Synchrotron radiation and Laser : Applications to material science and biology in the infrared frequency range

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Outline

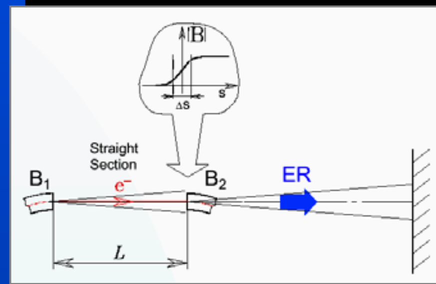
1. Synchrotron radiation: spectroscopy and microscopy
   - Infrared emission
   - Biological applications(microscopy)....
   - Surface Science – far infrared
   - Vibrational dynamics at surfaces

2. Infrared Lasers: non linear spectroscopy at surface and interface
   - Non linear spectroscopy at surfaces: SFG
   - Vibrational dynamics at surfaces

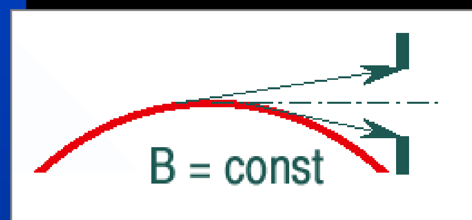
3. Future at Fouth Generation Light Source?

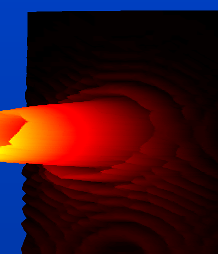
Synchrotron radiation: a bright source of Infrared photons

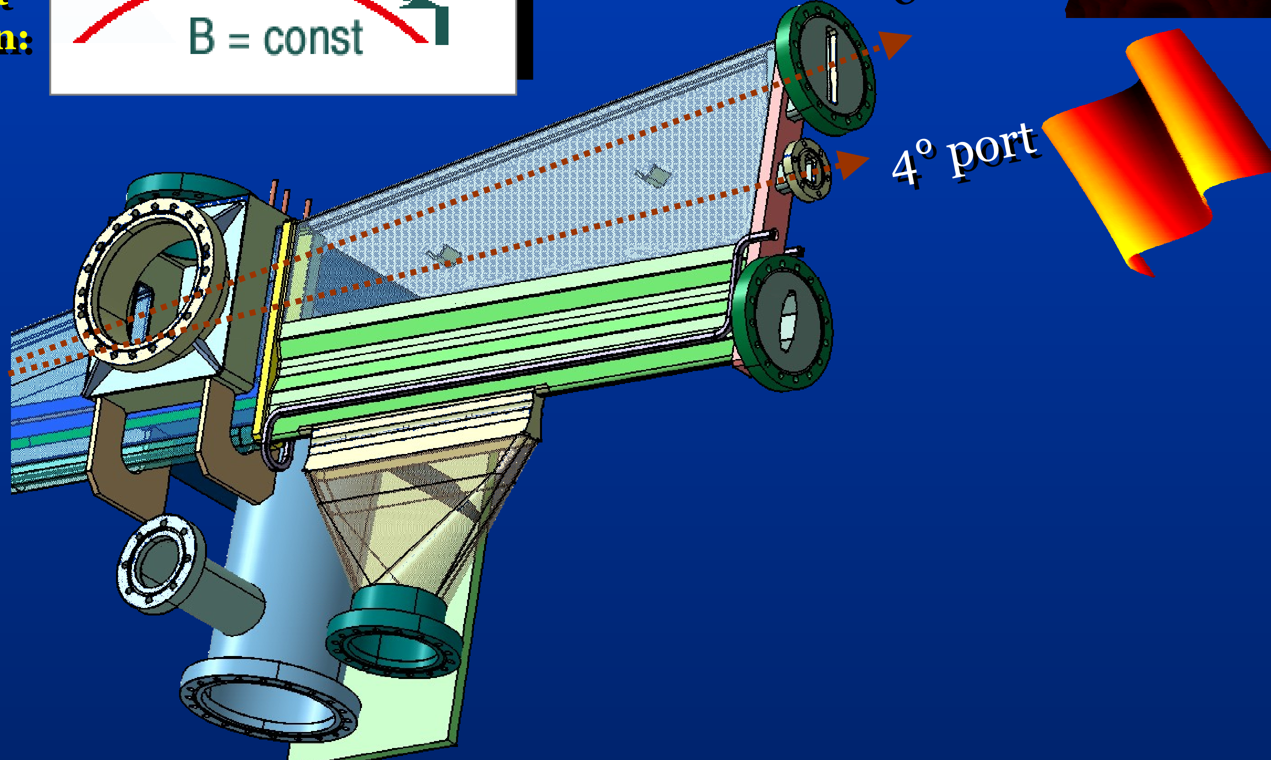
Edge emission:



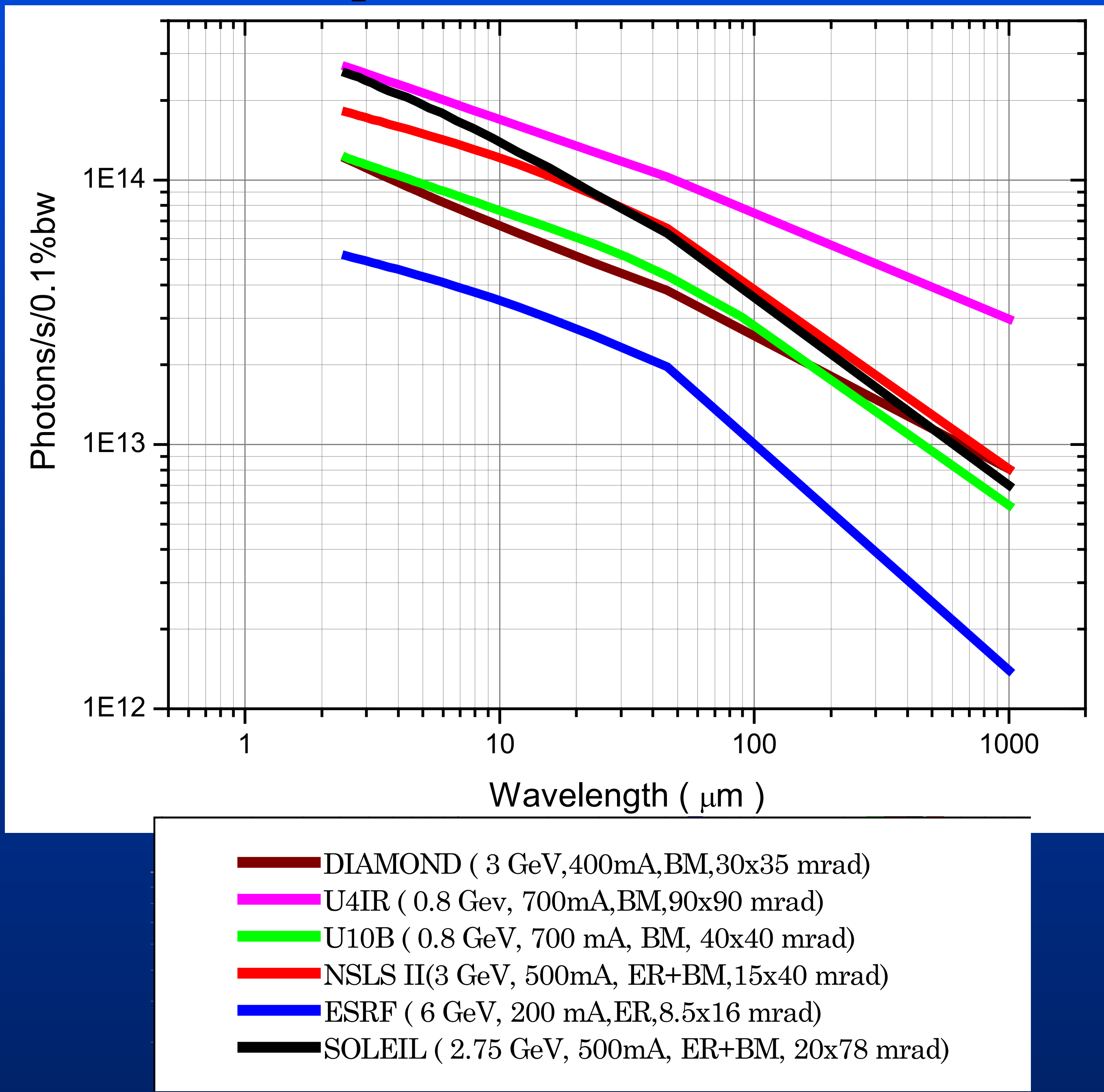
Bending magnet emission:





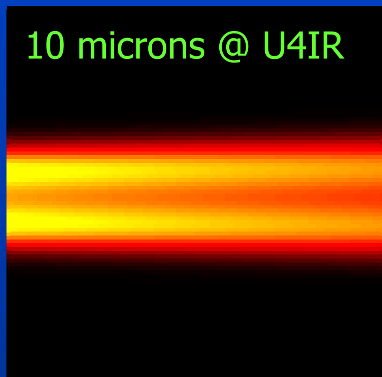


Flux comparison between various facilities

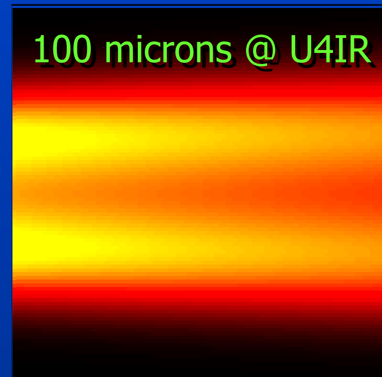


Infrared emission is well accounted for theoretically the SRW software(Oleg Chubar) (both flux and intensity profile)

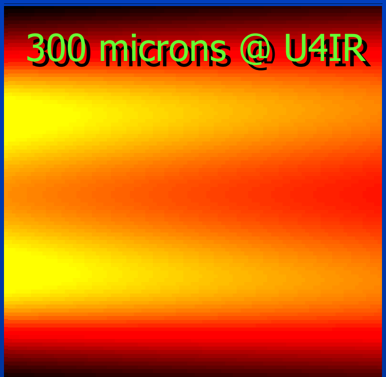
NSLS U4IR 90x90 mrad 700 mA



1.5769e+14 Photons/s/.1%bw

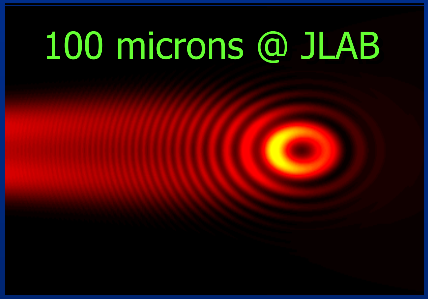


7.3359e+13 Photons/s/.1%bw

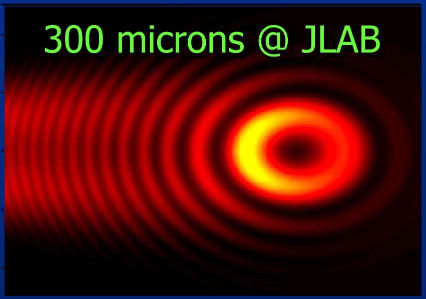


4.9233e+13 Photons/s/.1%bw

JLAB(G.Williams) 170x146 mrad 10 mA



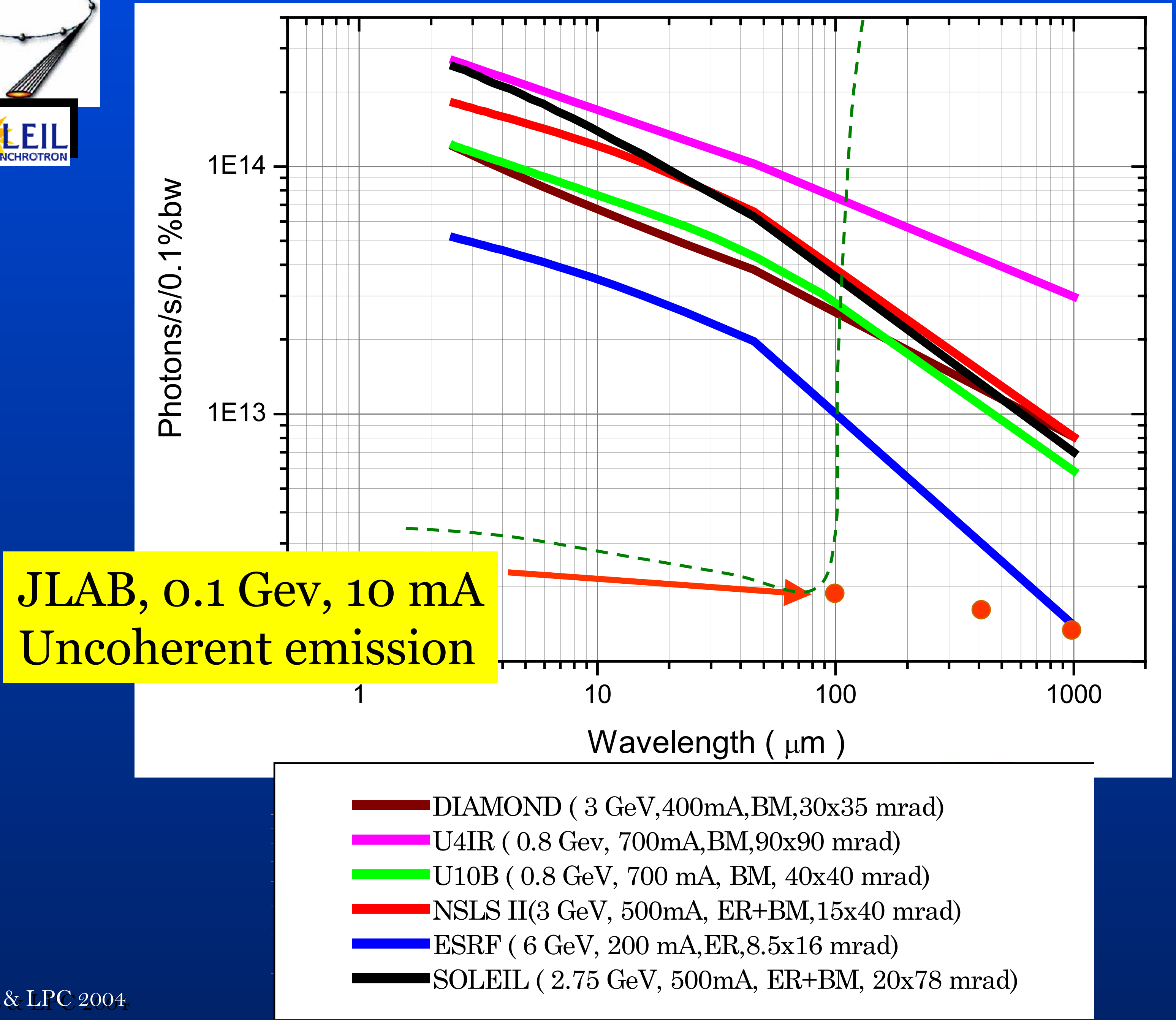
1.83021e+12 Phot/s/0.1%bw



1.53084e+12 Phot/s/0.1%bw

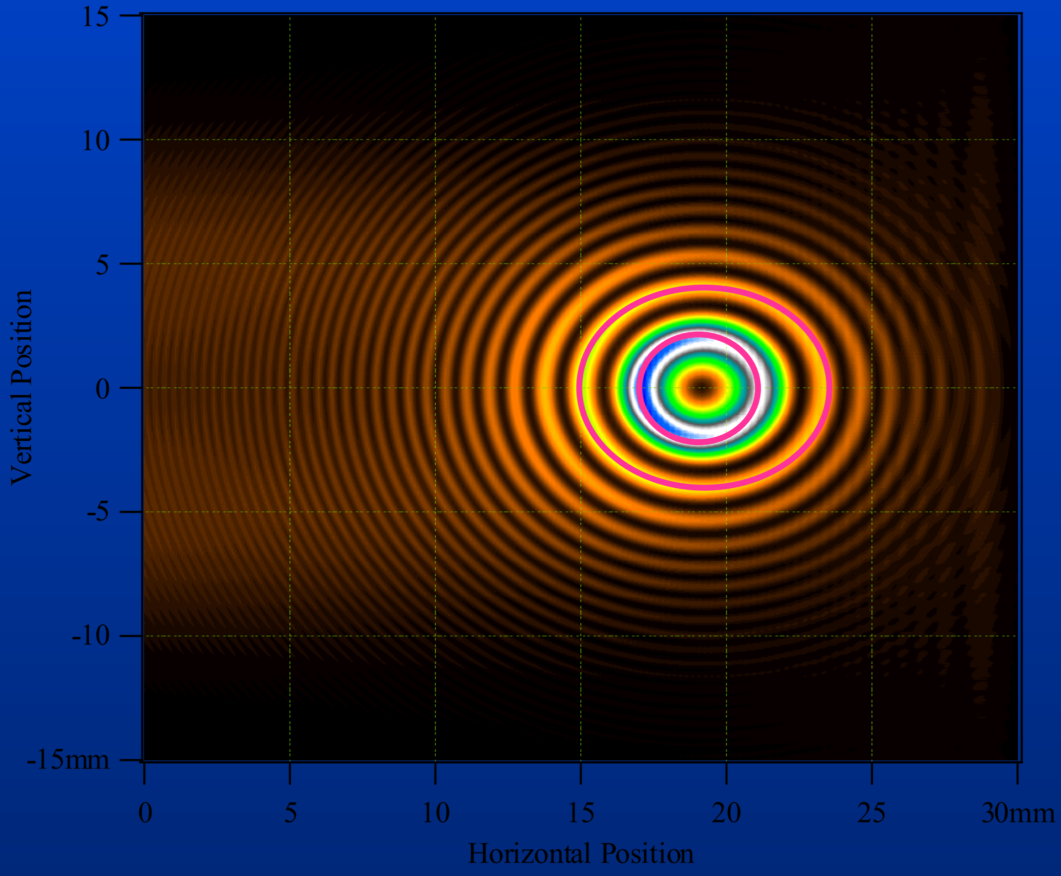
1.13926e+12 Phot/s/0.1%bw

Flux comparison between various facilities

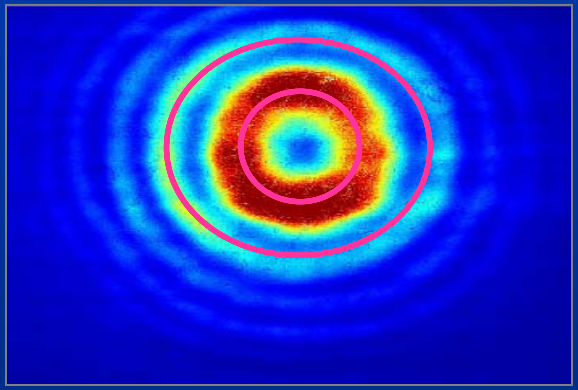


IR beamline @ ESRF

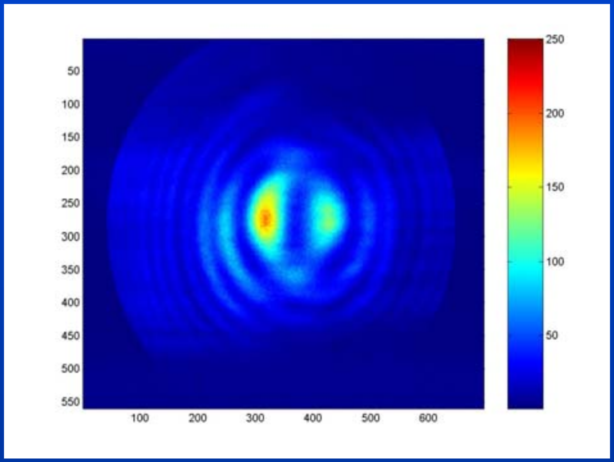
Calculated intensity profile
at 6.2 meters from source
λ=0.52 microns



