Vibrational spectroscopy of chiral molecules and adsorbates

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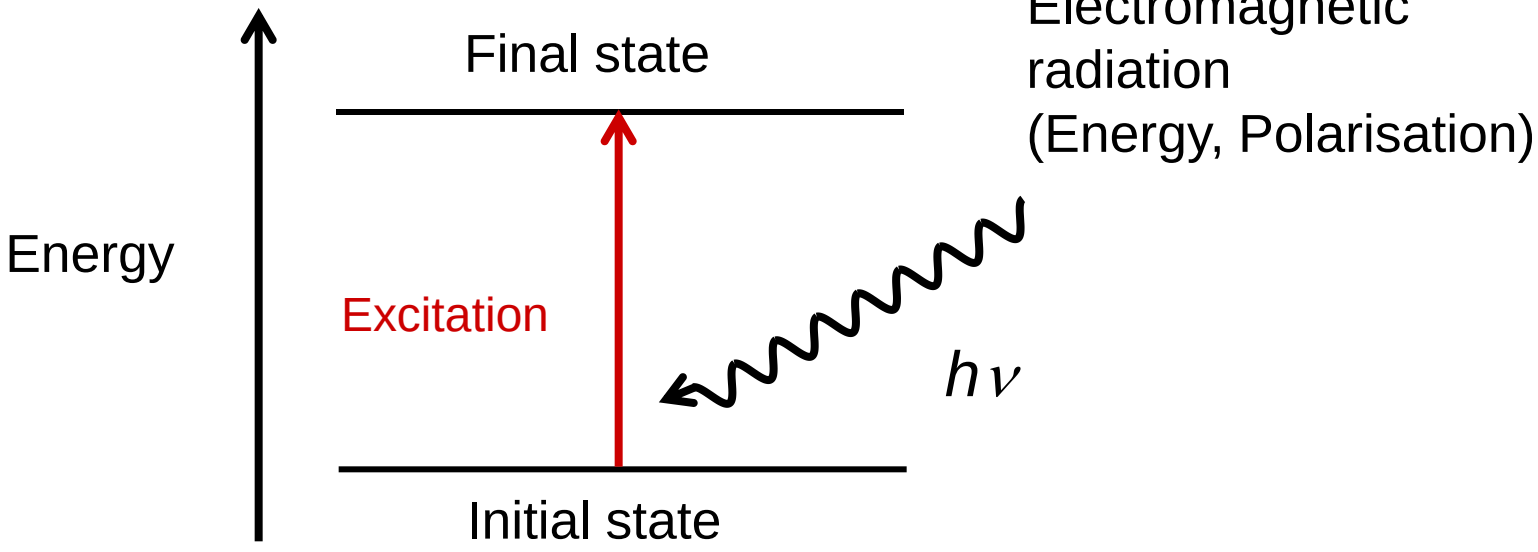
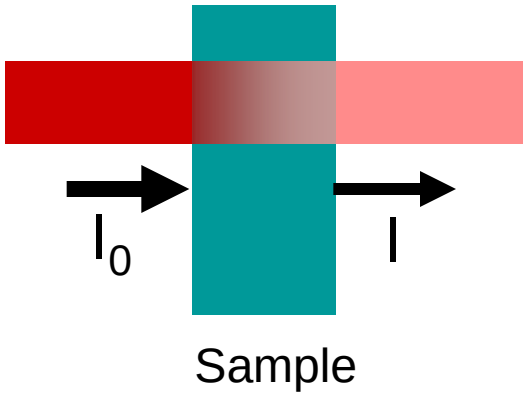
Outline

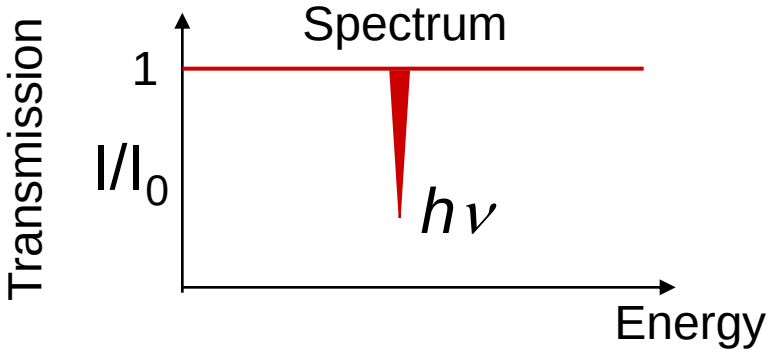
- Introduction
- IR spectroscopy of adsorbates
- Vibrational optical activity
  - Vibrational circular dichroism (VCD)
  - Raman optical activity (ROA)
- Chiral nanoparticles

Spectroscopy

(linear spectroscopy)

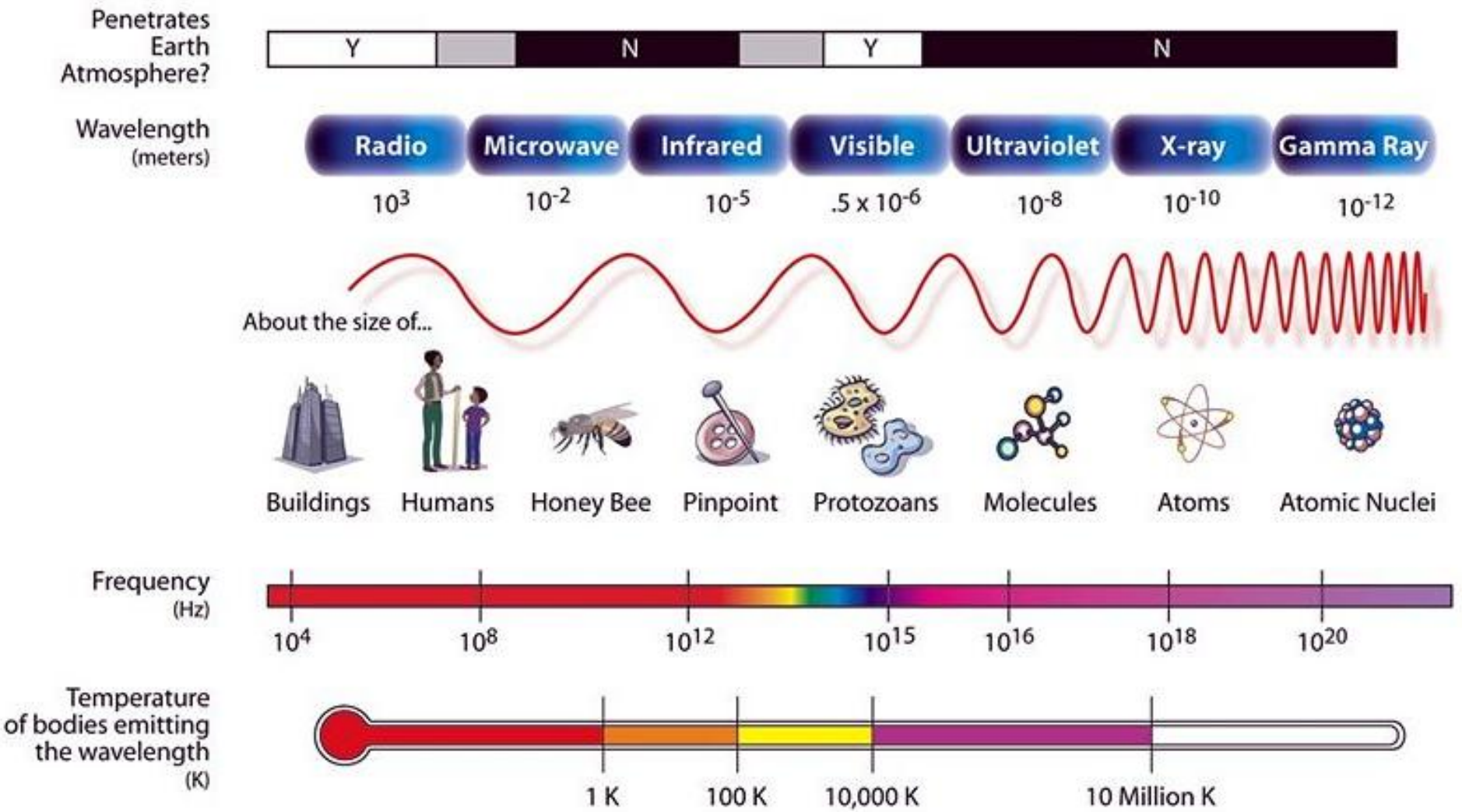






States: electronic, vibrational ….

