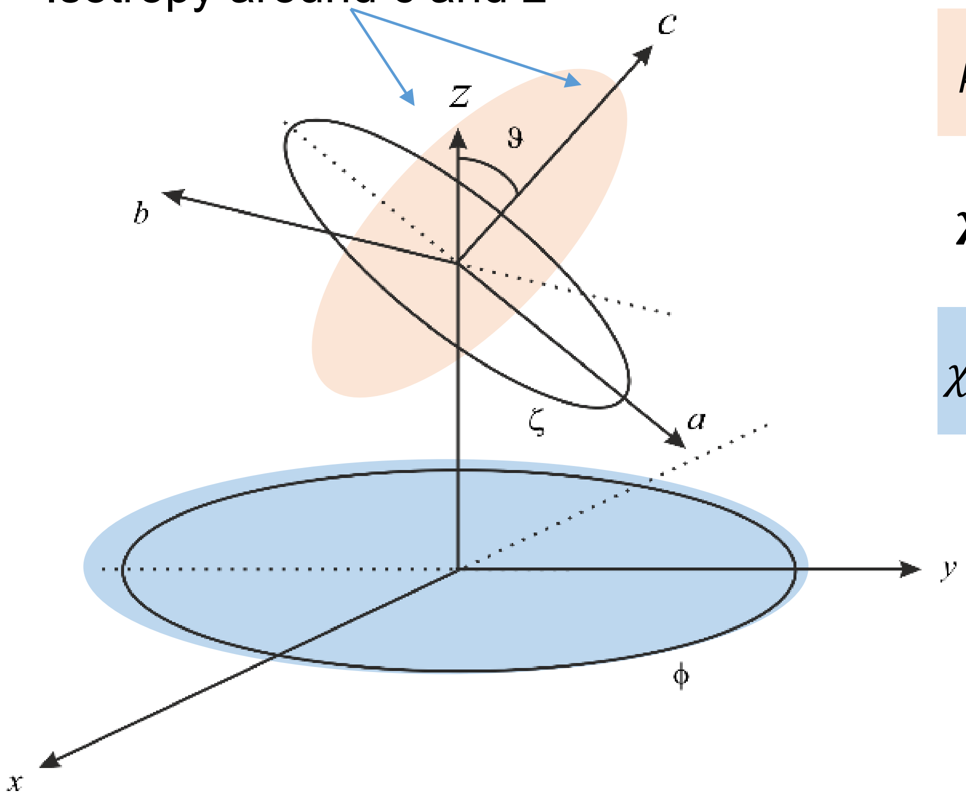
- Interface specific [Raman $\boxed{(\alpha_{ab})}$ x IR $\boxed{(\mu_c)}$ transition moments]
- Vibrational frequency $\boxed{\omega_{0n}}$ & linewidth $\boxed{\gamma_{0n}}$ chemical interactions
  - which molecules and their interactions
- Intensity: number of molecules @ interface $\boxed{(N)}$
  - how many molecules at interface
- For alkyl chains the ratio of the symmetric CH_3 and CH_2 modes provides information about the chain conformation
- Polarimetry: molecular orientation:
  Vary the direction of the e-m field: 8 P/S combinations
  Relate tilt angle to polarization ratios of light



Symmetric stretch

ChemPhysChem (2009), 10, 1380
Annu. Rev. Phys. Chem, (2012), 63, 353

Molecular tilt angle



Isotropy around c and z

Coordinate systems of the molecule ((a,b,c)) and the surface ((x,y,z)) as well as the rotational Euler angles ((ϕ,ϑ,ζ)) over which we need to rotate to transform one into the other.

$$\beta^{(2)}_{abc} = \frac{1}{2\hbar}\sum_{n}\frac{\bar{\alpha}_{ab}\bar{\mu}_c}{(\omega_{IR}-\omega_n)+i\gamma_n}$$

Molecule response

$$\boldsymbol{\chi}^{(2)}_{S} = \frac{N}{\epsilon_0}\langle\boldsymbol{\beta}^{(2)}\rangle$$

Surface response

$$\chi^{(2)}_{s,ijk} = \frac{N}{\epsilon_0}\sum_{a,b,c}\langle(\hat{\boldsymbol{\imath}}\cdot\hat{\boldsymbol{a}})(\hat{\boldsymbol{\jmath}}\cdot\hat{\boldsymbol{b}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{c}})\rangle_{\phi,\vartheta,\zeta}\,\beta^{(2)}_{abc}$$

i,j,k: any x,y,z coordinate

Possible to extract a tilt angle – assuming a certain distribution at the interface: isotropy (ϕ,ζ) drop out

Unknowns: value of $\bar{\alpha}_{ab}\bar{\mu}_c$ and tilt angle w.r.t surface normal ϑ

Intensity ~ $\mathrm{N}^2\cos^2(\vartheta)$

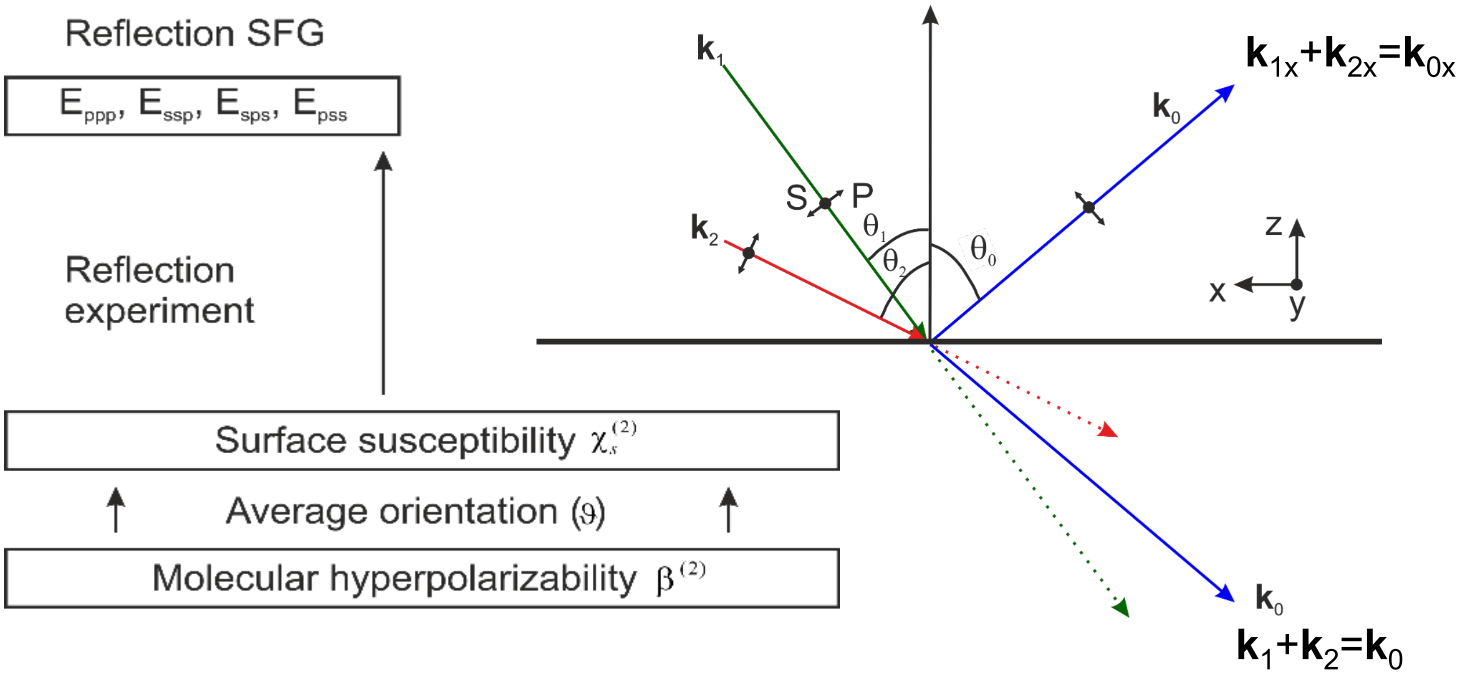
SHG and SFG experiments, like any optical experiment can be performed in

- Transmission
- Reflection
- Scattering
- Imaging geometry

As with linear reflection / refraction / scattering the sum of the ingoing wave vectors needs to match the outgoing one to achieve a continuous phase of the electromagnetic fields at the interface

The geometry of the experiment determines the relationship between the e-m fields and the molecular properties

Geometry determines relations between $\chi^{(2)}$ and emitted E-fields



Reflection SFG

E_{ppp}, E_{ssp}, E_{sps}, E_{pss}

Reflection experiment

Surface susceptibility $\chi_s^{(2)}$

Average orientation (ϑ)

Molecular hyperpolarizability $\beta^{(2)}$

Terminology of linear polarized light:
P: E-field and **k** are in the same plane as the surface normal

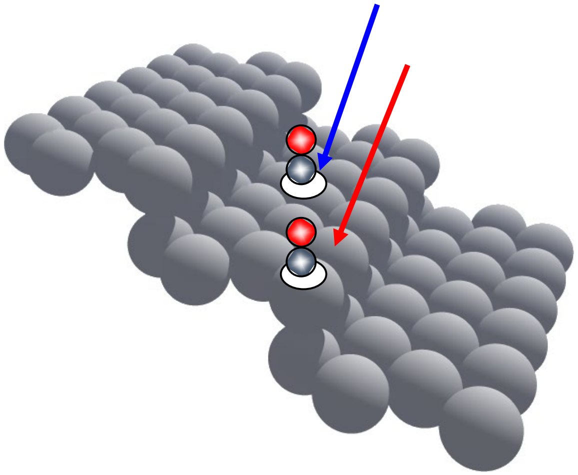
S: E-field and **k** are in a plane perpendicular to the surface normal

SFG: PSS = polarization of out, in, in fields
Convention: High frequency goes first