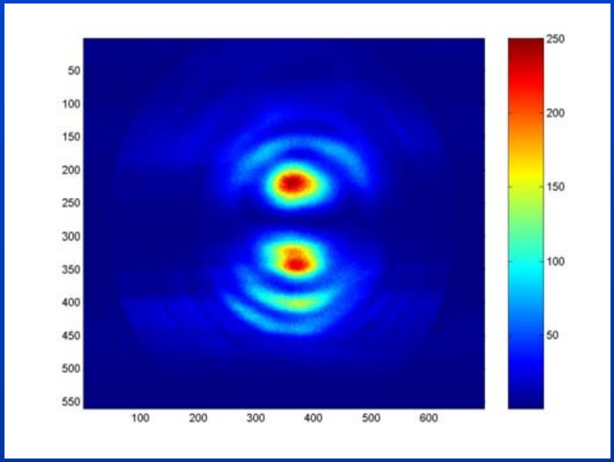
Recorded with a CCD camera
at 6.2 meters from source
λ= 0.52 microns



Edge radiation observed at IR beamline ESRF
CCD camera, 10m from source, filter=700nm

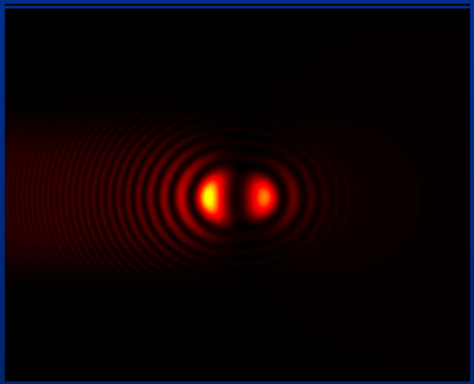


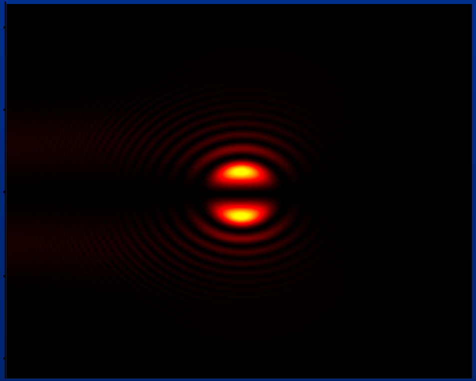
H-polarized



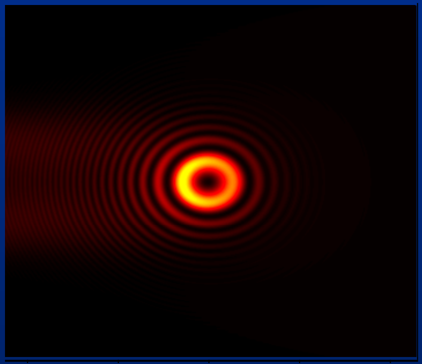
V-polarized

Simulation with finite-emittance electron beam

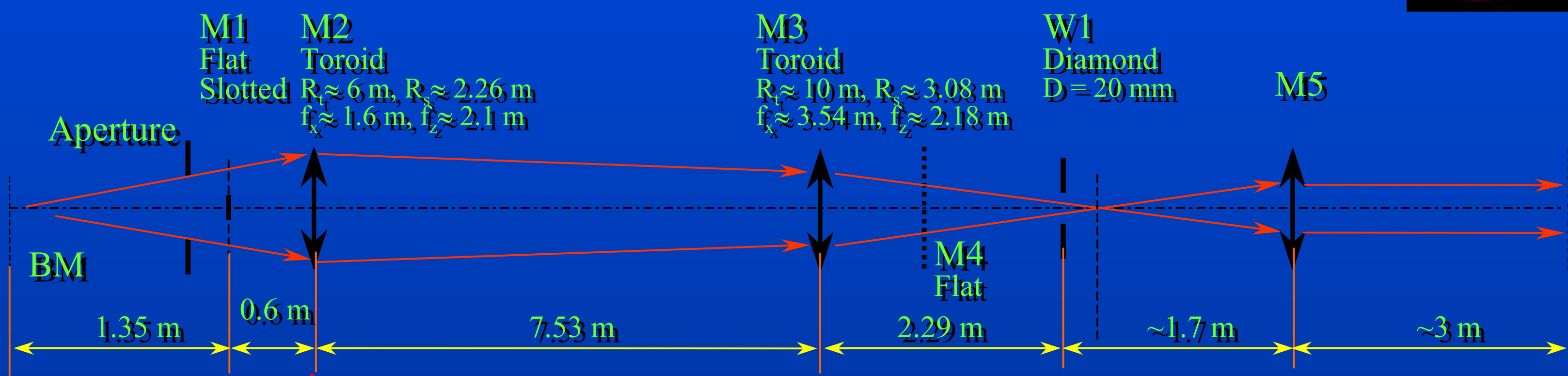




Total polarisation



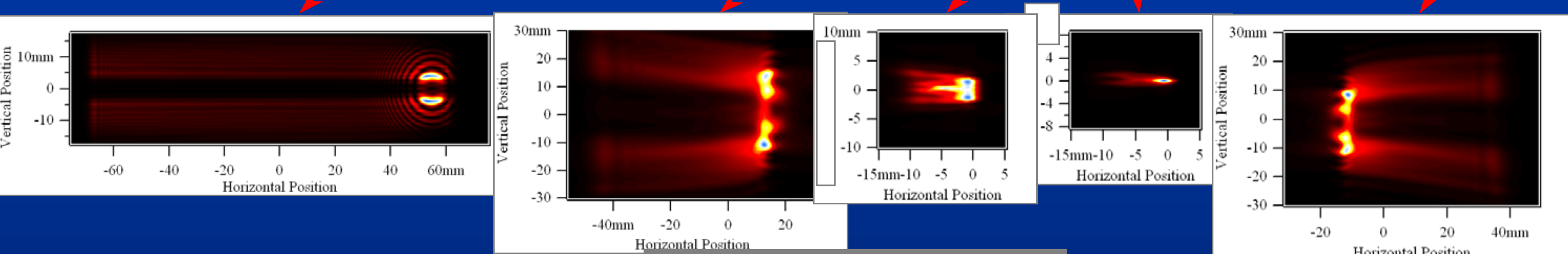
Detailed optimization: the SOLEIL case



Flux: 1.67×10^{14} Phot/s/0.1%bw

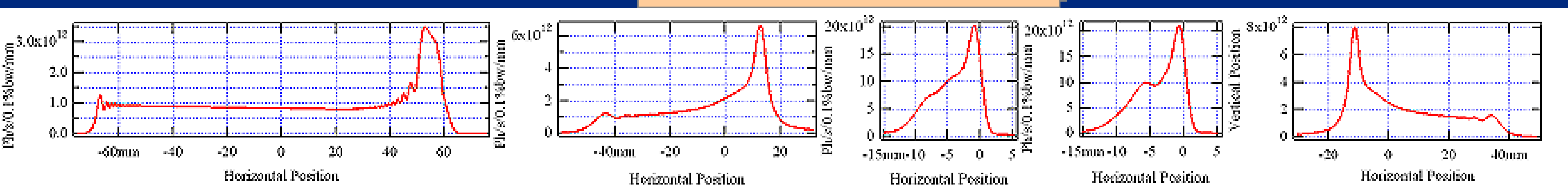
Flux: 1.35×10^{14} Phot/s/0.1%bw

Intensity Distributions at 10 µm Wavelength



Emission, wavefront propagation calculations: SRW code

Intensity Profiles

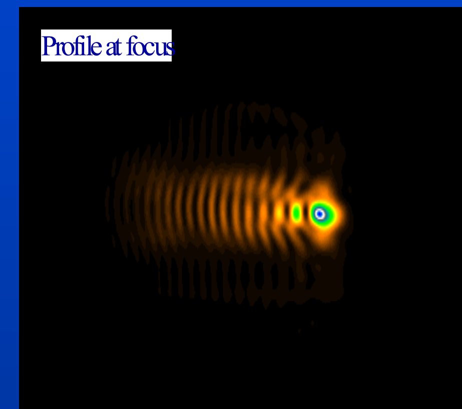


- Synchrotron Infrared Microscopy has become a very useful microanalytical technique in almost all synchrotron facilities

- It's a multidisciplinary technique

- One of the most active community= Biology

Coupling source with spectrometer



Microscope at ESRF-IR beamline

Synchrotron Infrared Microscopy

BRIGHTNESS (100 to 1000x)

+

BROADBAND

- Higher Spatial Resolution
- Better Signal-to-Noise
- Faster Data Collection

Spectroscopy

From high-contrast microspectroscopy to high-contrast imaging

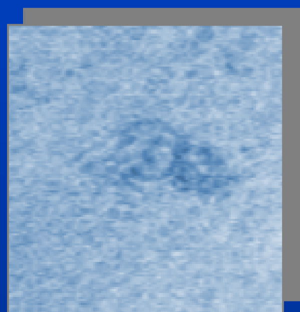
Biological applications of synchrotron IR microscopy:

- Single cell study
- Human tissues

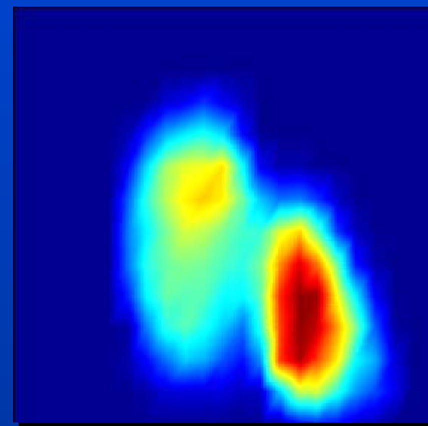
Cell differentiation

Induced by Phorbol Myristate Acetate (PMA)
(morphology and activity changes)

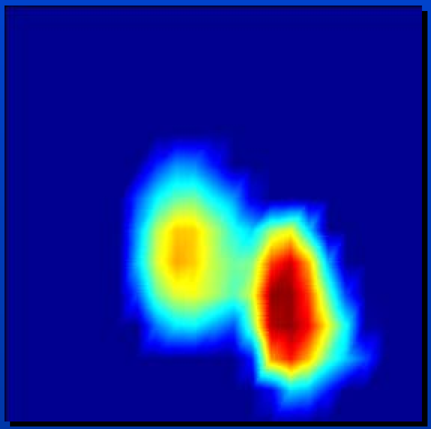
HL-60 few minutes after « activation »



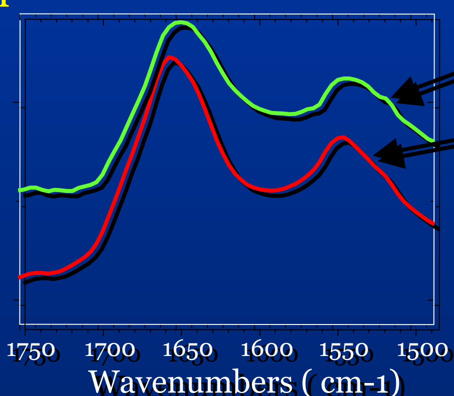
20 µm



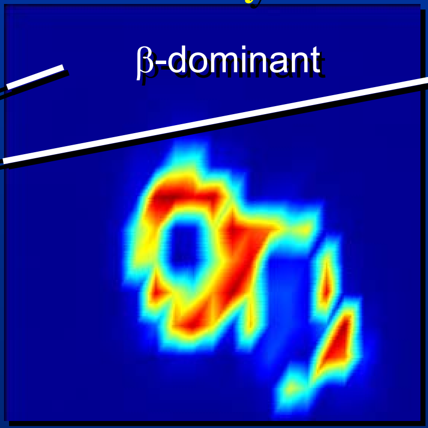
Lipids profile

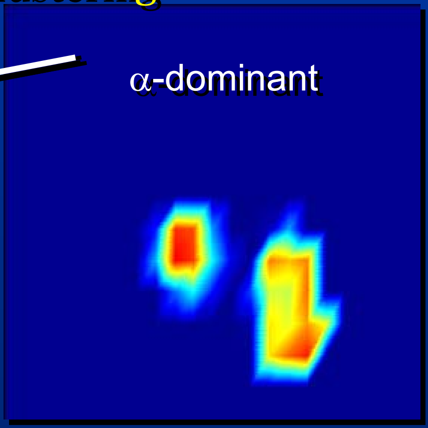


Protein profile
(Amide I)



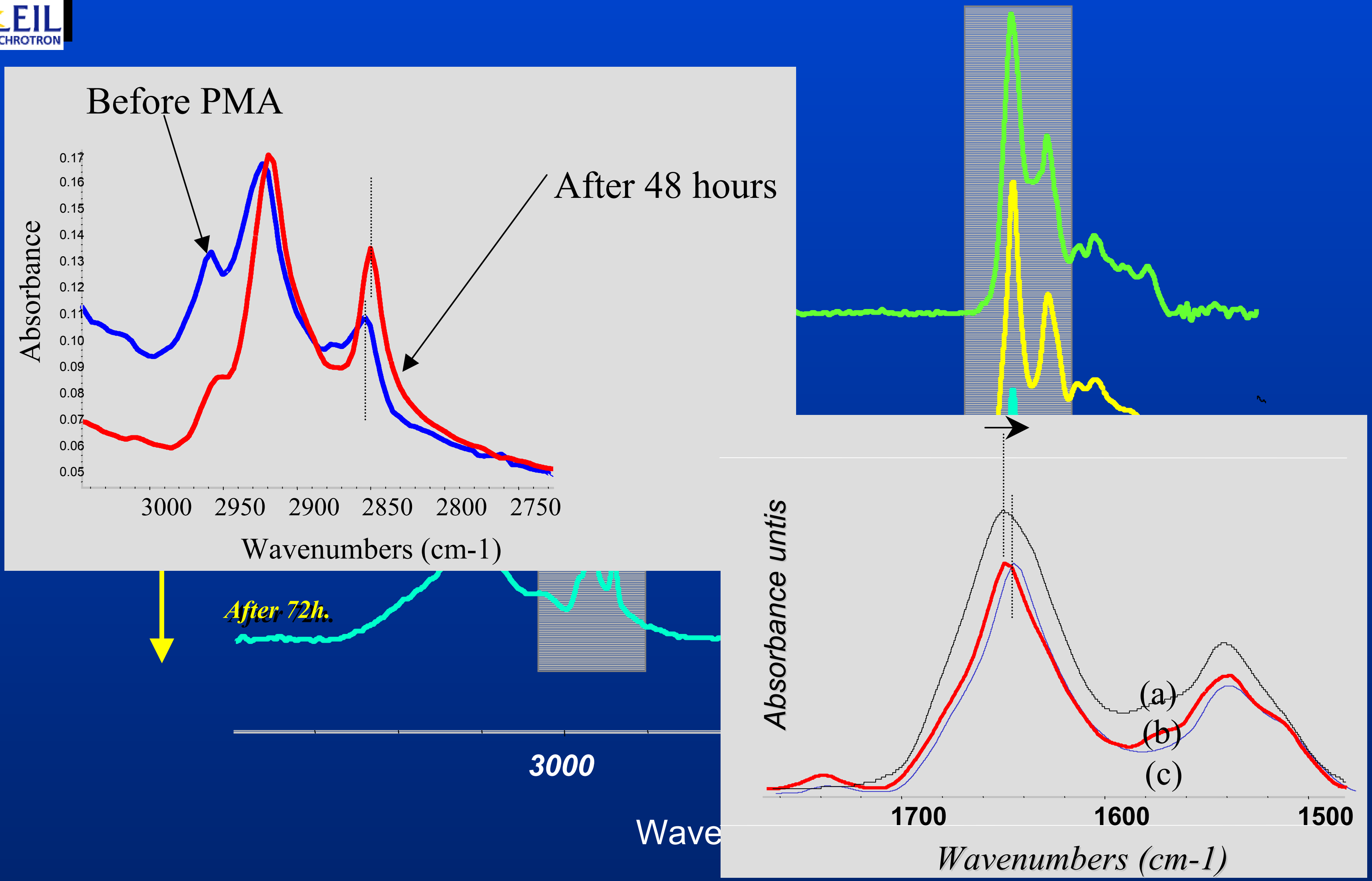
Fuzzy-c-means clustering



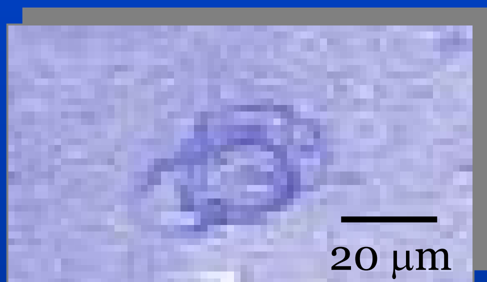


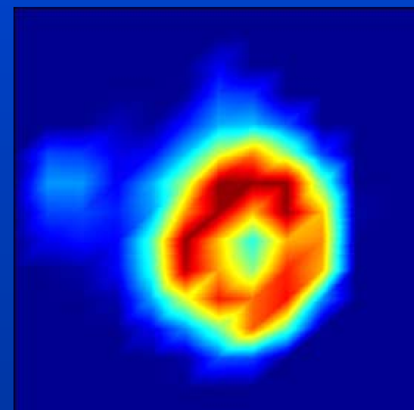
J.L. Teillaud, N. Jamin, L. Miller and P.Dumas

