Static, 2D, and time-resolved vibrational spectroscopy in bulk and at interfaces

Ellen Backus
University of Vienna and Max Planck Institute for Polymer Research Mainz

Part I

Interface specific vibrational spectroscopy

Introduction

Surfaces important for:

- Catalysis
- Electrochemistry
- Biochemistry
- …

Introduction

- How does the surface look like?
- What is the interaction of adsorbates with surface?
- How strongly are molecules bound?
- What is the reaction mechanism?

Required: molecular specific information at an interface

Solution: sum frequency generation spectroscopy
(as will be shown in this lecture)

Introduction

Required: molecular specific information at an interface

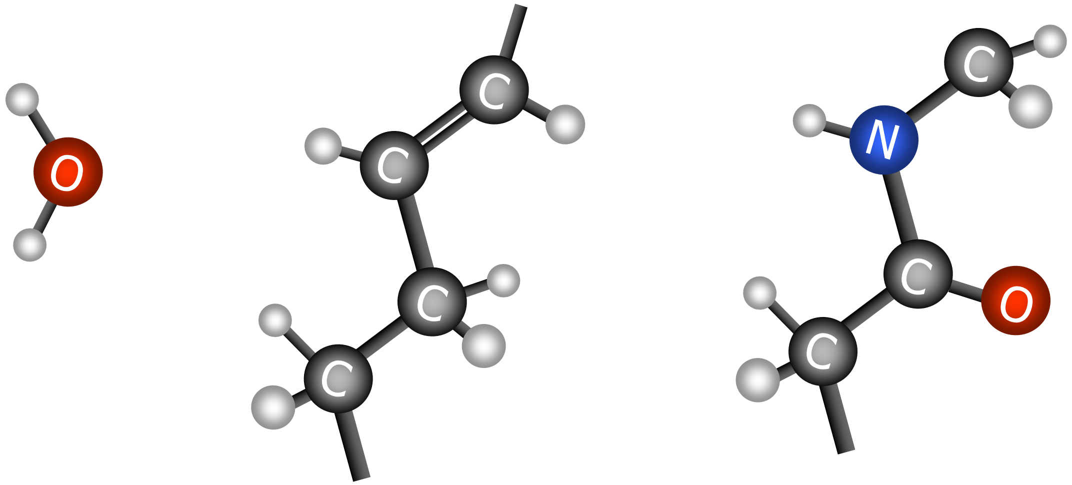
Two ingredients:

1. Molecular specificity
2. Surface sensitivity

Approach

The wiggling and jiggling of molecules is very specific

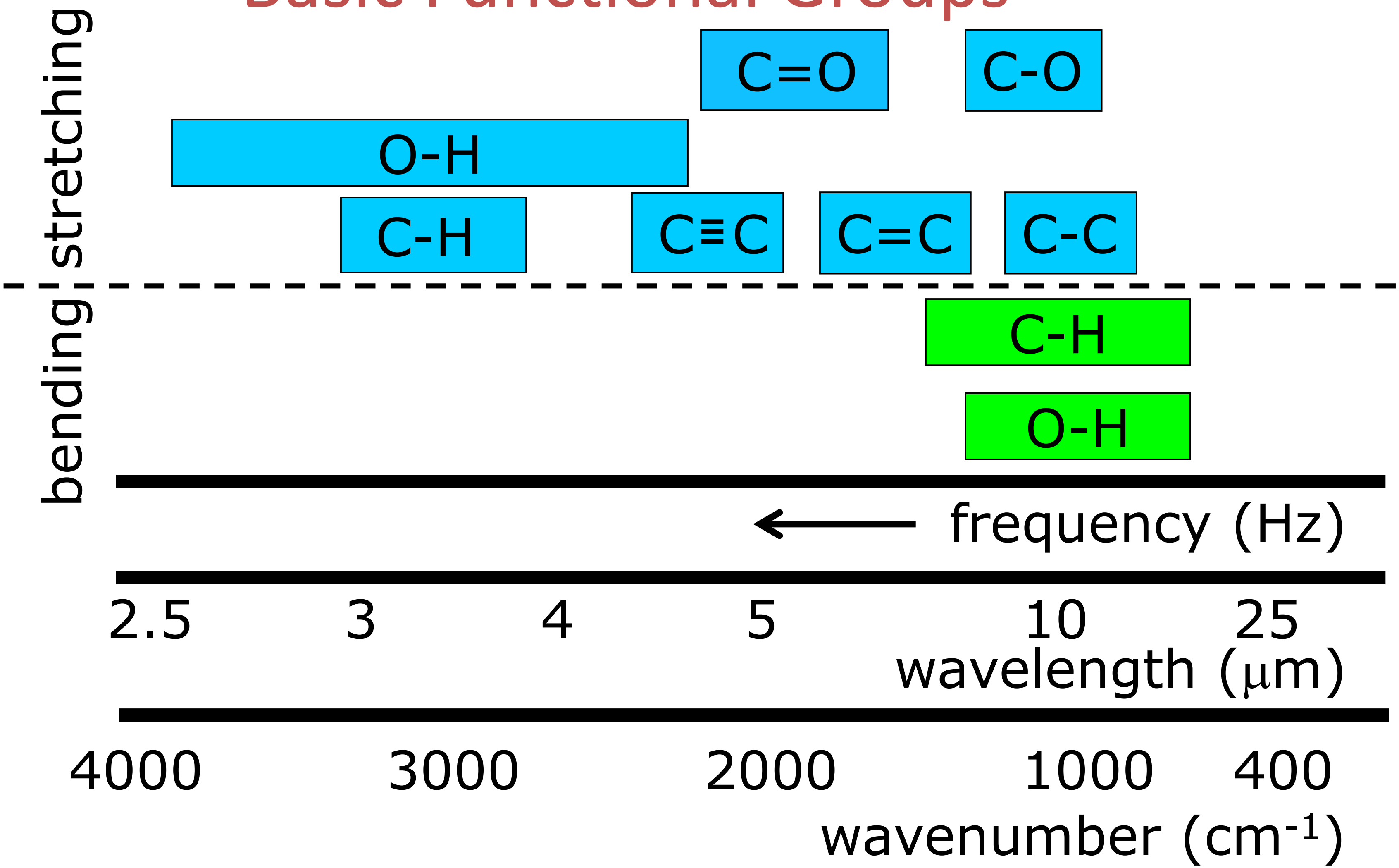
Water Lipids Proteins



A chemical bond is just like a spring: the oscillation frequency is given by the strength of the chemical bond and the masses of the atoms involved.

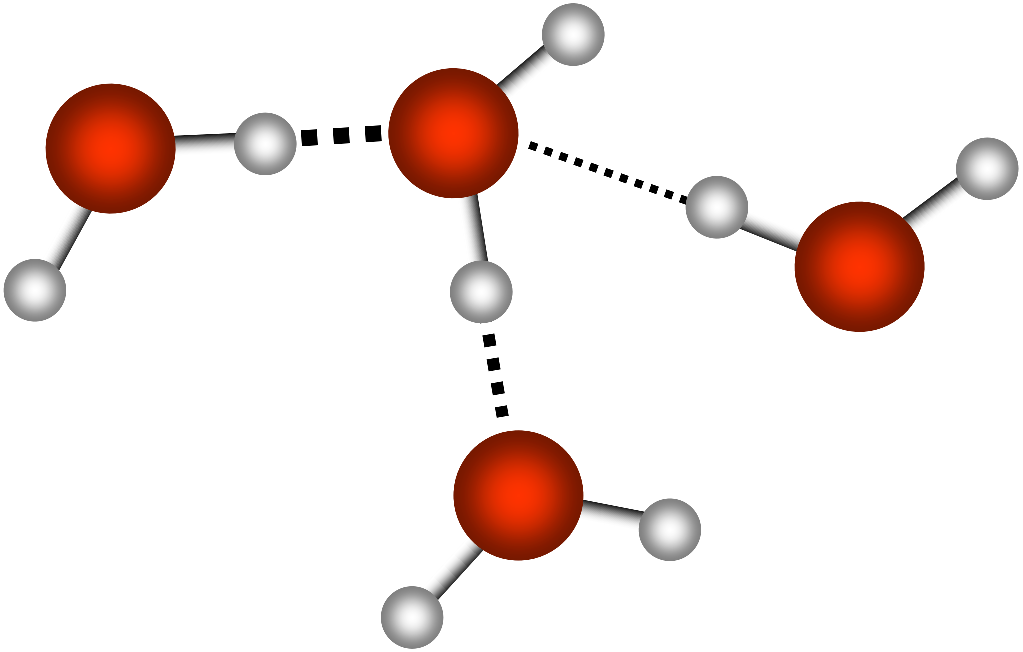
Vibrational frequencies

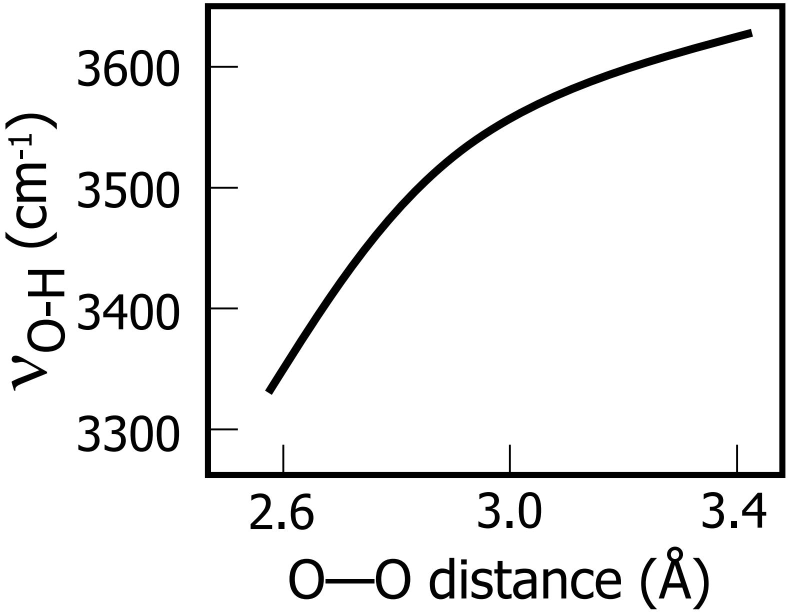
Basic Functional Groups



Sensitivity to environment

Water displays strong variation in H-bond strengths, which affect O—H stretch vibration

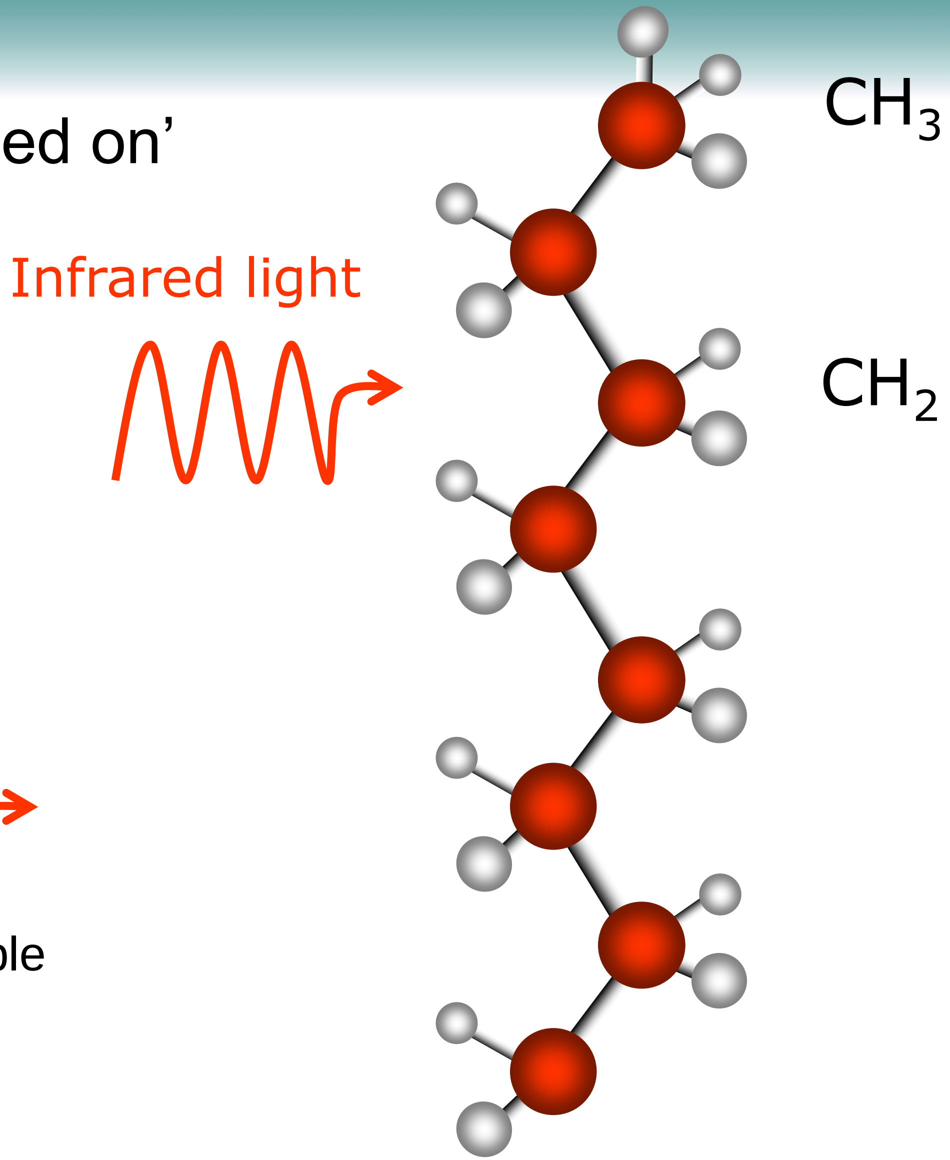




O—H stretch vibration is a marker of local water environment

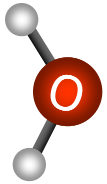
Approach

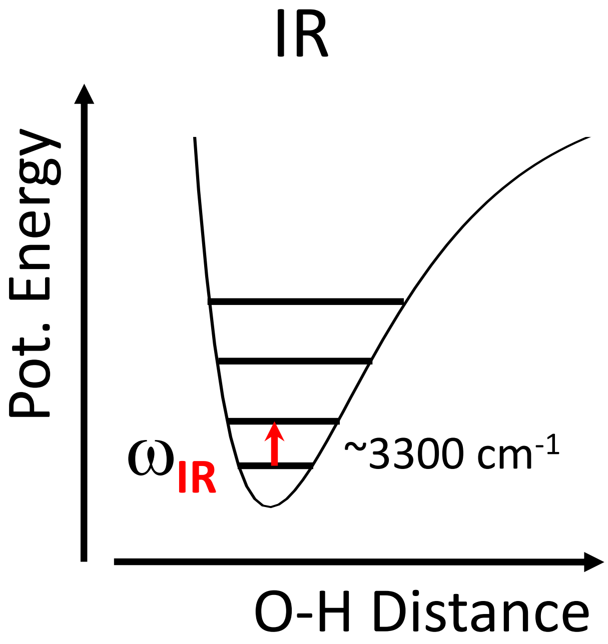
The vibration can be ‘switched on’ with infrared (IR) light