Examples Reflection SFG

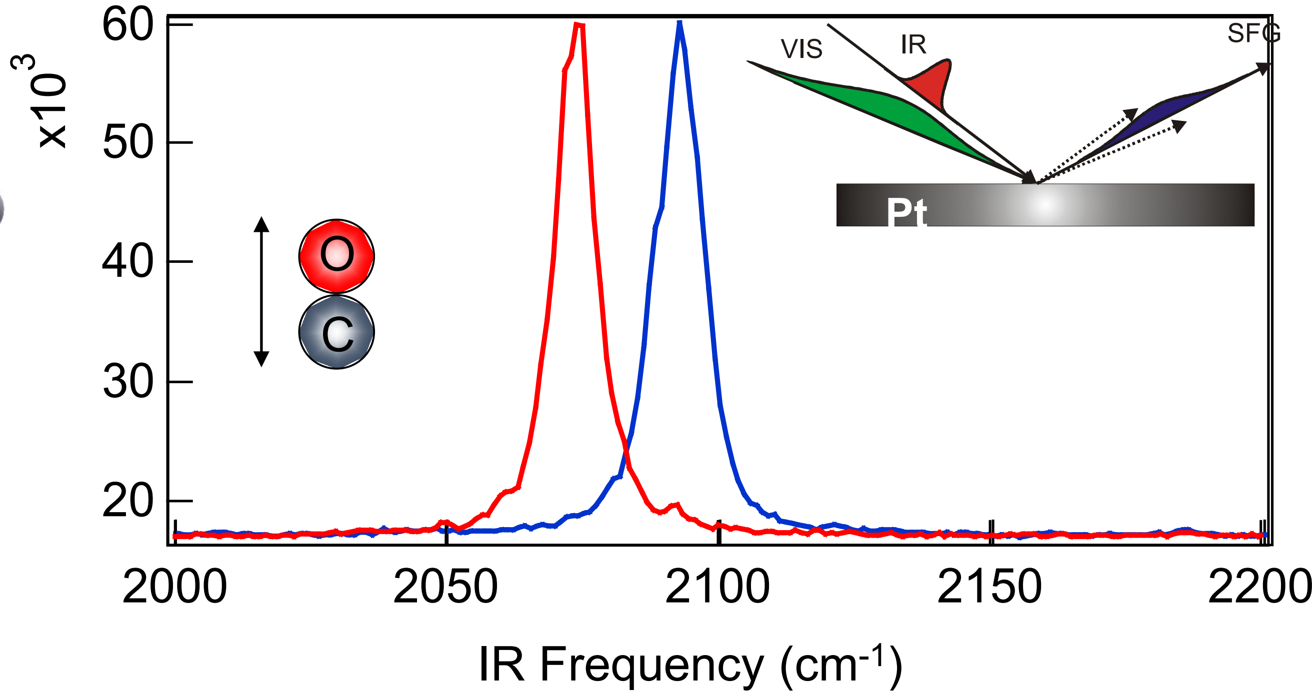
Reflection SFG in vacuum

slightly different chemical environment



stepped platinum with
different adsorption sites:
model system for a rough
catalyst in UHV

CO on stepped Pt

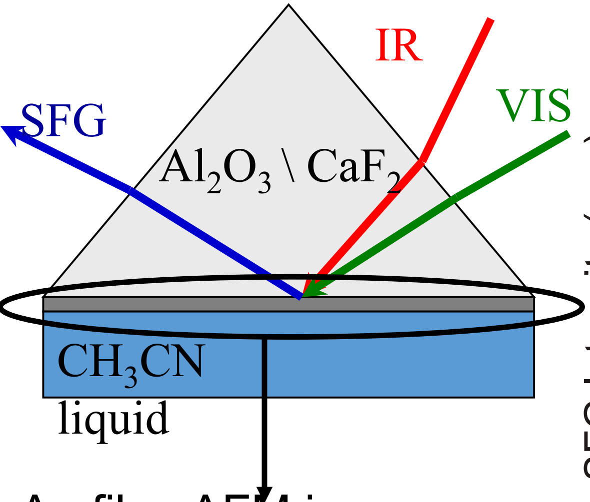


Different sites have a different resonance frequency

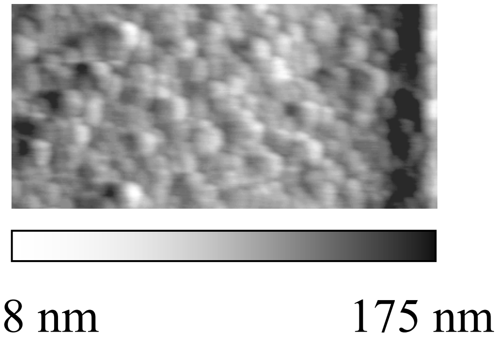
Distinguish between chemical binding sites

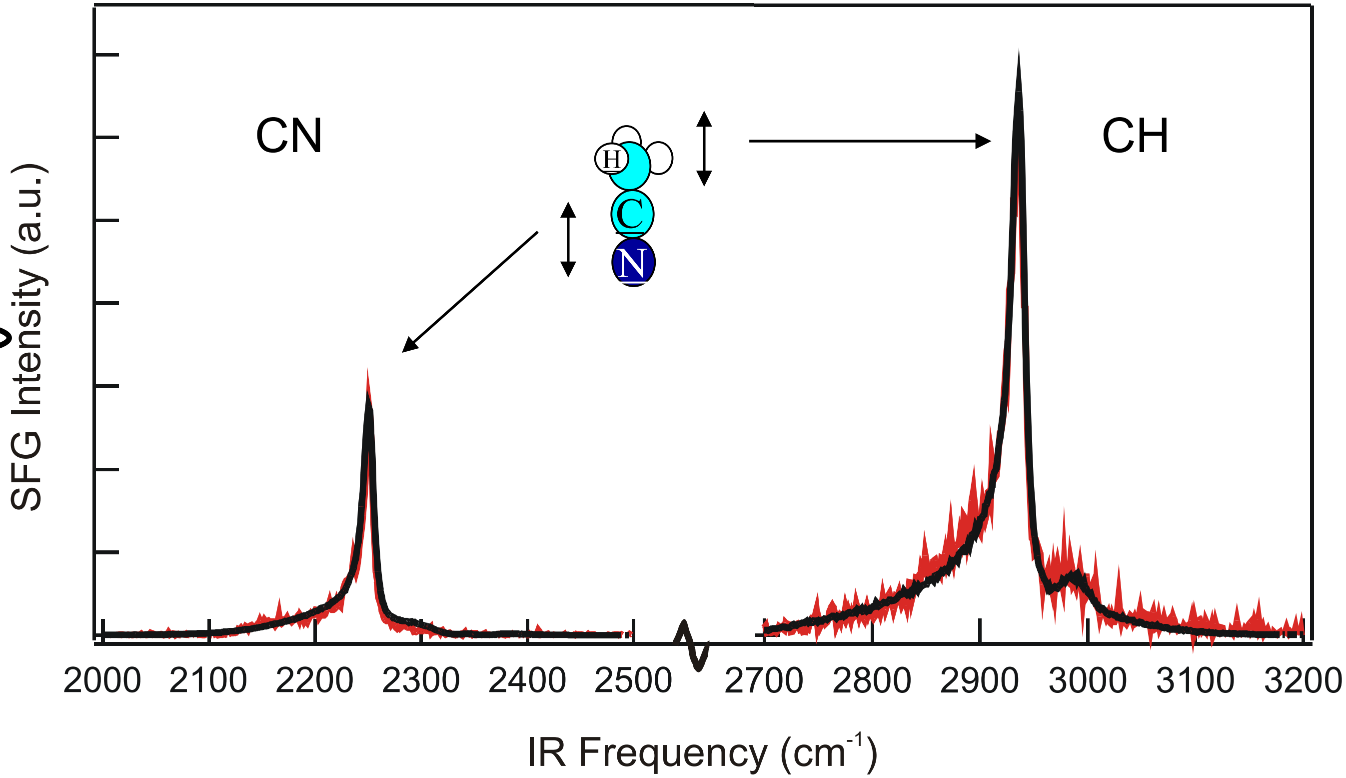
Reflection SFG: solid/liquid interface

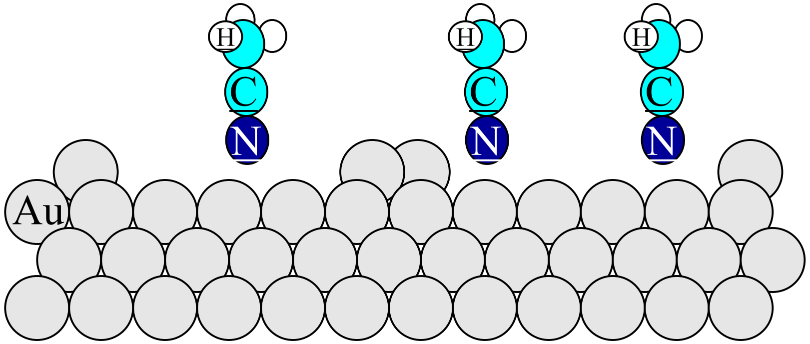
Evanescent wave method



Au film: AFM image



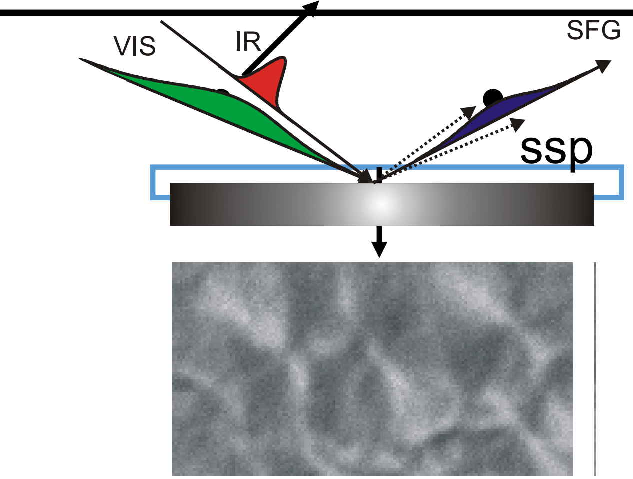




Frequency: Chemical specificity
Line width / shape: surface roughness

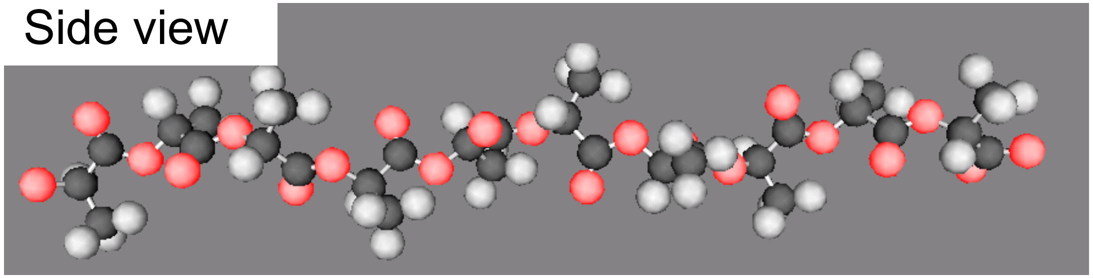
Roke et al.,**CPL**, 370, 227, 2003

Reflection SFG: polymer/air interface

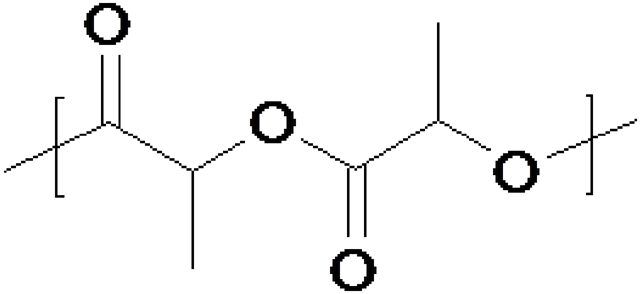


Poly –(L- lactic acid)