Spectra recorded with a 3x3 μm² aperture in the nucleus

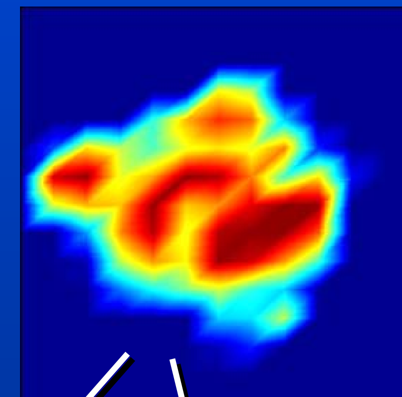


48 Hours after PMA…

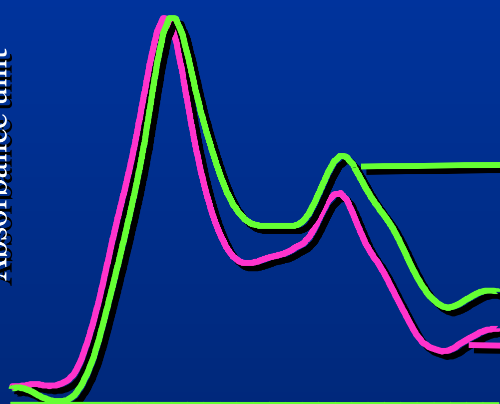


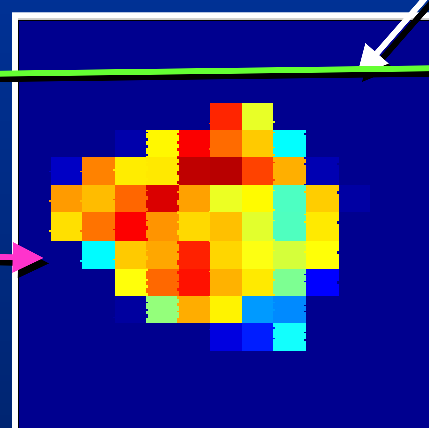


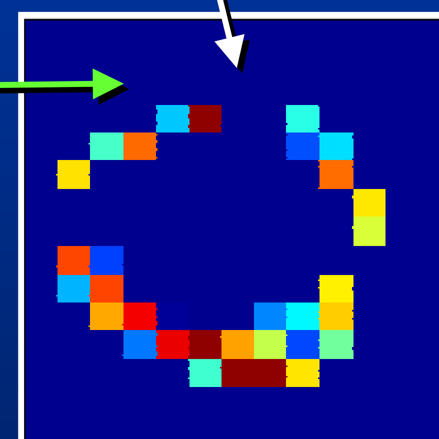
Intensity profile of lipids



Nucleus (Amide I)

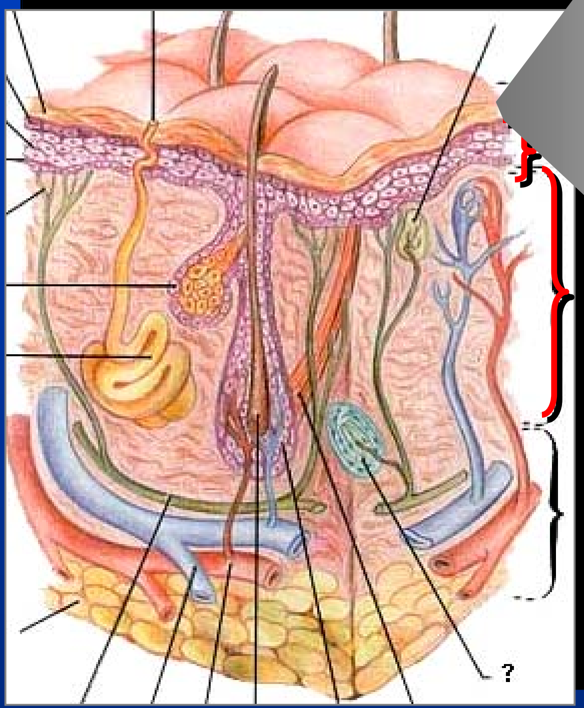




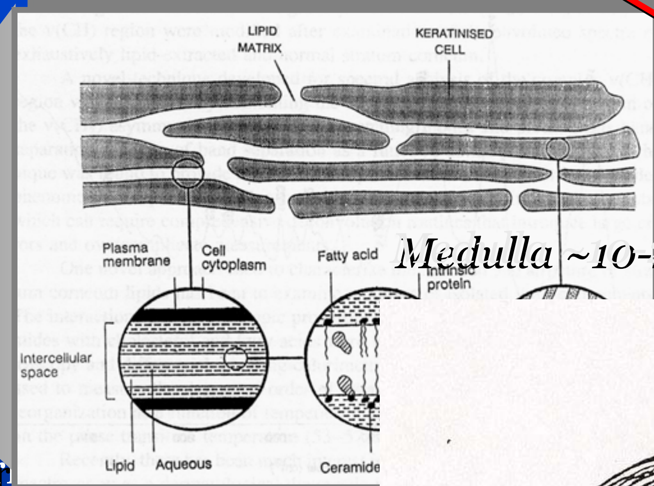


J.L. Teillaud, N. Jamin, L. Miller and P.Dumas

Skin and hair structures

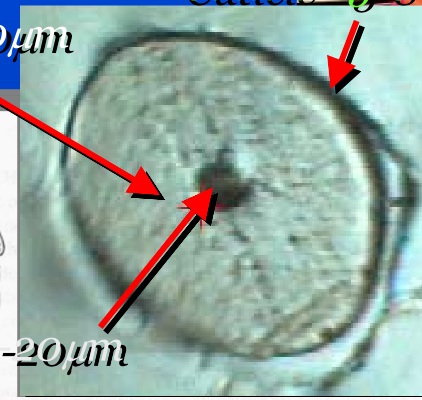


Der
>100 µm

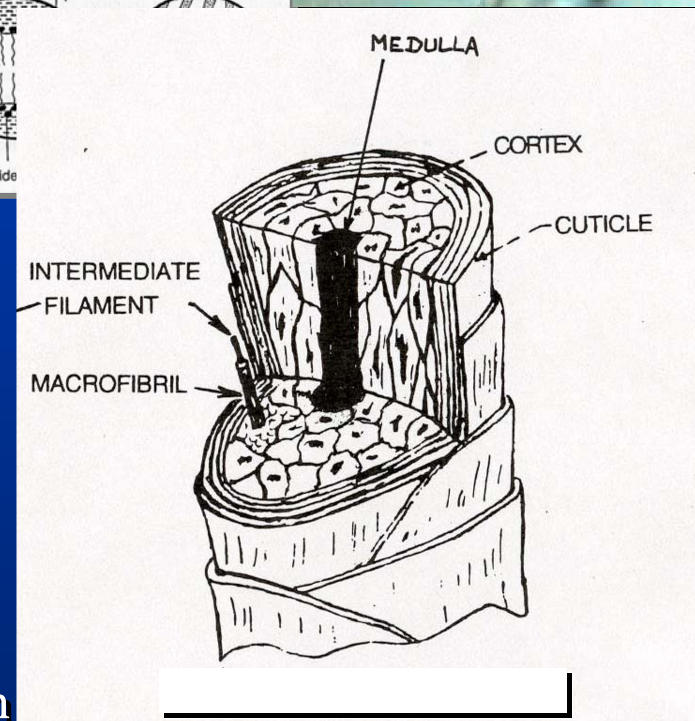


Cortex ~40-80µm

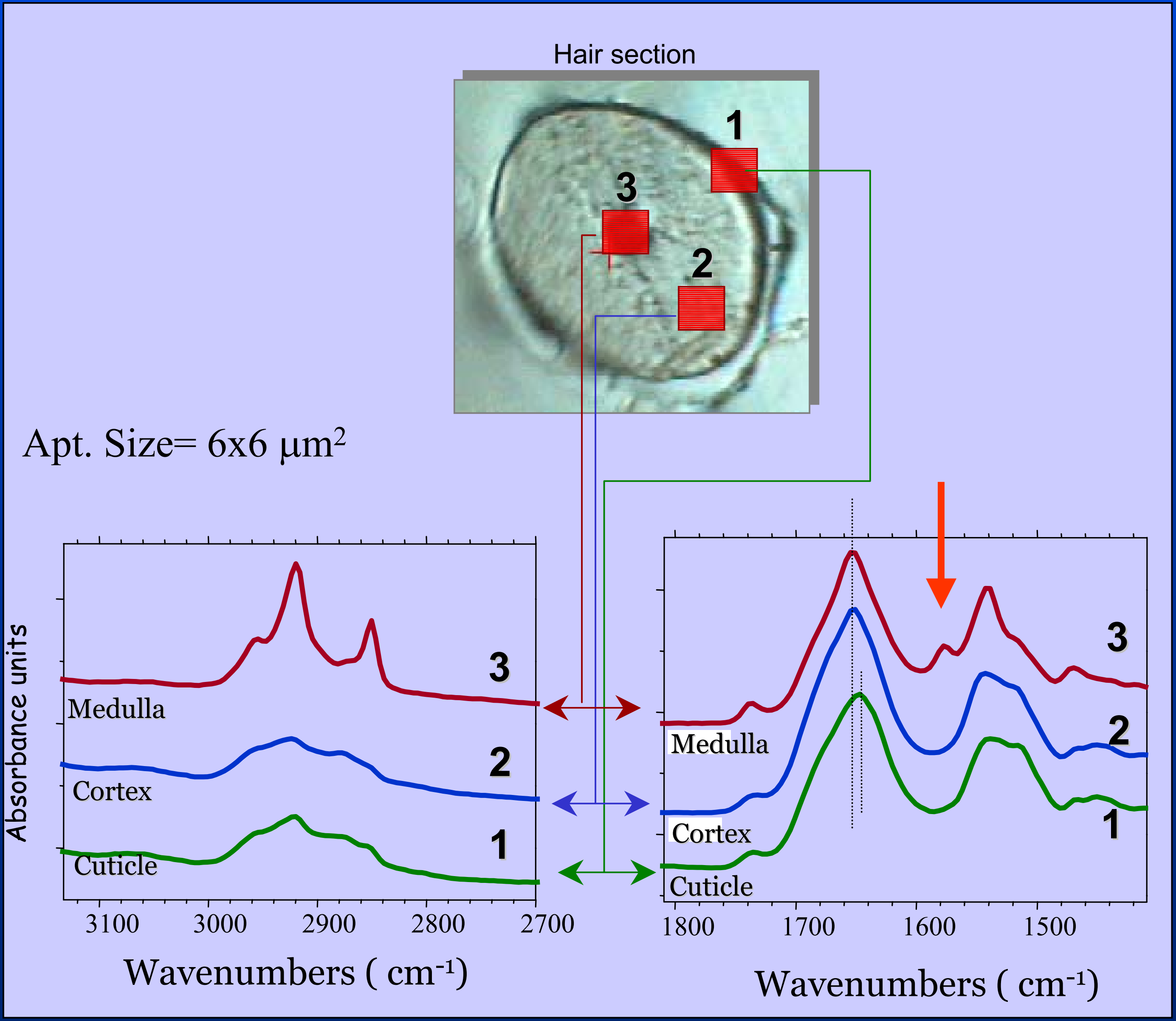
Cuticle ~5-8 µm



Medulla ~10-20µm

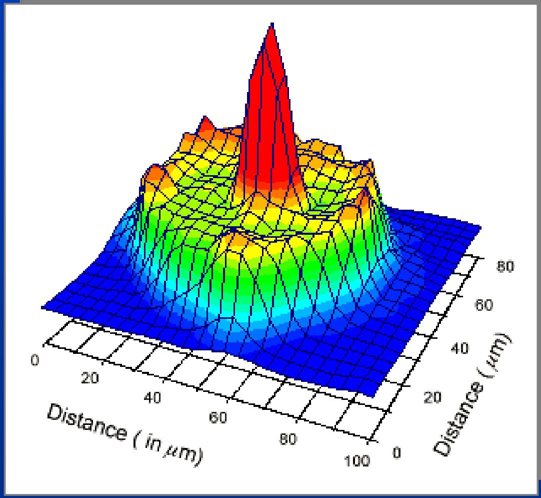


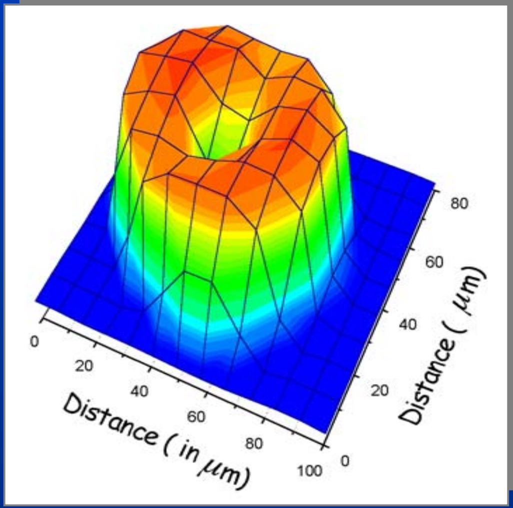
Need to understand the biochemical composition
with micron-range lateral resolution


Hair section
1
3
2
Apt. Size= 6x6 µm²
Absorbance units
3
Medulla
2
Cortex
1
Cuticle
3100
3000
2900
2800
2700
Wavenumbers (cm⁻¹)
3
Medulla
2
Cortex
1
Cuticle
1800
1700
1600
1500
Wavenumbers (cm⁻¹)