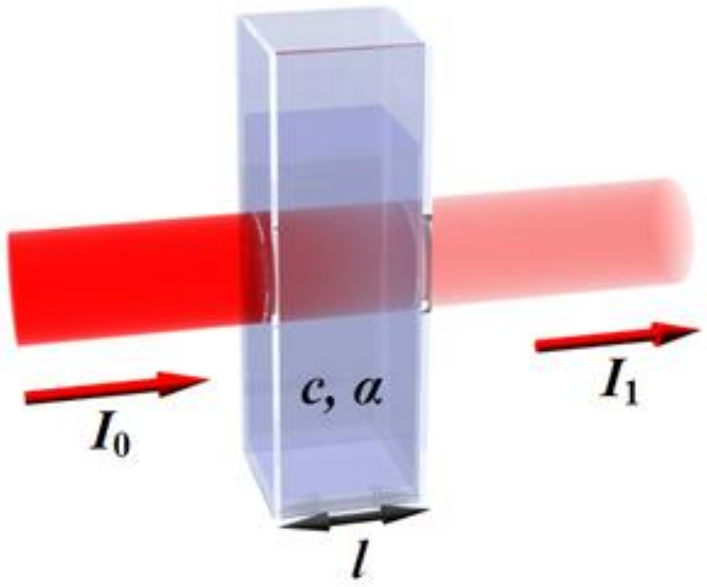
THE ELECTROMAGNETIC SPECTRUM



http://www.newworldencyclopedia.org/entry/Electromagnetic_spectrum

Beer-Lambert law

$$T = \frac{I}{I_0} = 10^{-\alpha \ell} = 10^{-\varepsilon \ell c}$$



T : Transmittance
ℓ : path length
ε : molar extinction coefficient
c : concentration

Beer-Lambert law

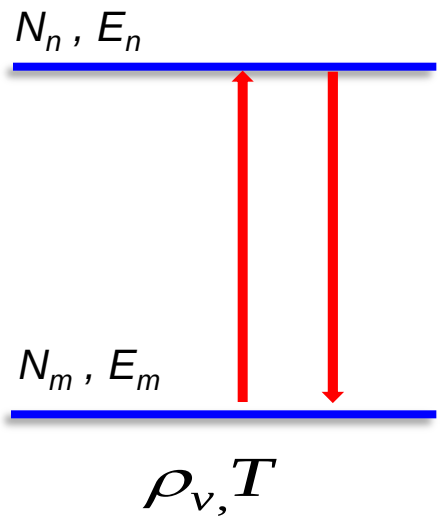
$$A = -\log T = -\log_{10}\left(\frac{I}{I_0}\right) = \varepsilon c l = \alpha l$$

A: Absorbance: It is proportional to the concentration (or number density)

If the concentration is expressed in moles/L the **molar extinction coefficient (*ε*)** is used in $L \cdot mol^{-1} \cdot cm^{-1}$ sometimes in converted SI units of $m^2 \cdot mol^{-1}$.

ε is characteristic for a molecule and a transition: How is it related to the wavefunctions of a molecule?

Einstein coefficients



Rate of change of population N_n of state n

$$\frac{dN_n}{dt} = B_{mn}\rho_\nu N_m - B_{nm}\rho_\nu N_n - A_{nm}N_n$$

Spontaneous emission

In thermal equilibrium:
total rate of emission =
total rate of absorption

Steady state $$\frac{dN_n}{dt} = 0 \rightarrow \frac{N_n}{N_m} = \frac{B_{mn}\rho_\nu}{B_{nm}\rho_\nu + A_{nm}}$$

Boltzmann Distribution $$\frac{N_n}{N_m} = e^{-h\nu_{mn}/kT} \Rightarrow \rho_\nu = \frac{A_{nm}}{B_{nm}}\left(\frac{1}{e^{h\nu/kT}-1}\right) \qquad (B_{nm} = B_{mn})$$

For Blackbody radiation:
radiation density $$\rho_\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1} \Rightarrow \frac{A_{nm}}{B_{nm}} = 8\pi h\left(\frac{\nu}{c}\right)^3$$

Relation between Einstein coefficients and wave functions

Transition rate $$W_{nm} = B_{nm}\rho_\nu = \frac{|\mu_{nm}|^2}{6\varepsilon_0\hbar^2}\rho_\nu$$

Einstein coefficient of stimulated absorption $$\frac{|\mu_{nm}|^2}{6\varepsilon_0\hbar^2} \equiv B_{nm}$$

Transition dipole moment $$\mu_{nm} = \int \psi_n^* \mu \psi_m d\tau$$

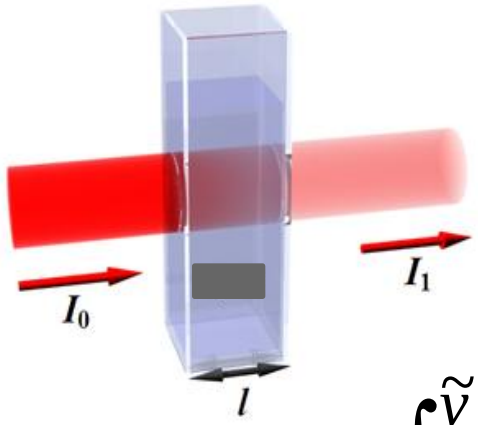
operator $\mu = \sum_i q_i r_i$

B_{nm} may be found experimentally in the case of an absorption experiment

Absorption cross-section σ = $h\nu B_{nm}$

" probability of absorption of a photon per molecule "

Beer-Lambert Law : $$A = -\log T = -\log_{10}\left(\frac{I}{I_0}\right) = \varepsilon c l$$



$$\varepsilon = \frac{\sigma N_A}{\ln 10} = \frac{N_A h\nu B_{nm}}{\ln 10}$$

$$\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon(\tilde{\nu})d\tilde{\nu} = \frac{N_A h\tilde{\nu}_{nm} B_{nm}}{\ln 10} \qquad N_n << N_m$$

$$Note: \sigma N l = \varepsilon c l * \ln 10 \Rightarrow \sigma\left[m^2\right] = \frac{0.2303}{N_A}\varepsilon\left[L mol^{-1} cm^{-1}\right]$$

#/m^3 m #/N_A*liter cm

Transition dipole moment and intensity of vibrational bands

$$R^{v',v''} = \int \psi_{v'}^{*} \vec{\mu}(r) \psi_{v''} dr$$

μ: dipole moment

Expansion of dipole moment in a Taylor series around the equilibrium position

$$\vec{\mu} = \vec{\mu}_{eq} + (\frac{d\vec{\mu}}{dr})_{eq} q + \frac{1}{2}(\frac{d^2\vec{\mu}}{dr^2}) q^2 + ...$$

q: displacement from equilibrium

$$R^{v',v''} = \vec{\mu}_{eq} \underbrace{\int \psi_{v'}^{*} \psi_{v''} dr}_{0} + (\frac{d\vec{\mu}}{dr})_{eq} \underbrace{\int \psi_{v'}^{*} q \psi_{v''} dr}_{\neq 0} + ...$$

$$Intensity : I \propto \left| R^{v',v''} \right|^2 \propto \left(\frac{d\vec{\mu}}{dr} \right)_{eq}$$

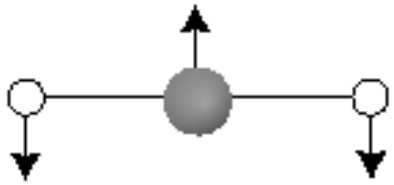
Intensity (selection rules) I

When is a vibration infrared active?

$$\left(\frac{\partial \mu}{\partial Q}\right) \neq 0$$

symmetrical stretching

Not IR active



scissoring (bending in the plane of the paper)

IR active

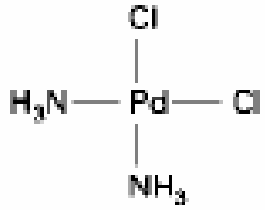
Intensity (selection rules) II

$$B_{12} \propto \left| \int \psi_1 \hat{\mu} \psi_2 dr \right|^2$$

Ψ_1 and Ψ_2 are the ground and excited state wavefunctions, μ is the dipole moment operator and integration is over all space. The integral can only be non zero if the function being integrated has a totally symmetric component within the point group of the molecule.
μ transforms like the functions x, y and z. This means that we can observe an IR transition when the excited state wavefunction belongs to the same irreducible representation as either x, y or z.

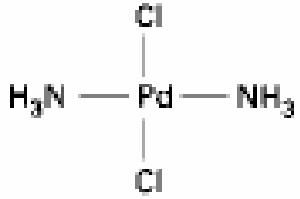
At this point group theory comes into play!

Symmetry / Group theory



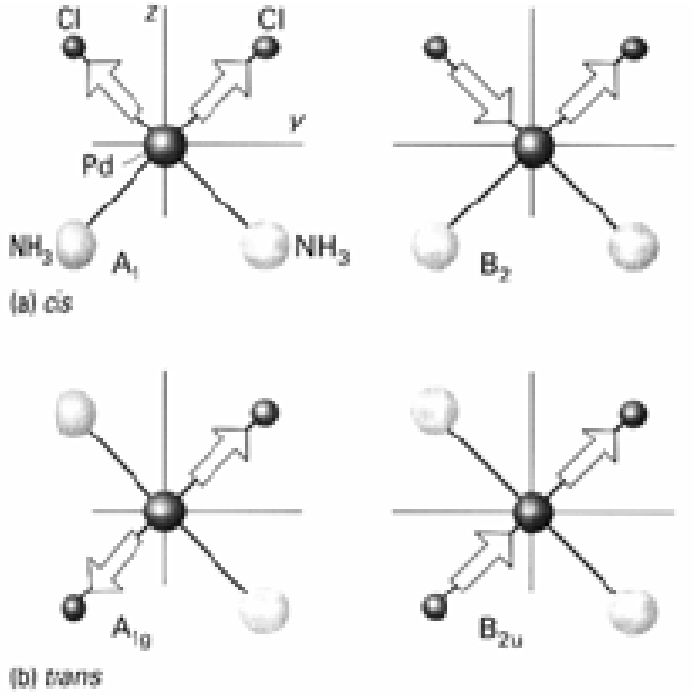
C_{2v}

16 *cis*-$[PdCl_2(NH_3)_2]$



D_{2h}

17 *trans*-$[PdCl_2(NH_3)_2]$



4.36 Some of the Pd–Cl stretching modes of a $[PdCl_2(NH_3)_2]$ square-planar complex. The motion of the Pd atom (which preserves the center of mass of the molecule) is not shown.