Compare IR light without and with sample

Vibrational infrared spectroscopy



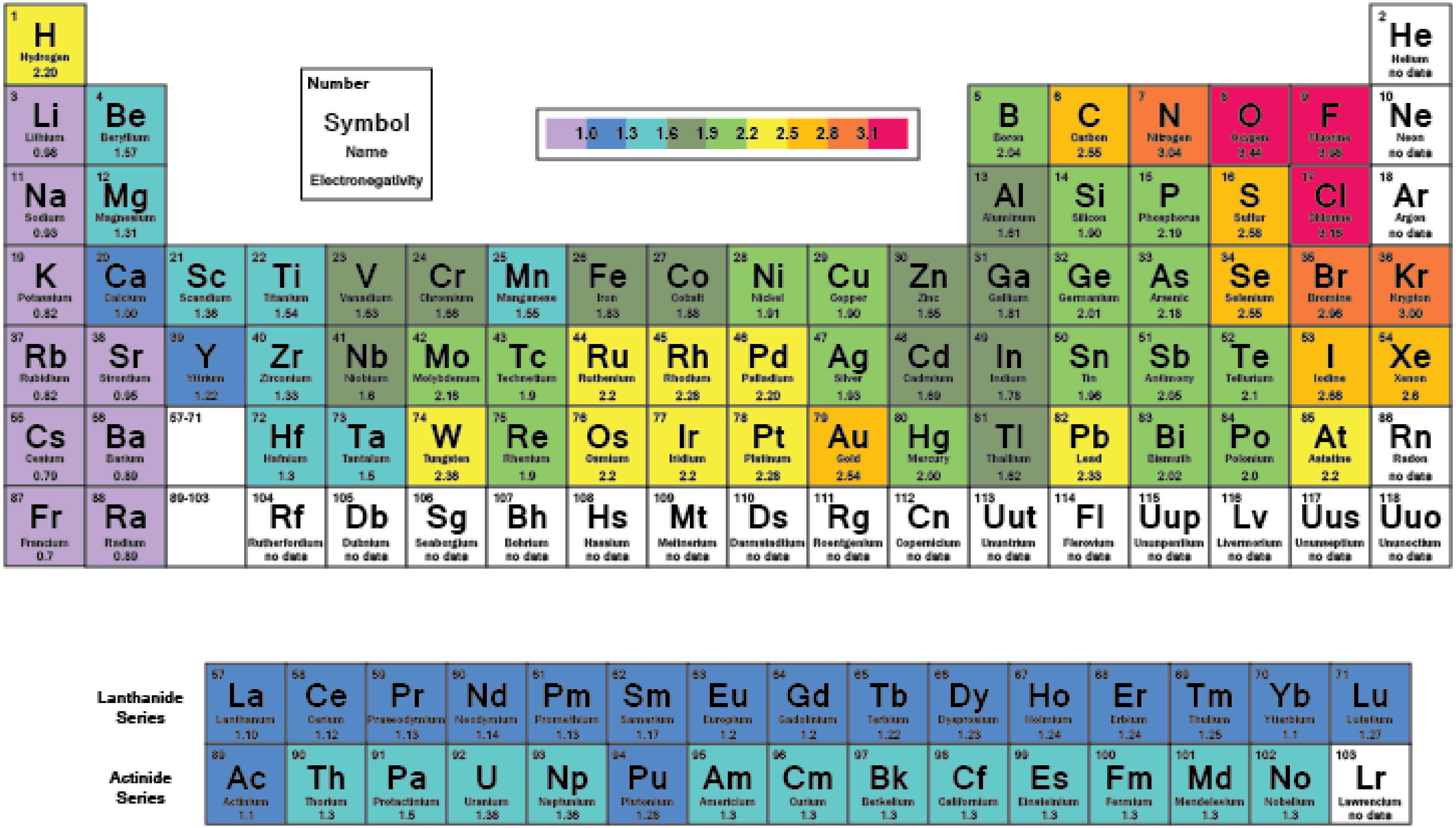


- With background, IR detection
- Not sensitive
- Not surface specific

<u>Selection rule</u>

dipole moment of molecule should change during vibration

Electronegativity



Number
Symbol
Name
Electronegativity

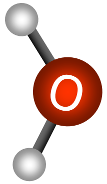
1.0 1.3 1.6 1.9 2.2 2.5 2.8 3.1

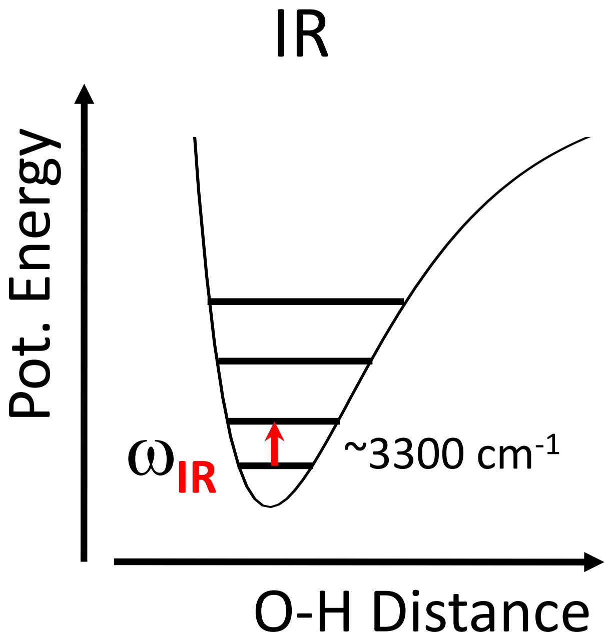
1 H Hydrogen 2.20																	2 He Helium no data
3 Li Lithium 0.98	4 Be Beryllium 1.57											5 B Boron 2.04	6 C Carbon 2.55	7 N Nitrogen 3.04	8 O Oxygen 3.44	9 F Fluorine 3.98	10 Ne Neon no data
11 Na Sodium 0.93	12 Mg Magnesium 1.31											13 Al Aluminum 1.61	14 Si Silicon 1.90	15 P Phosphorus 2.19	16 S Sulfur 2.58	17 Cl Chlorine 3.16	18 Ar Argon no data
19 K Potassium 0.82	20 Ca Calcium 1.00	21 Sc Scandium 1.36	22 Ti Titanium 1.54	23 V Vanadium 1.63	24 Cr Chromium 1.66	25 Mn Manganese 1.55	26 Fe Iron 1.83	27 Co Cobalt 1.88	28 Ni Nickel 1.91	29 Cu Copper 1.90	30 Zn Zinc 1.65	31 Ga Gallium 1.81	32 Ge Germanium 2.01	33 As Arsenic 2.18	34 Se Selenium 2.55	35 Br Bromine 2.96	36 Kr Krypton 3.00
37 Rb Rubidium 0.82	38 Sr Strontium 0.95	39 Y Yttrium 1.22	40 Zr Zirconium 1.33	41 Nb Niobium 1.6	42 Mo Molybdenum 2.16	43 Tc Technetium 1.9	44 Ru Ruthenium 2.2	45 Rh Rhodium 2.28	46 Pd Palladium 2.20	47 Ag Silver 1.93	48 Cd Cadmium 1.69	49 In Indium 1.78	50 Sn Tin 1.96	51 Sb Antimony 2.05	52 Te Tellurium 2.1	53 I Iodine 2.66	54 Xe Xenon 2.6
55 Cs Cesium 0.79	56 Ba Barium 0.89	57-71	72 Hf Hafnium 1.3	73 Ta Tantalum 1.5	74 W Tungsten 2.36	75 Re Rhenium 1.9	76 Os Osmium 2.2	77 Ir Iridium 2.2	78 Pt Platinum 2.28	79 Au Gold 2.54	80 Hg Mercury 2.00	81 Tl Thallium 1.62	82 Pb Lead 2.33	83 Bi Bismuth 2.02	84 Po Polonium 2.0	85 At Astatine 2.2	86 Rn Radon no data
87 Fr Francium 0.7	88 Ra Radium 0.89	89-103	104 Rf Rutherfordium no data	105 Db Dubnium no data	106 Sg Seaborgium no data	107 Bh Bohrium no data	108 Hs Hassium no data	109 Mt Meitnerium no data	110 Ds Darmstadtium no data	111 Rg Roentgenium no data	112 Cn Copernicium no data	113 Uut Ununtrium no data	114 Fl Flerovium no data	115 Uup Ununpentium no data	116 Lv Livermorium no data	117 Uus Ununseptium no data	118 Uuo Ununoctium no data

Lanthanide Series	57 La Lanthanum 1.10	58 Ce Cerium 1.12	59 Pr Praseodymium 1.13	60 Nd Neodymium 1.14	61 Pm Promethium 1.13	62 Sm Samarium 1.17	63 Eu Europium 1.2	64 Gd Gadolinium 1.2	65 Tb Terbium 1.22	66 Dy Dysprosium 1.23	67 Ho Holmium 1.24	68 Er Erbium 1.24	69 Tm Thulium 1.25	70 Yb Ytterbium 1.1	71 Lu Lutetium 1.27
Actinide Series	89 Ac Actinium 1.1	90 Th Thorium 1.3	91 Pa Protactinium 1.5	92 U Uranium 1.38	93 Np Neptunium 1.36	94 Pu Plutonium 1.28	95 Am Americium 1.3	96 Cm Curium 1.3	97 Bk Berkelium 1.3	98 Cf Californium 1.3	99 Es Einsteinium 1.3	100 Fm Fermium 1.3	101 Md Mendelevium 1.3	102 No Nobelium 1.3	103 Lr Lawrencium no data

http://sciencenotes.org/wp-content/uploads/2014/05/PeriodicTableElectronegativity.png

Vibrational infrared spectroscopy





- With background, IR detection
- Not sensitive
- Not surface specific

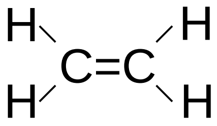
<u>Selection rule</u>

dipole moment of molecule should change during vibration

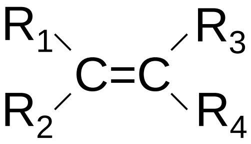
Which molecules are infrared active?

C=O

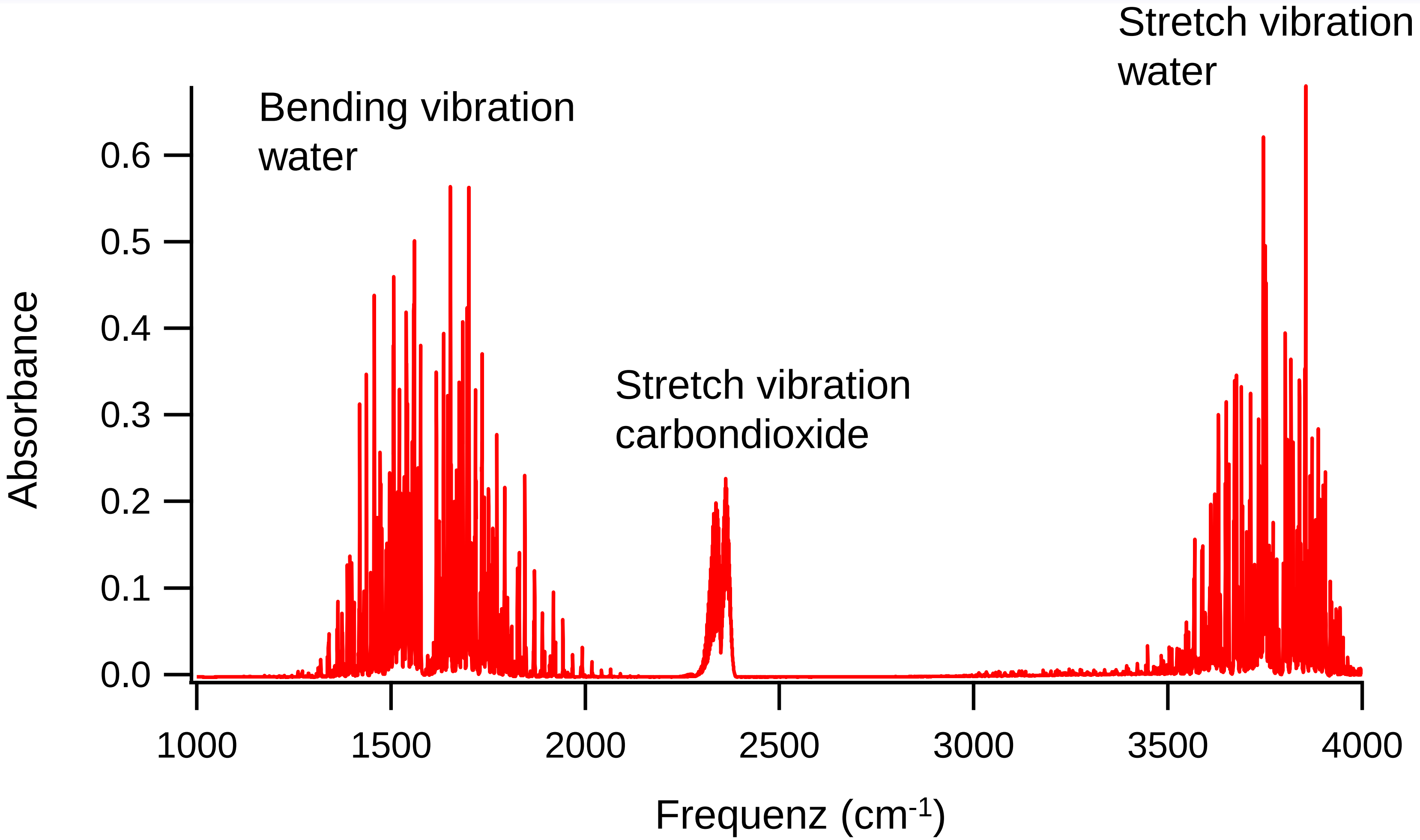
N=N



O=C=O

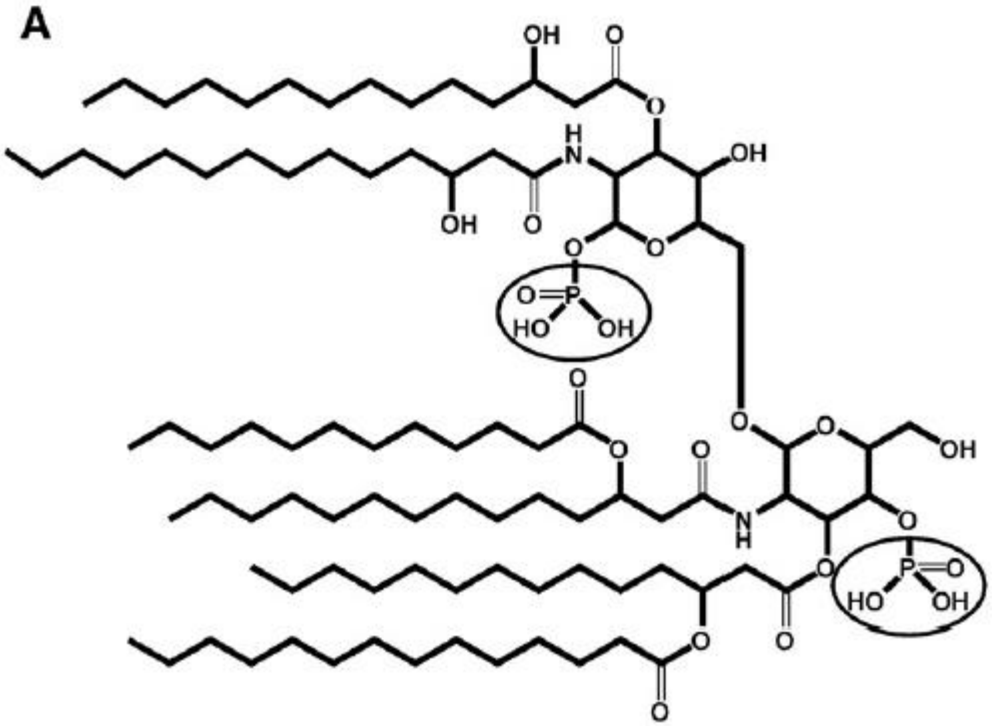


IR spectrum air

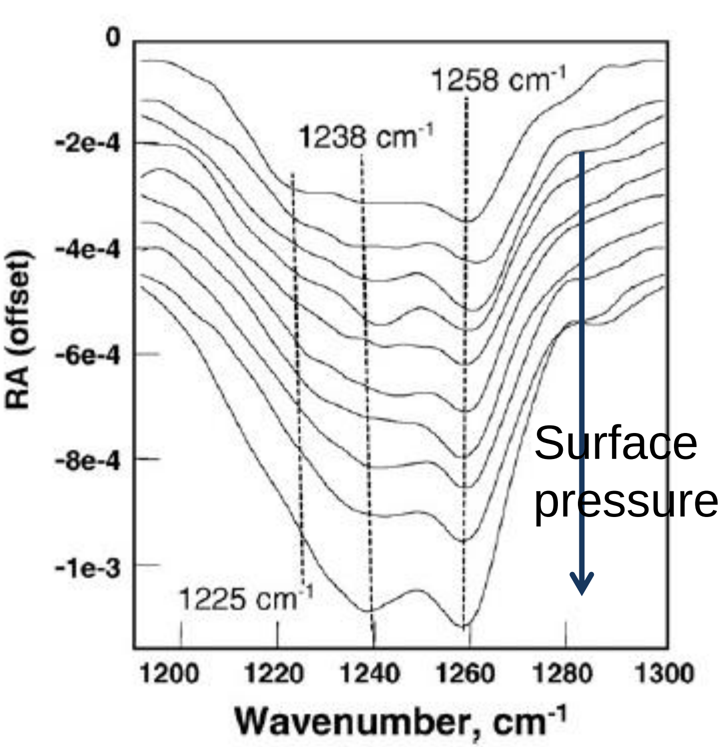


Rotational transitions on top of the vibrations

IRRAS water-lipid monolayer



Phosphate vibrations
1258 cm^{-1}: unhydrated
1238 cm^{-1}: monohydrated
1225 cm^{-1}: dihydrated