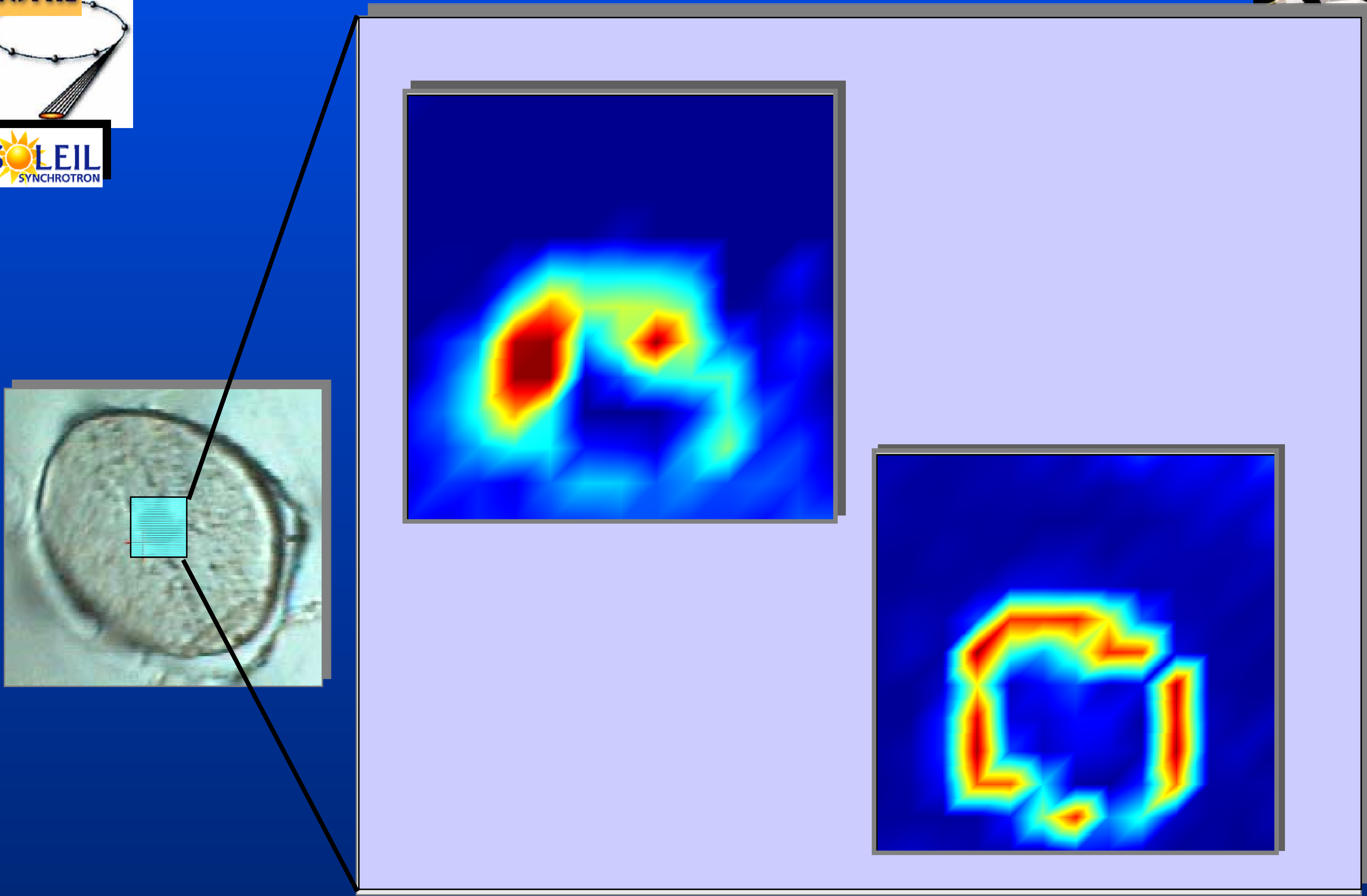
Lipid profile

Protein profile

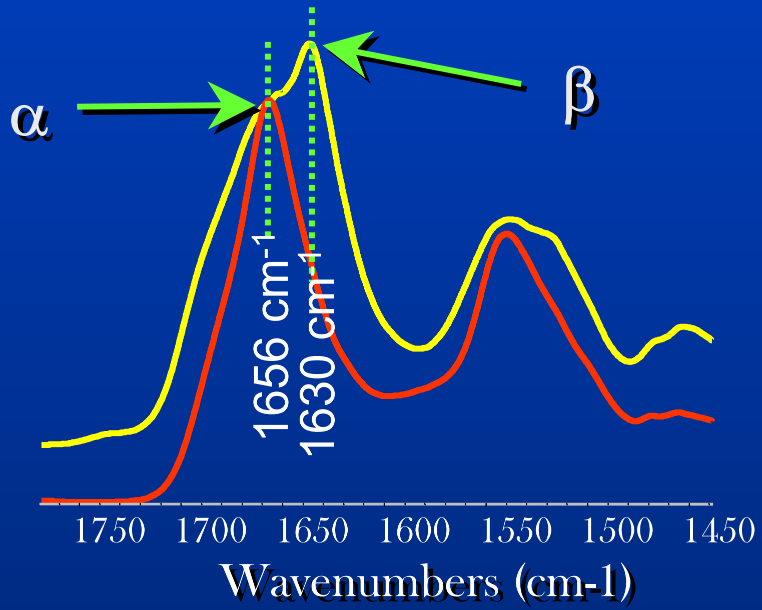


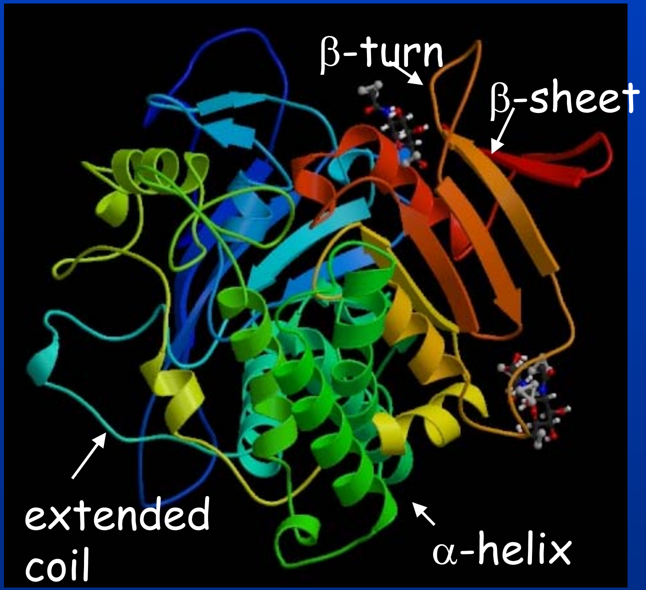


Intern.J. of Cosmetics Science. **23** *1-6* (2001) 369-374

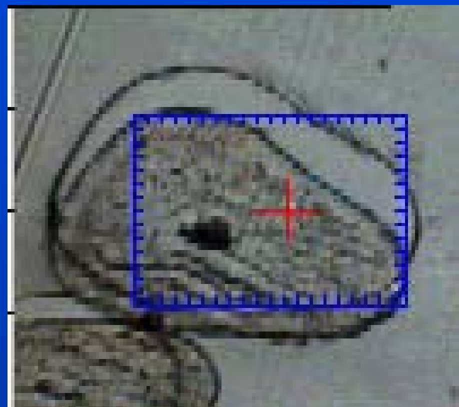


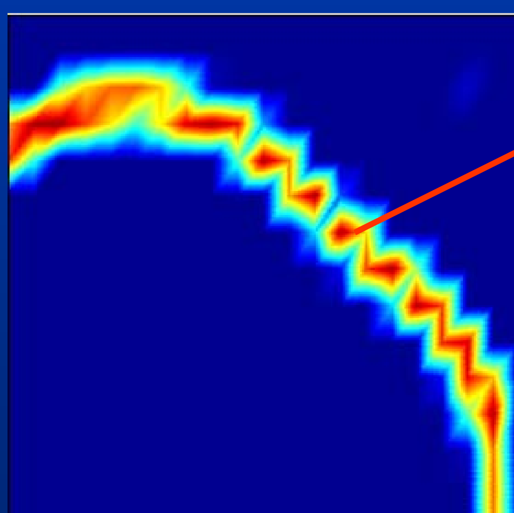
But, there are also structural informations within an IR spectrum of biological samples

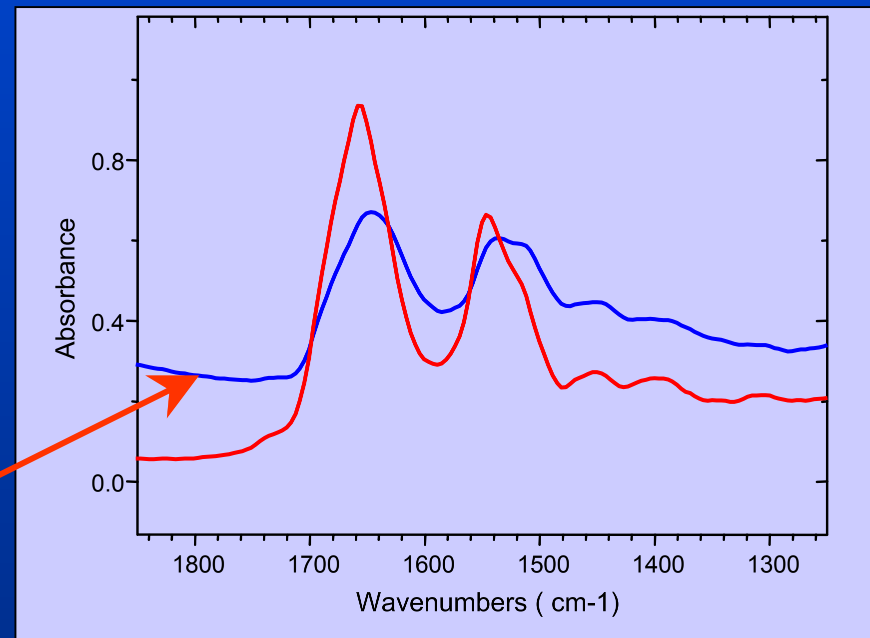




Imaging of the secondary structure of proteins in cuticle

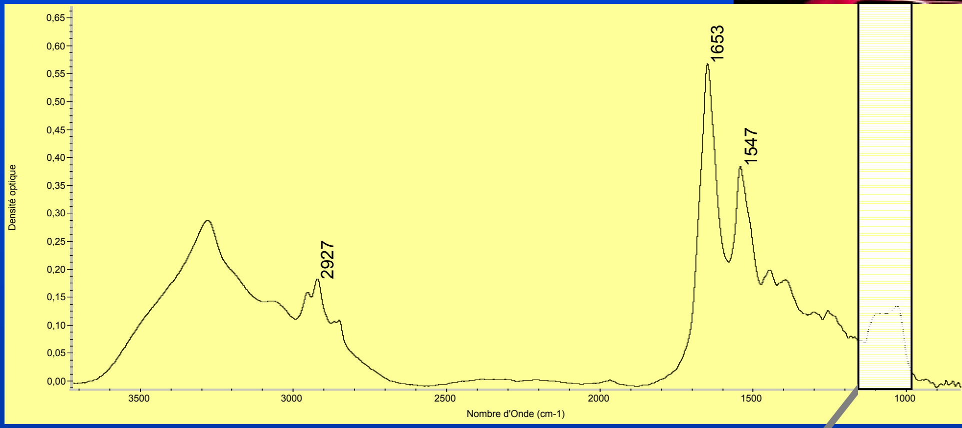


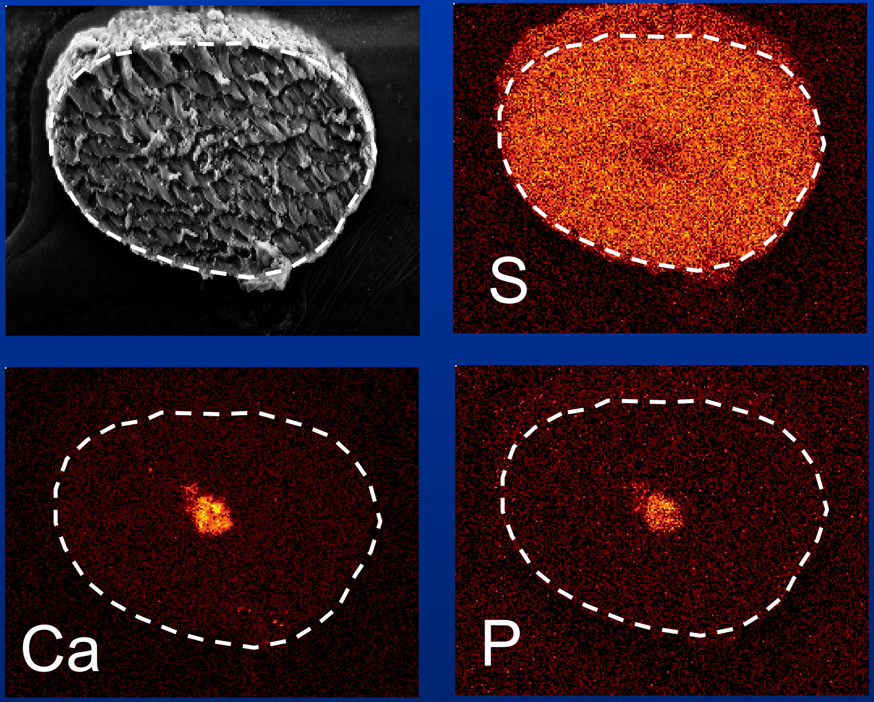


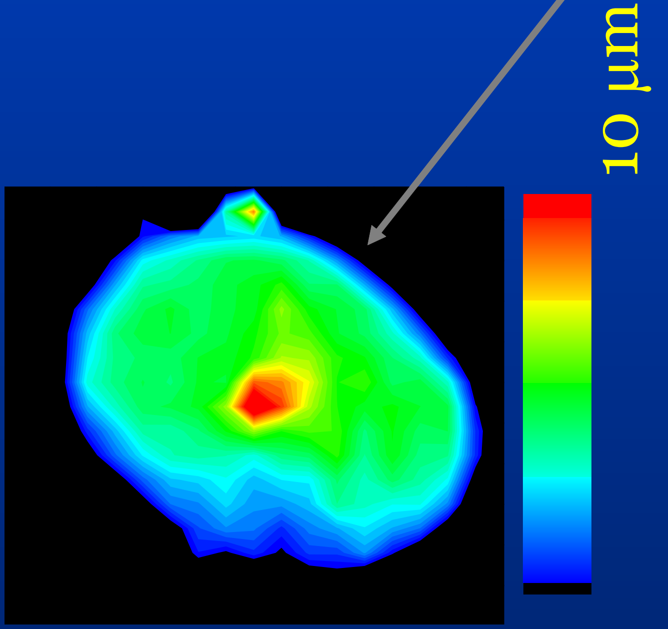


Fuzzy c-means clustering
Cytospec software

3000 years old mummy





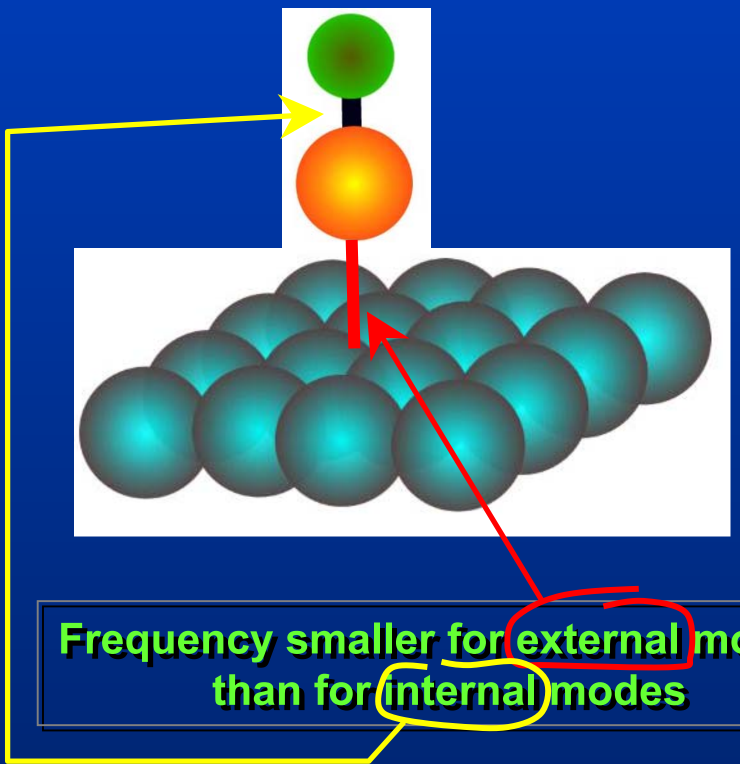


Far Infrared Spectroscopy is benefiting a lot from the synchrotron source:

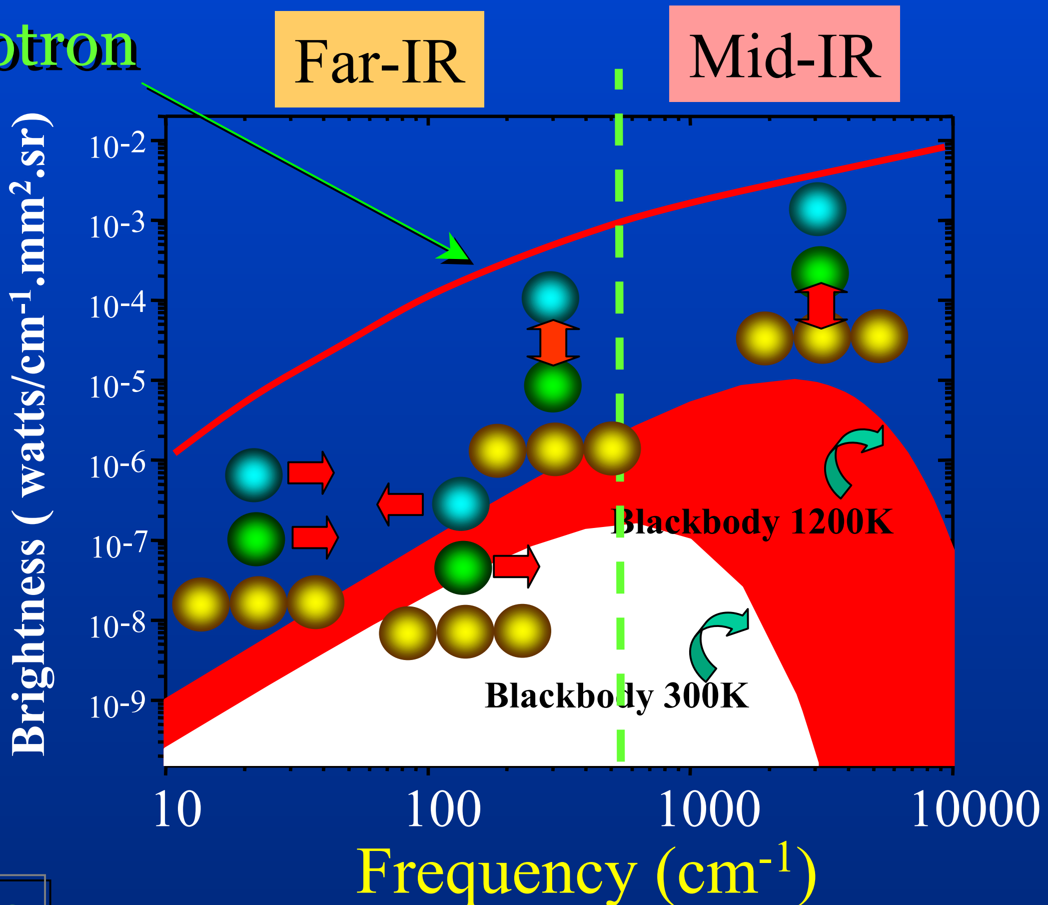
Surface Science was among the first discipline
to use the synchrotron source in the far-IR , for:

Detection of low frequency modes (bonding of adsorbates)
... and vibrational dynamics

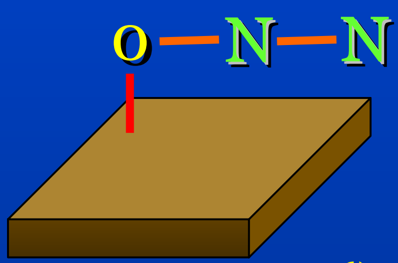
Focus on the adsorbate-subtrate motion



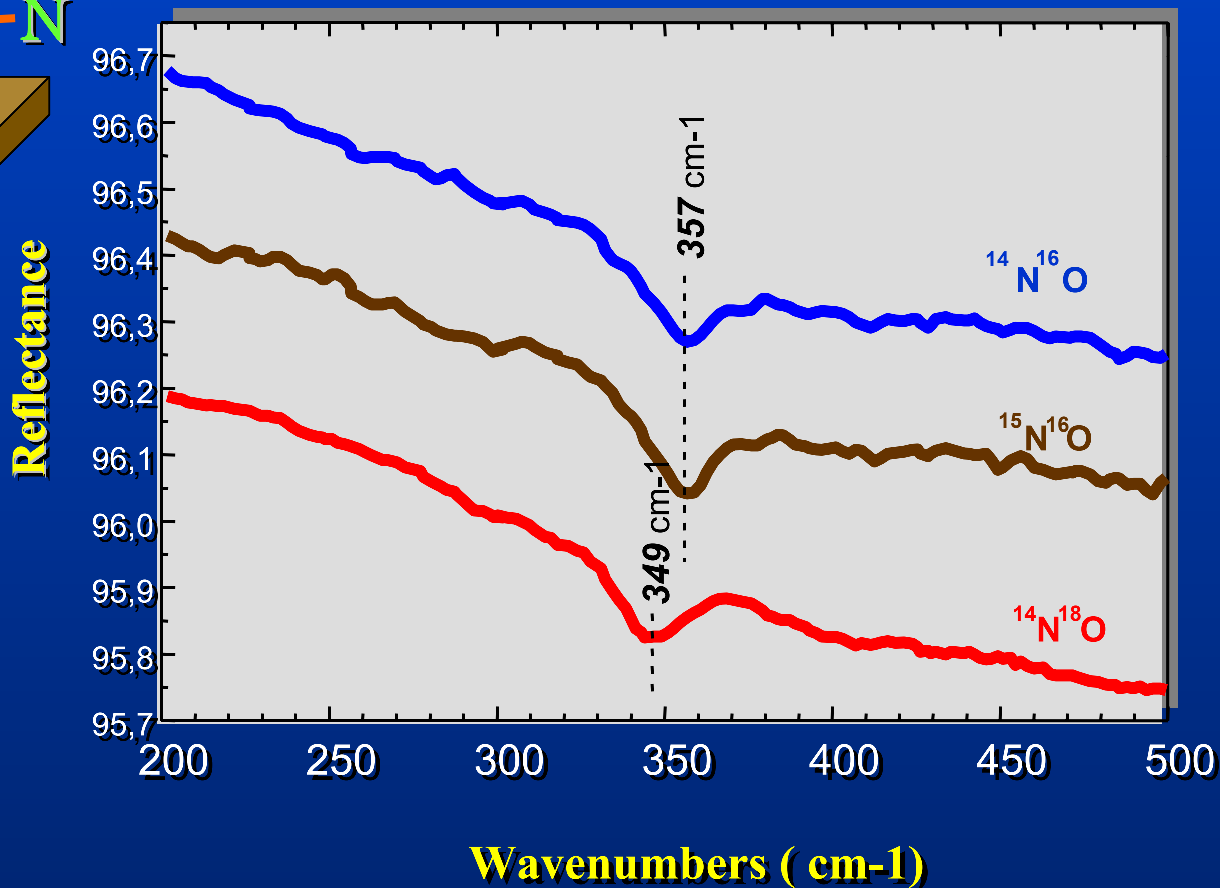
Frequency smaller for external modes than for internal modes



Cu-O modes: isotopic effect



Cu(100)

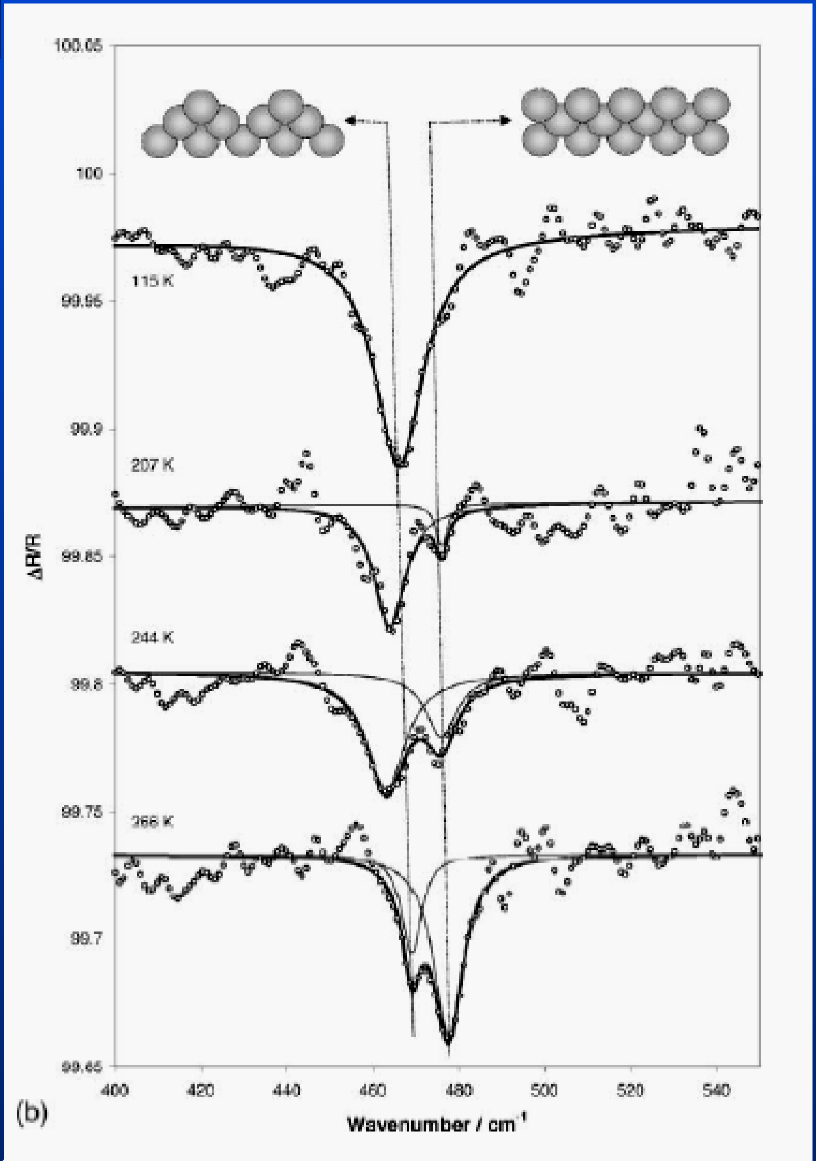


P.Dumas, M.Suhren,C.J.Hirschmugl,Y.J.Chabal et G.P.Williams

Surf. Sci. 371(1997)200.

Far-IR spectroscopy at surfaces provide unravelled details about the adsorbate bonding, thanks to the high resolution of the IR technique (as compared to HREELS)

CO on Pt{110}



From C.J. Baily, M. Surmann, and A.E. Russel
Surf. Science 523(2003)111

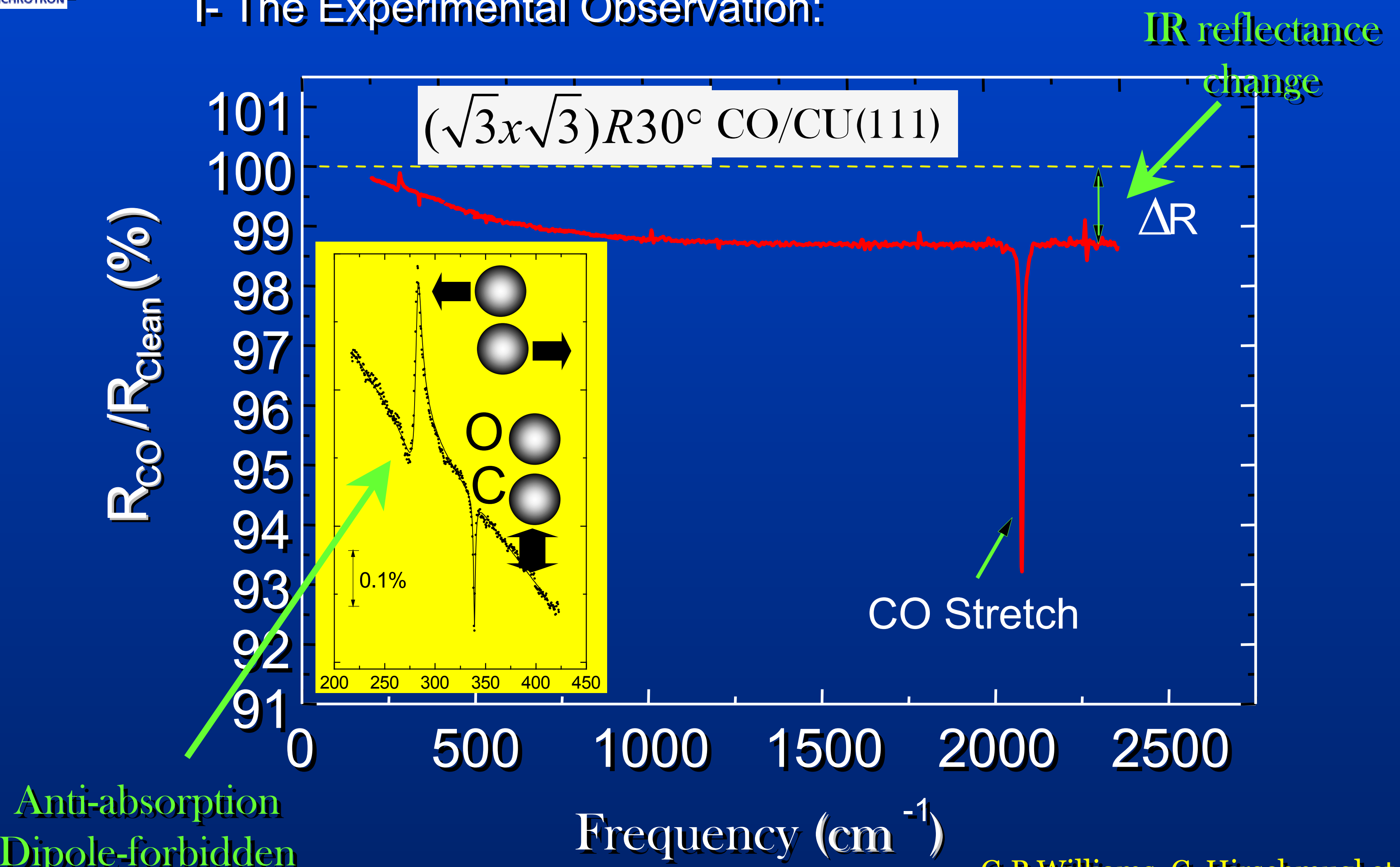
Missing-row reconstruction

of clean Pt surface not lifted

upon low temperature adsorption of CO

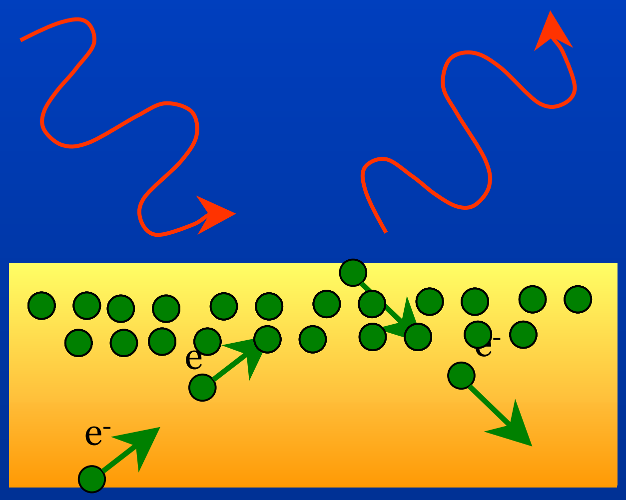
Vibrational dynamic: adsorbate-induced electronic change in metallic substrate

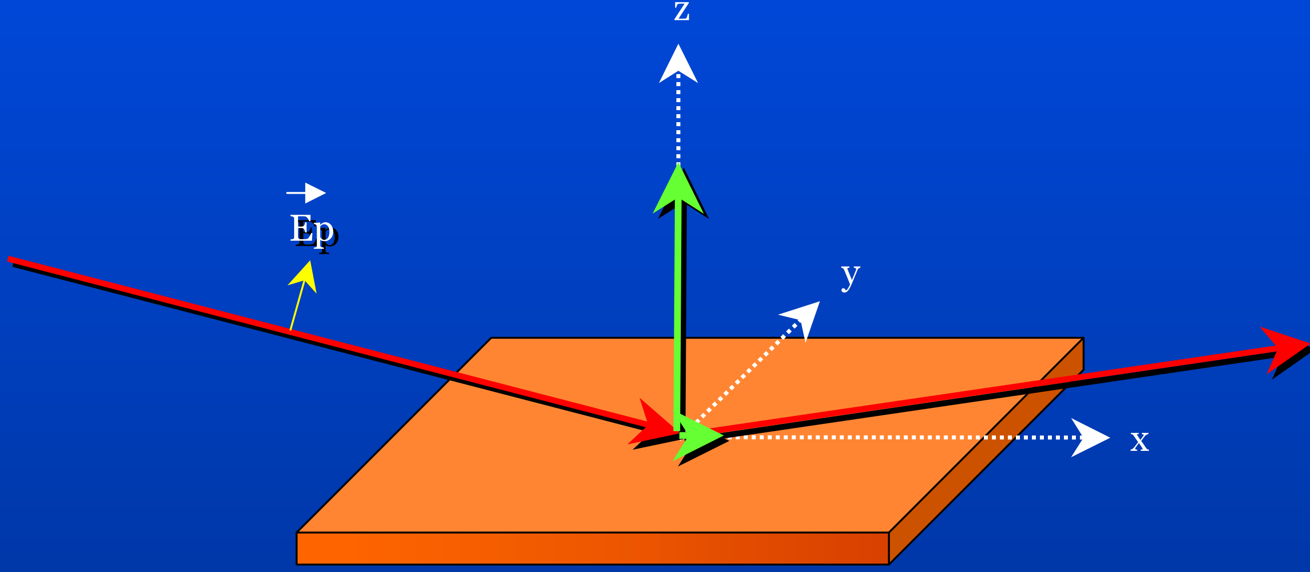
I- The Experimental Observation:

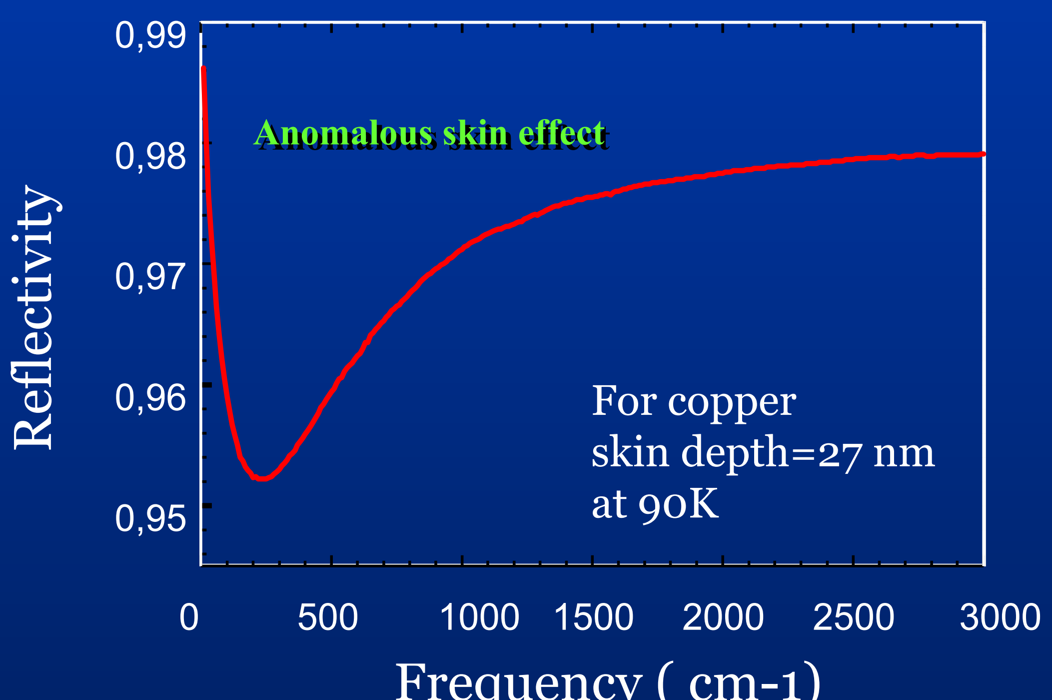


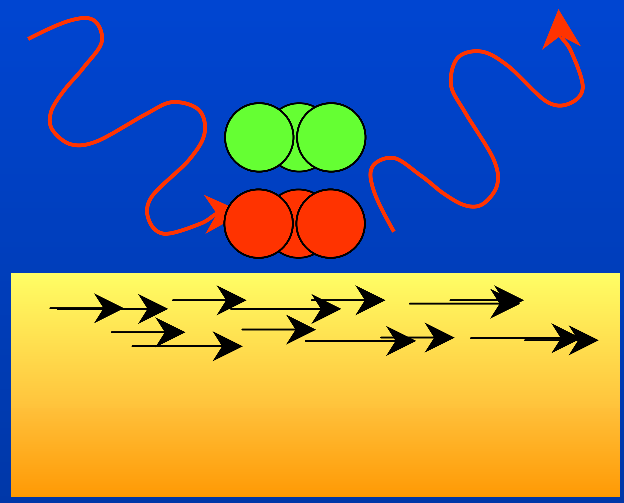
G.P.Williams, C. Hirschmugl et al.