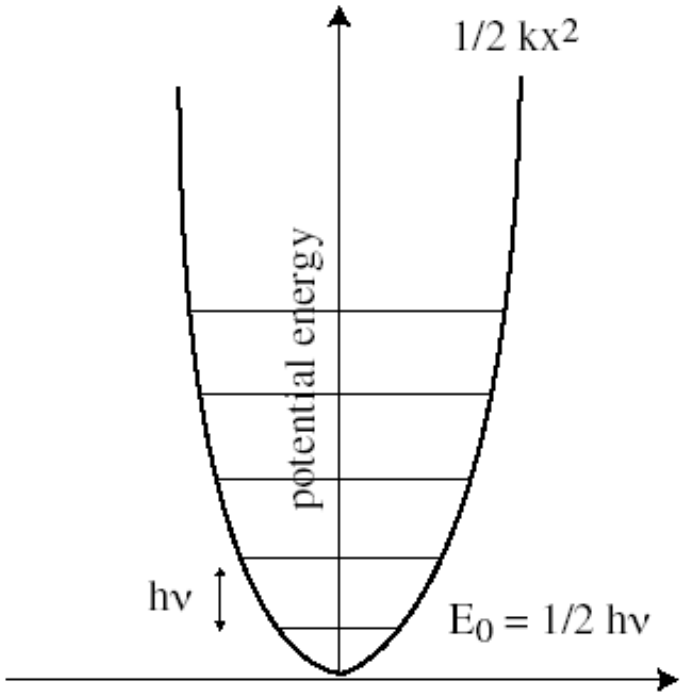
What is the difference?

Harmonic Oscillator

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dq^2}+\frac{1}{2}kq^2\psi = E_{vib}\psi$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

k is the force constant, μ the reduced mass q is the displacement from the equilibrium position.



$$E = (n+\frac{1}{2})h\nu$$

For molecules with more than two atoms
-> Normal mode analysis

What can we learn from spectroscopy?

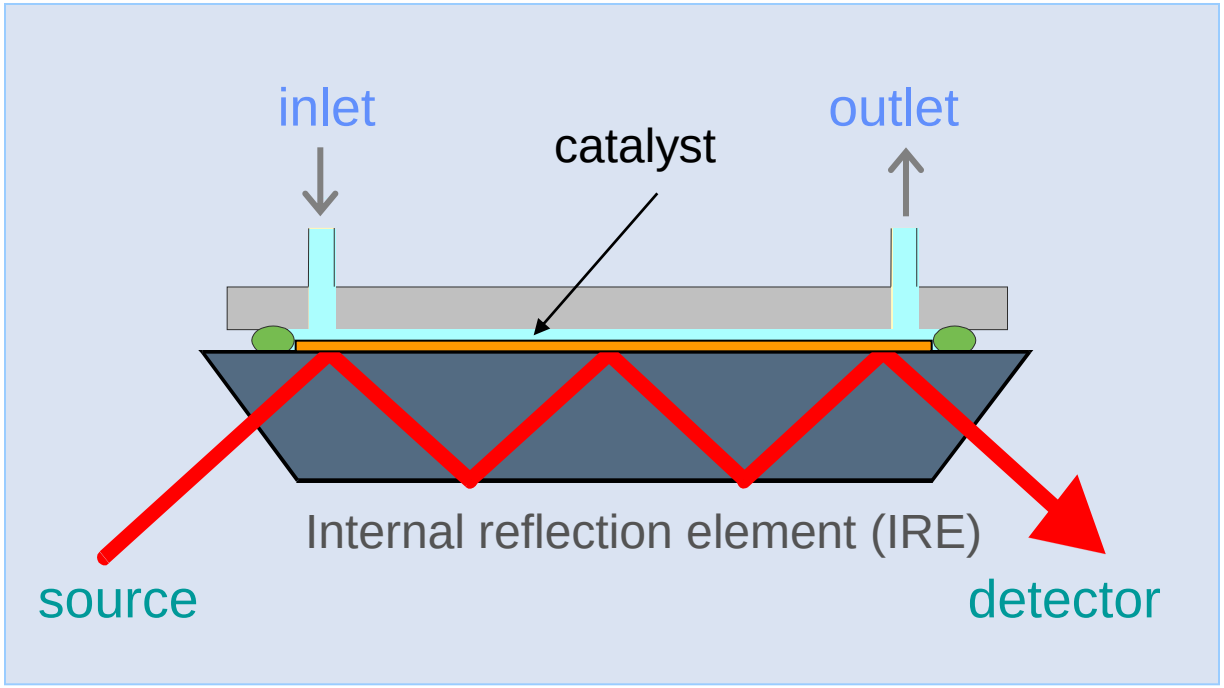
- Identify species
- Quantify
- Structure determination
- Orientation
- Interactions
- „Imaging“
-
-
-

Infrared spectroscopy of adsorbates
(IR spectroscopy of interfaces)