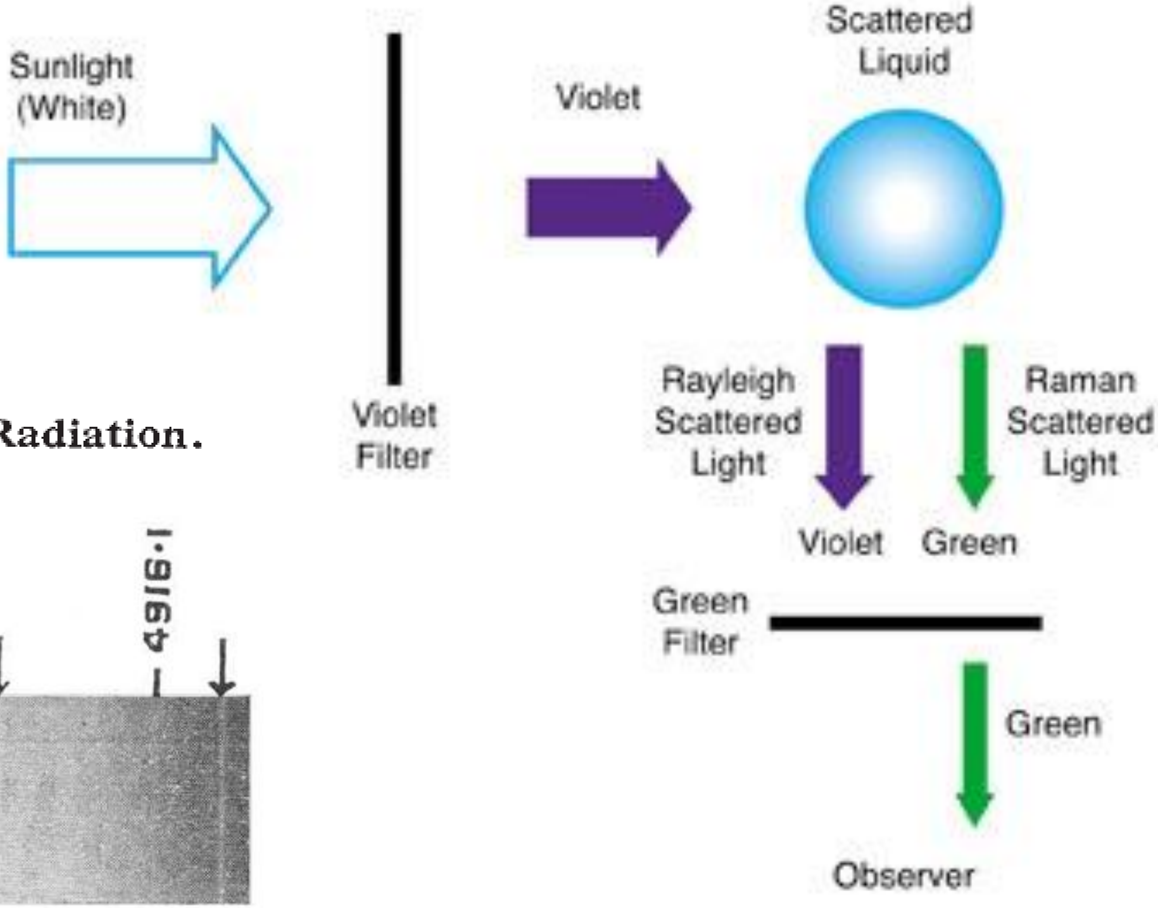
Surface pressure

Upon compression, relative peak intensities changes, revealing a structural or environmental change in the vicinity of the lipid polar head group.

R. Mendelsohn et al. / Biochimica et Biophysica Acta 1798 (2010) 788–800

Scattering experiment

Raman und Krishnan



Sunlight (White)

Violet Filter

Violet

Scattered Liquid

Rayleigh Scattered Light

Raman Scattered Light

Violet

Green

Green Filter

Green

Observer

The Negative Absorption of Radiation.

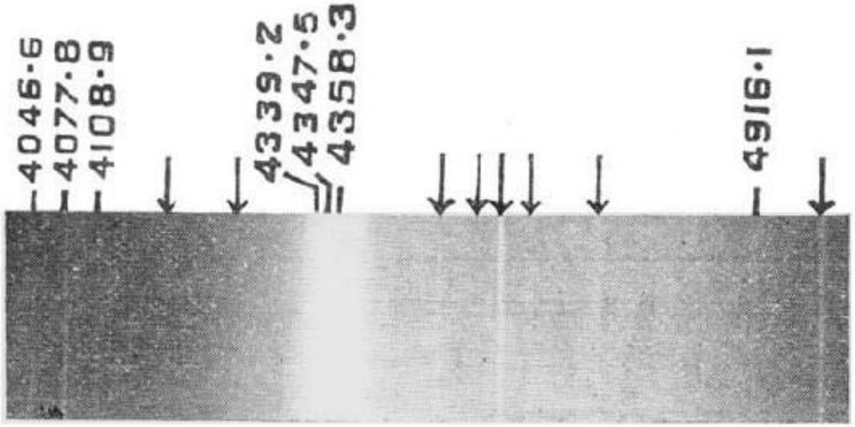
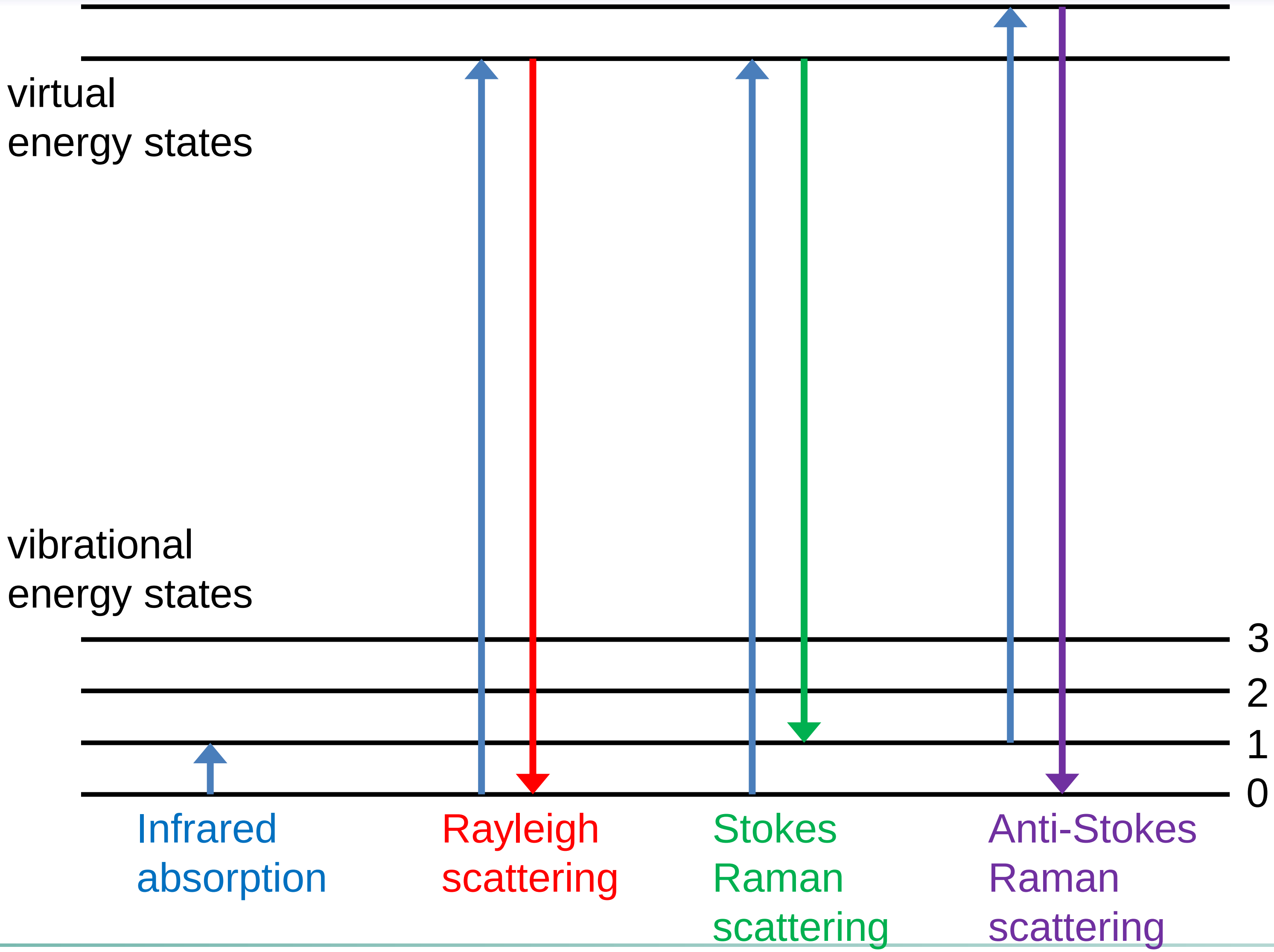


FIG. 1.

Nature 122 (1928) 12

Raman energy-level diagram



virtual
energy states

vibrational
energy states

3
2
1
0

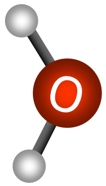
Infrared
absorption

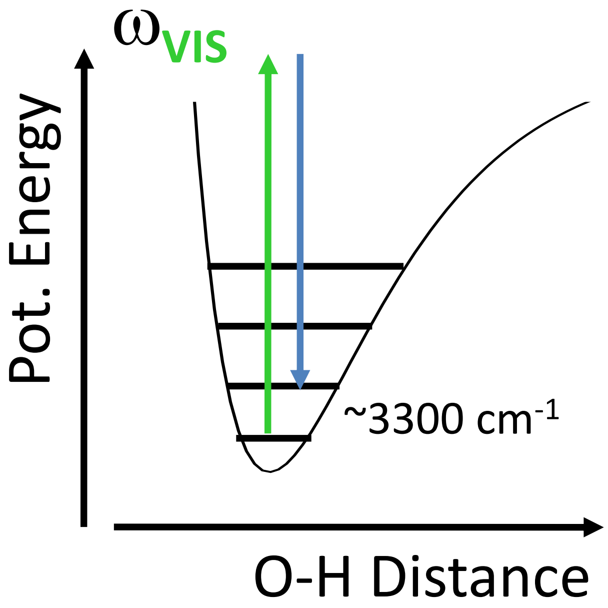
Rayleigh
scattering

Stokes
Raman
scattering

Anti-Stokes
Raman
scattering

Vibrational Raman spectroscopy





- With background, VIS detection
- Not sensitive
- Not surface specific
- Suited for microscopy

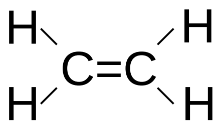
Selection rule

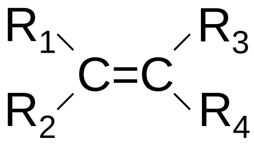
polarizability (tendency of charge distribution to be distorted by external electromagnetic field) of molecule should change during vibration

Which molecules are Raman active?

N=N

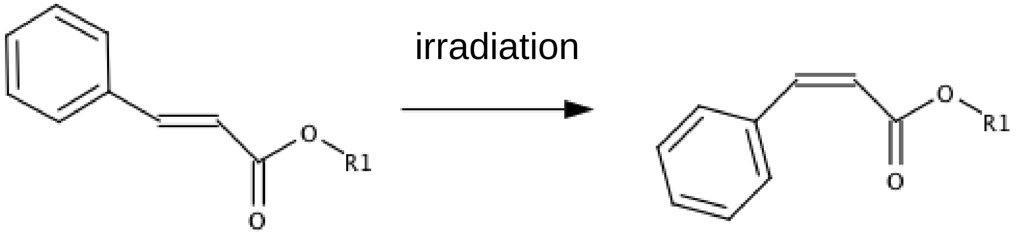
C=O





O=C=O

Compare IR and Raman

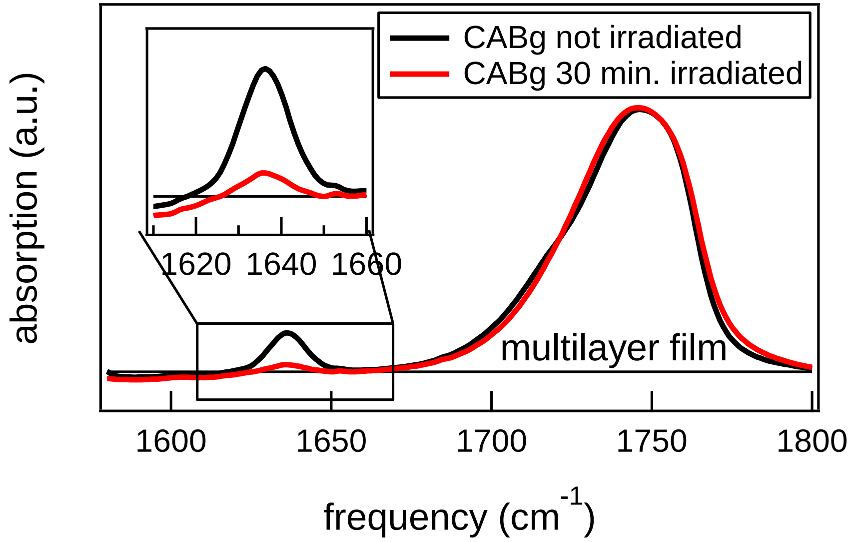


trans

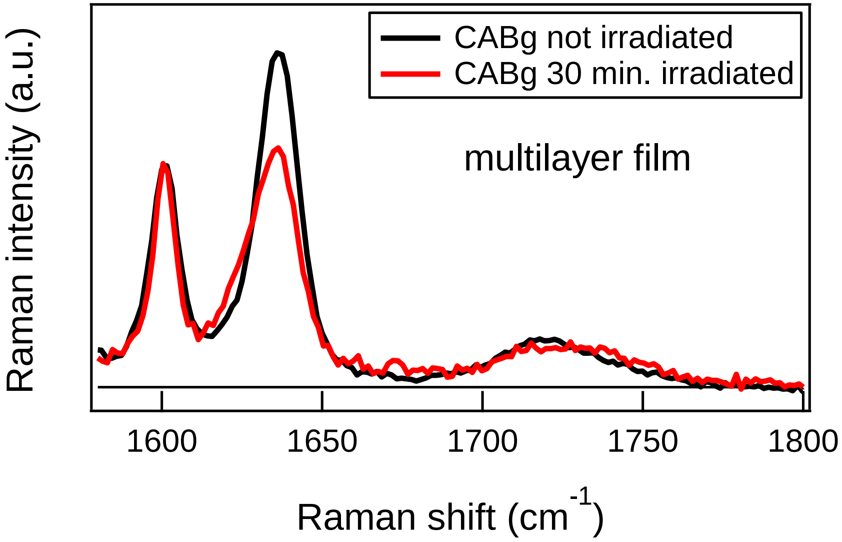
cis

1600: C=C stretch benzene
1640: C=C stretch
1750: C=O stretch

infrared



Raman



Vibrational spectroscopy

- Identification of functional groups on a molecule: label-free molecular info
- Shape and frequency of spectral response reflects local molecular environment
- Absorbance follows Beer's Law:

  Abs=extinction coefficient*concentration*pathlength

  $\Rightarrow$ can do quantitative analysis

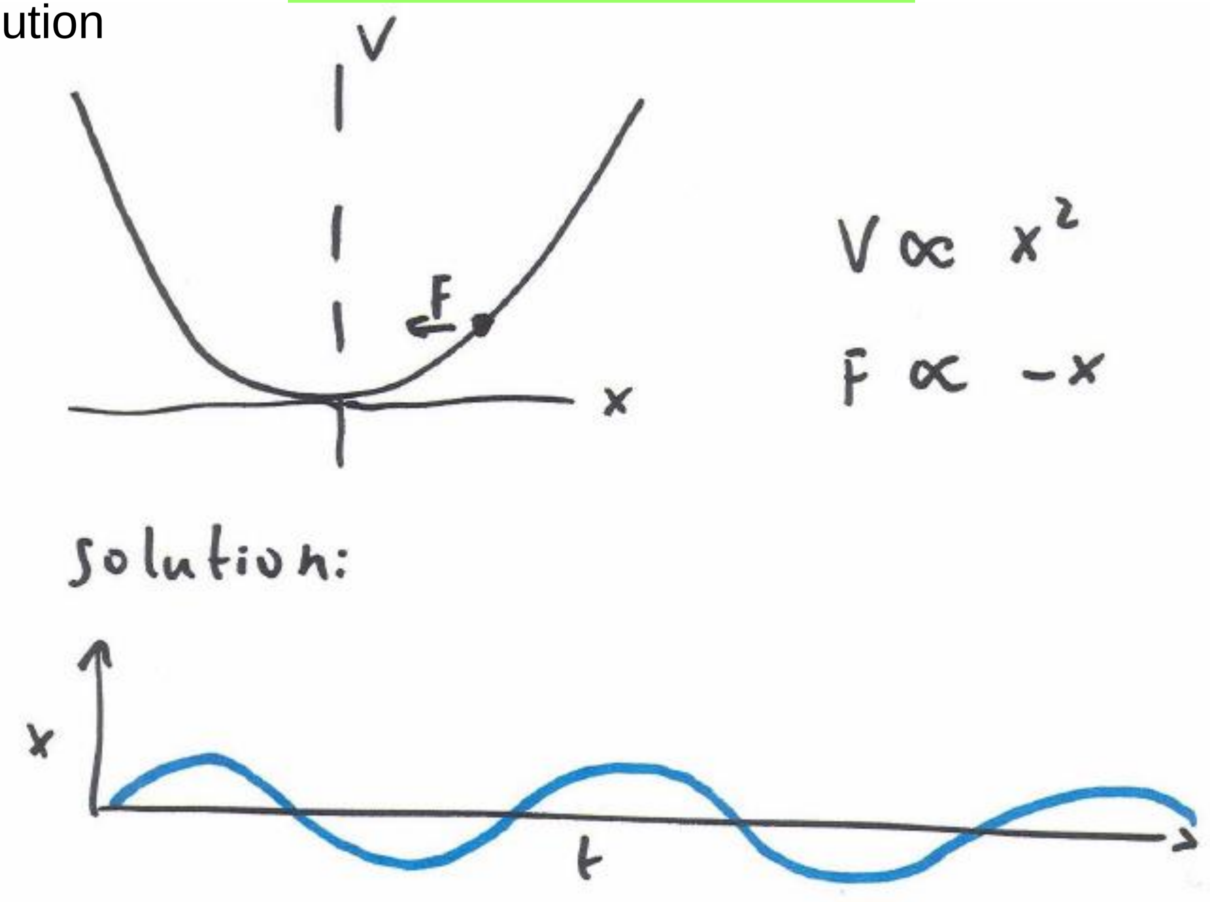
- But….. need advanced methods to investigate surfaces/interfaces

Linear optics

Polarization P:
non-equilibrium
charge distribution
created by E

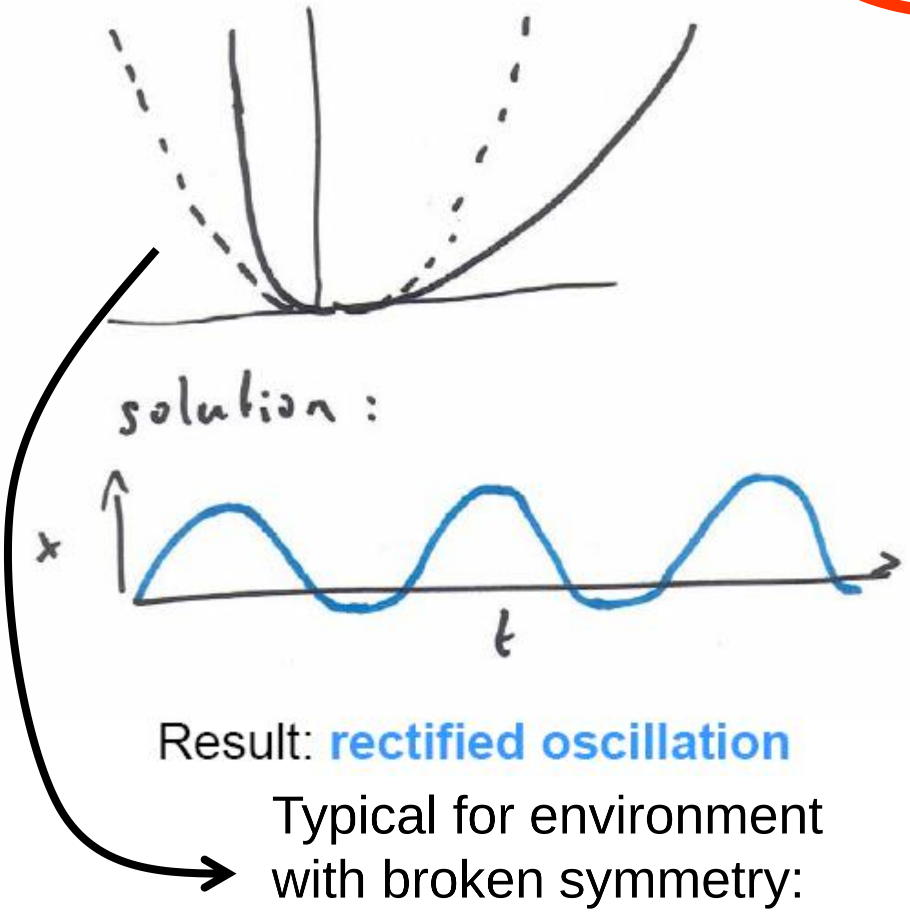
$$P(\omega) = \epsilon_0\ \chi(\omega) E(\omega)$$

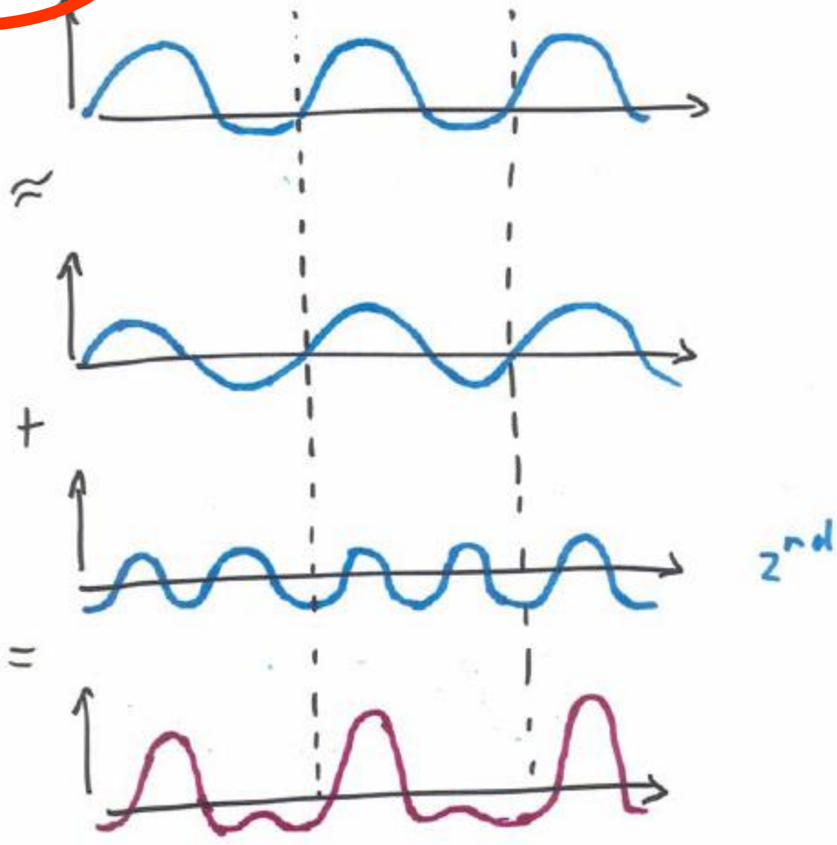
with $\chi = \chi^{(1)}$



Nonlinear optics

$$P(t) \propto \chi^{(1)} E(t) + \boxed{\chi^{(2)} E^2(t)} + \chi^{(3)} E^3(t) + \cdots.$$





Result: **rectified oscillation**

Typical for environment
with broken symmetry:
Surface / interface

First second harmonic experiment

1961, 694 nm light on quartz plate

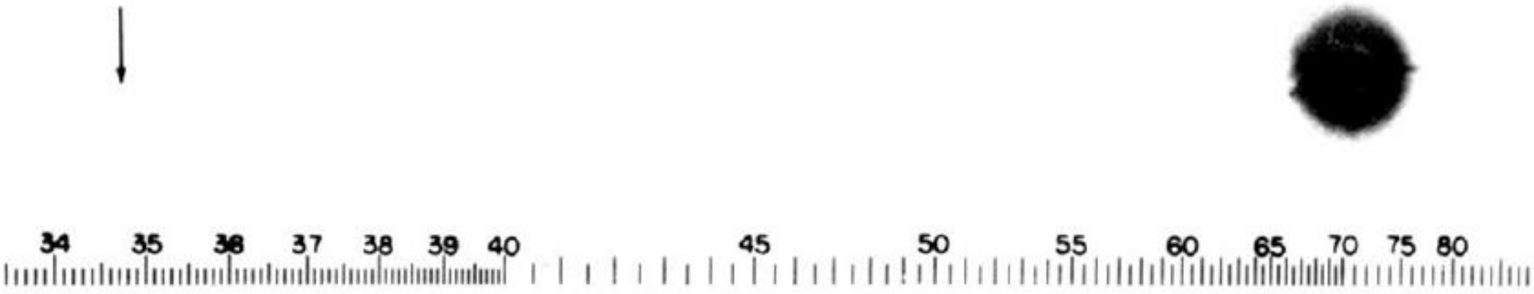


FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

Phys. Rev. Lett. **1961,** *7,* 118-119

Theory: nonlinear optics

The electric field of a light wave propagating through a medium exerts a force on the electrons of the molecules. Low intensity light, then

$$\mu = \mu_0 + \alpha E$$

polarisability of molecular electrons

static permanent dipole

The sum of the molecular electric dipoles gives rise to a bulk polarisation:

$$P = \varepsilon_0 \chi^{(1)} E$$ (considering only the induced polarisation)

$\chi^{(1)}$ is average of α

By increasing field strength, non-linearity terms become important:

$$\mu = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \ldots$$

first order hyperpolarisability

second order hyperpolarisability

Theory: nonlinear optics

$$P(t) \propto \chi E(t)$$

$$\propto \chi^{(1)} E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 + \ldots$$

Theory: nonlinear optics

$$P(t) \propto \chi E(t)$$

$$\propto \chi^{(1)} E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 + \ldots$$

Second Harmonic Generation

Optical Rectification

$$P^{(2)}(t) \propto \chi^{(2)} \begin{pmatrix} E_1^2\left(\cos(2\omega_1 t) + \cos((\omega_1 - \omega_1)t)\right) + \\ E_2^2\left(\cos(2\omega_2 t) + \cos((\omega_2 - \omega_2)t)\right) + \\ 2E_1E_2\left(\cos((\omega_1 + \omega_2)t) + \cos((\omega_1 - \omega_2)t)\right) \end{pmatrix}$$

Sum Frequency Generation

Difference Frequency Generation

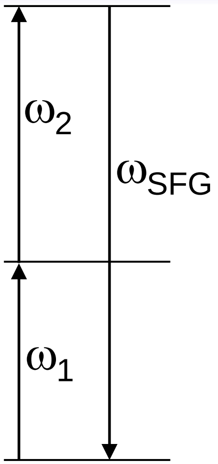
Topic of this lecture

Theory: nonlinear optics

$$P^{(2)} \propto \chi^{(2)} E_1 E_2$$

$$\mu = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \dots$$

$$\chi^{(2)}_{\alpha\beta\gamma} \propto N \sum_{\alpha\beta\gamma} \beta_{\alpha\beta\gamma}$$



$\chi^{(2)}$ has molecular information and is thus the interesting observable to obtain in an experiment

$$E_{\mathrm{SFG}}(\omega_{\mathrm{SFG}}) \propto P^{(2)}(\omega_{\mathrm{SFG}})$$

$$I_{\mathrm{SFG}}(\omega_{\mathrm{SFG}}) = \left|E_{\mathrm{SFG}}(\omega_{\mathrm{SFG}})\right|^2$$

$$I_{\mathrm{SFG}}(\omega_{\mathrm{SFG}}) \propto \left|\chi^{(2)}(\omega)\right|^2 I(\omega_1) I(\omega_2)$$

$\chi^{(2)}$ obtained by measuring the intensity of the SFG signal

Prove of SFG forbidden in centrosymmetric media

Perform a ‘gedanken’ experiment:

$$P^{(2)} \propto \chi^{(2)} E E$$

Apply inversion symmetry operation

$$P^{(2)} = -P^{(2)}, E = -E, \chi^{(2)} = \chi^{(2)}_{\text{inverted}}$$ for centrosymmetric medium

$$-P^{(2)} \propto \chi^{(2)} (-E)(-E) = \chi^{(2)} E E$$

$$\Rightarrow \chi^{(2)} = 0$$

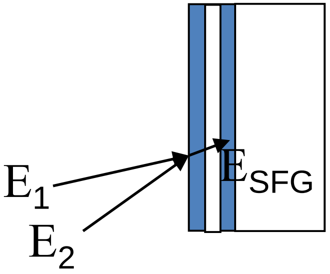
At surface symmetry is broken
⇒ SFG allowed at surface, but forbidden in bulk

Theory: nonlinear optics

Two requirements to obtain SFG signal from bulk materials:

1. phase matching condition

signal from every slab has to interfere positively



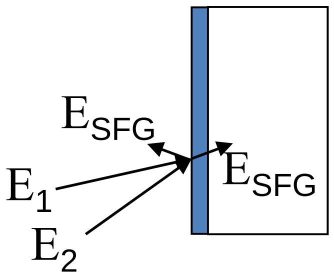
2. material should have a nonzero second-order susceptibility

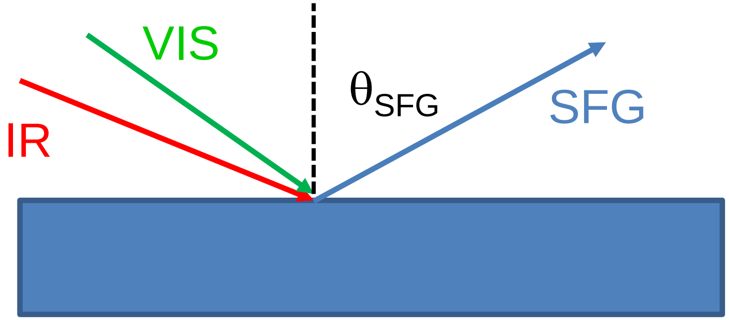
which is not the case for a centrosymmetric medium

At surface symmetry is broken
⇒ SFG allowed at surface, but forbidden in bulk

Theory: nonlinear optics

At surface symmetry is broken for a thin region (~one molecular diameter in thickness) and therefore SFG signal can be generated in reflection and transmission geometry.