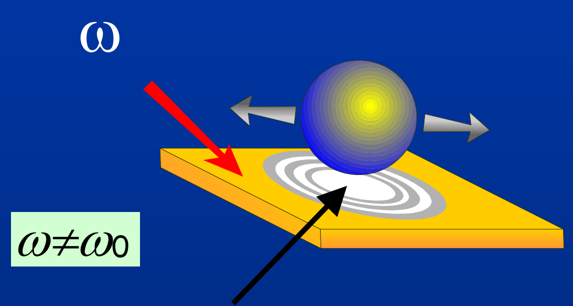
To make the story short...




z
Ep
y
x

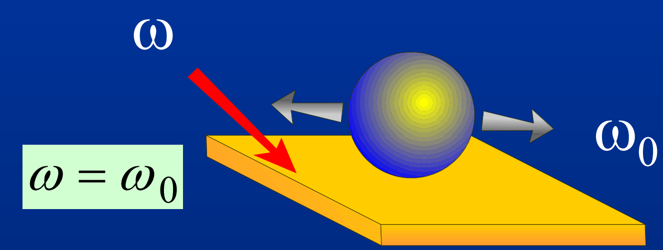

0,99
0,98
0,97
0,96
0,95
Reflectivity
Anomalous skin effect
For copper
skin depth=27 nm
at 90K
0
500
1000
1500
2000
2500
3000
Frequency (cm-1)



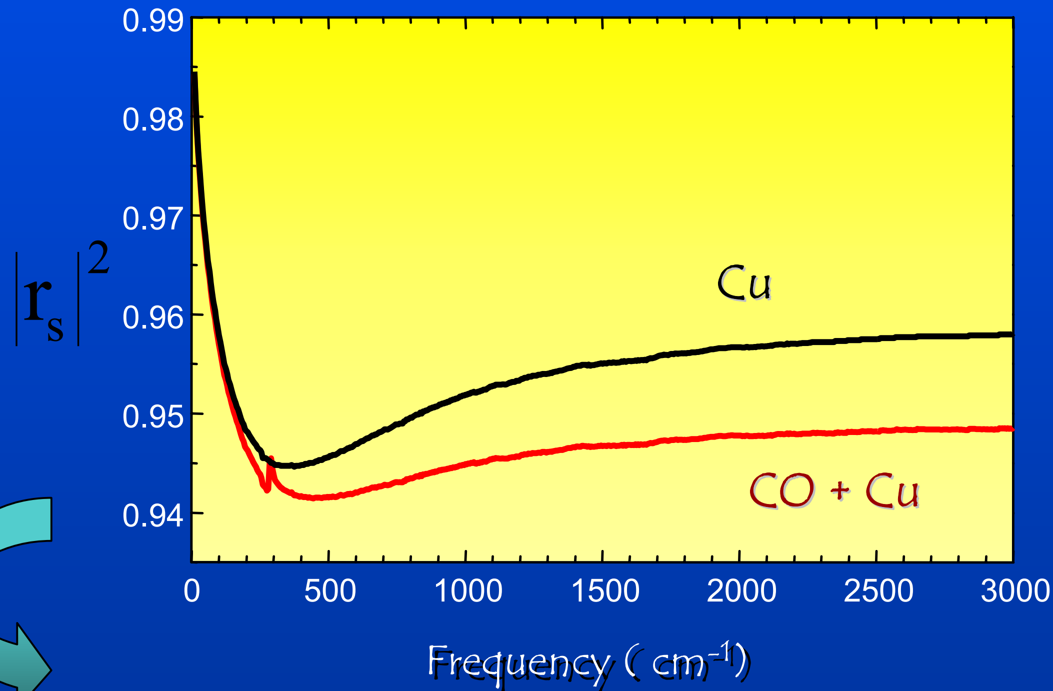


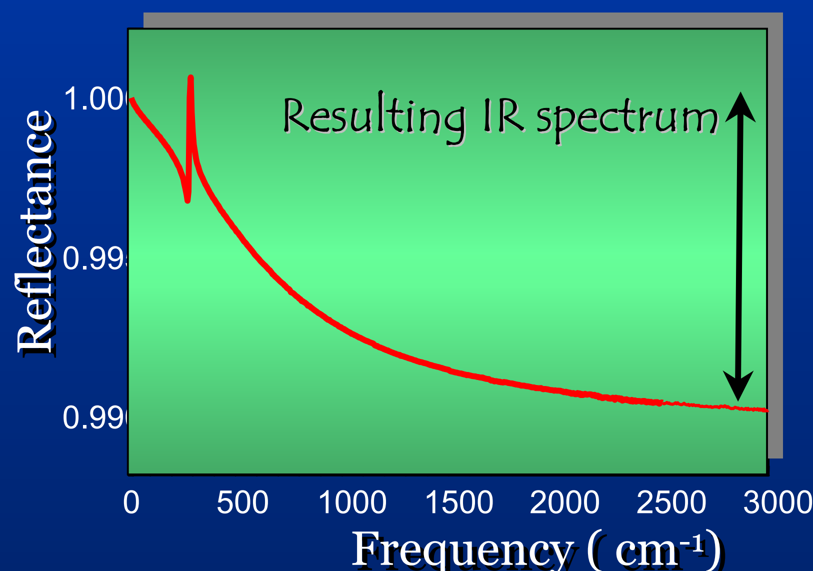
Friction force

$$f = M\eta v_{//}$$



No Friction!!





$$\Delta R_p = -\frac{4}{c}\frac{n_a}{n}\frac{M}{m}\frac{\eta}{\cos\theta}$$

$$\Delta W = \frac{n_a M \eta}{(ned)^2}$$

Resistance change!

Persson defines:

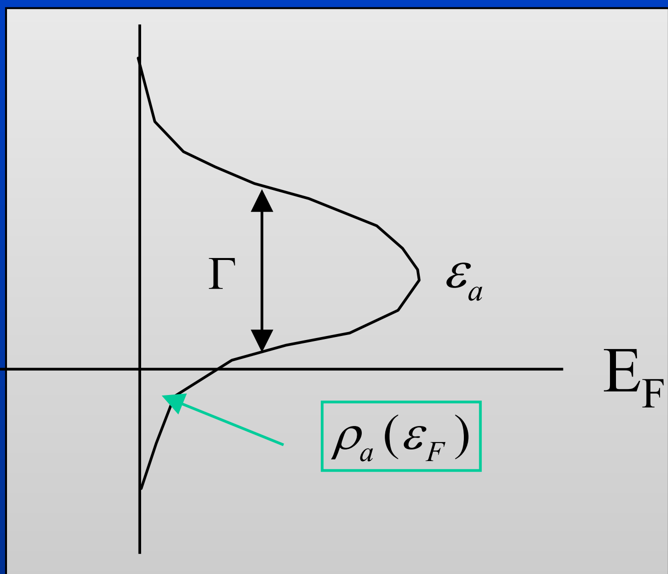
$$\eta = \frac{1}{\tau_{e-h}} = \frac{n_e^2 e^2}{M n_a}\left[l_f \rho_S \right]$$

See: Phys. Rev.B 44(1991)3277 and Surf. Sci. 363(1996)354

e-h* lifetime for frustrated translation of molecules adsorbed at surfaces:

- by resistance change measurement if film is very thin
- by infrared reflectance change on monocrystal

... and both dependant on the density of states at E_F



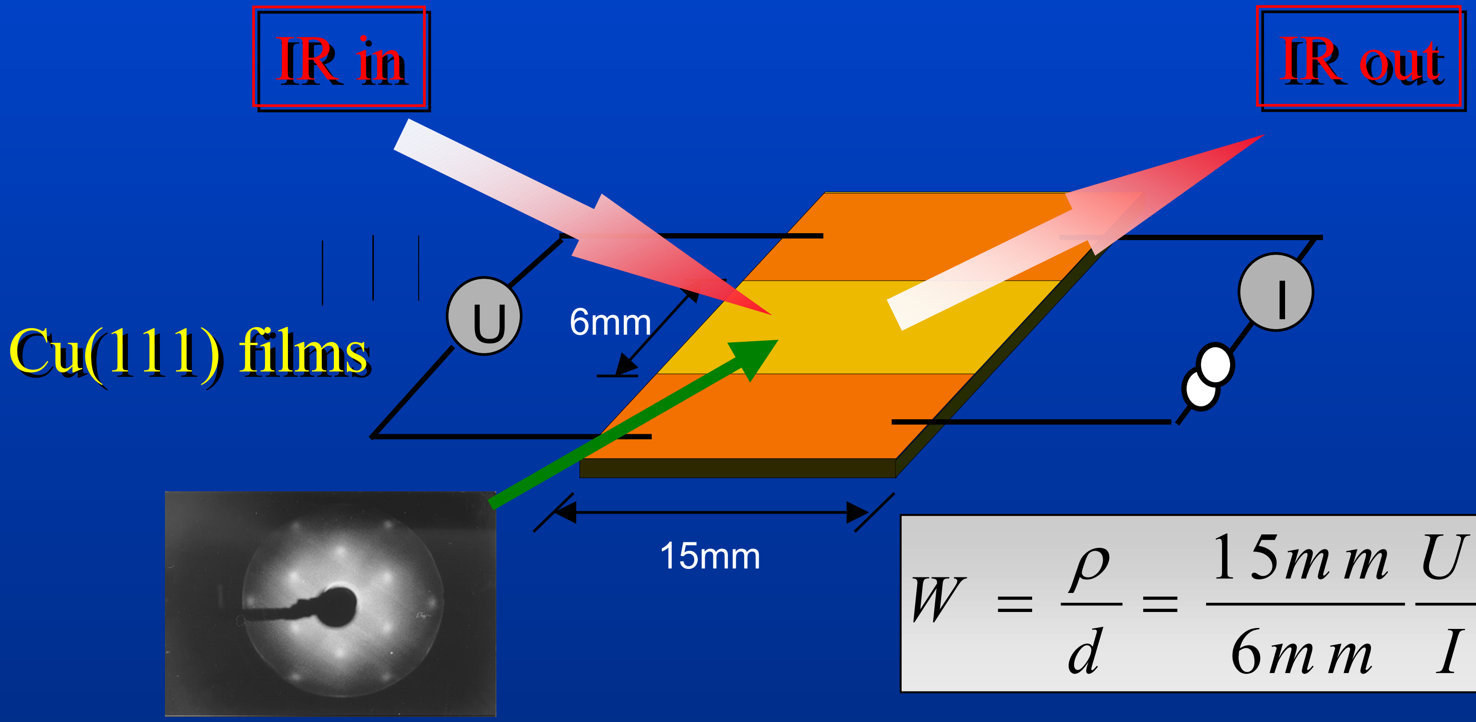
$$\eta\omega_F = \varepsilon_F$$

$$k_{//} = k_F \sin\Theta$$

$$\frac{1}{\tau_{e-h}} = 2\frac{m}{M}\omega_F \Gamma \rho_a(\varepsilon_F)\rangle \sin^2\Theta \langle$$

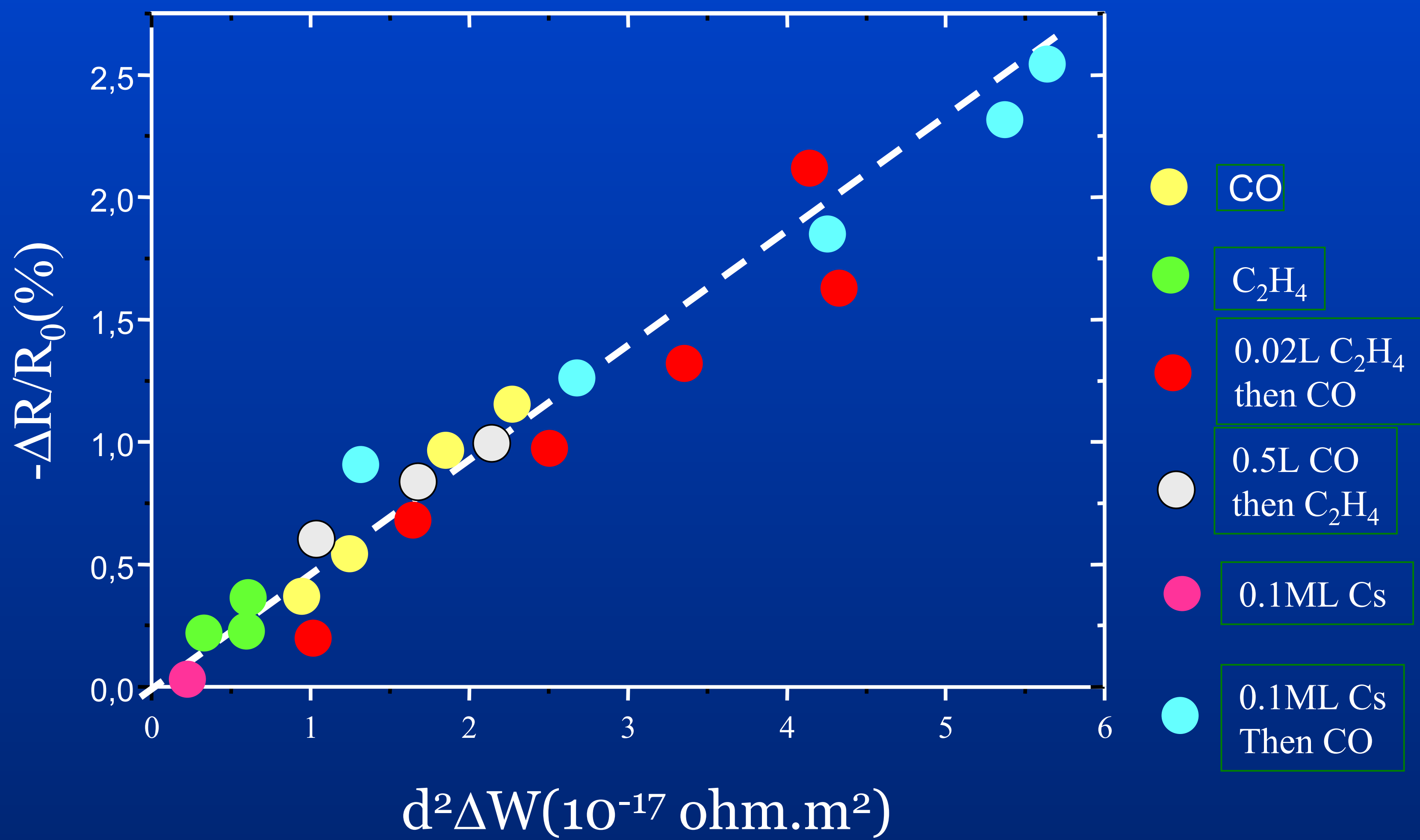
$$\rho_a(\varepsilon_F) \approx \frac{1}{\Pi}\frac{\Gamma/2}{(\varepsilon_a - \varepsilon)^2 + (\Gamma/2)^2}$$

The resistance of thin metal film
as well as its reflectivity
can be tuned by shifting the position
of the adsorbate resonant state



$$W = \frac{\rho}{d} = \frac{15mm}{6mm}\frac{U}{I}$$

M. Hein, A. Otto, P. Dumas and G.P. Williams


-ΔR/R0(%)
0,0
0,5
1,0
1,5
2,0
2,5
0
1
2
3
4
5
6
d²ΔW(10⁻¹⁷ ohm.m²)
CO
C2H4
0.02L C2H4 then CO
0.5L CO then C2H4
0.1ML Cs
0.1ML Cs Then CO

Electronic damping can be determined using either resistance change (when possible) or by reflectivity change (thick crystal..)