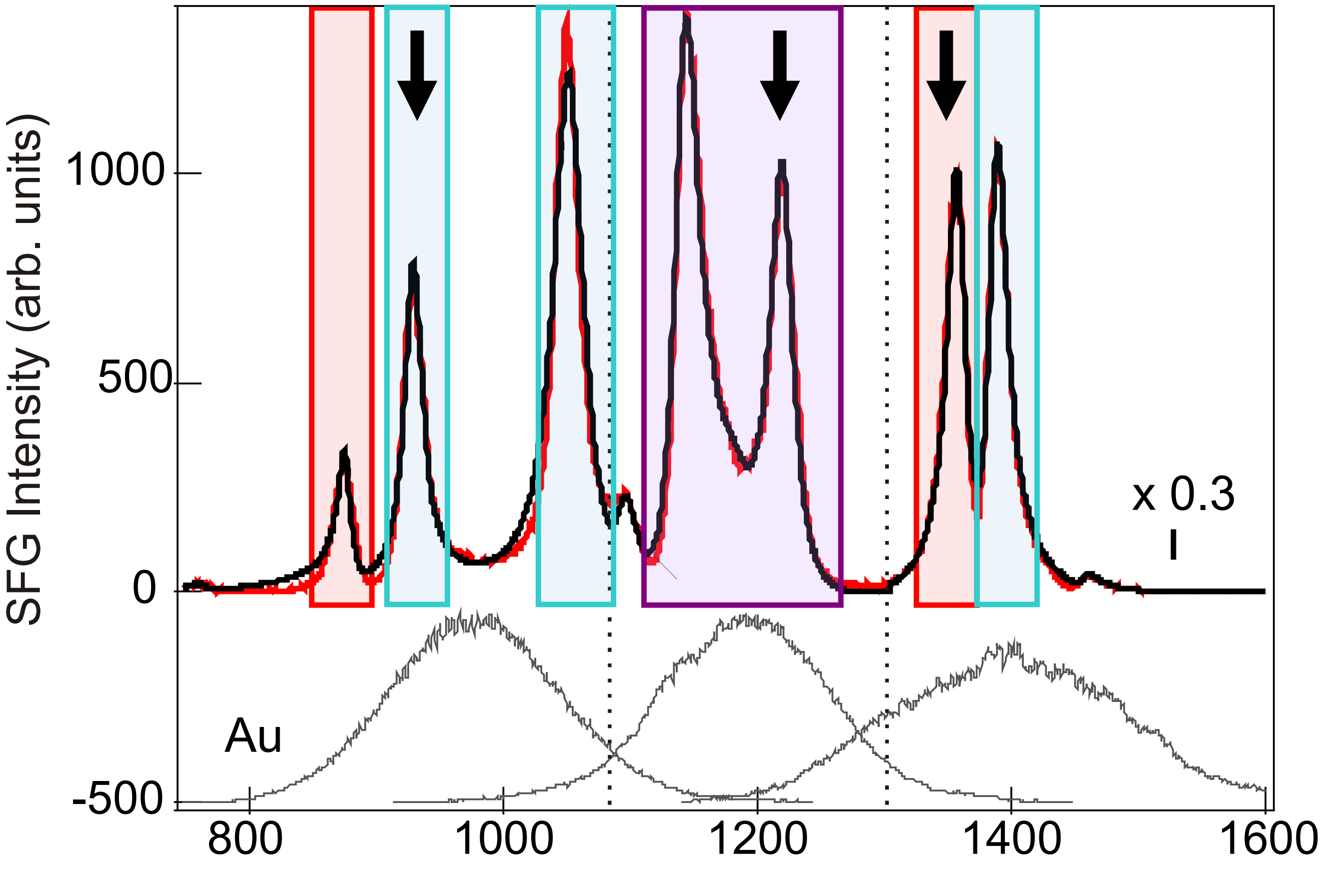
- Bio-degradable & biocompatible
- Mechanical properties
- Medicine development and implants

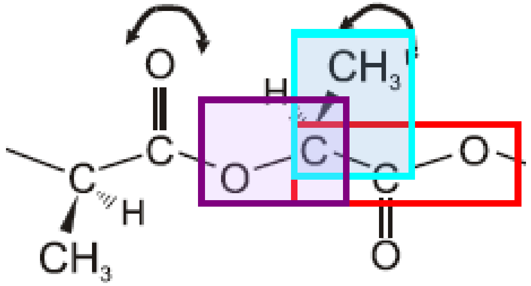


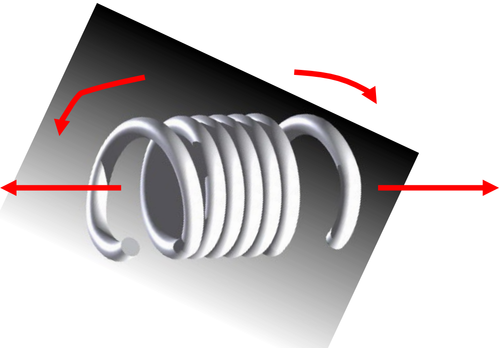
Complex 3D structure with α helices



Reflection SFG: polymer/air interface





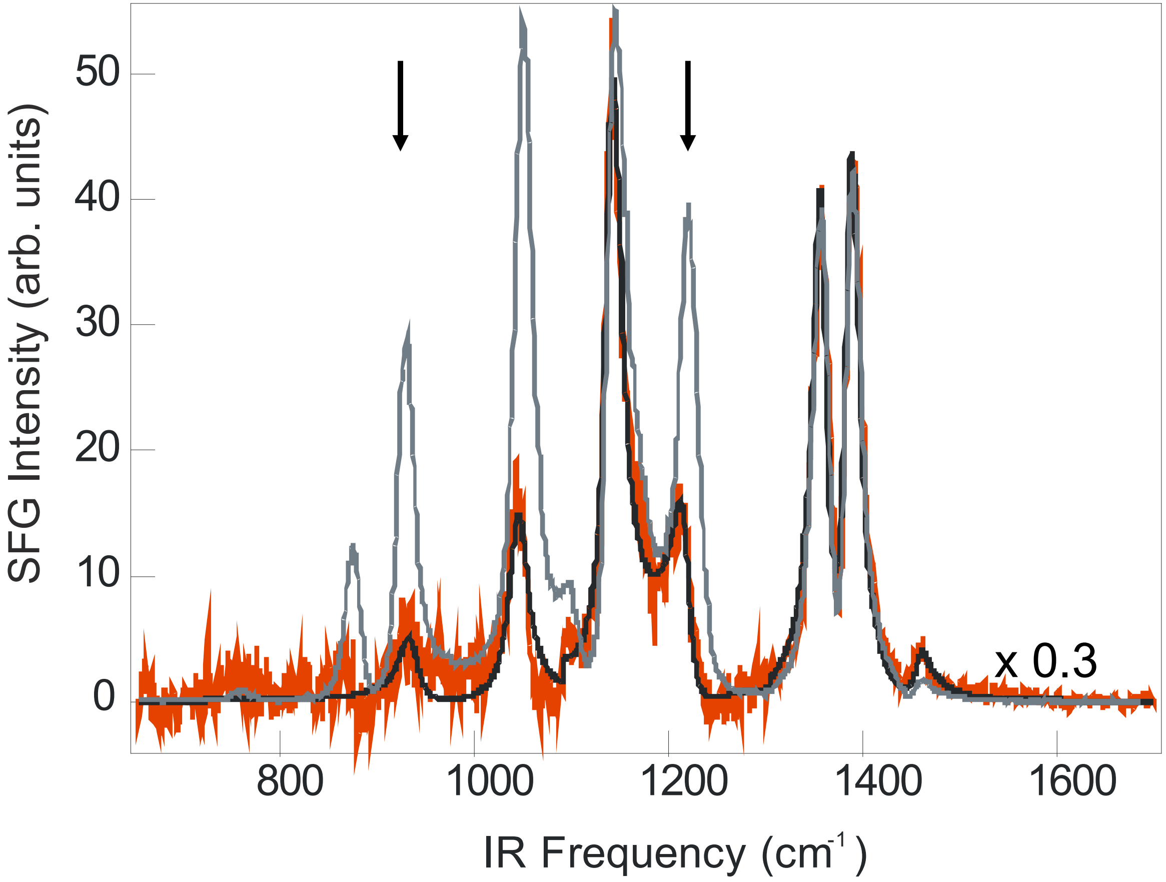


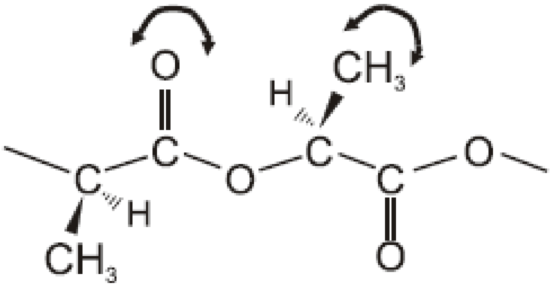
Crystalline form: helical coils are present at interface
skeleton oriented parallel to the interface

J. Phys. Chem. C, (2008), 221, 7531 -7534.

Reflection SFG: polymer/air interface

Amorphous vs **crystalline** surface





- less pronounced helical modes
- skeletal modes have the same frequency
- 20 x less signal, less chain order

Low frequencies are sensitive to 3D structure

J. Phys. Chem. C, (2008), 221, 7531 -7534.

What about charged interfaces?

Any particular effects?