Phase matching: conservation of momentum parallel to surface

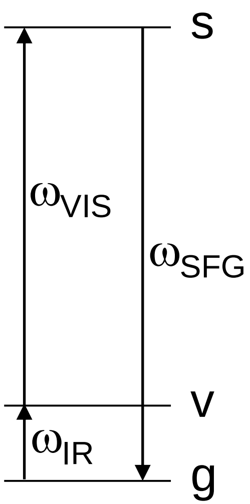
$$n_{SFG}\omega_{SFG}\sin\theta_{SFG} = n_{IR}\omega_{IR}\sin\theta_{IR} + n_{VIS}\omega_{VIS}\sin\theta_{VIS}$$

How to obtain molecular information?

Sum frequency generation

- Infrared spectroscopy molecular specific
- Second-order nonlinear process, like SFG, surface specific

$\Rightarrow$ vibrational sum-frequency generation spectroscopy gives molecular information of an interface



ω_{IR}: resonant with molecular vibration
ω_{VIS}: in general nonresonant

ω_{SFG}: in visible region $\Rightarrow$ “easy” to detect

Theory: nonlinear optics

$$P^{(2)} \propto \chi^{(2)} E_1 E_2$$

$$\chi^{(2)}_{\alpha\beta\gamma} \propto N \sum_{\alpha\beta\gamma} \beta_{\alpha\beta\gamma}$$

$$\boxed{\beta_{\alpha\beta\gamma} = \frac{1}{2\hbar} \frac{M_{\alpha\beta} A_\gamma}{\left(\omega_\upsilon - \omega_{IR} - i\Gamma\right)}}$$

$$M_{\alpha\beta} = \sum_s \left[\frac{\langle g|\mu_\alpha|s\rangle\langle s|\mu_\beta|v\rangle}{\hbar\left(\omega_{SF} - \omega_{sg}\right)} - \frac{\langle g|\mu_\beta|s\rangle\langle s|\mu_\alpha|v\rangle}{\hbar\left(\omega_{VIS} + \omega_{sg}\right)} \right]$$

Raman transition moment

$$A_\gamma = \langle v|\mu_\gamma|g\rangle$$

Infrared transition moment

A.G. Lambert et al.
Appl. Spectr. Rev. 40 (2005) 103

Theory summary

$$P^{(2)}(\omega_{\mathrm{SFG}}) \propto \chi^{(2)}(\omega) E(\omega_{\mathrm{VIS}}) E(\omega_{\mathrm{IR}})$$

$$E_{\mathrm{SFG}}(\omega_{\mathrm{SFG}}) \propto P^{(2)}(\omega_{\mathrm{SFG}})$$

$$I_{\mathrm{SFG}}(\omega_{\mathrm{SFG}}) = \left| E_{\mathrm{SFG}}(\omega_{\mathrm{SFG}}) \right|^2$$

$$\boxed{I_{\mathrm{SFG}}(\omega_{\mathrm{SFG}}) \propto \left| \chi^{(2)}(\omega) \right|^2 I(\omega_{\mathrm{VIS}}) I(\omega_{\mathrm{IR}})}$$

Molecular characteristics are present in $\chi^{(2)}$

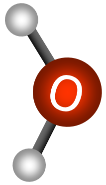
$$\chi = \chi_{NR} + \chi_R$$

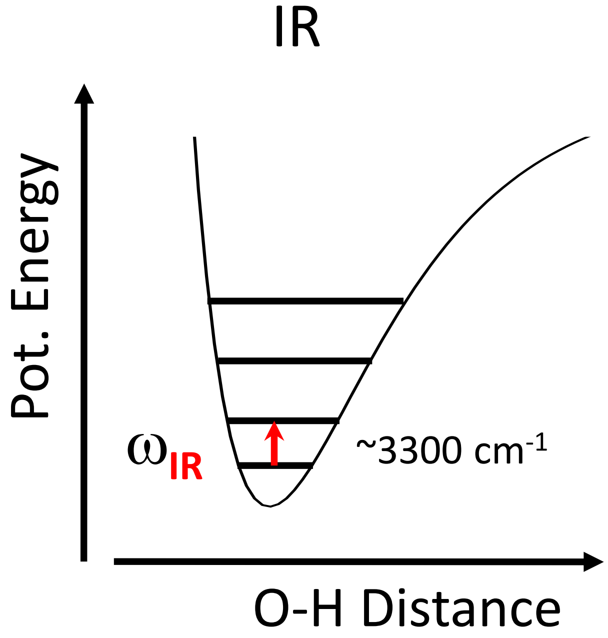
$$\chi_R = \sum_n \frac{N_n M_n A_n}{\omega_{IR} - \omega_n + i\Gamma_n}$$

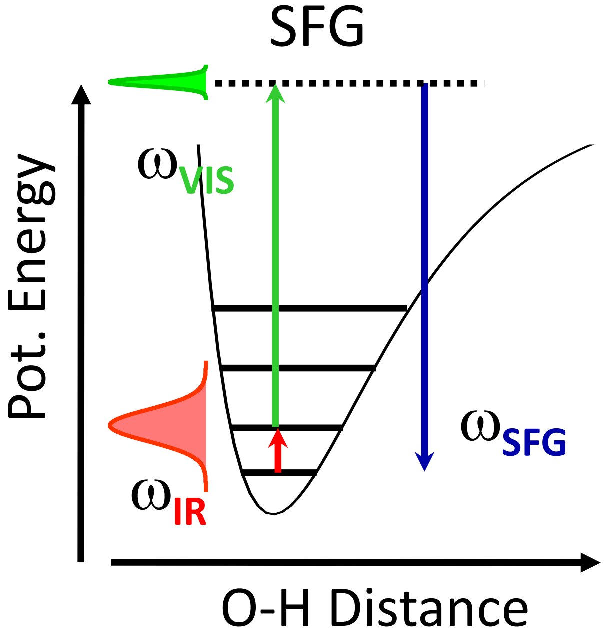
N: number of molecules
M: polarizability (Raman)
A: dipole moment (infrared)
ω: frequency
Γ: linewidth

For SFG a vibration has to be both IR and Raman active!
Large signal if $\omega_{IR}=\omega_n$, i.e. on resonance

Sum-frequency generation





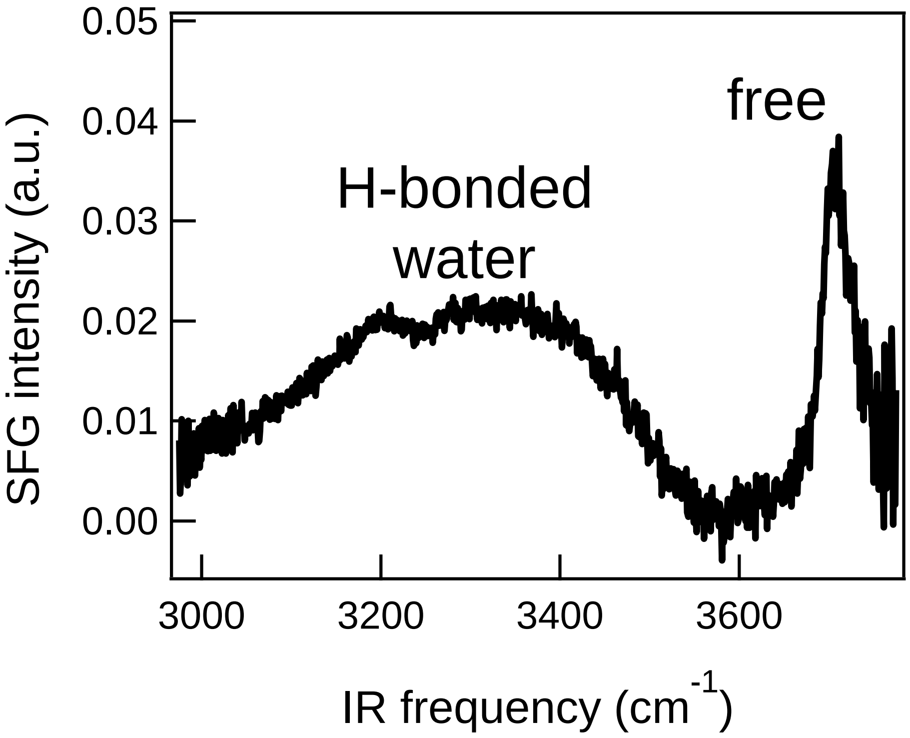


- With background, IR detection
- Not sensitive
- Not surface specific
- Ill-suited for microscopy

- Background-free, visible detection
- Sensitivity: 10^{-3} ML
- Surface specific, because $I_{SFG} \sim \chi^{(2)}$ for inversion symmetry: $\chi^{(2)}=0$

Obtain *molecular* surface picture: Spatially unresolved, but surface specific

Water-air SFG spectrum



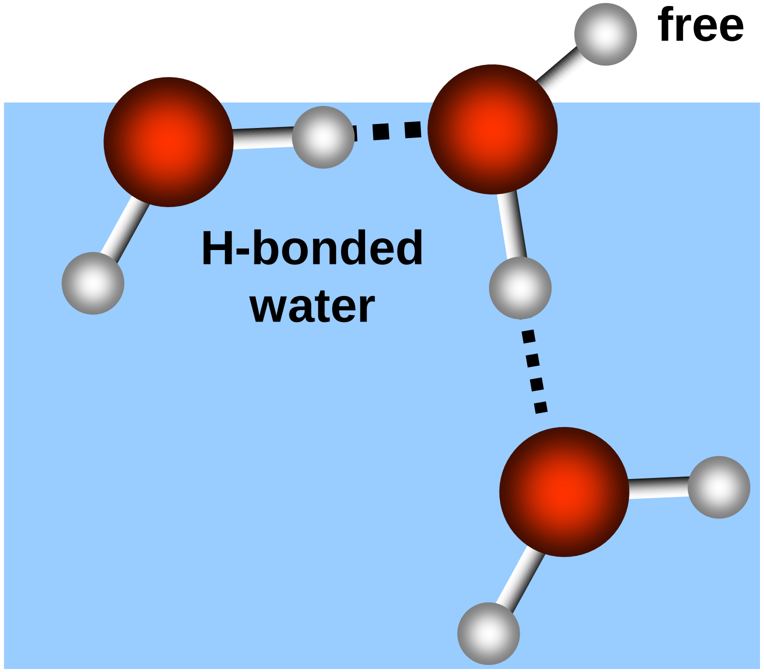
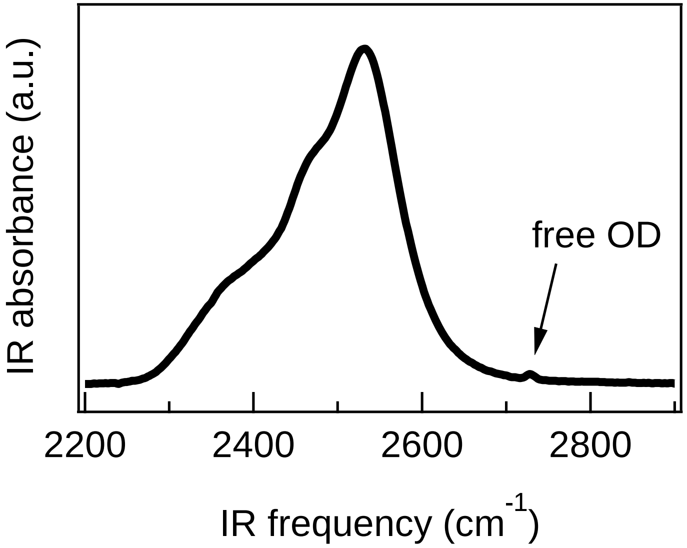
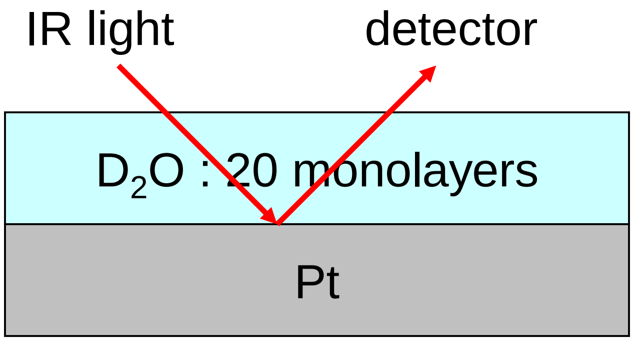