- ATR-IR spectroscopy
- Orientation measurements
- Case studies

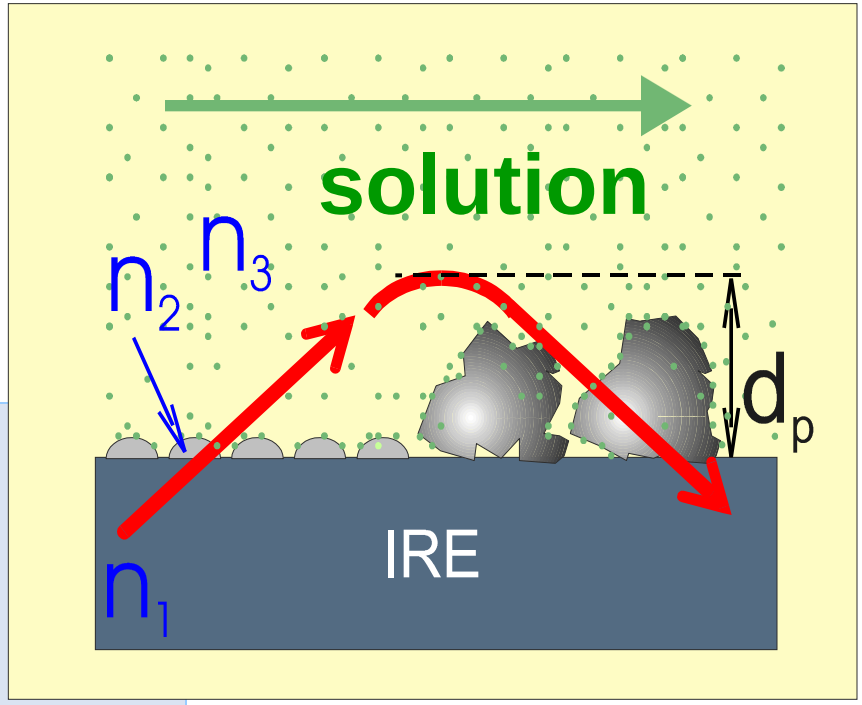
ATR-IR spectroscopy

flow-through cell

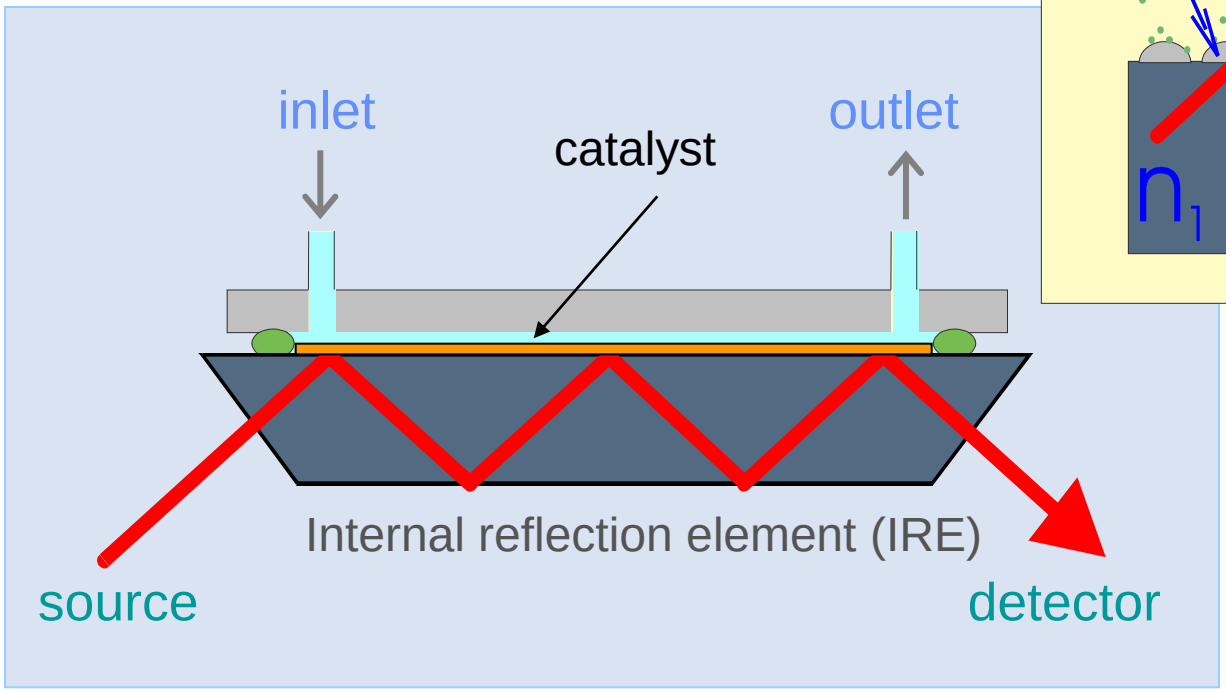


ATR: Attenuated total reflection

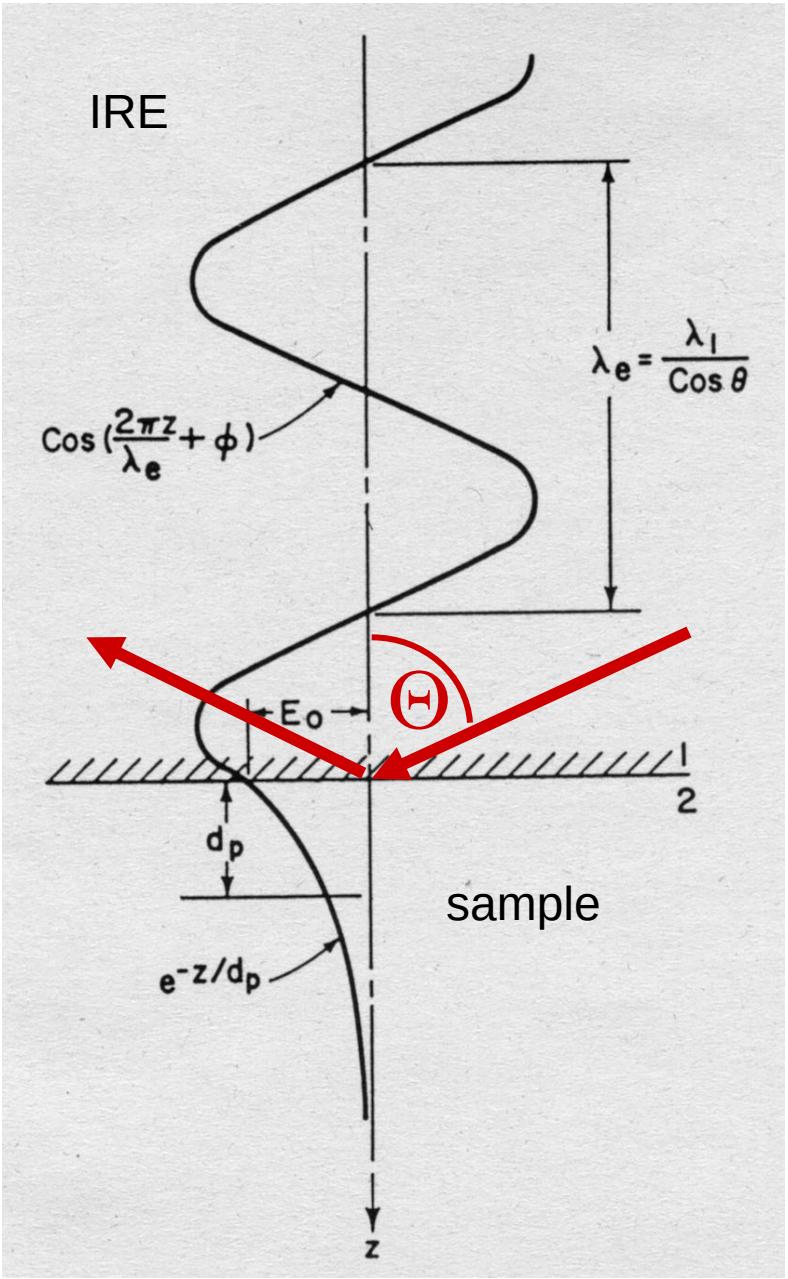
ATR-IR spectroscopy



flow-through cell



Electric field at interface for ATR



$$d_p = \frac{\lambda_1}{2\pi\sqrt{\sin^2\theta - {n_{21}}^2}}$$

$$E = E_0 e^{\frac{-z}{d_p}}$$

z: distance from the interface

d_p: Penetration depths (typically on the order of a μm in the IR). Distance from interface where the electric field has decayed to 1/e of its value E_0 at the interface

λ_1: Wavelength in medium 1

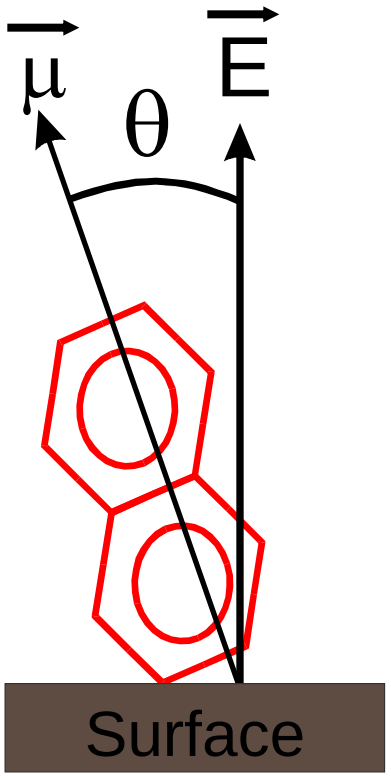
$n_{21}=n_2/n_1$: Refractive indices of internal refelection element (IRE) and sample

Θ: Angle of incidence

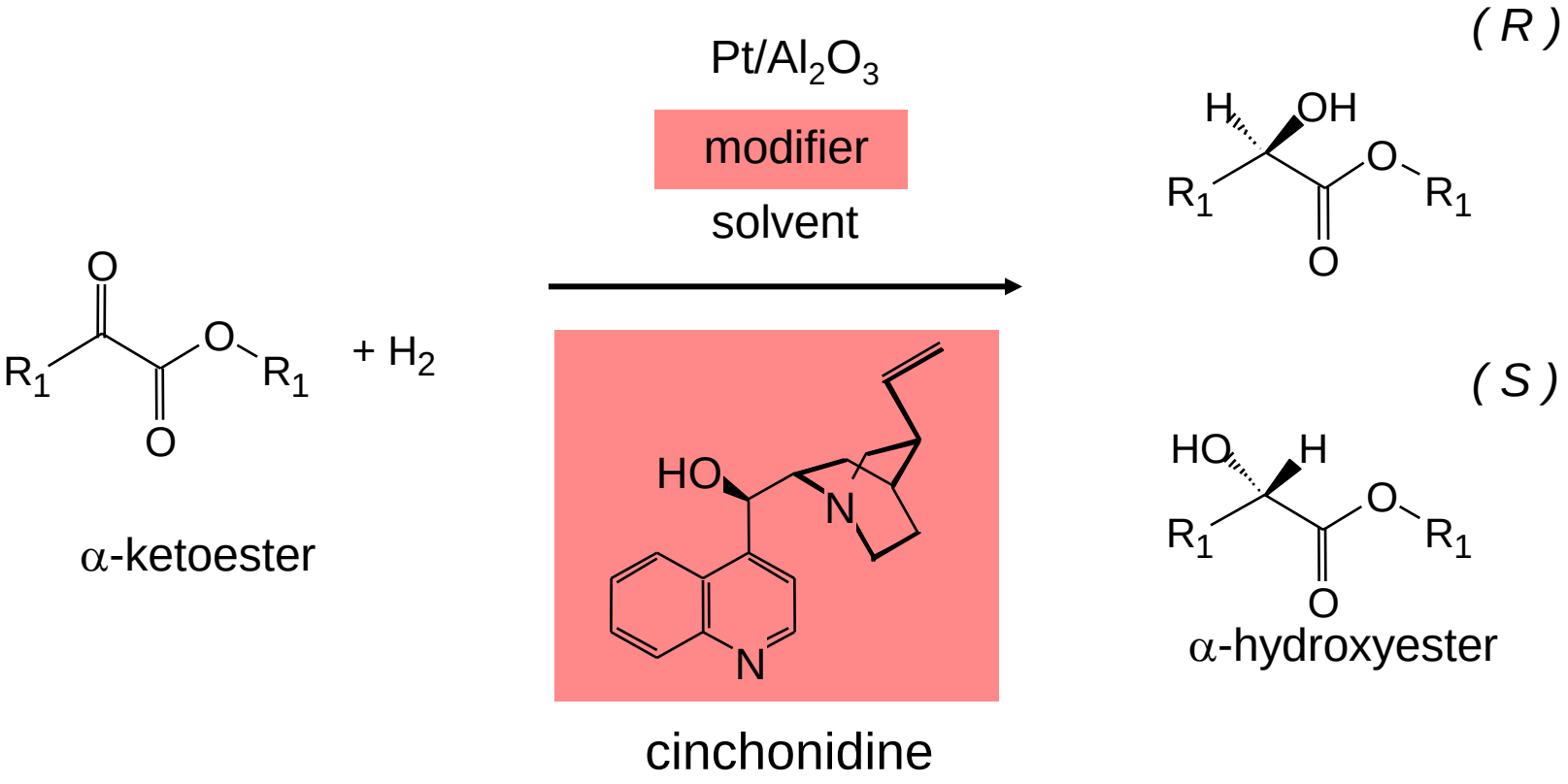
Orientation measurements

- Make use of polarized light
- For flat (model) systems
- Usually no net orientation for powder samples

$$I \propto (\vec{\mu} \bullet \vec{E})^2 = \left|\vec{\mu}\right|^2 \left|\vec{E}\right|^2 \cos^2(\theta)$$