Interfacial electrostatics

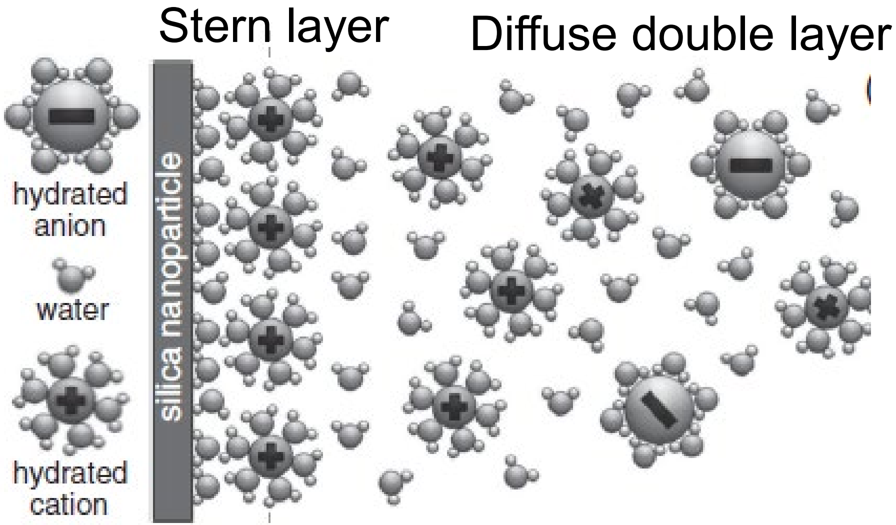
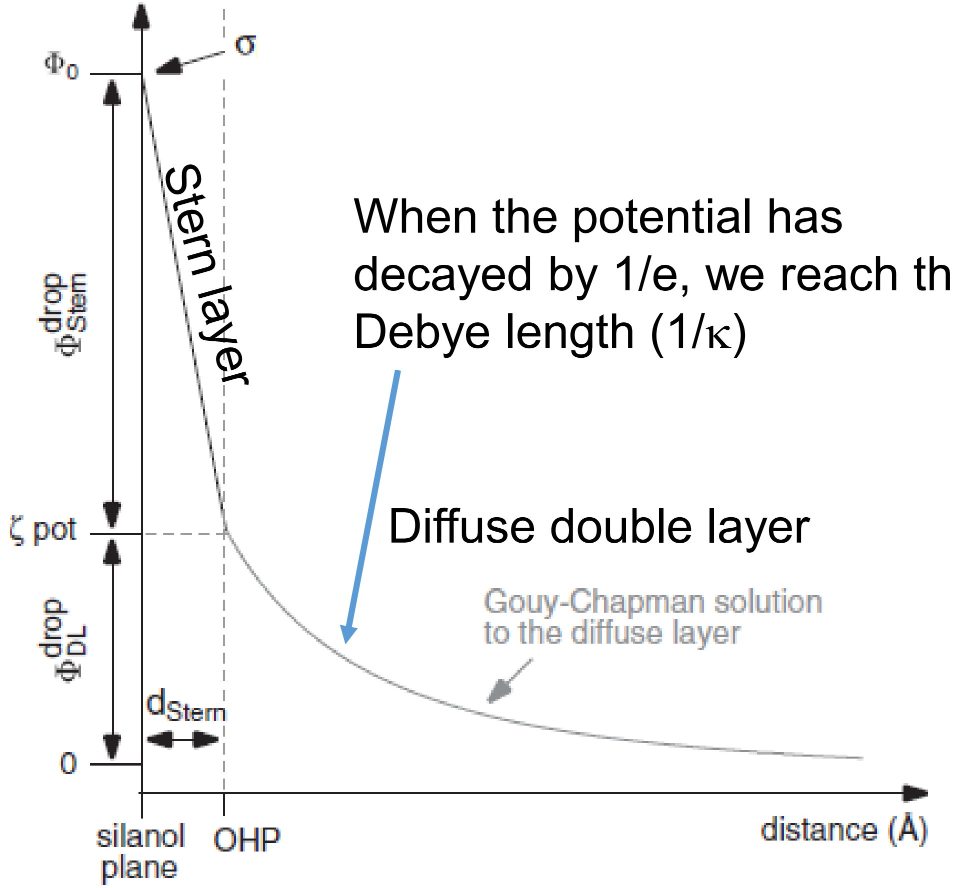


Illustration: PRX 2016, 6, 011007

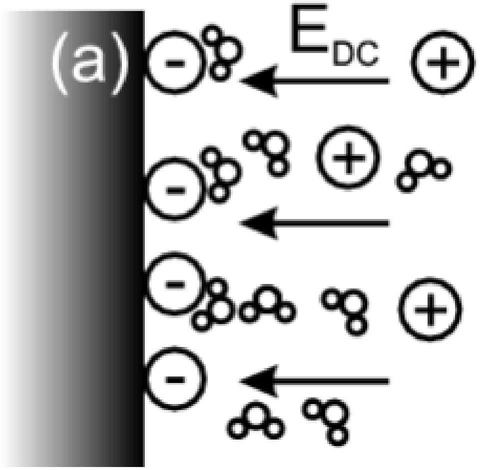


When the potential has decayed by 1/e, we reach the Debye length (1/κ)

Most interfaces in nature are charged
The electrostatic field from this charge decays into the solution and dramatically alters the surface structure, chemistry and physical properties

How to measure this field ?
There are no methods available to measure a surface potential

Interfacial source polarization



Near a charged interface E_{DC} is very high (~10^6 – 10^8 V/m)

E_{DC} acts as third optical input field: a $\chi^{(3)}$ process:

$\omega_0 = \omega_1 + \omega_2$ SFG, second order, $\chi^{(2)}$

$\omega_0 = \omega_1 + \omega_1$ SHG, second order, $\chi^{(2)}$

$\omega_0 = \omega_1 + \omega_2 + 0$ SFG, third order, $\chi^{(3)}$

$\omega_0 = \omega_1 + \omega_1 + 0$ SHG, third order, $\chi^{(3)}$

Total Nonlinear Polarization (SHG) is sum of 2 and 3 photon interactions:

$$\mathbf{P}_{\mathrm{NL}}(\omega_0 = 2\omega_1) = \mathbf{P}^{(2)}(\omega_0) + \mathbf{P}^{(3)}(\omega_0) + \cdots$$

Interfacial water

Dipoles that interact with a DC field

Possible to find electric potential at interface with *just* an optical measurement!

The interfacial source polarization

$$\mathbf{P}_{\mathrm{NL}}(\omega_0 = 2\omega_1) = \mathbf{P}^{(2)}(\omega_0) + \mathbf{P}^{(3)}(\omega_0) + \cdots$$

$$\mathbf{E}(\omega_1) = \mathrm{E}_0 e^{-i(k_1 r - \omega_1 t)}\,\mathbf{u}$$

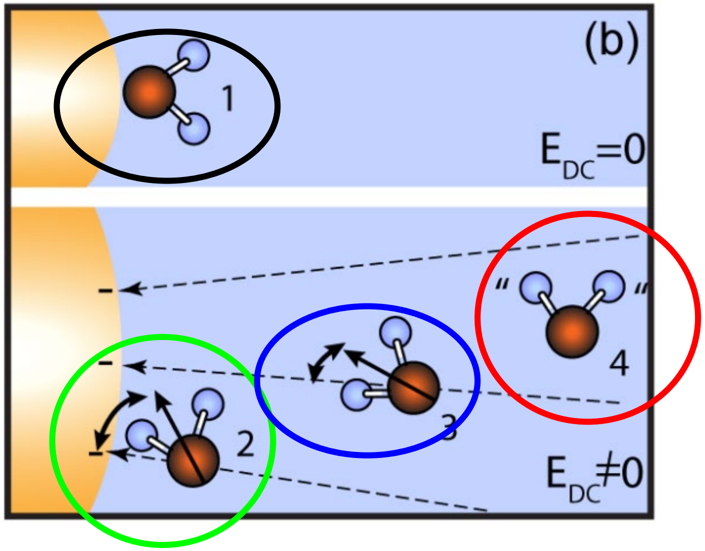
$$\mathbf{P}^{(2)}(\omega_0) = \boxed{\epsilon_0 \boldsymbol{\chi}_s^{(2)}} : \mathbf{E}_1(\omega_1)\mathbf{E}_2(\omega_1)$$

2 fields $\leftarrow\rightarrow$ $\chi^{(2)}$

$$\mathbf{P}^{(3)}(\omega_0, z) = \epsilon_0 \boldsymbol{\chi}^{(3)\prime} : \mathbf{E}_1(\omega_1)\mathbf{E}_2(\omega_1)\mathbf{E}_{\mathrm{DC}}(z, \omega = 0)$$

3 fields $\leftarrow\rightarrow$ $\chi^{(3)}$

Three sources for third order interaction



Diffuse double layer (DDL)

$$P^{(3)}(\omega_0, z) =$$

$$\epsilon_0 N_m \boxed{< {\beta_{iso}}^{(3)} >} E_1(\omega_1)E_2(\omega_1)E_{\mathrm{DC}}(z) +$$

$$\epsilon_0 N_m \boxed{< \beta^{(2)} >} \frac{2\mu_{DC}}{3kT} E_1(\omega_1)E_2(\omega_1)E_{\mathrm{DC}}(z) +$$

$$\epsilon_0 N_s \boxed{< {\beta_s}^{(2)} >} \frac{2\mu_{DC}}{3kT} E_1(\omega_1)E_2(\omega_1)E_{\mathrm{DC}}(z)$$

Combined in $\boldsymbol{\chi}^{(3)\prime}$

Linearized Boltzmann equation
= fraction of aligned water

Intensity is proportional to surface potential (Φ_0)

$$\mathrm{I}(\omega_0) \sim |\, P^{(2)}(\omega_0) + P^{(3)}(\omega_0)|^2$$

$$P^{(3)}(\omega_0) = \epsilon_0\, E_1(\omega_1, k_1) E_2(\omega_1, k_1) \int_0^{\infty} \chi^{(3)\prime} E_{DC}(z)\, dz$$

Sum all z contributions

$$P^{(3)}(\omega_0) = \epsilon_0\, E_1(\omega_1) E_2(\omega_1) \int_0^{\infty} \chi^{(3)\prime} E_{DC}(z)\, e^{\mathrm{i}\,\Delta k_z z} dz$$

Fields ($e^{-i(k_1 r - \omega_1 t)}$) change phase away from interface

$$P^{(3)}(\omega_0) \;= \epsilon_0 \chi^{(3)\prime}\, E_1(\omega_1) E_2(\omega_1) \int_0^{\infty} \left(-\frac{d}{dz}\Phi(z)\right) e^{\mathrm{i}\,\Delta k_z z} dz$$

Definition of potential

$$\Phi(z) = \Phi_0 e^{-\kappa z}$$

Exponentially decaying potential; κ is the inverse Debye length

$$I(\omega_0) \;\propto \mathrm{I}_1(\omega_1)\mathrm{I}_2(\omega_2) \left| \chi_s^{(2)} + \chi^{(3)\prime}\, \Phi_0 \frac{\kappa}{\kappa - i\Delta k_z} \right|^2$$

Solution via partial integration

$$\Delta k_z = k_{1z} + k_{1z} - k_{0z}$$

Gonella, Luetgebaucks, Roke, J. Phys. Chem. C 2016, 120, 9165

Second Harmonic Scattering (SHS) / SH Imaging

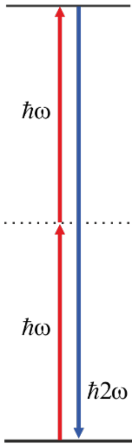
SHS is around since 1965* – but mostly for probing fluorophores