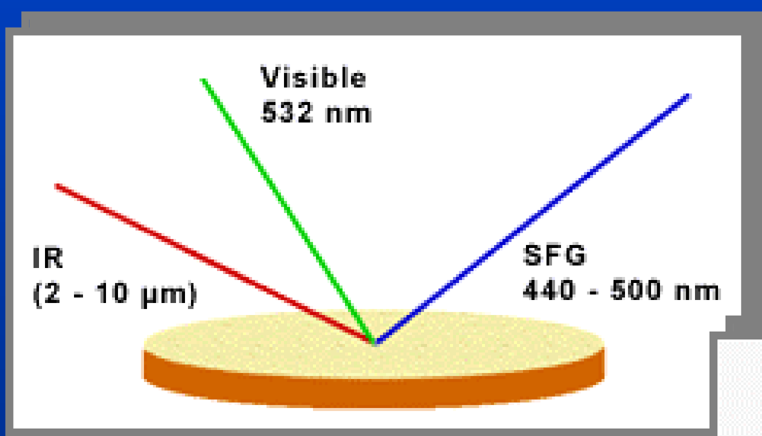
	From resistance	From IR
	$\tau_{e-h}(x10^{12}s.)$	$\tau_{e-h}(x10^{12}s.)$
CO/Cu(111) bulk	-	46
NO/Cu(111) bulk	-	11
CO/Cu(111) 40 nm	36	45
CO/Cu(111) 50 nm	32	35
O/Cu(111) 50 nm	12	19
C_2H_4/Cu(111) 33 nm	213	235

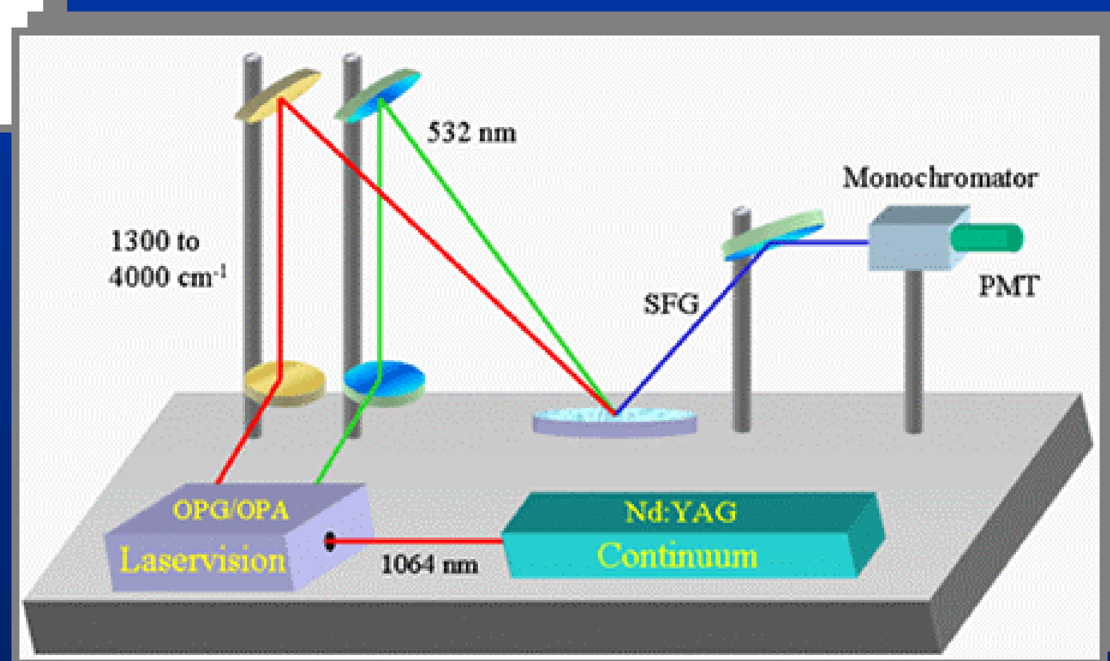
Non linear spectroscopy with lasers
Surface and Interfaces studies

Sum Frequency Generation

Non linear process generated strickly at interfaces

$$\propto N_S \, L_{IR} L_{Vis} L_{SFG} \left|\frac{\partial \mu}{\partial \xi}\right|^2 \left|\frac{\partial \alpha}{\partial \xi}\right|^2 \frac{U_{IR}\, U_{Vis}}{A\, T}$$





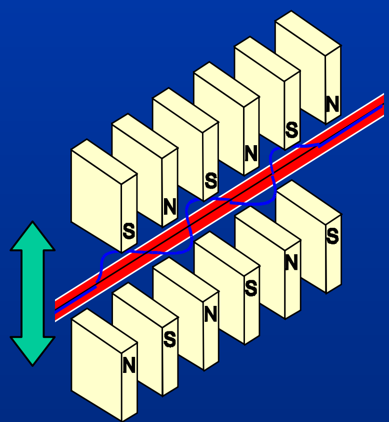
SFG experimental set-up

Tunable infrared laser sources

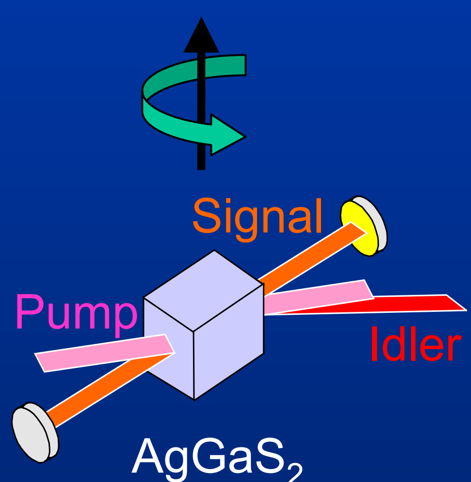
CLIO FEL
6-20 µm
5 ps

OPO
2.5-10 µm
11 ps

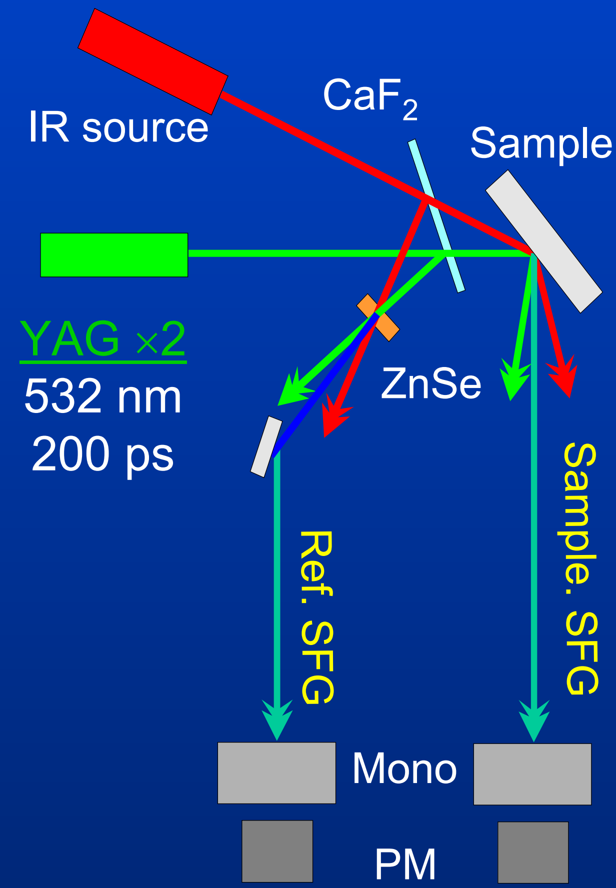
$$\omega_I(\theta) = \omega_{Pump} - \omega_S(\theta)$$



Undulator



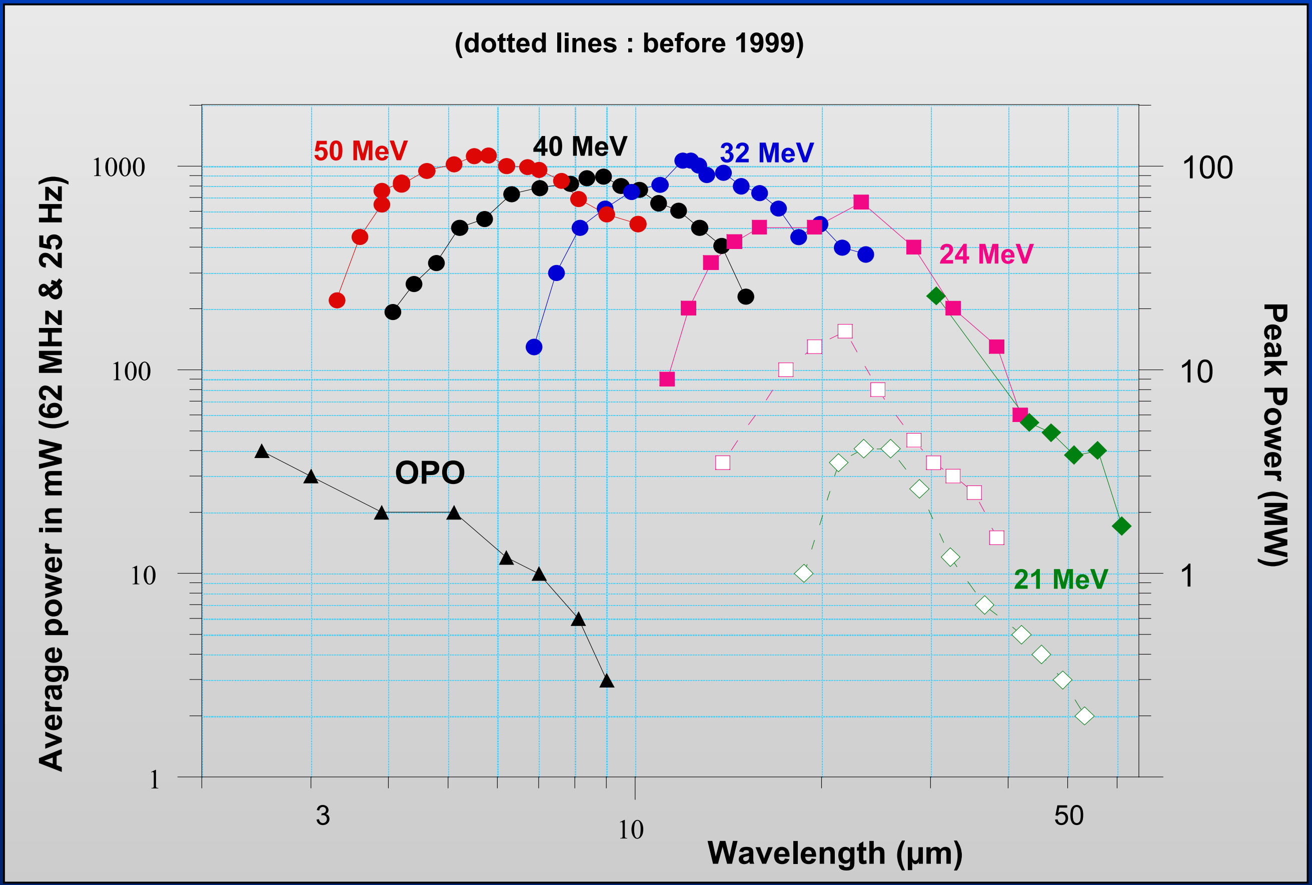
Set-up

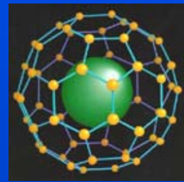


The IR-FEL CLIO at LURE (J.M. Ortega)

(20 - 50 MeV) room temperature 3 GHz RF linac based infrared free-electron laser (3 - 60 µm)

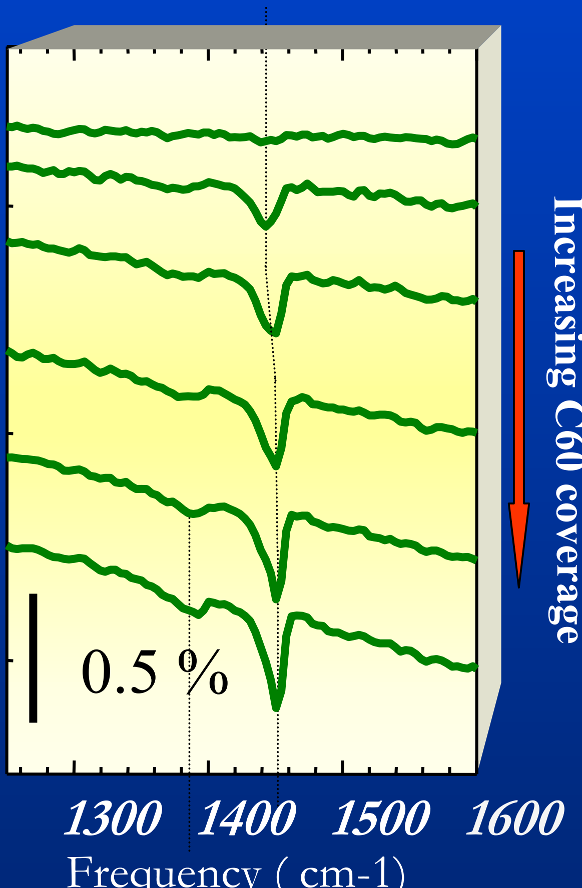
Spectral range of CLIO + OPO



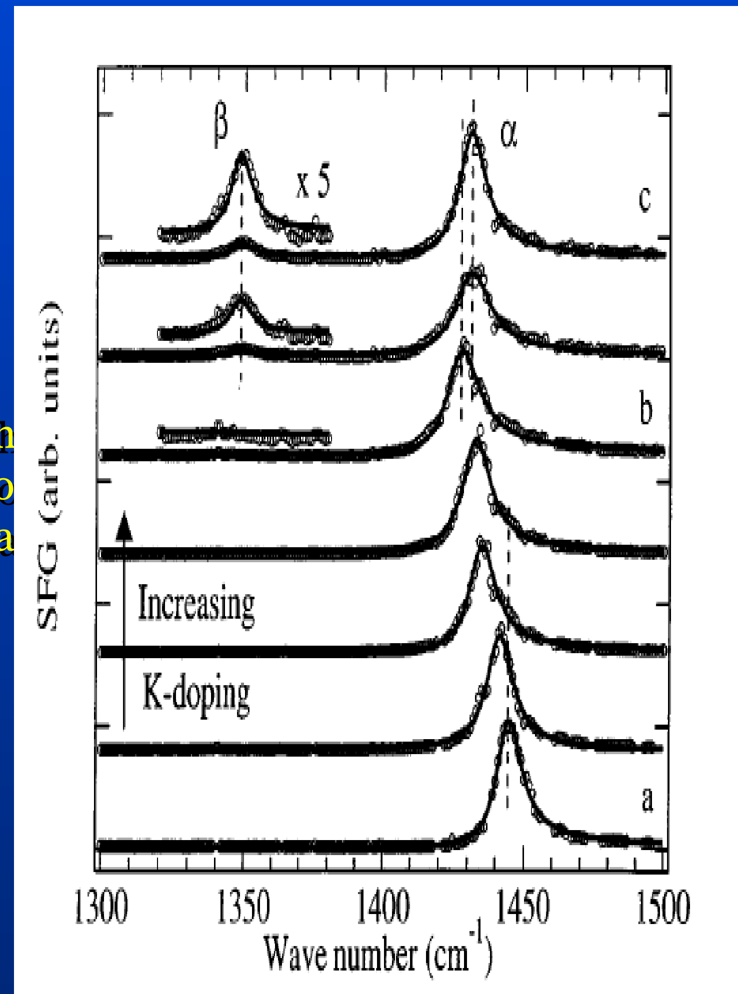


C_{60} adsorbed on Ag(111)

IR spectra

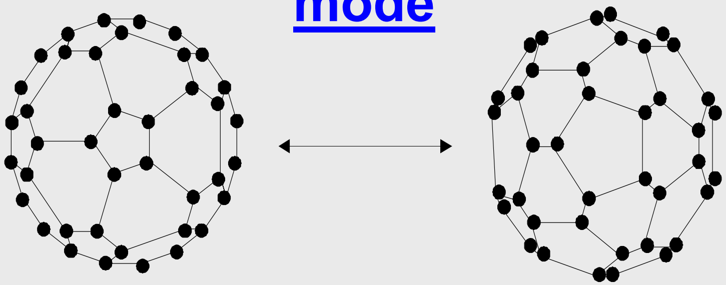


Th... e mode?
To... out, since
Ba...

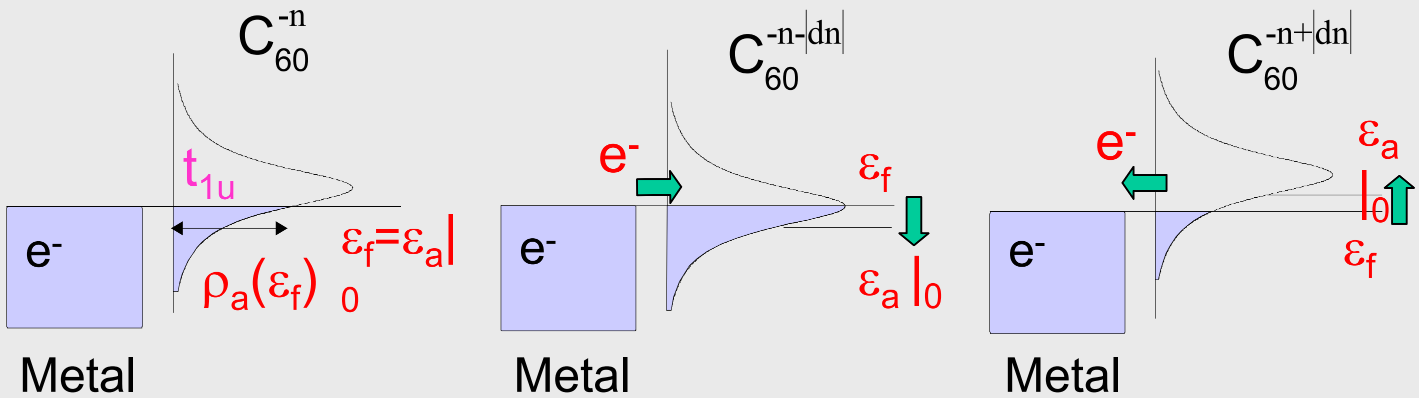


Electronic Tuning of Dynamical Charge Transfer at an interface: K doping of C60/Ag(111)"
A.Peremans, Y.Caudano, P.A.Thiry, **P.Dumas**, A.Le Rille, W.Zheng and A.Tadjeddine
Phys. Rev. Lett. 78 (1997)2999.