Heterogeneous enantioselective hydrogenation of α-functionalized ketones (case study)



Orito et al., 1979

Heterogeneous enantioselective catalysis

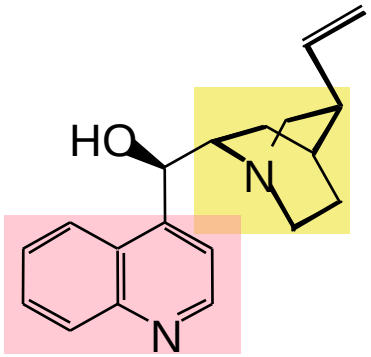
- Structure of the active site?
  - How does the chiral modifier adsorb on the catalyst surface?

→ In situ ATR spectroscopy

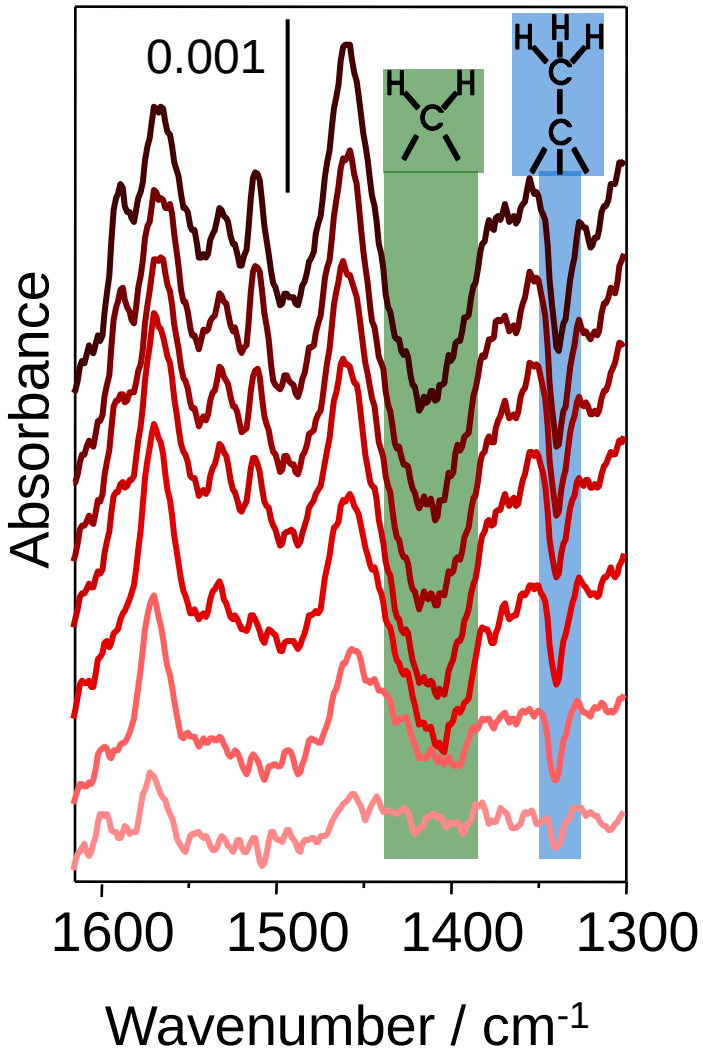
Why in situ?

Cinchonidine (CD) adsorption on Pt/Al_2O_3 film

10° C; H_2-saturated CH_2Cl_2



- Adsorption mode depends on coverage
- Competition with solvent for adsorption sites

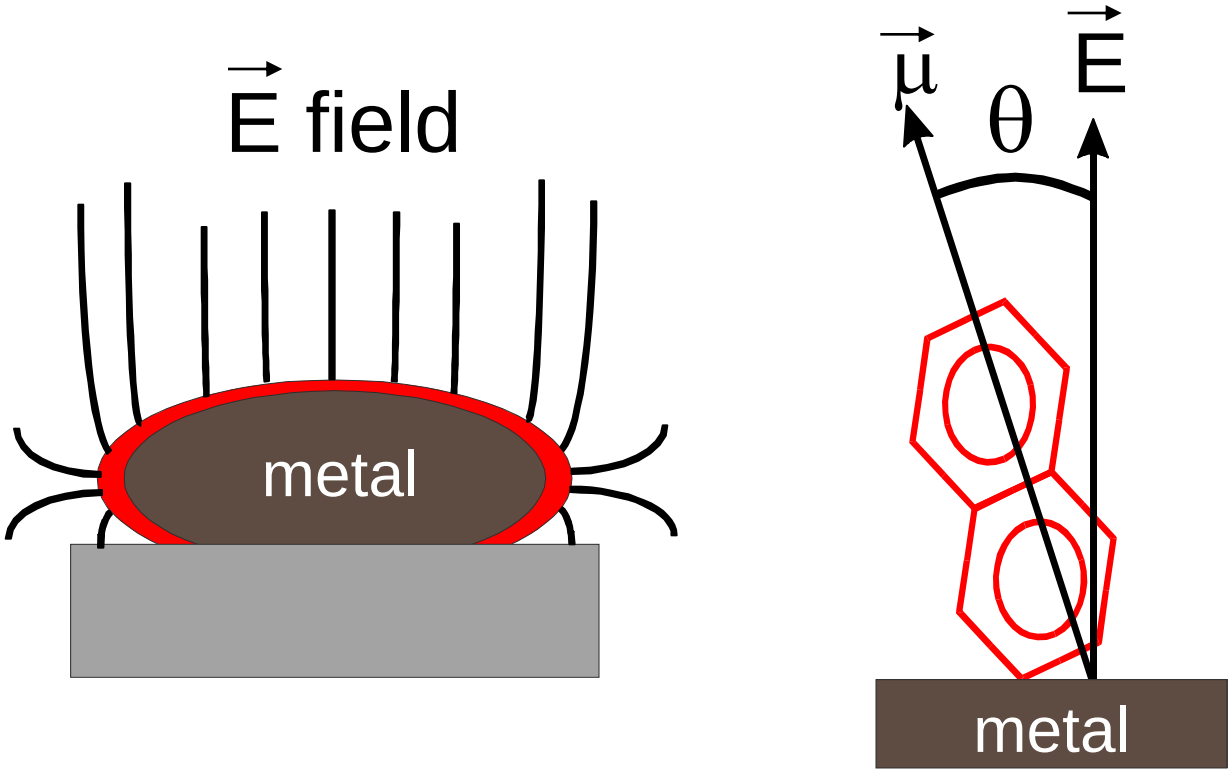


CD concentration

- 2.8×10^{-5} M
- 1.9×10^{-5} M
- 1.0×10^{-5} M
- 0.6×10^{-5} M
- 0.4×10^{-5} M
- 0.2×10^{-5} M
- 0.1×10^{-5} M

D. Ferri, T. Bürgi, J. Am. Chem. Soc. **123**, 12074 (2001)

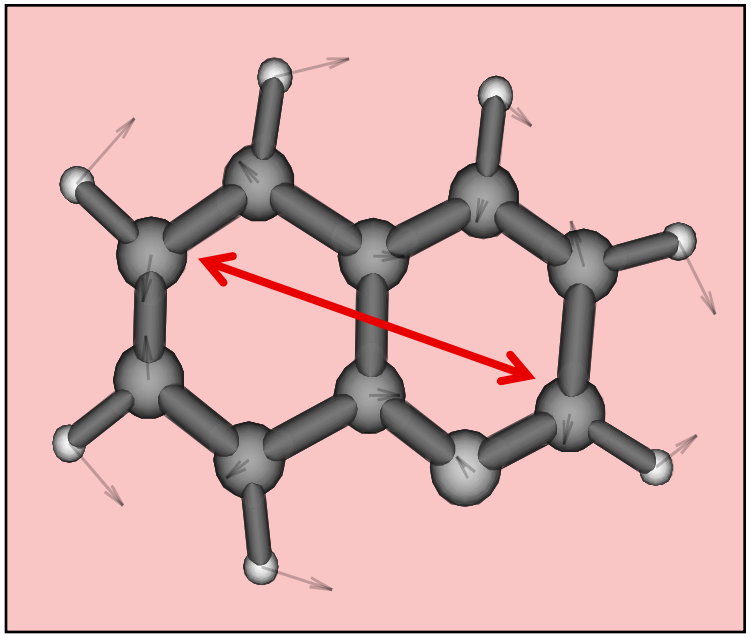
Determination of the orientation of an adsorbate on a metal surface