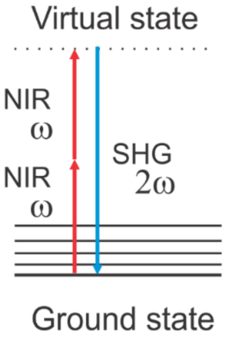
Resonant: response derives from fluorophores

Asymmetric distribution of fluorophores

Non-Resonant: response equal in magnitude for all non-centrosymmetric (dipolar) molecules in solution

But non-resonant nonlinear processes are exceptionally weak – this response has not been practically useful for a long time**





First experiments:
*Hyper Rayleigh scattering in liquids: Terhune et al, PRL, 1965
***First high throughput: Opt. Express* (2013), 21, 815 - 821

Second Harmonic Generation

SHG is a special form of SFG: all general equations derived for SFG are true for SHG

- For non-resonant SHG there is no chemical specificity since all molecules respond identically.
- Far away from resonance: $\chi^{(2)} = \frac{e^3}{\epsilon_0 m^2 \omega_0^4 d^4}$ no bond specific information
- In aqueous systems **water is so much more abundant than anything else** that the intensity nearly always derives from oriented water. Example: a lipid interface will have water:lipid = 100:1 and the intensity will be 10^4:1

$$I_i(\omega_0) \sim \left| P_i^{(2)}(\omega_0) + P_i^{(3)}(\omega_0) \right|^2$$

$$P_i^{(2)}(\omega_0) = \epsilon_0\, \chi_{ijk}^{(2)}(\omega_0; \omega_1, \omega_1)\, E_j(\omega_1) E_k(\omega_1)$$

$$P_i^{(3)}(z, \omega_0) = \epsilon_0 \int_0^\infty \chi_{ijkl}^{\prime(3)}(\omega_0; \omega_1, \omega_1, 0)\, E_j(\omega_1) E_k(\omega_1) E_l(z, \omega = 0)\, dz$$

$$I(\omega_0) \propto \mathrm{I}_1(\omega_1)\mathrm{I}_2(\omega_2) \left| \chi_s^{(2)} + \chi^{(3)\prime}\, \Phi_0 \frac{\kappa}{\kappa - i\Delta k_z} \right|^2$$

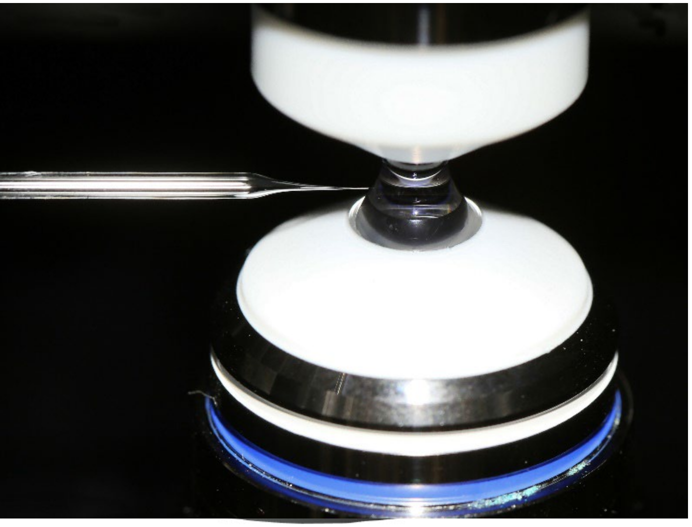
Definition surface potential

$$\Phi_0 = -\int_0^\infty E(z, \omega = 0)\, dz$$

No spectral information: **advantage**: simple connection with surface potential (Φ_0)

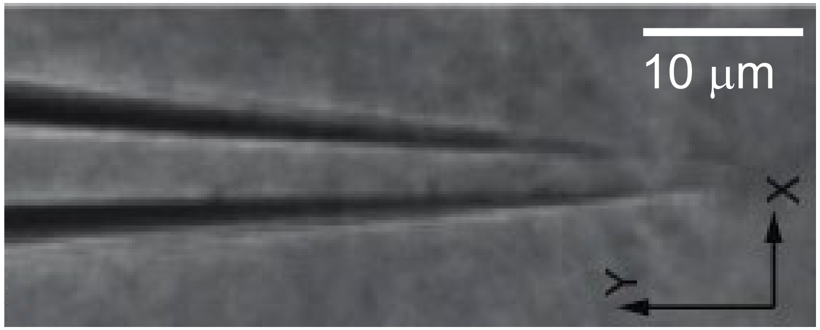
Use SHG to image the surface potential

Surface potential imaging



Glass micro-capillary immersed in water with ionic strength of 10 mM

Wide field phase contrast image



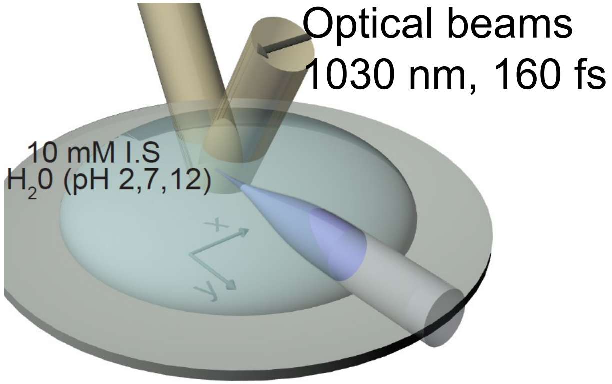
Take SH images in XXX polarization

Convert intensity scale to surface potential scale

Vary pH (2, neutral, 12)

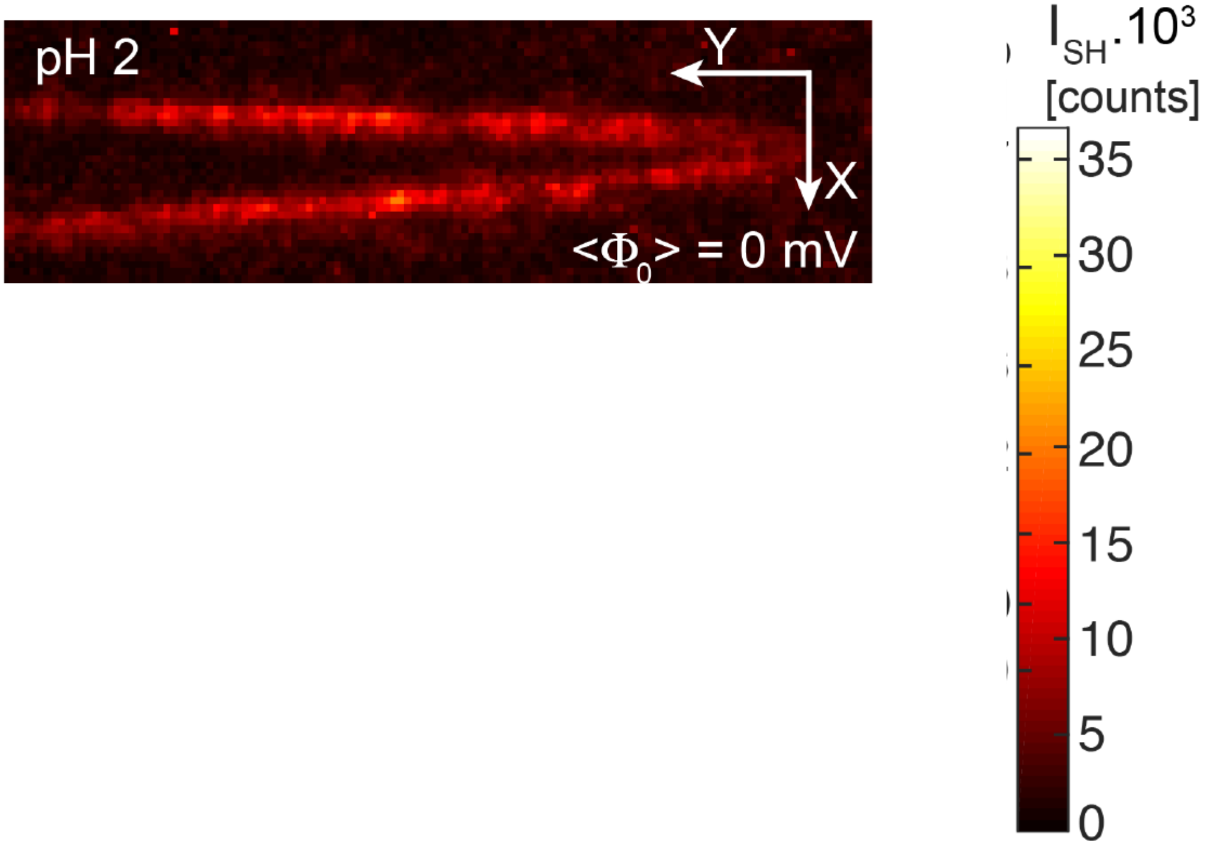
Macias, Nahalks, Okur, Roke, Science (2017) 357, 784-788

Surface potential imaging



Glass micro-capillary immersed in water
1 s/image (250 ms possible)
Average of 5 images