Illustration: surface specificity

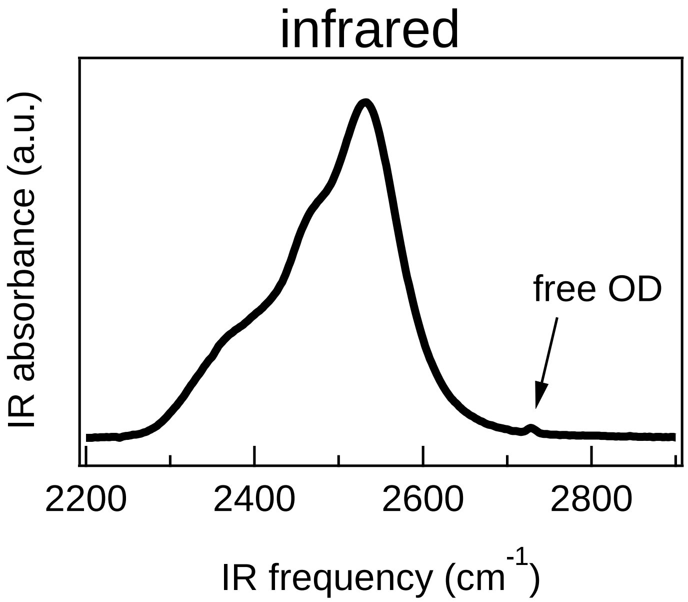
infrared

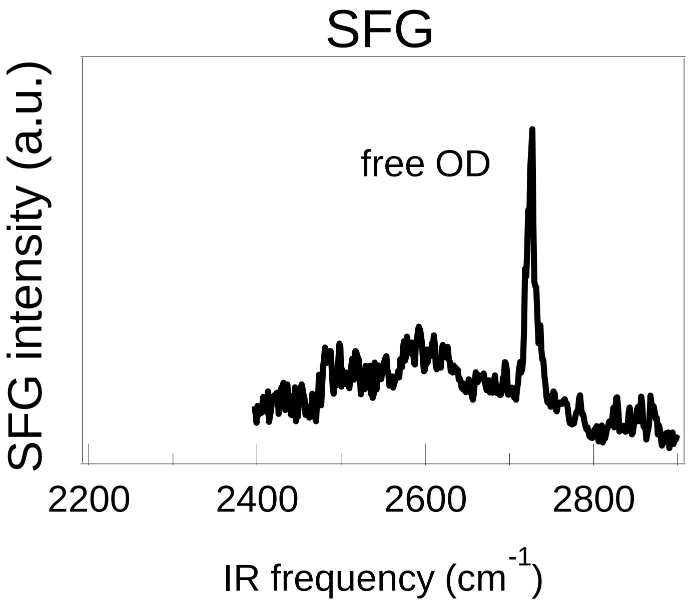


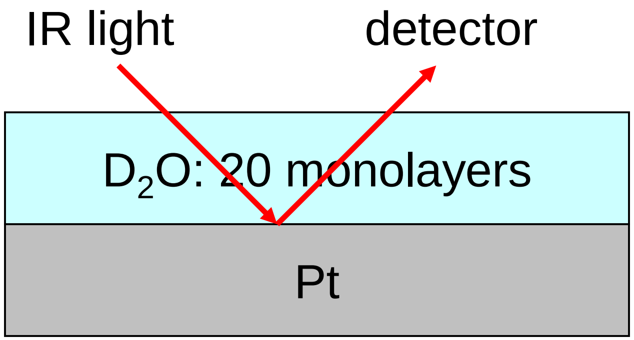


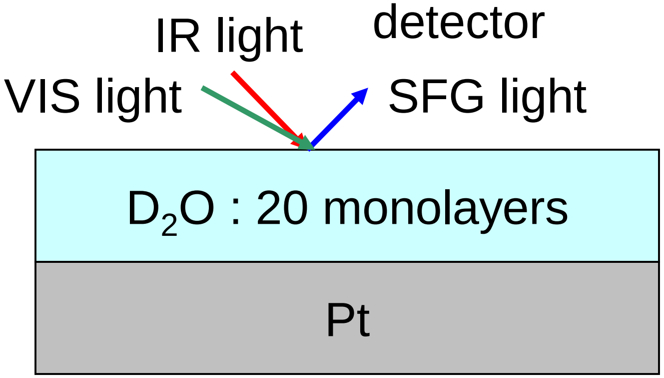
SFG

Illustration: surface specificity


infrared

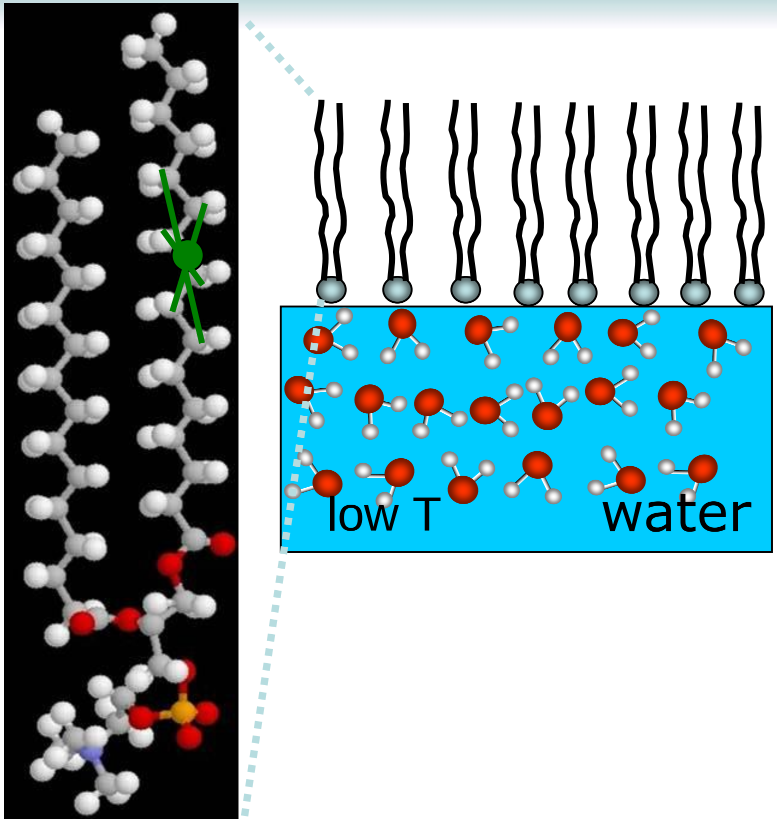

SFG

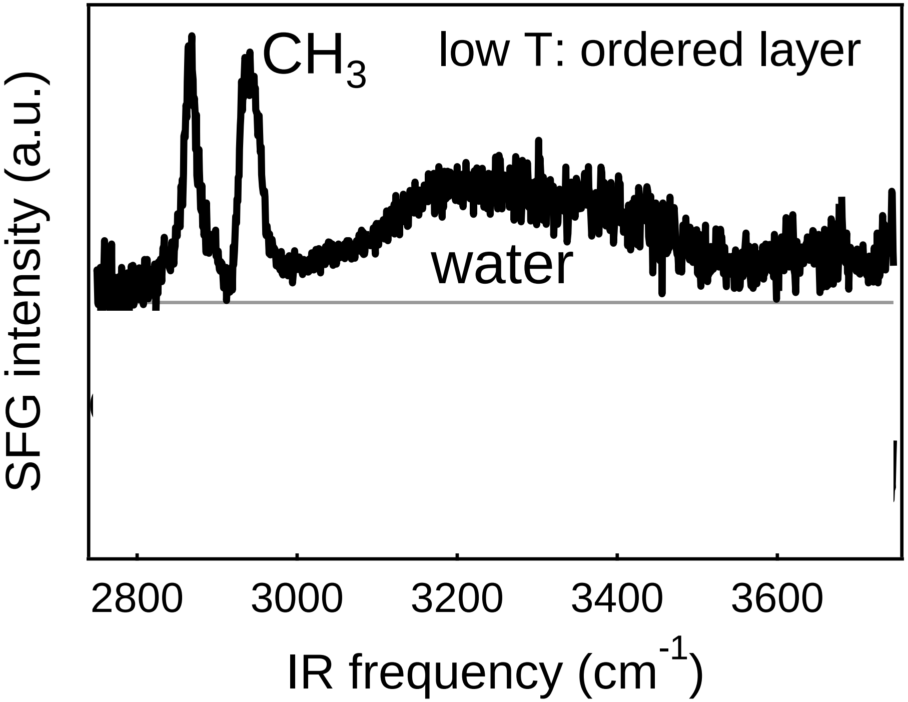




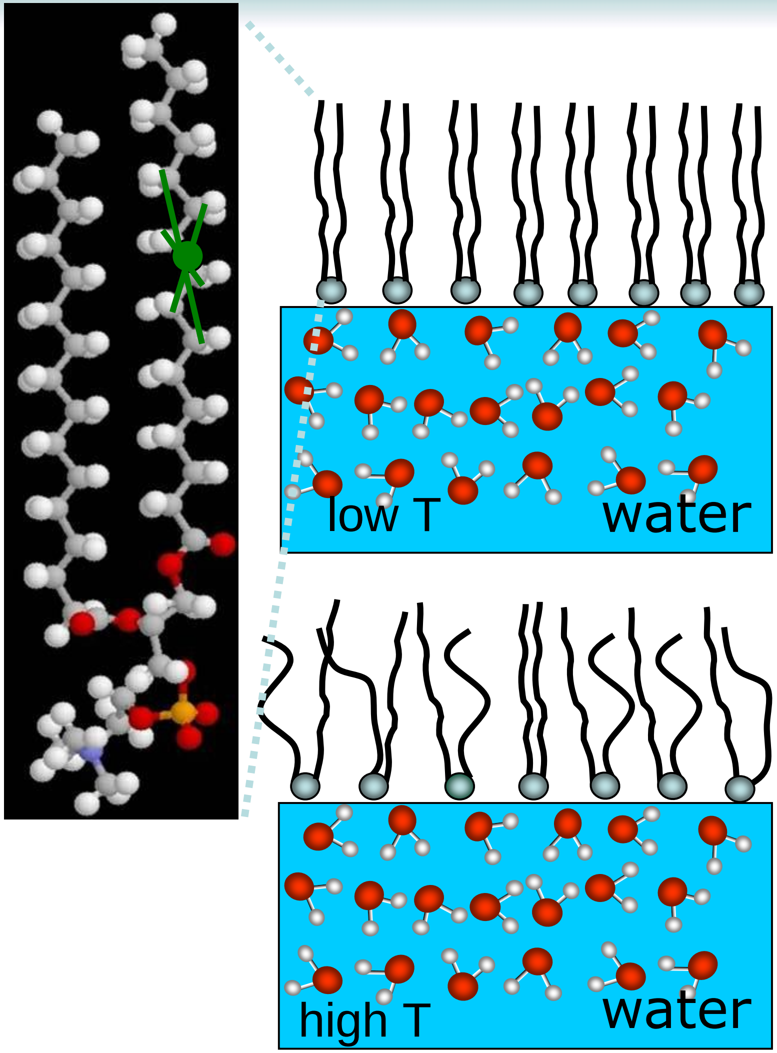
SFG: surface specific

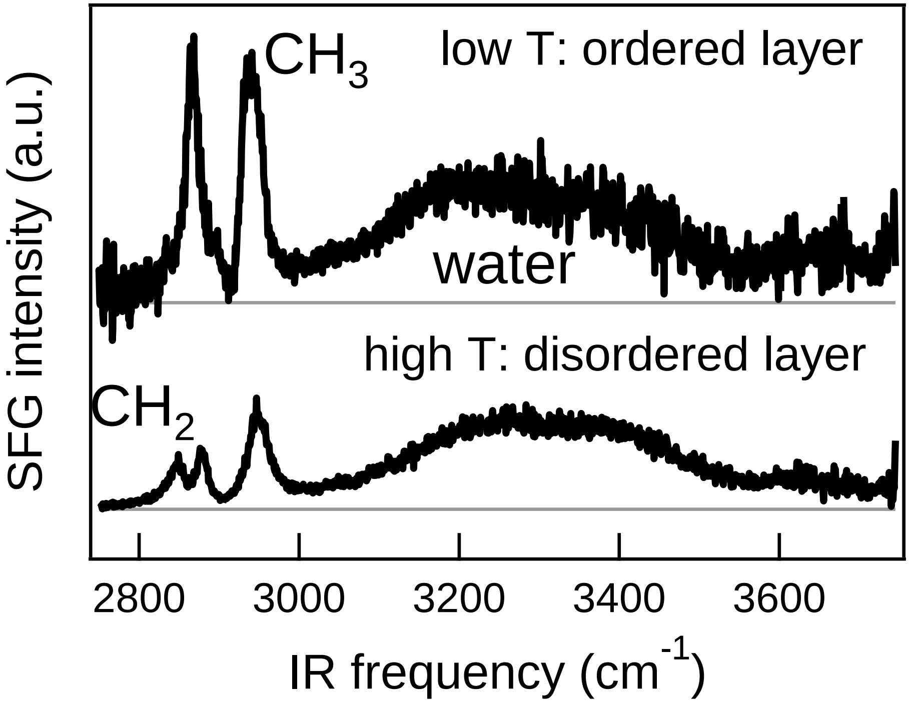
SFG forbidden by centrosymmetry





SFG forbidden by centrosymmetry





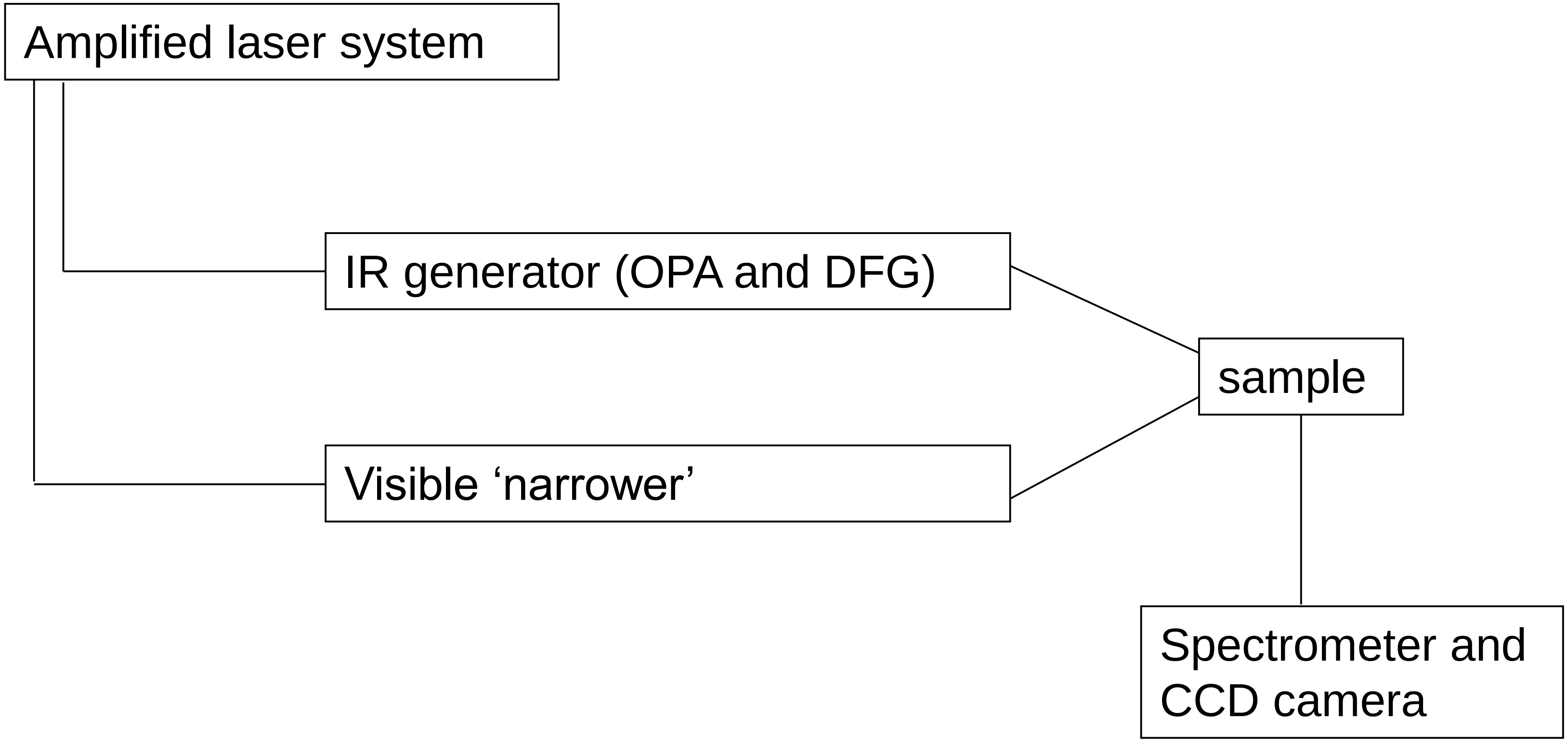
⇒ SFG forbidden in centro-symmetric media and therefore sensitive to order in the tails

SFG: what can we learn?