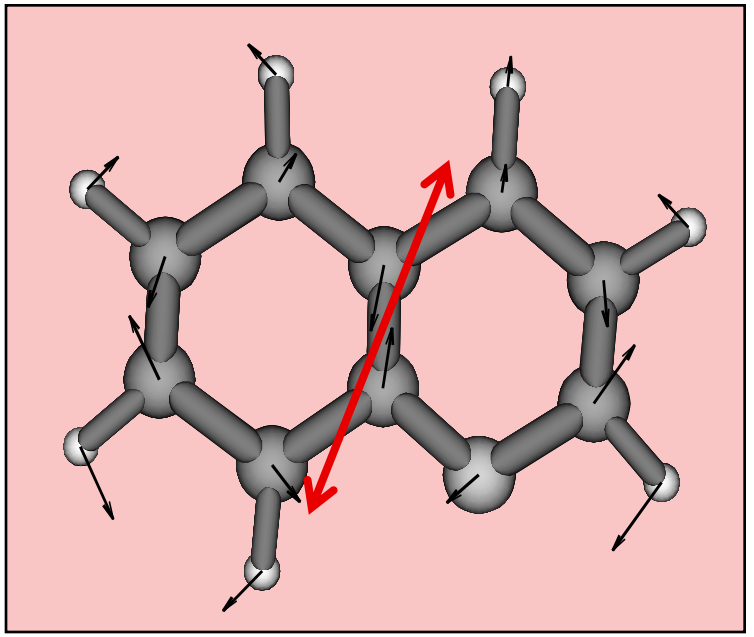
$$I \propto (\vec{\mu} \bullet \vec{E})^2 = \left|\vec{\mu}\right|^2 \left|\vec{E}\right|^2 \cos^2(\Theta)$$

Orientation of dynamic dipole moment μ associated with a vibrational mode

Quantum chemical calculations

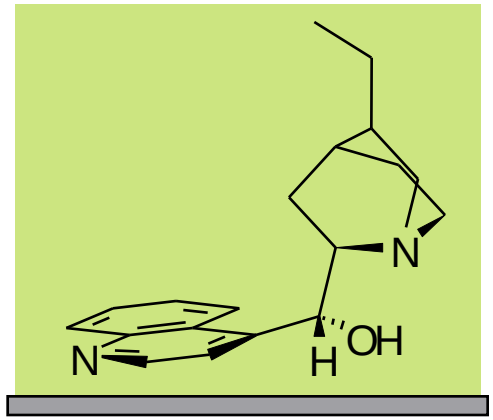


1510 / 1530 cm^{-1}

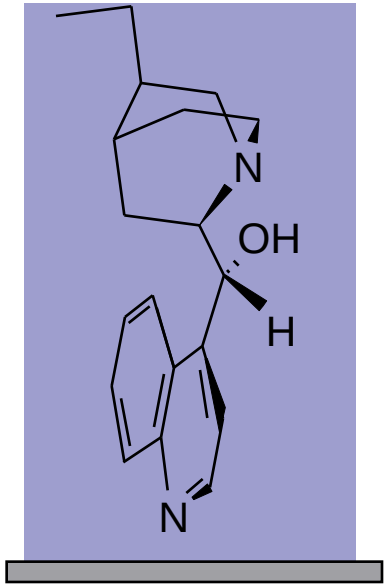


1569 cm^{-1}

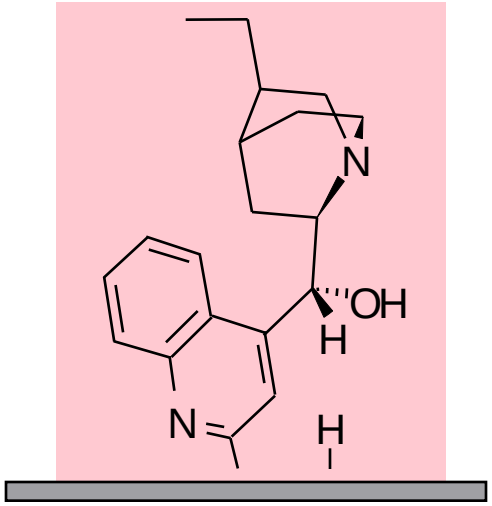
Summary: Adsorption of cinchonidine on Pt



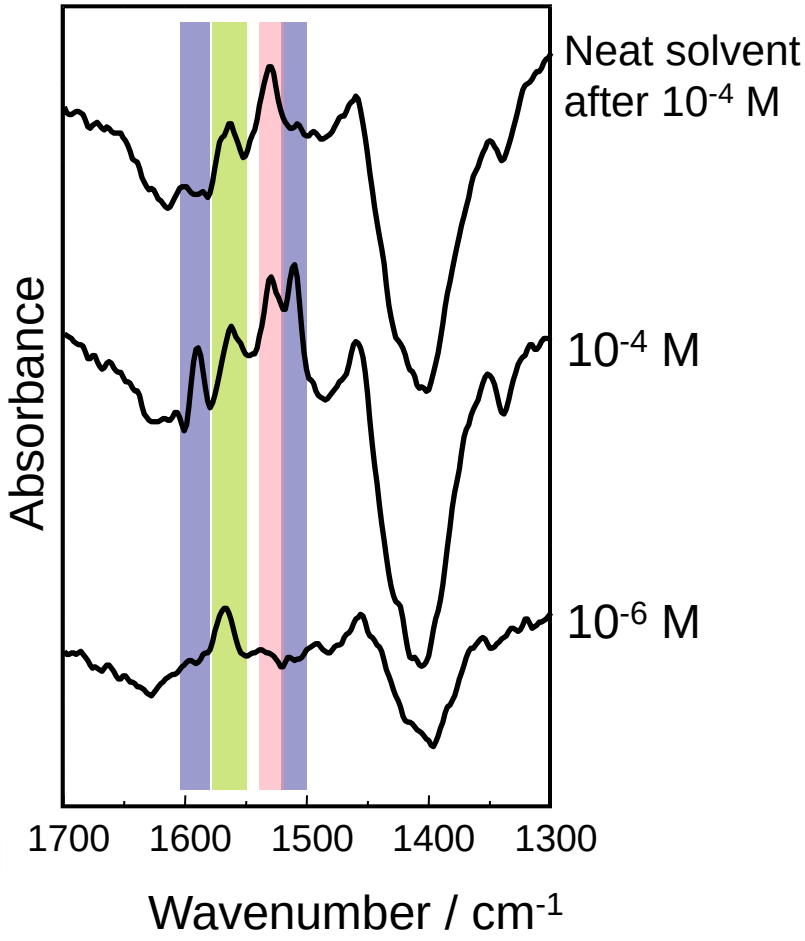
- Low coverage
- Strongly adsorbed



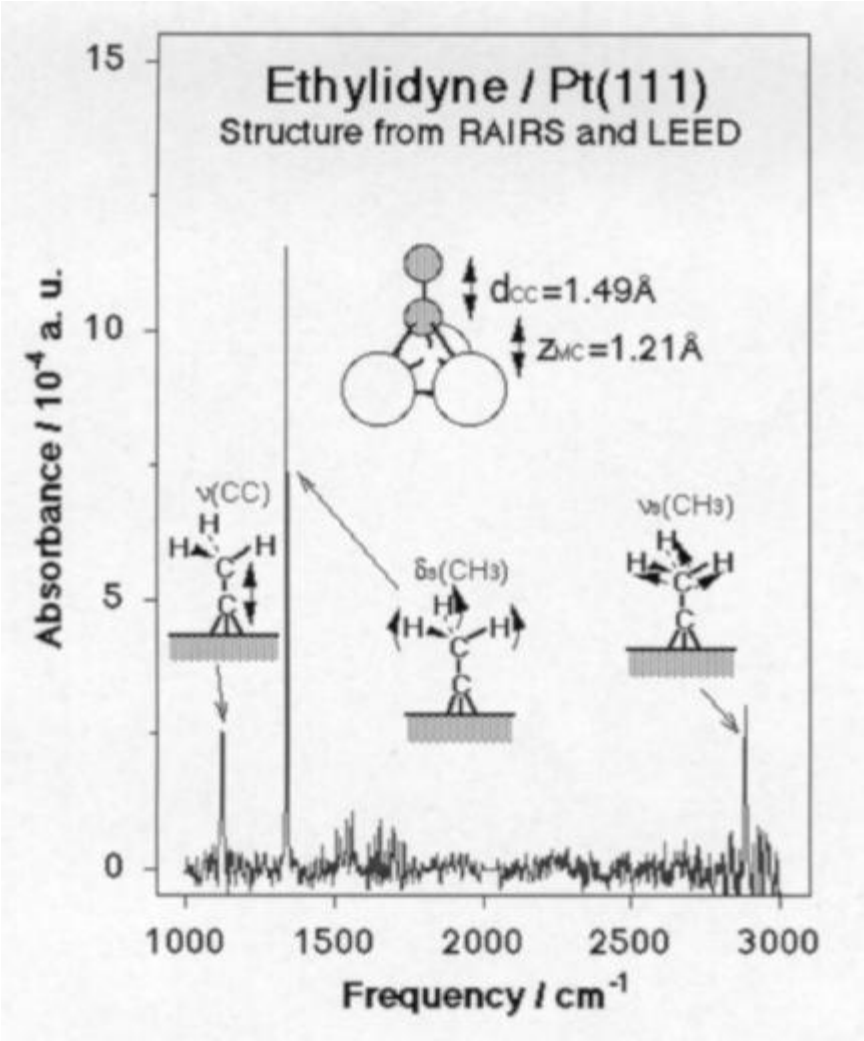
- High coverage
- Weakly adsorbed
- N lone pair bonded