X,Y res: 188 nm
Z res: 520 nm



Average SH intensity increases with increasing pH

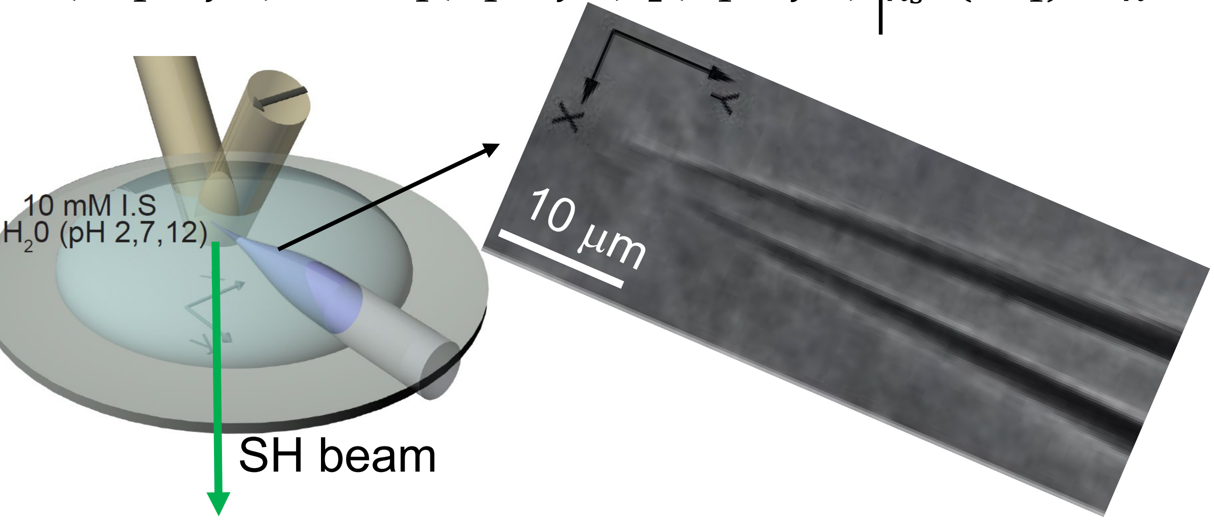
Science (2017) 357, 784-788

Surface potential imaging

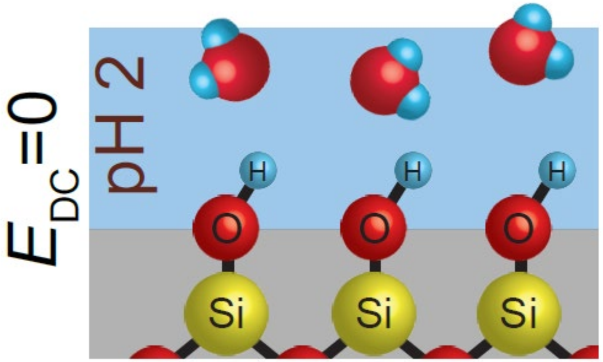
The emitted transmitted intensity

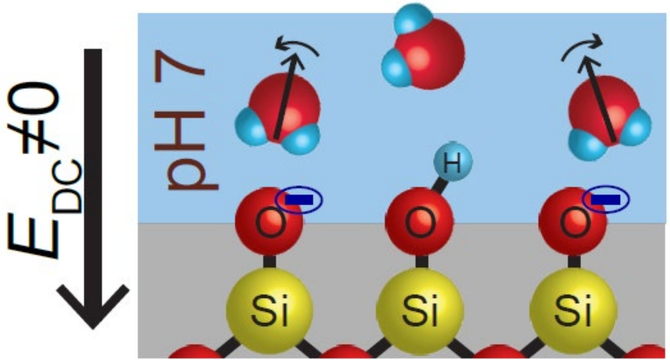
$$I(2\omega_1, x, y, t) \propto \mathrm{C} \cdot \mathrm{I}_1(\omega_1, x, y, t)\mathrm{I}_2(\omega_1, x, y, t) \left| \chi_s^{(2)}(2\omega_1) + \chi^{(3)\prime}(2\omega_1)\, \Phi_0(x, y, t) \underbrace{\frac{\kappa}{\kappa - i\Delta k_z}}_{\downarrow} \right|^2$$

=1 for transmission geometry



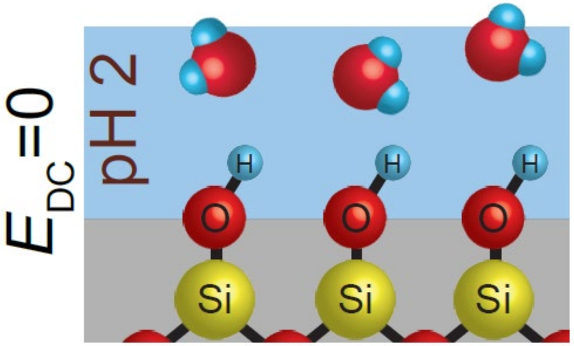
The surface charge density and potential change when the pH is changed

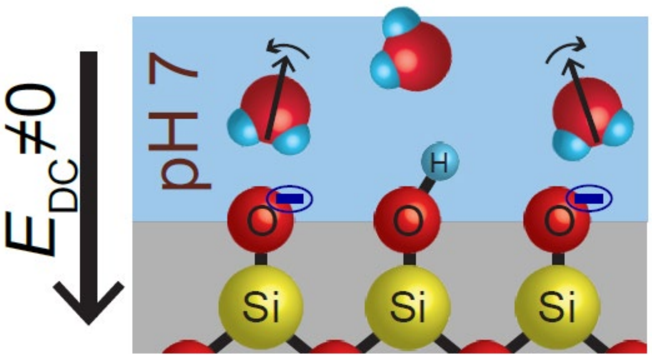




Science (2017) 357, 784-788

Surface potential imaging





To compute $\Phi_0(x,y)$ we need to use three assumptions:

1. At the point of zero charge:
$\langle \Phi_0(pzc) \rangle = 0$ mV

$$\chi_s^{(2)} = \sqrt{\frac{\langle I(pH=2) \rangle}{C}}$$

2. $\chi_s^{(2)}$ is pH independent and constant in x,y

3. At neutral pH, the average surface charge density is the one reported in the literature*, using -2 μC/cm², 0.91 nm for average charge density / Stern layer thickness:
$\langle \Phi_0(pH=7) \rangle$ =-114 mV

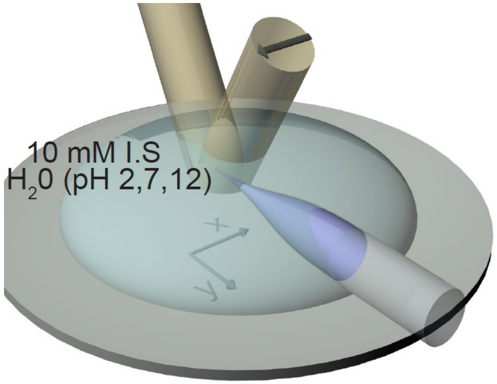
Result:

$$\boxed{\Phi_0(x,y,t) = \frac{\sqrt{I(x,y,t)} - \sqrt{\langle I(pH=2) \rangle}}{\sqrt{\langle I(pH=7) \rangle} - \sqrt{\langle I(pH=2) \rangle}} \langle \Phi_0(pH=7) \rangle}$$

Colloid Polym. Sci. 273, 926 (1995).
Angew. Chem. Int. Ed. 55, 3790 (2016).

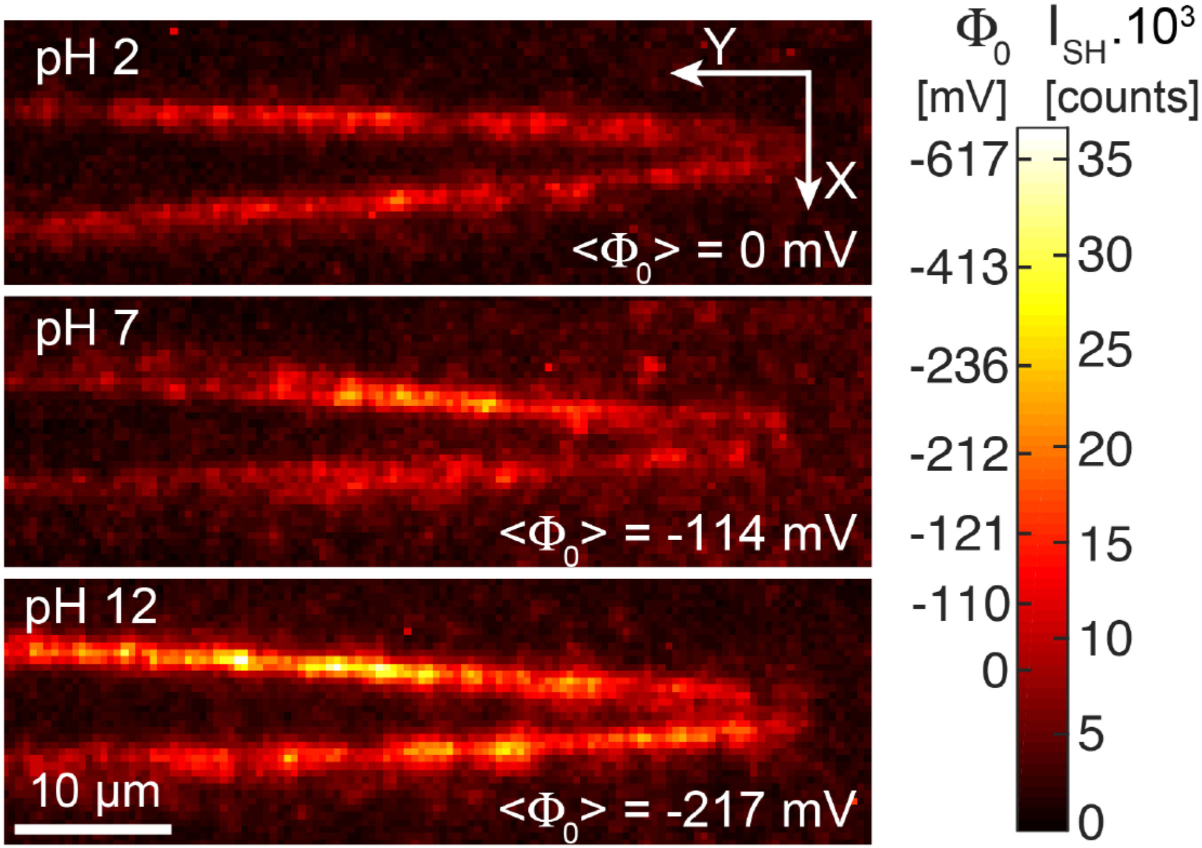
Science (2017) 357, 784-788

Surface potential imaging



Glass micro-capillary immersed in water
1 s/image (250 ms possible)
Average of 5 images

X,Y res: 188 nm
Z res: 520 nm



Retrieve a surface potential map / video: $\Phi_0(x, y, t)$
Observe real electrostatic energy landscape at a surface – outside idealized conditions and in 3D

Science (2017) 357, 784-788

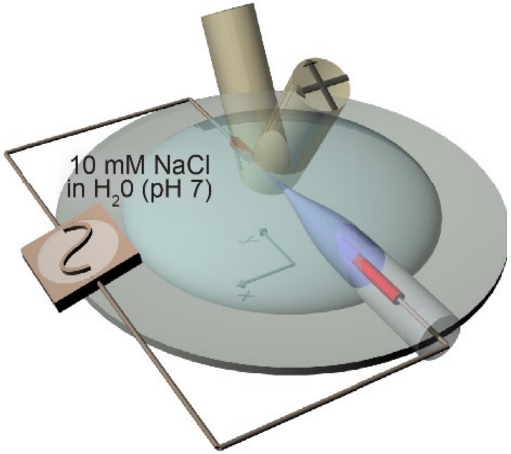
Science (2017) 357, 784-788

In SH / SF experiments like these …

How many water molecules are oriented?