SFG ‘selection rules’:

- Forbidden in centrosymmetric media
- Surface specific
- Vibrational mode has to be Raman and IR active

Layout femtosecond SFG setup



Amplified laser system

IR generator (OPA and DFG)

Visible ‘narrower’

sample

Spectrometer and CCD camera

ps- vs fs-SFG setup

picosecond-SFG setup

Pro

- High frequency resolution

Contra

- Scan the IR frequency

femtosecond-SFG setup

Pro

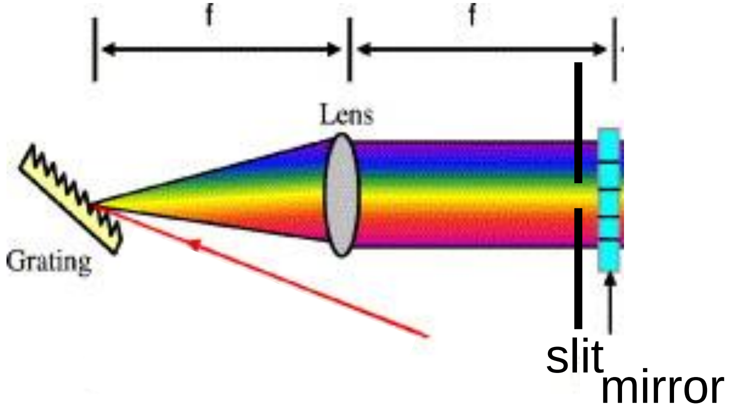
- All frequencies in once
- High time resolution for pump-probe experiments

Contra

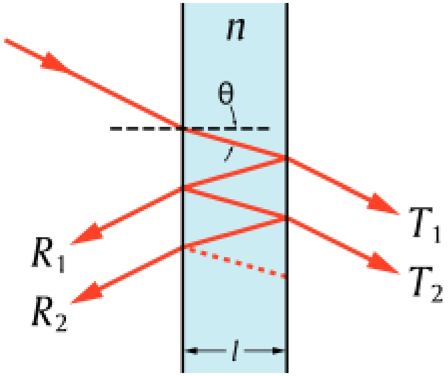
- Additional optics needed to generate narrowband visible

Pulseshaper and etalon

Pulseshaper



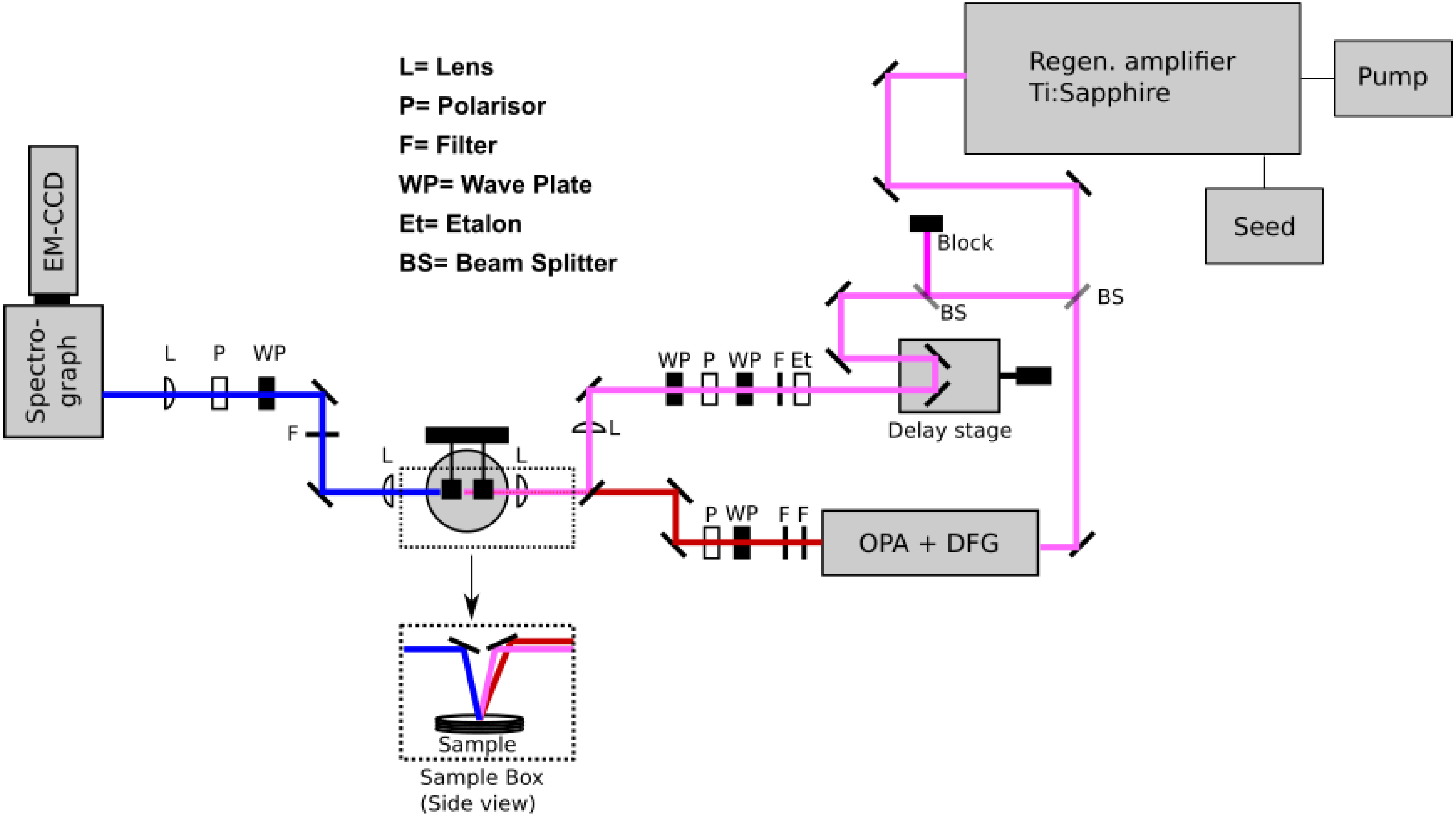
Etalon



Phase shift between two succeeding reflections:

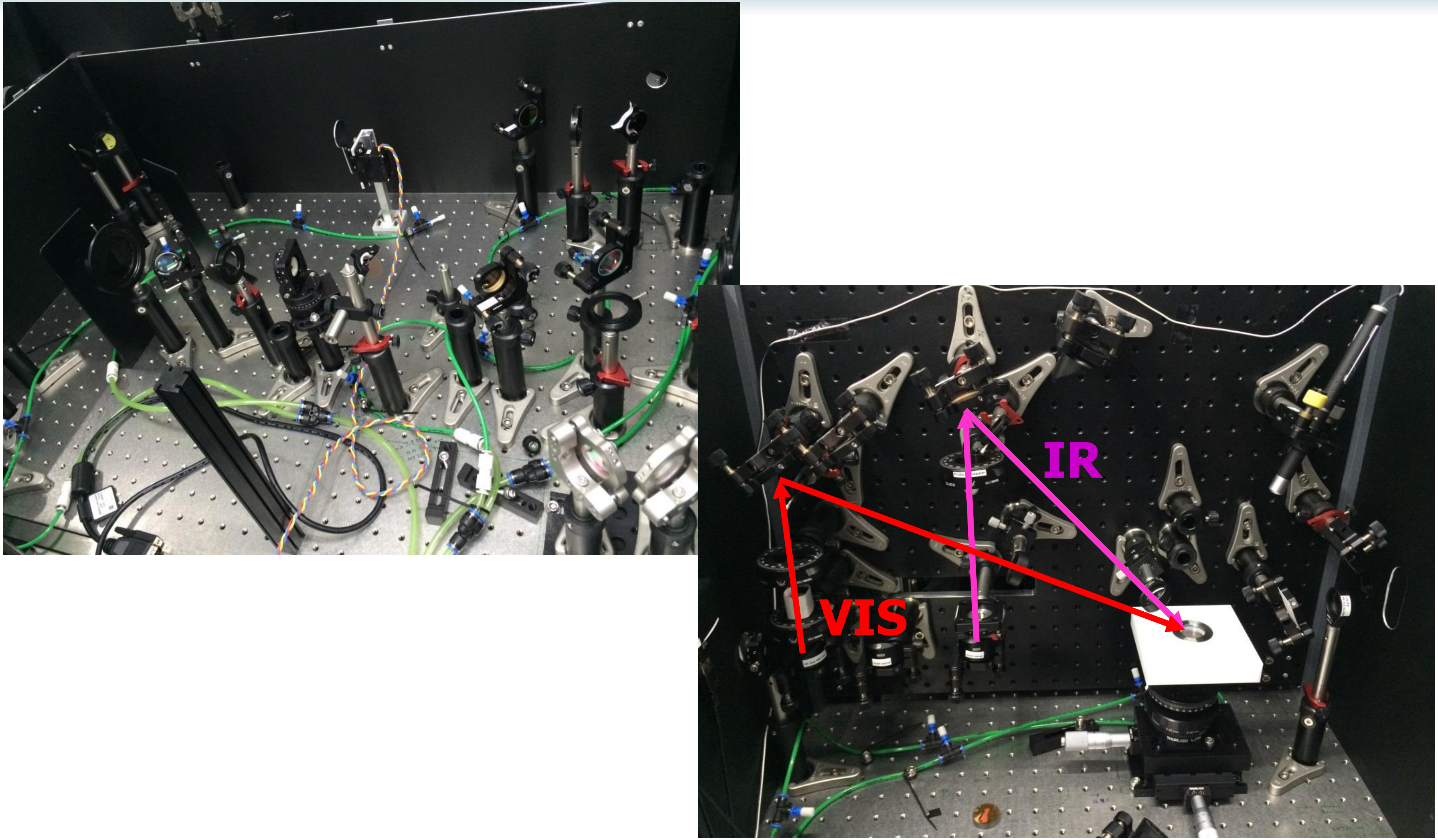
$$\delta = \left(\frac{2\pi}{\lambda}\right) 2nl\cos\theta$$

SFG setup



Slide from Sudipta Das

SFG setup



Summary I

- SFG sensitive to surfaces

- Molecular information can be obtained: i.e. ordering of tails, angle, structure (e.g. α-helix or β-sheet)

- Femtosecond laser used to have broad bandwidth to have spectrum all in once

Part II

2D-IR spectroscopy

Two coupled vibrational oscillators

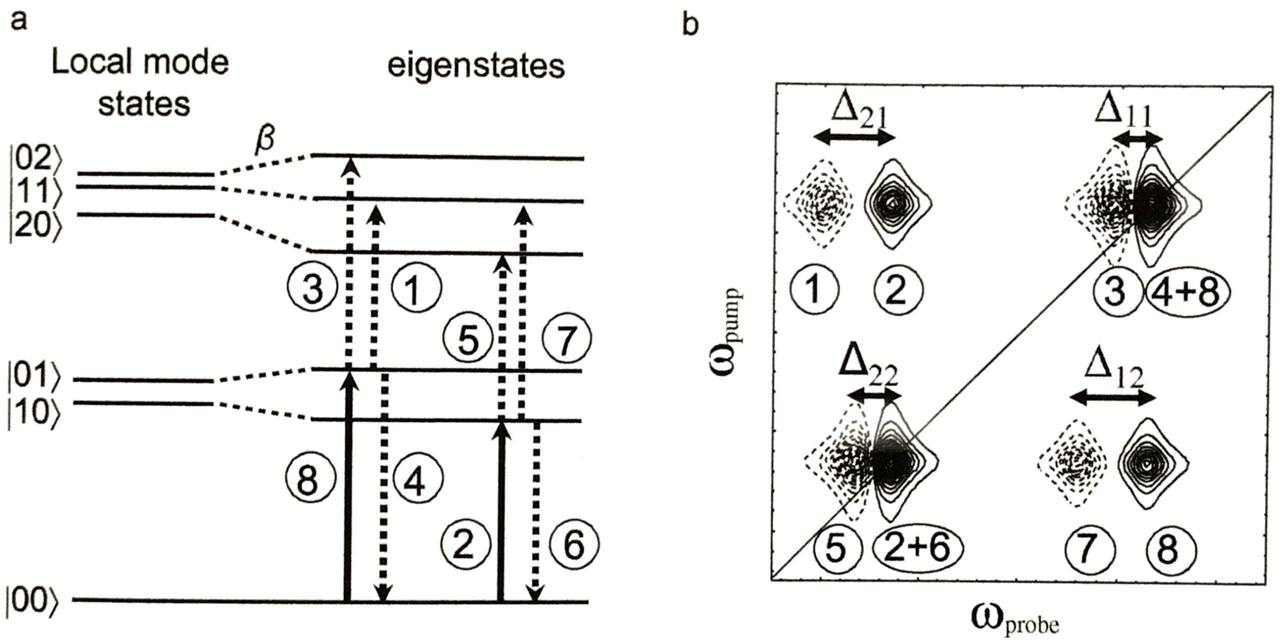
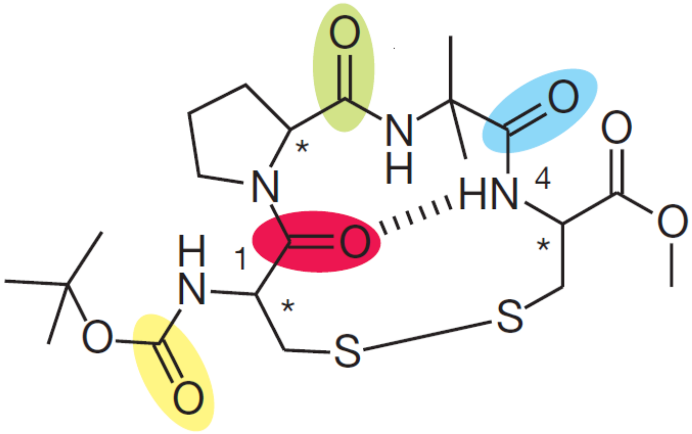


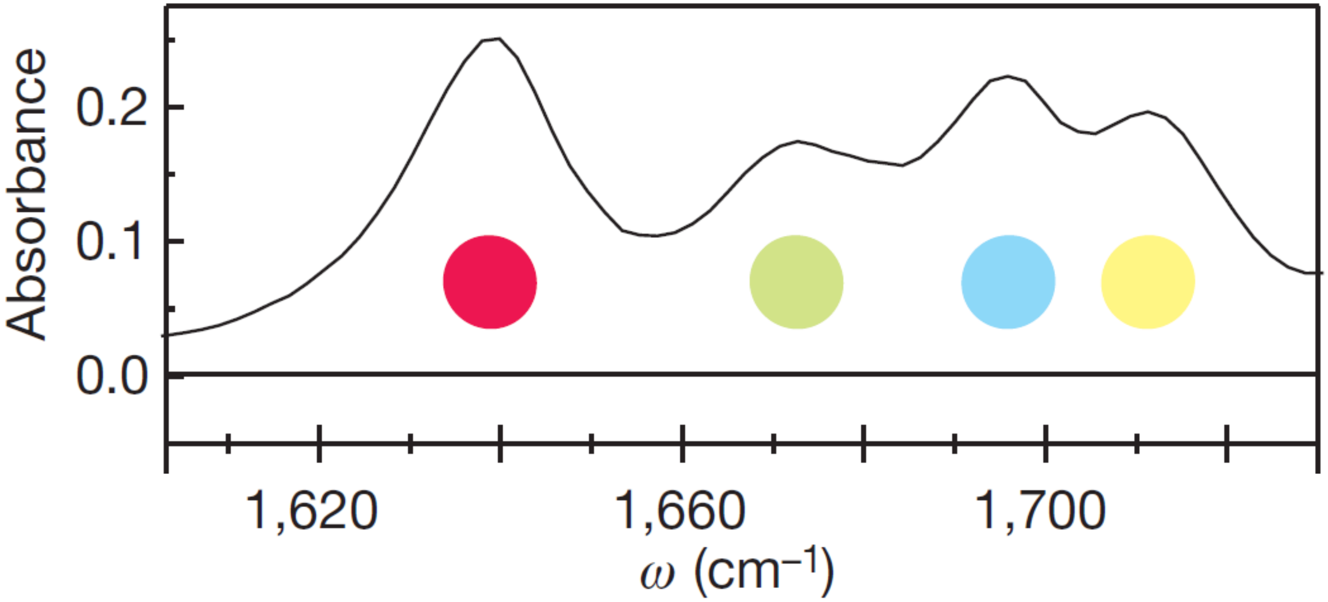
Figure 1.5 (a) Level scheme of two coupled oscillators before coupling (local modes) and after coupling (eigenstates). The dipole-allowed transitions are depicted. The solid arrows represent the pump process, the dotted arrows the probe process. (b) Resulting 2D IR spectrum. Solid contour lines represent negative response (bleach and stimulated emission), dotted contour lines positive response (excited state absorption). The labels (1)–(8) relate each peak in the 2D IR spectrum to the corresponding transition in the level scheme.