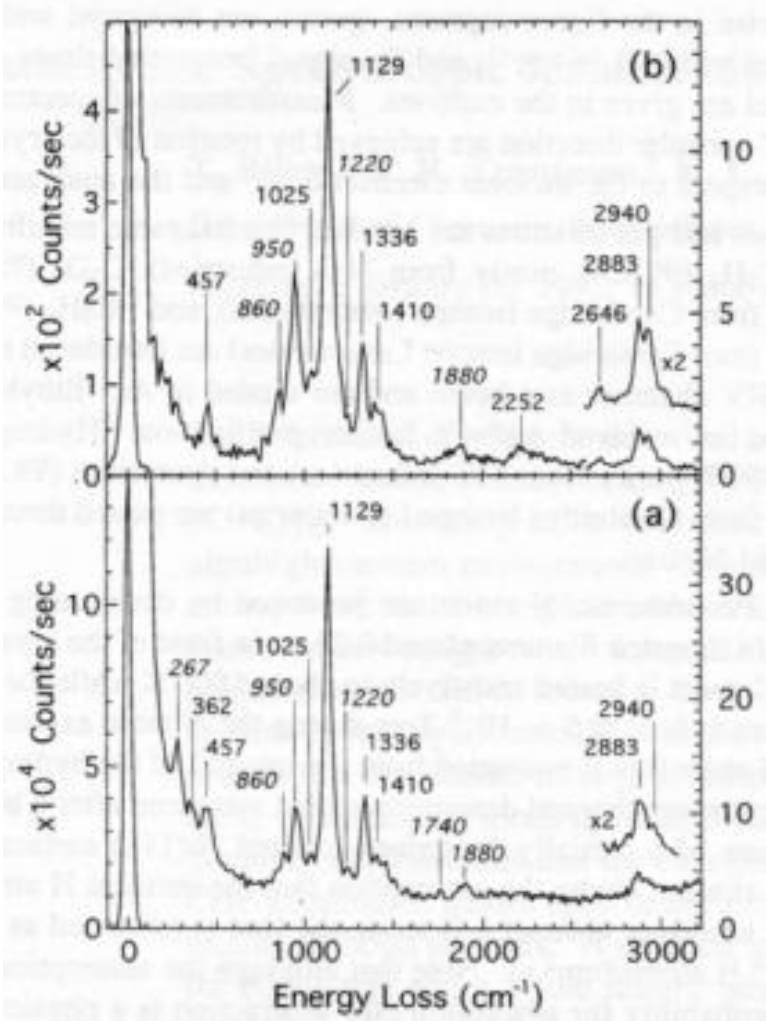
- Strongly adsorbed



Metal surface selection rule: Ethylidyne on Pt
Comparison between IRRAS and EELS



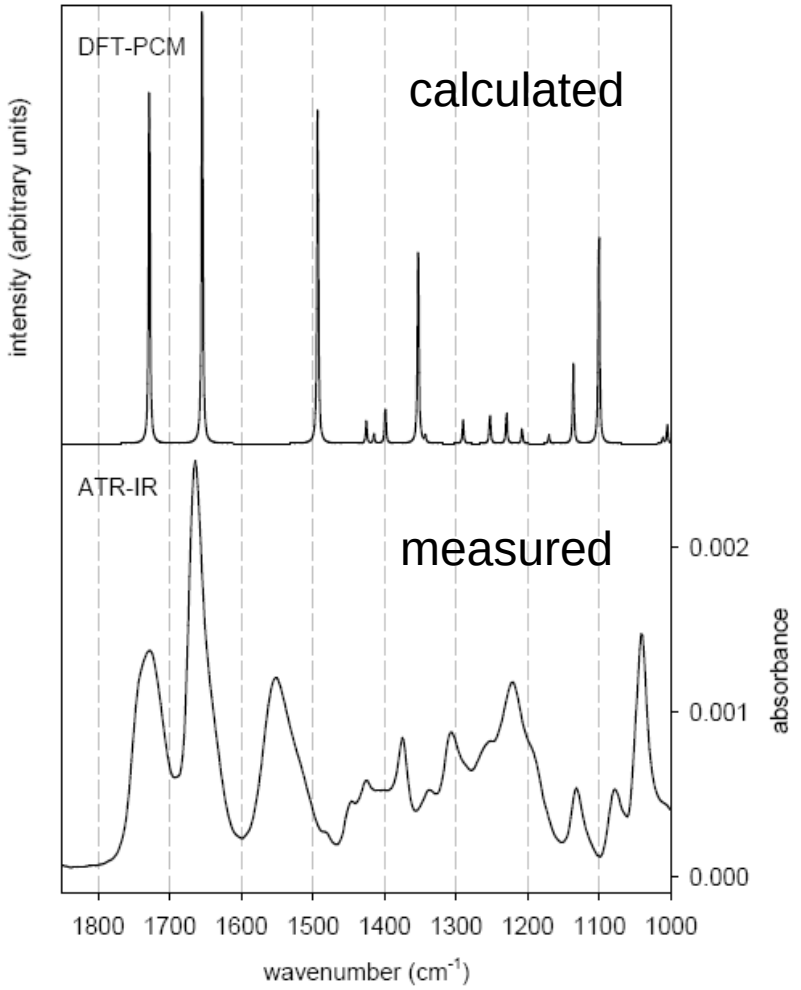
IRRAS

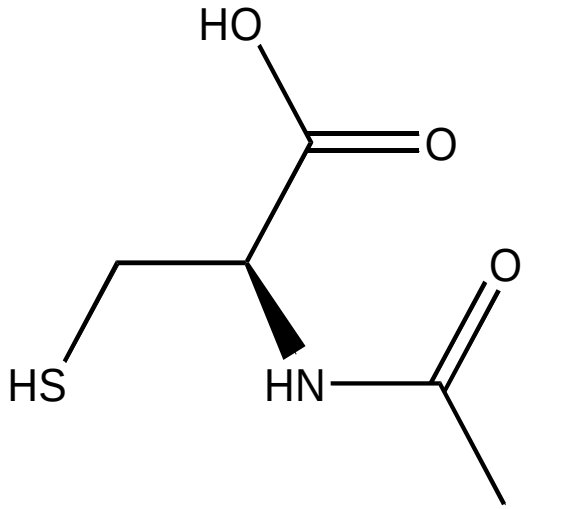


EELS: a) specular; b) off specular

Self-assembly of N-acetyl-L-cysteine on gold

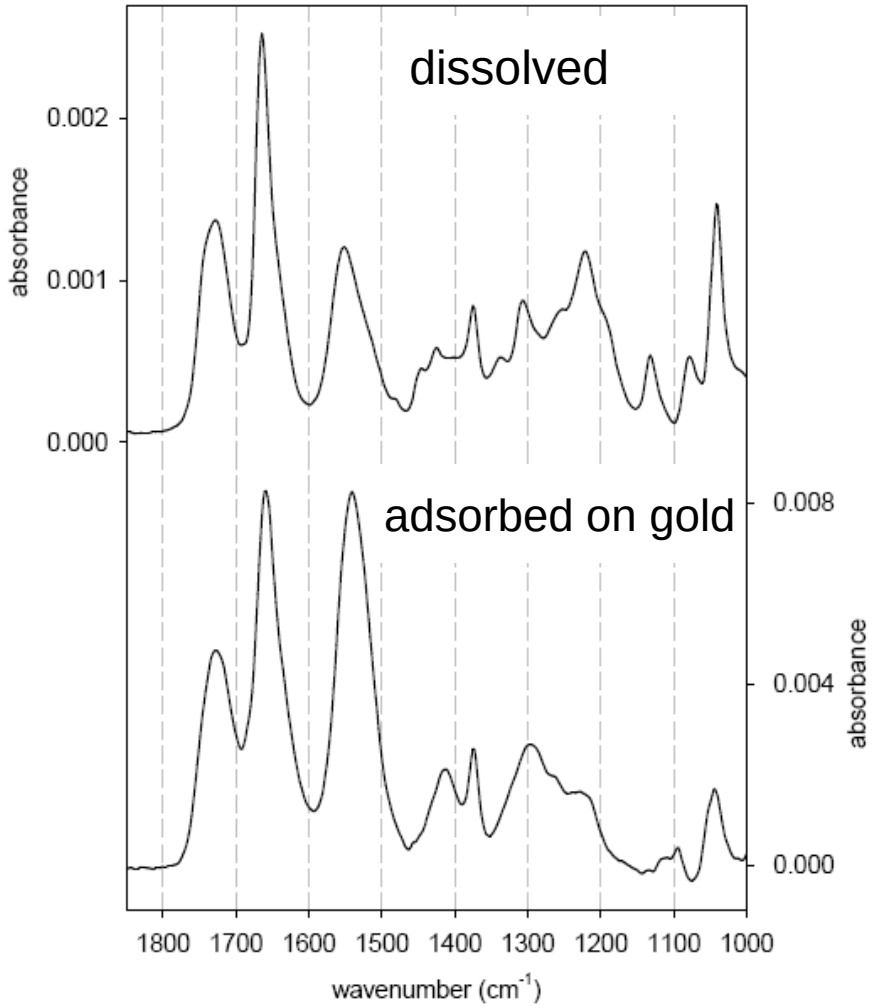
Infrared spectrum of dissolved NALC





N-acetyl-L-cysteine (NALC)