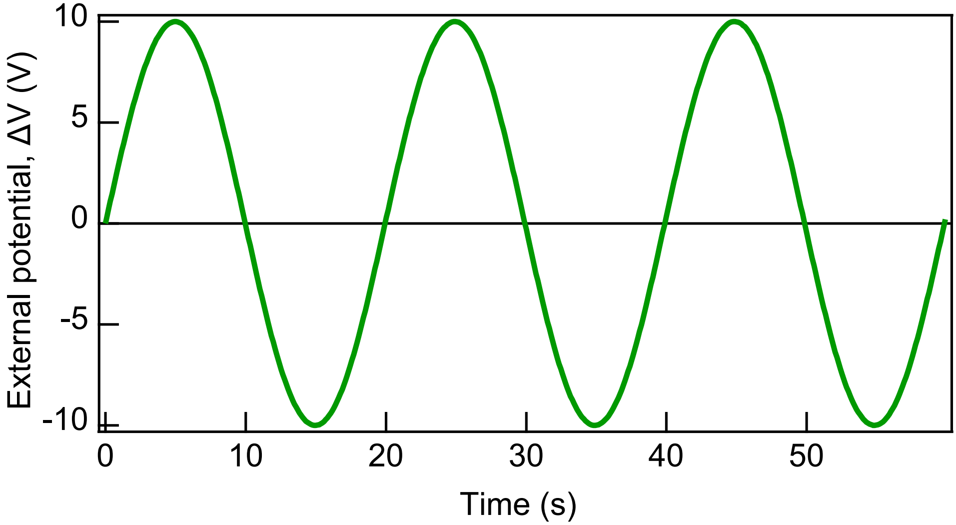
How does the intensity / contrast relate to the actual number of oriented water molecules ?

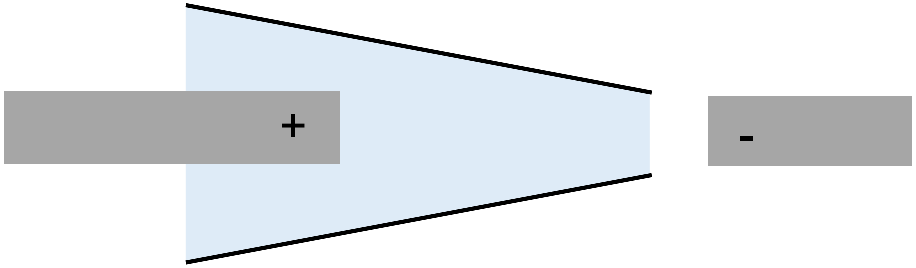
Dynamic Imaging of Water



$$V(t) = V_0 \sin ft$$

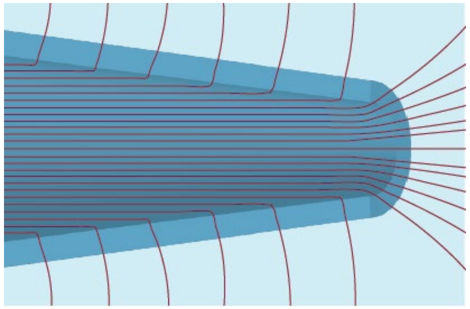
f=0.05 Hz
20 s period



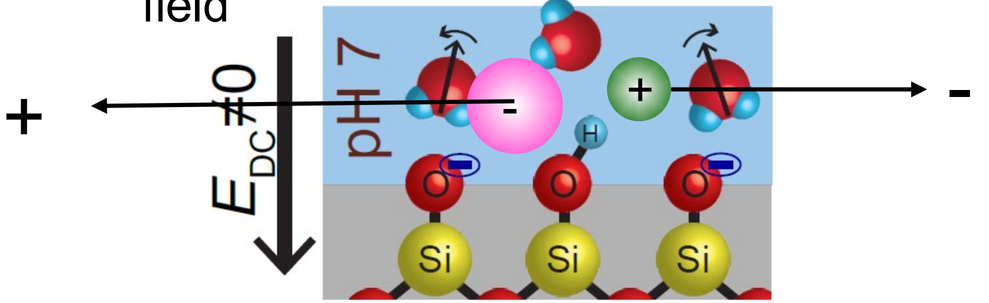


~0.5 mm thick Ag electrodes
Tip opening: 1 μm

Inside Tip:
Field lines are concentrated in the narrow opening

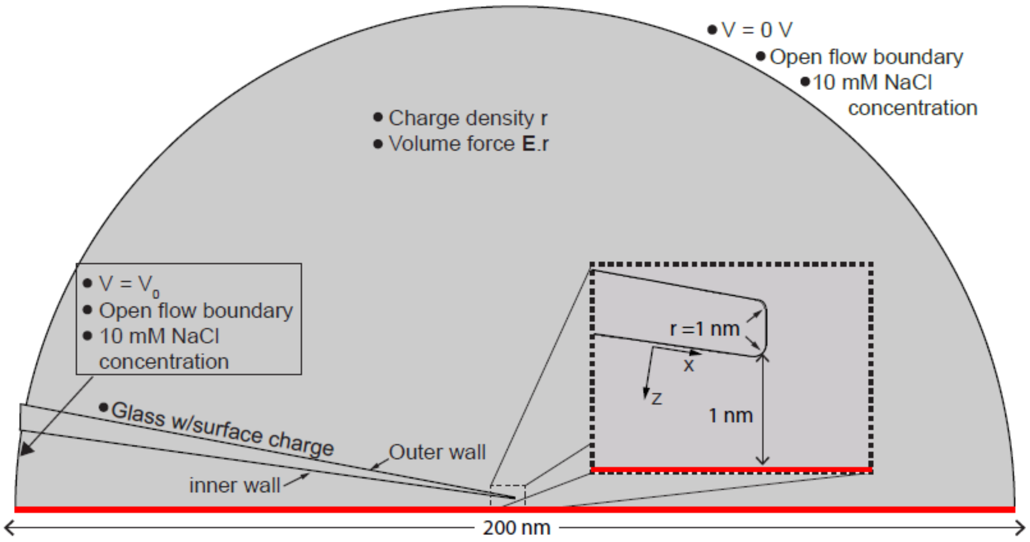


Inside electric double layer:
Separation of charges by external field



Model (COMSOL)

Science (2017) 357, 784-788



Numerical solution to equations describing surface charge and charge flow

Solve Poisson-Nernst-Planck-Stokes Equations to numerically extract the charge density and electric field / potential in the capillary:

$$\boldsymbol{J}_i = -D_i \nabla c_i - \frac{D_i}{RT} z_i F c_i \nabla \Phi(\boldsymbol{r}) + c_i \boldsymbol{u}$$

$$\nabla^2 \Phi(\boldsymbol{r}) = -\frac{\rho(\boldsymbol{r})}{\varepsilon_0 \varepsilon_r}$$

$$\eta \nabla^2 \boldsymbol{u} = \rho_e(\mathbf{r}) \nabla \Phi(\boldsymbol{r}) + \nabla P$$

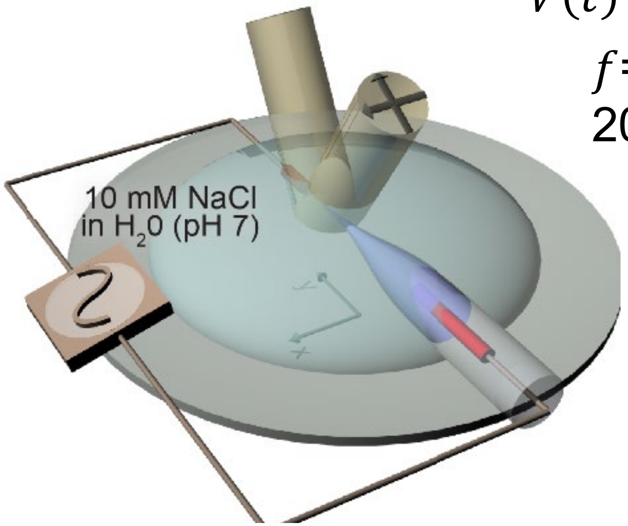
$$\rho_e(\boldsymbol{r}) = F \sum_i z_i c_i(\boldsymbol{r})$$

J: ion flux
c: concentration
D: diffusion constant
Φ: Electric Potential
ρ: Charge density
z: Valency
P: pressure of the liquid
u: velocity of liquid
η: dynamic viscosity
i: species

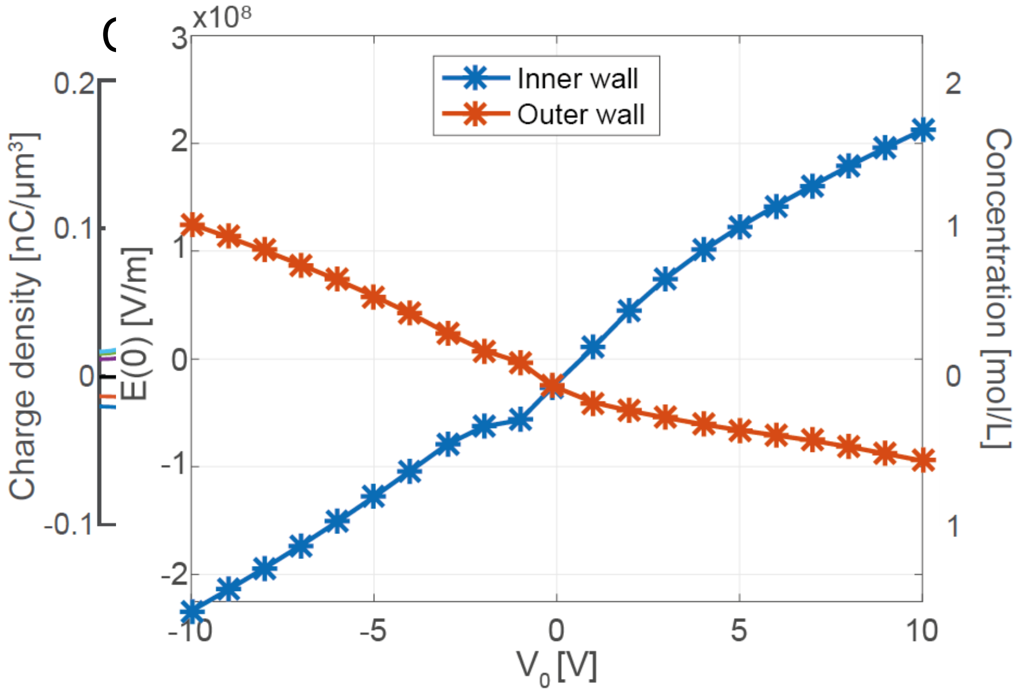
Dynamic surface imaging

$$V(t) = V_0 \sin ft$$

f=0.05 Hz
20 s perio

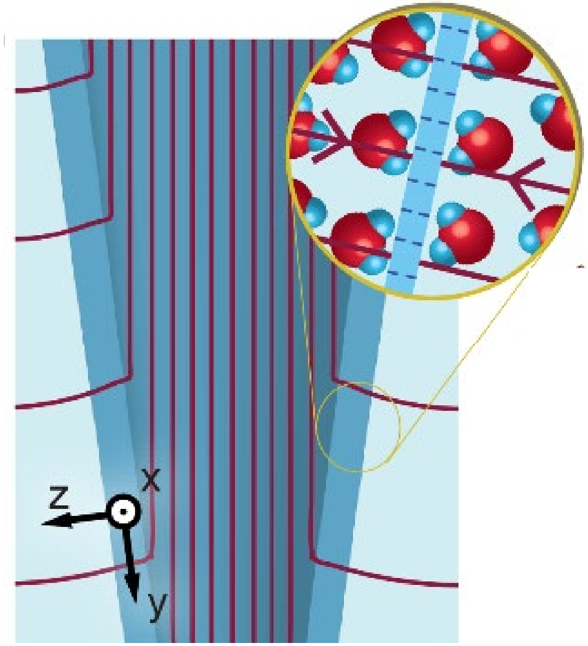


E-field at interface



The external bias redistributes the Na^+ and Cl^- ions in the DDL leading to different charge densities and surface electrostatic field amplitudes