P. Hamm and M. Zanni, Concepts and methods of 2D infrared spectroscopy, Cambridge

Transient 2D-IR of peptide

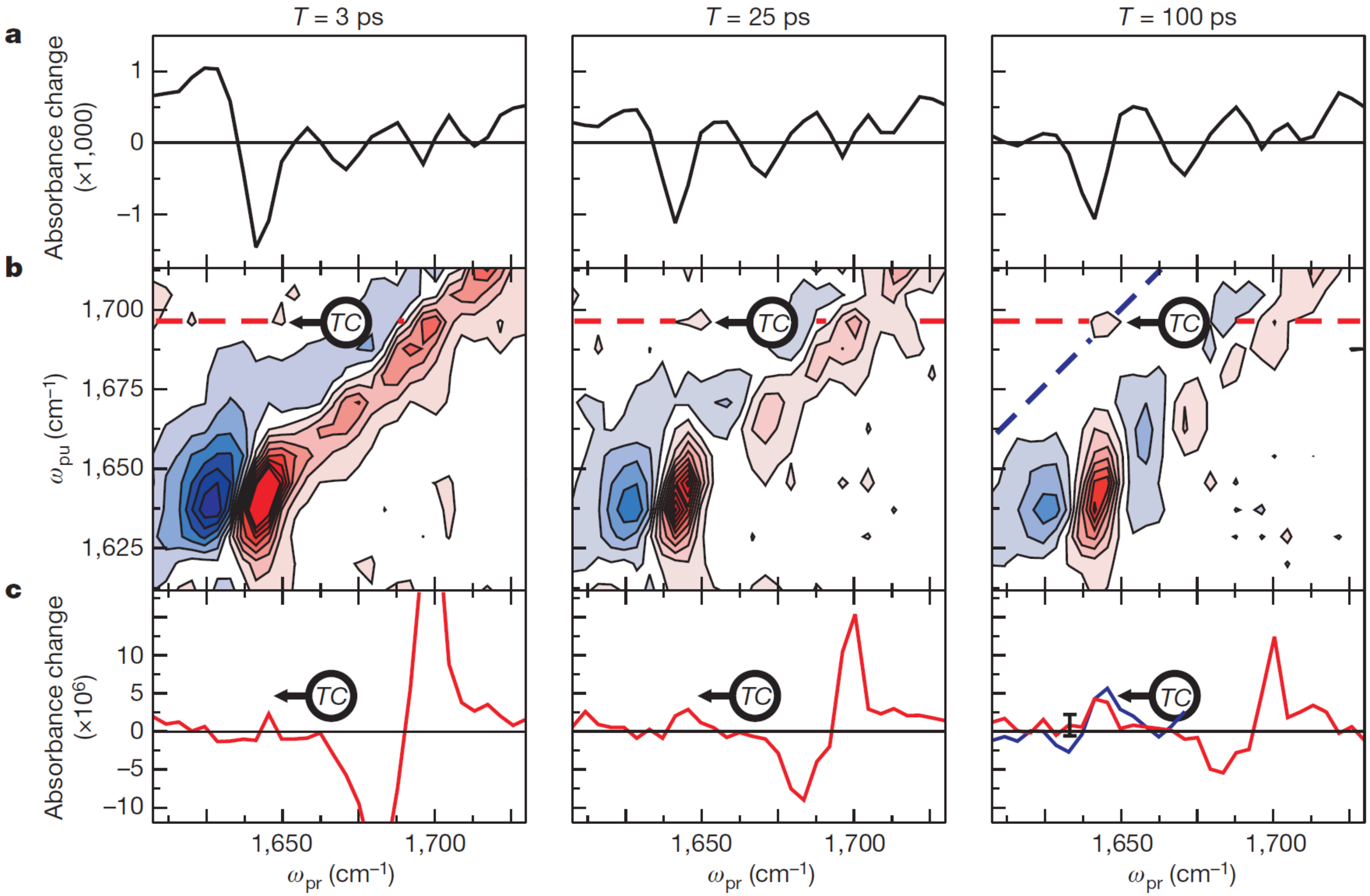


Photolysis of the S-S bond with laser results in partly unfolding of peptide



Nature 444 (2006) 469

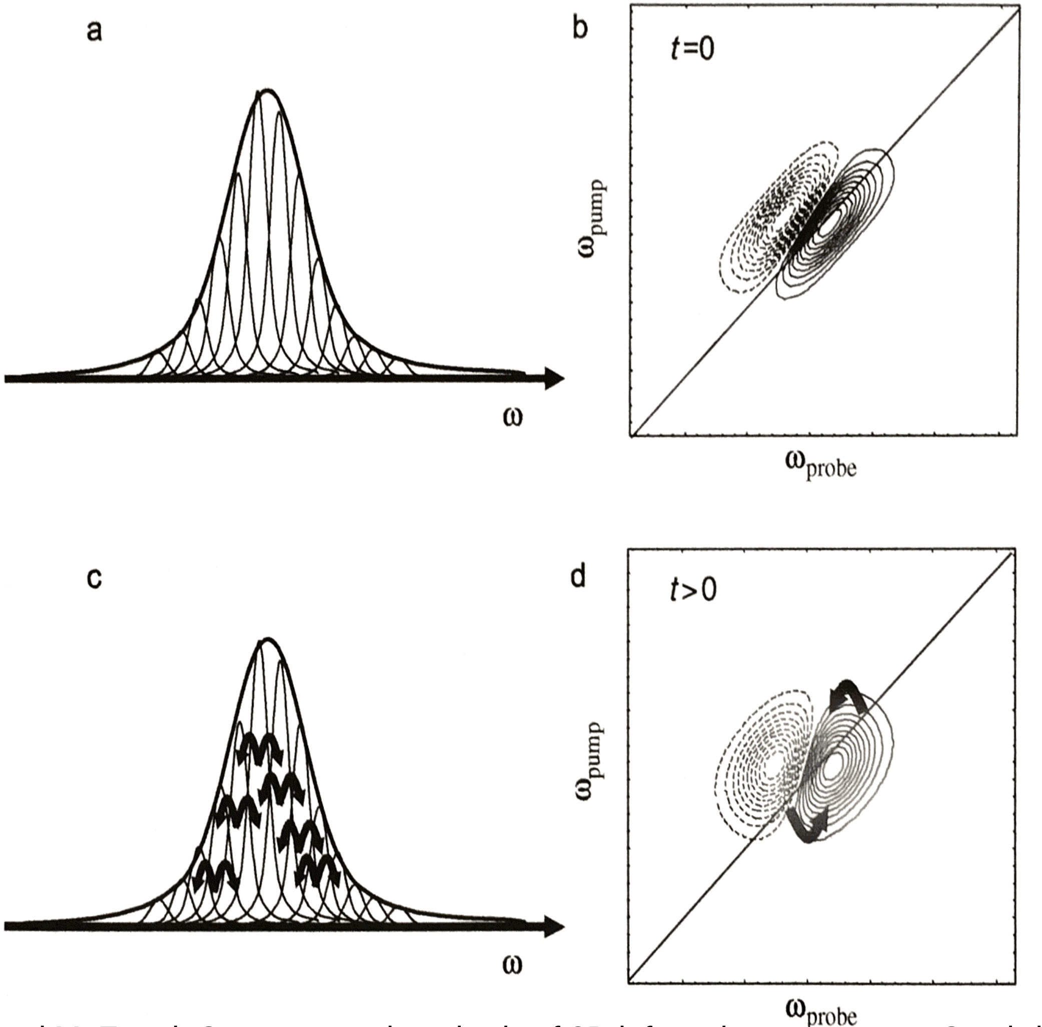
Transient 2D-IR of peptide



Nature 444 (2006) 469

TC: transient cross peak between 1640 and 1700 cm^{-1} peak increasing in time due to partially unfolding of peptide

Line broadening



Inhomogeneously broadened transition

At early times

At later times

P. Hamm and M. Zanni, Concepts and methods of 2D infrared spectroscopy, Cambridge

Line broadening

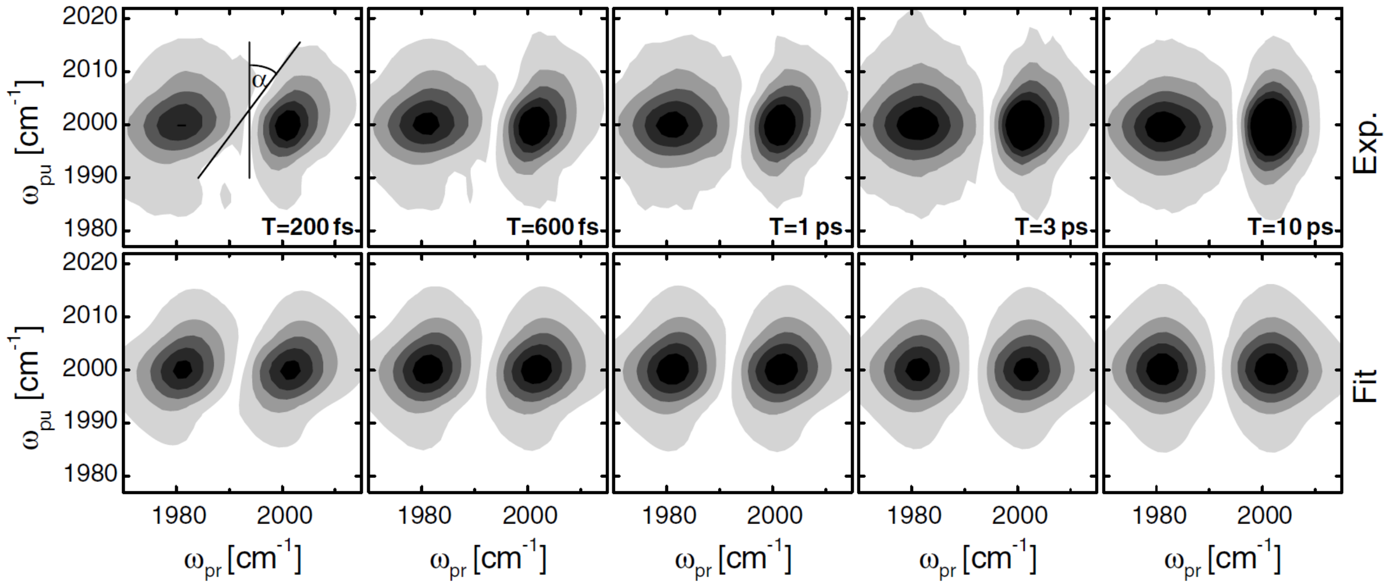


Fig. 2. Top: experimental 2D-IR spectra of $^{13}C^{15}N^{-}$ dissolved in D_2O for population times $T = 200$ fs, 600 fs, 1 ps, 3 ps and 10 ps, respectively. The negative peak is due to bleach/stimulated emission of the 0–1 transition, the positive peak due to 1–2 excited state absorption. Bottom: global fit of the experimental data, using Eq. (1) as model for the frequency fluctuation correlation function, and revealing the parameters in Table 1 as result. Contour levels are linearly spaced and symmetric around zero. In the top-left panel, the definition of the tilt angle plotted in Fig. 3 is indicated.

Chem. Phys. 341 (2007) 5

Chemical exchange

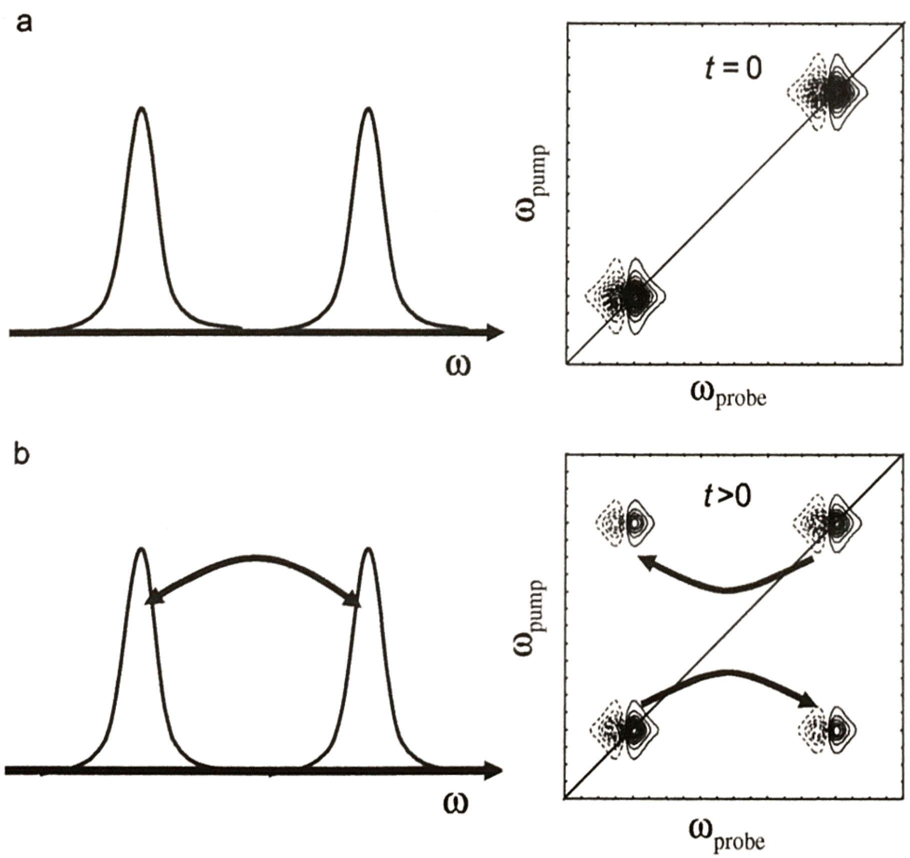


Figure 1.8 2D IR spectrum of a system undergoing chemical exchange with (a) no pump–probe delay and (b) a delay that is roughly that of the exchange.

P. Hamm and M. Zanni, Concepts and methods of 2D infrared spectroscopy, Cambridge

Chemical exchange

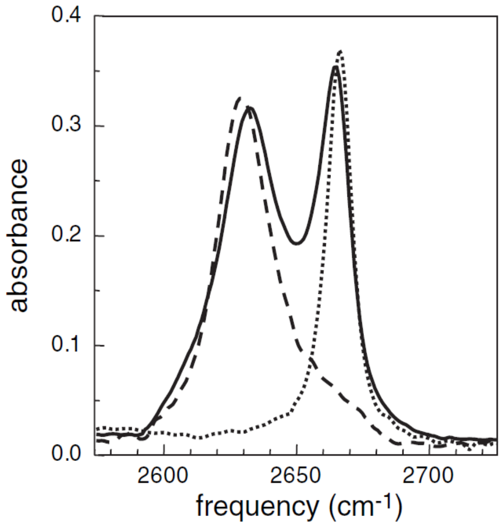
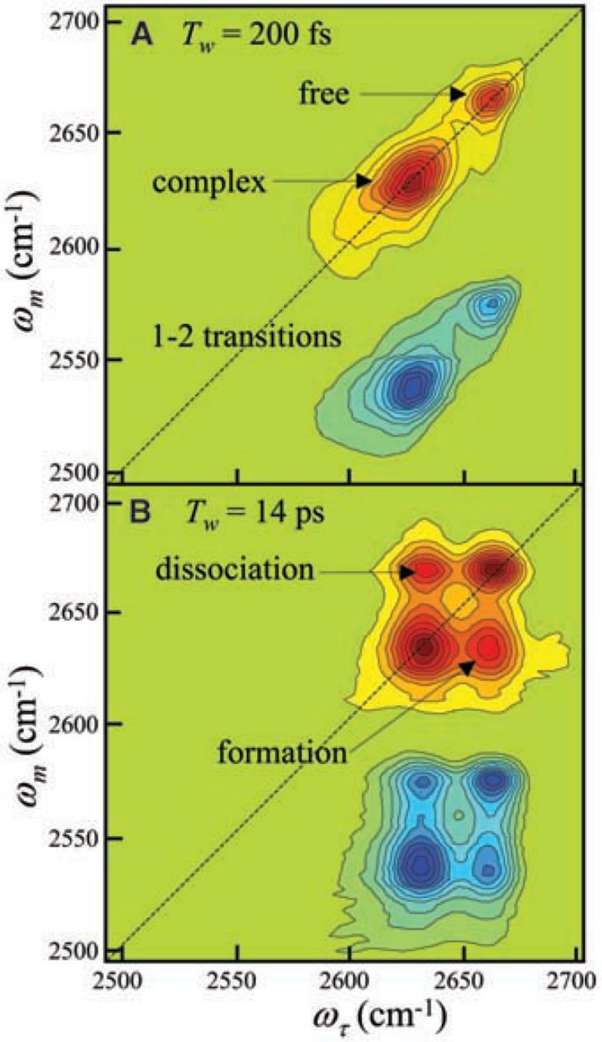


Fig. 2. FT-IR absorption spectra of the OD stretch of phenol-OD (hydroxyl H replaced with D) in CCl_4 (free phenol, dotted curve), phenol in benzene (benzene-phenol complex, dashed curve), and phenol in the mixed benzene-CCl_4 solvent (2:5 molar ratio), which displays absorptions of both free and complexed phenol (solid curve).



Science 309 (2005) 1338