Self-assembly of N-acetyl-L-cysteine on gold

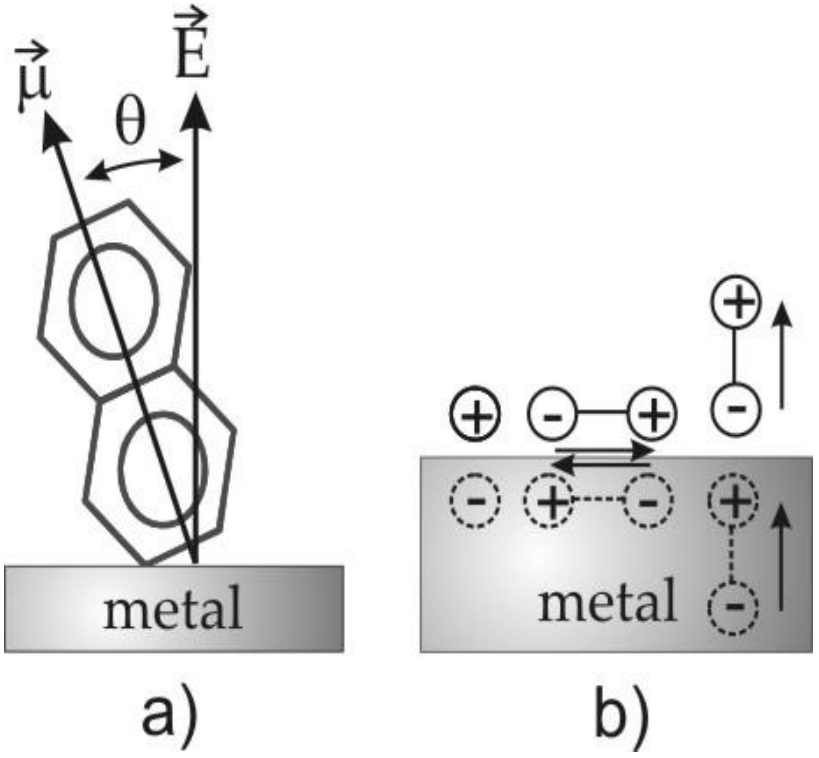


random

oriented

Investigation of Self-Assembled Monolayers

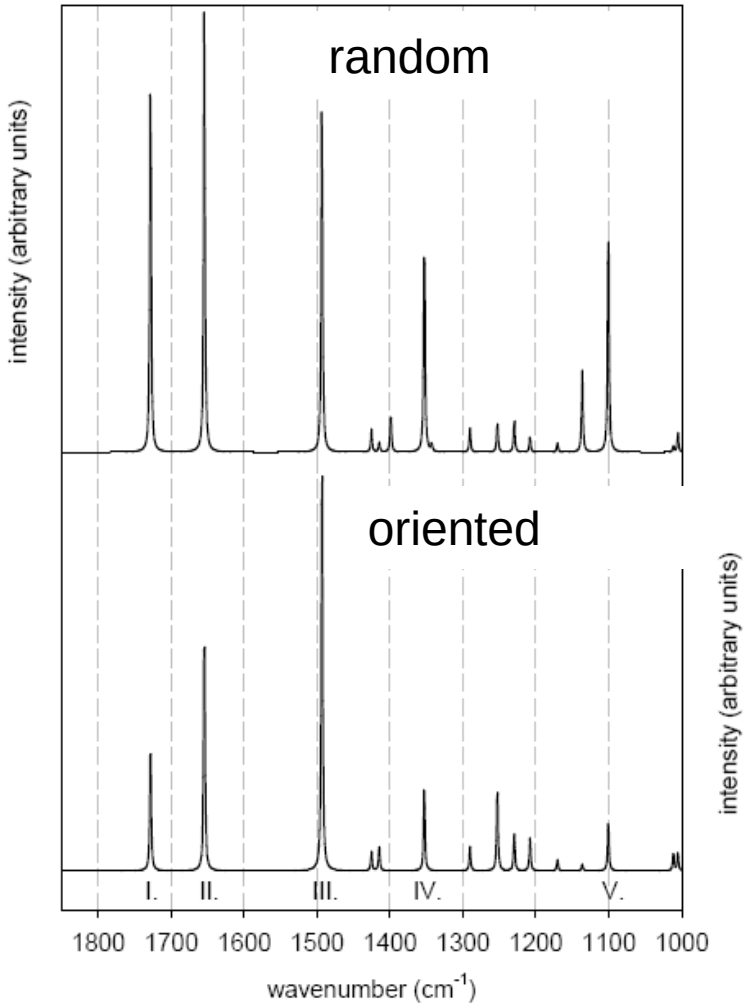
Orientation measurements



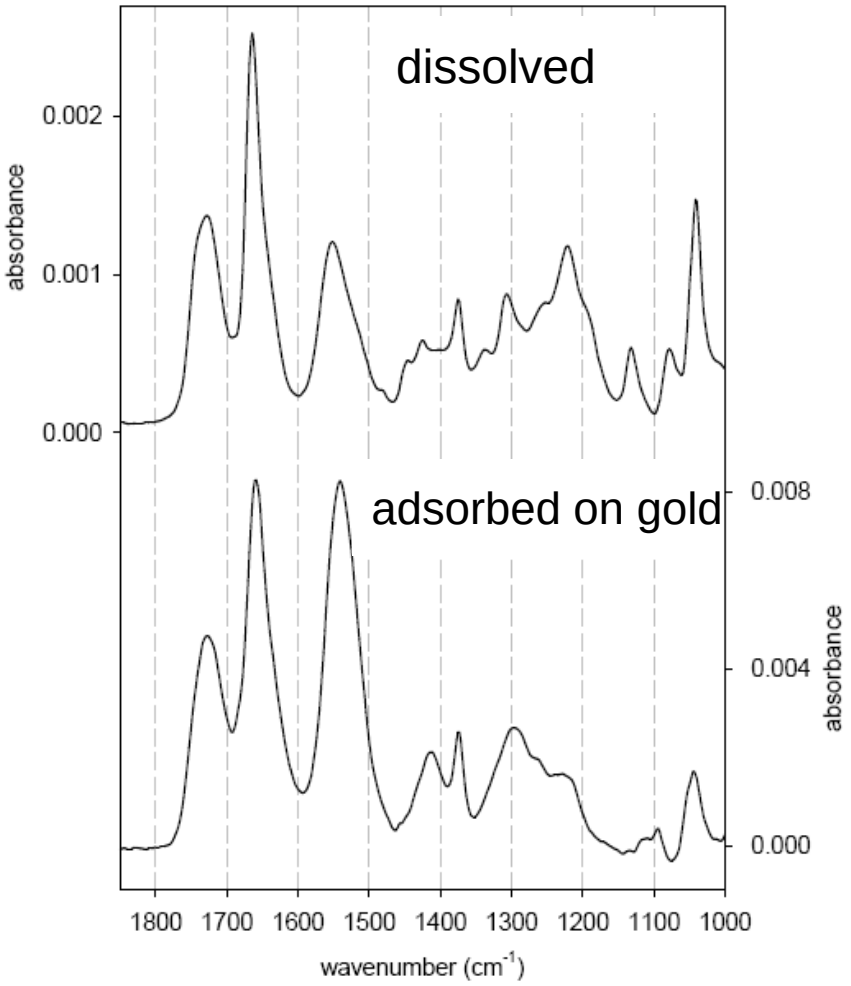
$$I \propto (\vec{\mu} \bullet \vec{E})^2 = \left|\vec{\mu}\right|^2 \left|\vec{E}\right|^2 \cos^2(\Theta)$$

Self-assembly of N-acetyl-L-cysteine on gold

Effect of orientation on the spectrum



Self-assembly of N-acetyl-L-cysteine on gold



Orientation of NALC on gold
(at the beginning of adsorption)