Water molecules follow those field lines and are made to rotate

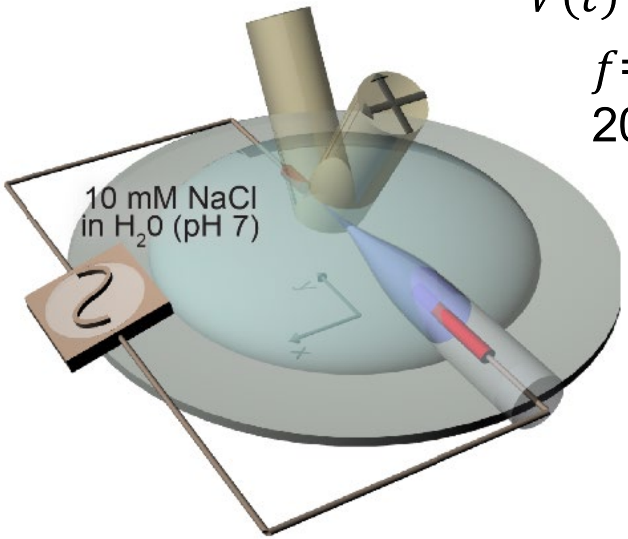


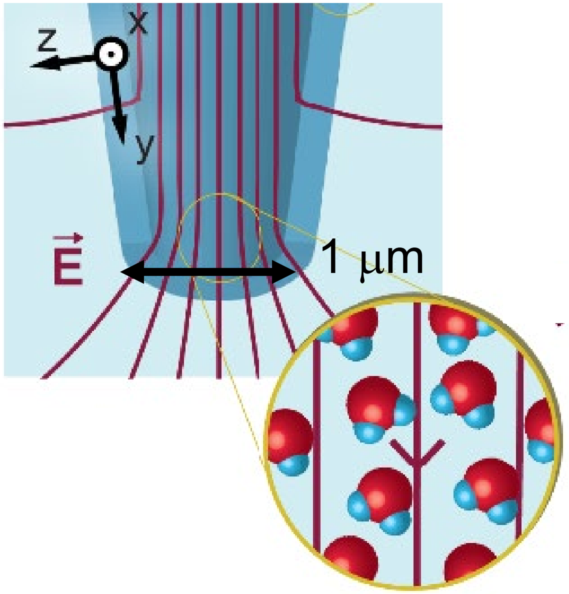
Science (2017) 357, 784-788

Dynamic SH imaging of water in a pore

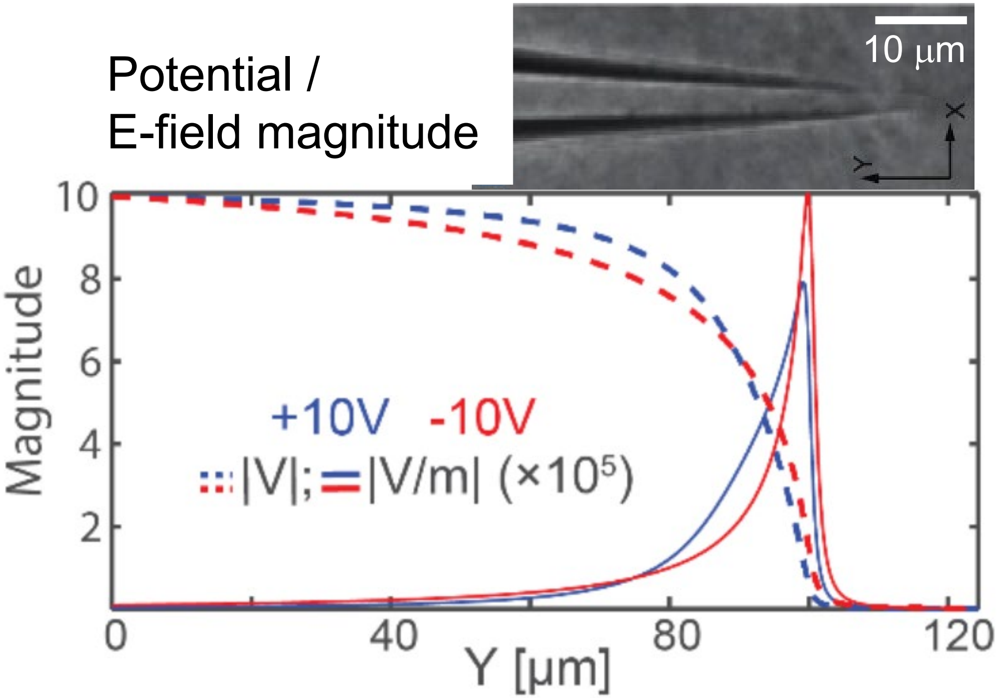
$V(t) = V_0 \sin ft$

f=0.05 Hz
20 s period





Potential /
E-field magnitude



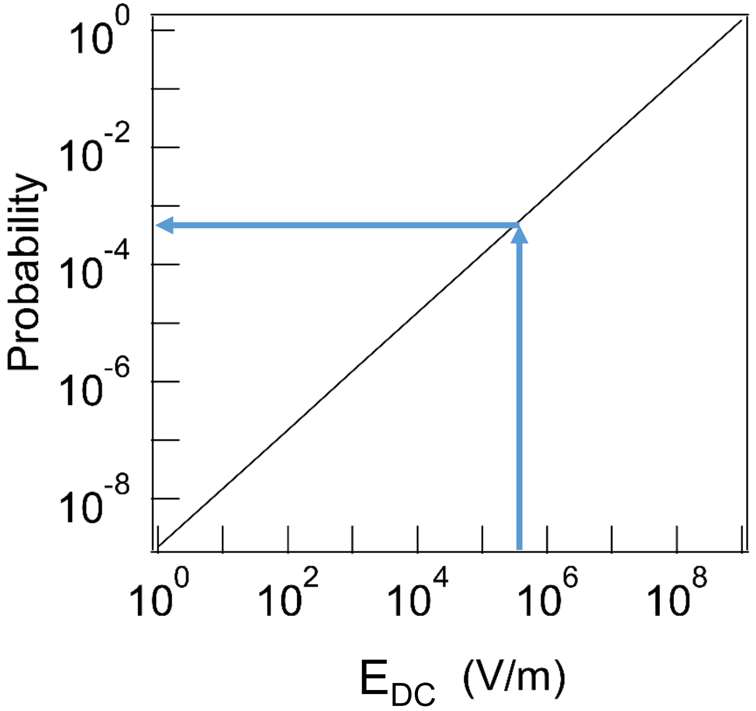
Inside the 1 µm wide opening the electrostatic field reaches values of $E_{DC}=10^6$ V/m

Science (2017) 357, 784-788

Oriented Water?– use Boltzmann Distribution

Probability to find an oriented water molecule

$$P = \frac{\int_0^\pi \cos\theta\, e^{-\frac{\mu E}{kT}} \sin\theta\, d\theta}{\int_0^\pi e^{-\frac{\mu E}{kT}} \sin\theta\, d\theta}$$



With $E_{DC}=10^6$ V/m a fraction of $5\ 10^{-4}$ water molecules are oriented.

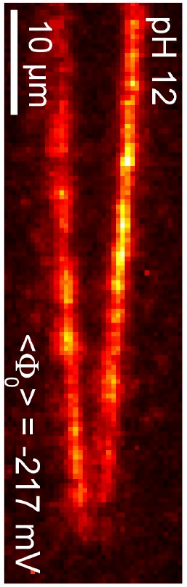
Volume of 1 pixel: $7.5\ 10^{-17}$ L
~ 55 mol/L = molar volume for room temp water (=density / molar mass)

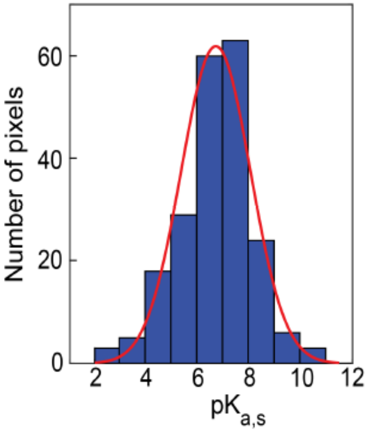
$1.2 \cdot 10^6$ oriented water molecules / pixel

At interface: Similar analysis shows that 64 % of the SH intensity from E_{DC}-field oriented water originates from within a 1 nm thick slab

Science (2017) 357, 784-788

SH imaging of water





SH imaging of surface potentials and chemical reaction constants

- High throughput SH imaging of aqueous interfaces can be performed on millisecond time scales
- Surface potential images can be constructed
- Structural heterogeneities are observed that inform about dynamic chemical reactivity differences

- Dynamically oriented water can be imaged with 250 ms acquisition time
- Very sensitive – a tiny fraction of water can be seen

C. Macias-Romero, I. Nahalka, H. I. Okur, S. Roke, Science (2017) 357,10.1126/science.aal4346

Key concepts Lecture 12

Measuring interfaces – 2 strategies:
(1) - Using reflective properties – total internal reflection, Brewster angle, metal surfaces – in combination with specific engineered surfaces /geometries it is possible to measure vibrational spectra of interfaces.
(2) - Using symmetry selection rules in combination with second-order nonlinear spectroscopy / imaging provides intrinsic interface specificity

- Some principles behind non-linear optics
- Vibrational SFG: how spectra can be understood and what they reveal
- SH imaging: how SH contrast is interpreted for resonant and non-resonant conditions – possibility to quantify the surface potential in space and time and determine contrast and probing depth