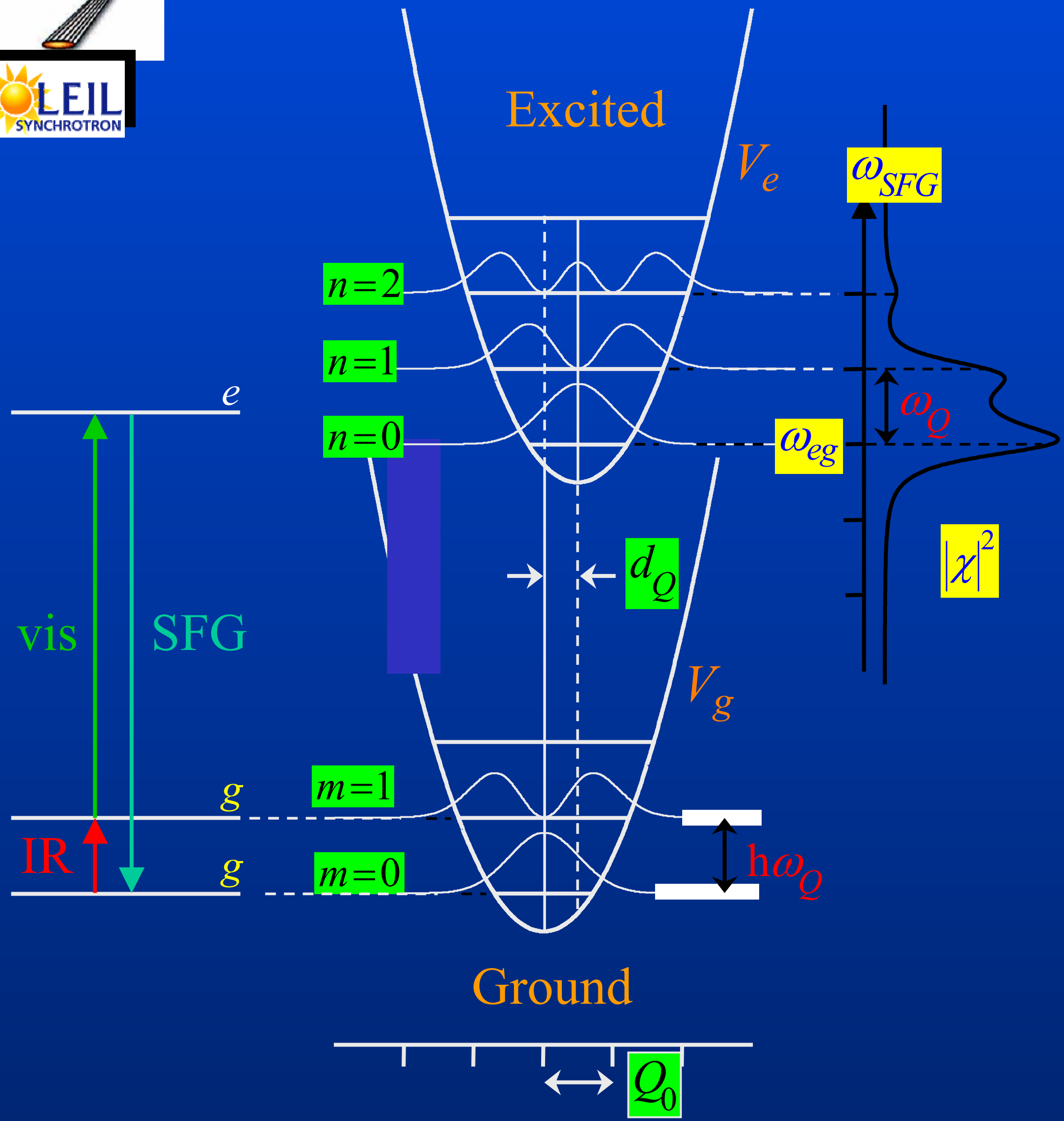
Interfacial dynamic charge transfer



Vibrational ground state



Doubly resonant SFG spectroscopy



Coupled vibration and electronic transition

Harmonic potential shift (d_Q) and coupling constant (S_Q)

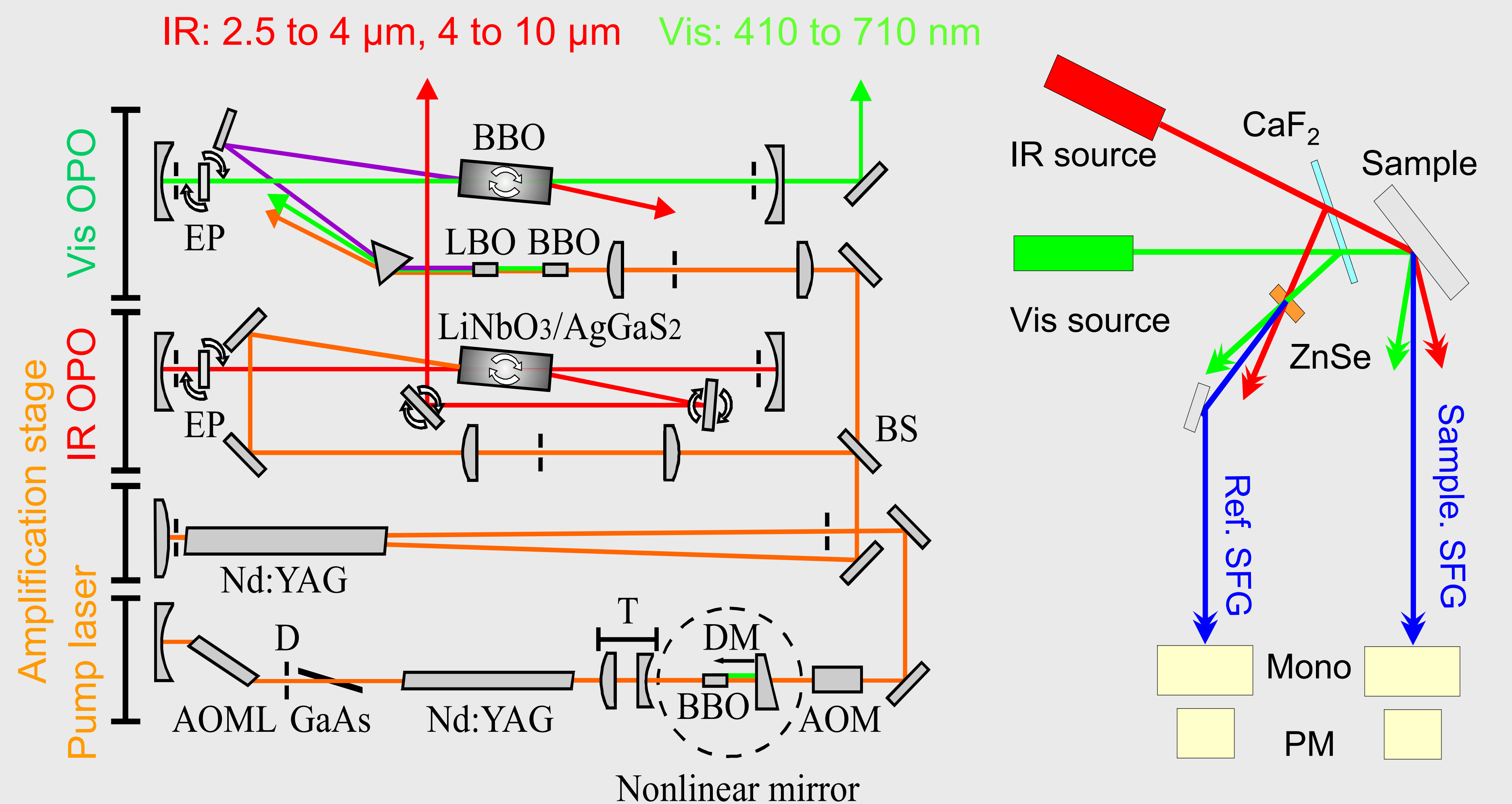
$$S_Q = \frac{1}{2\hbar}\omega_Q d_Q^2$$

Two (IR & SFG) resonances:[1]

$$\chi^{(2)} \propto \frac{1}{\omega_{IR} - \omega_Q + i\gamma_Q} \times \sum_{n=0}^{\infty} \frac{f\left(S_Q, n\right)}{\omega_{SFG} - \left(\omega_{eg} + n\omega_Q\right) + i\gamma_{eg}}$$

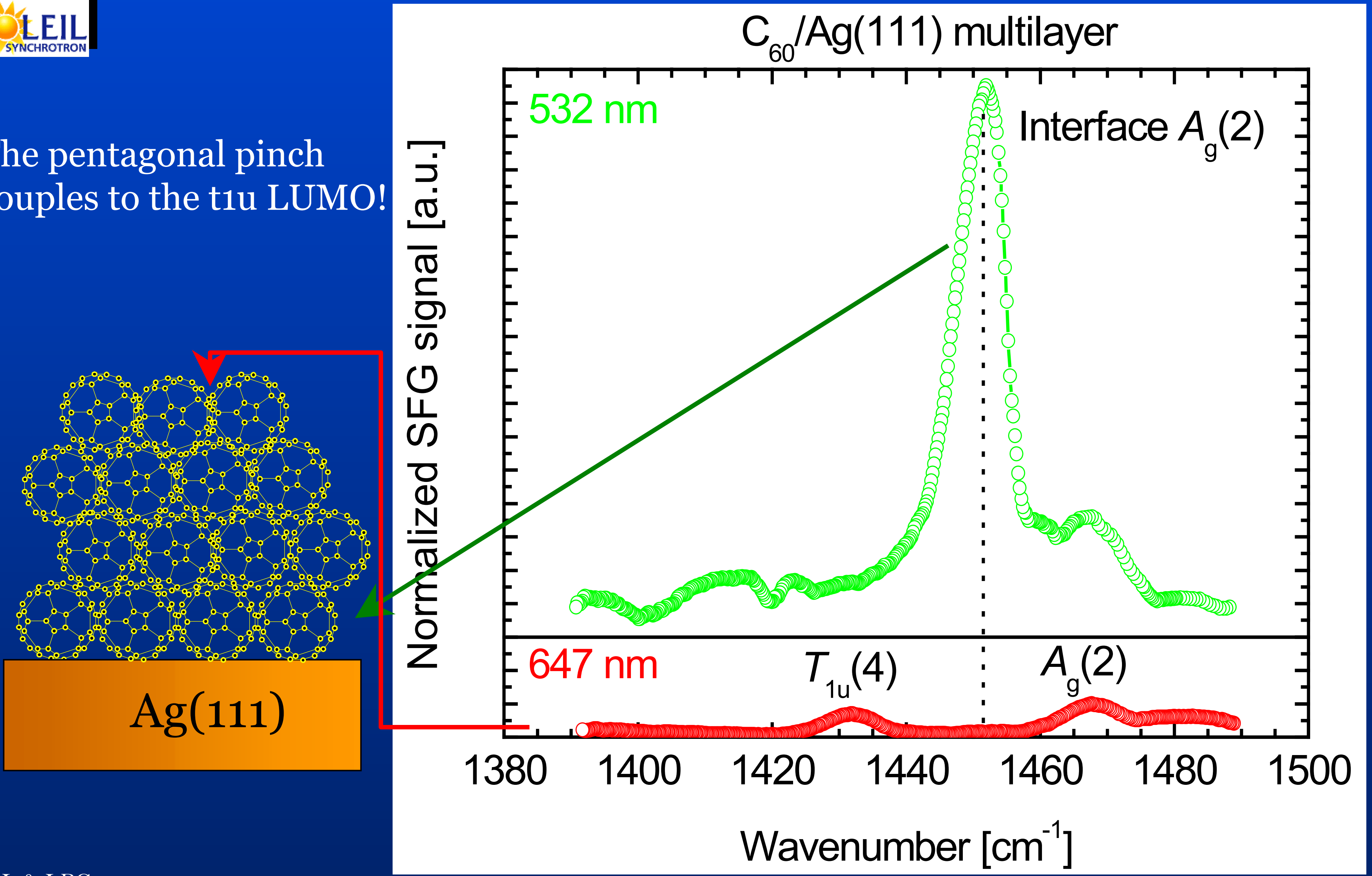
[1]M. Hayashi *et al*, J. Phys. Chem. A 106 (2002) 2271.

SFG experimental set-up



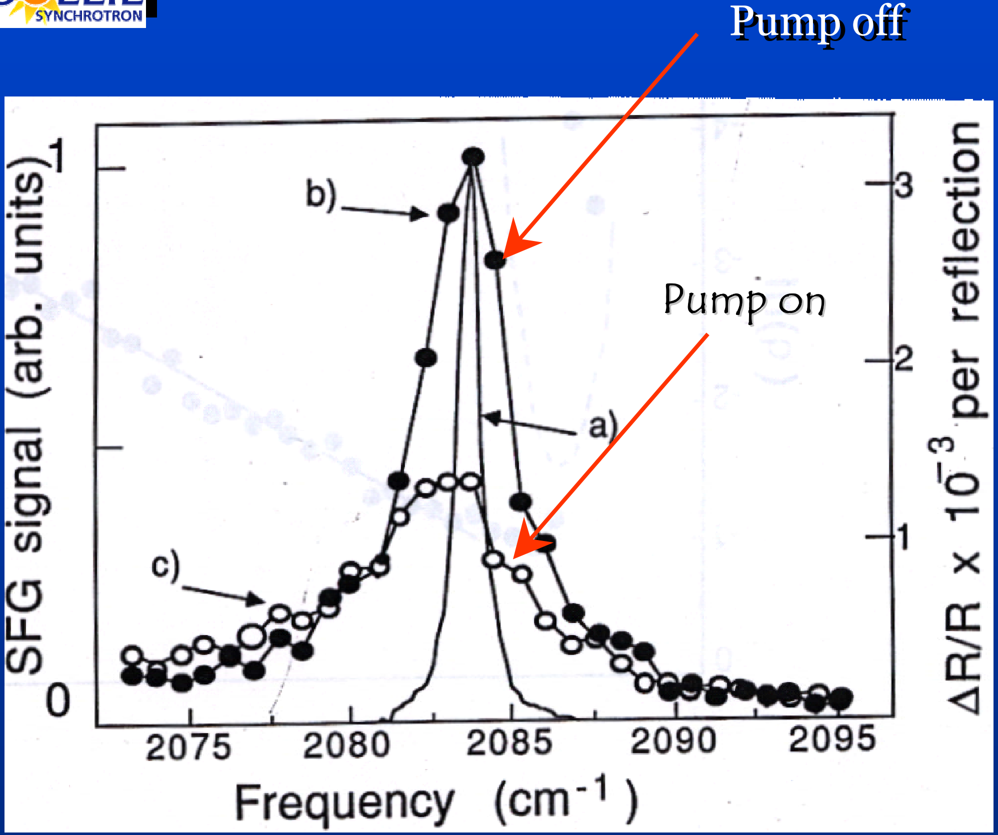
DR-SFG of C_{60}/Ag(111) interfaces: multilayer

The pentagonal pinch couples to the t1u LUMO!

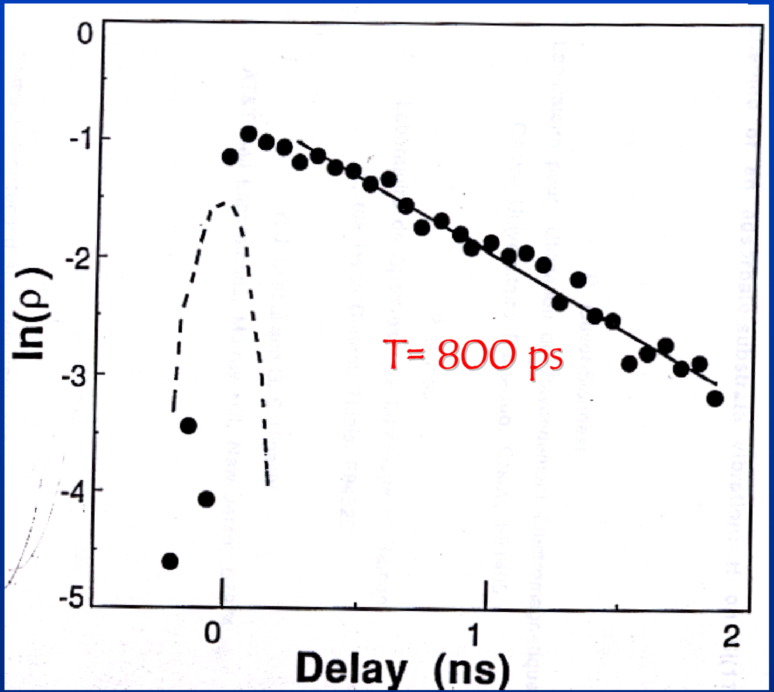


Vibrational dynamics with SFG

H-Si(111)-(1x1)



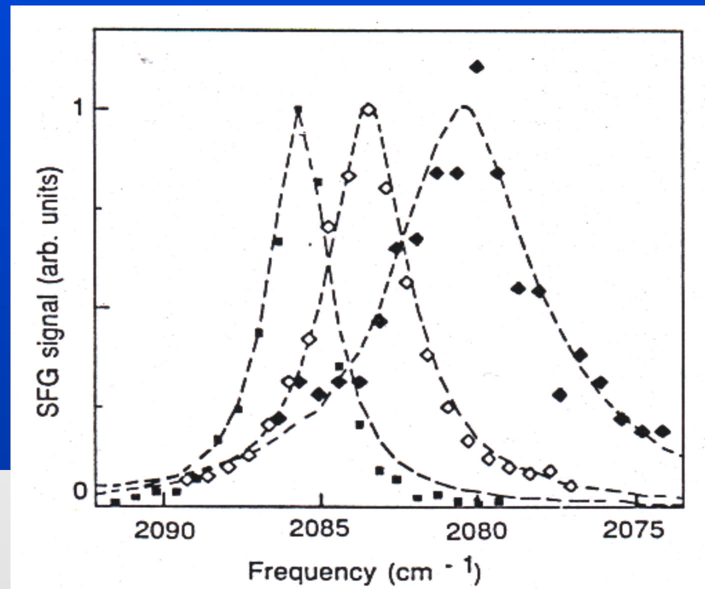
Obvious depopulation of the ground state upon pumping at the resonnant frequency



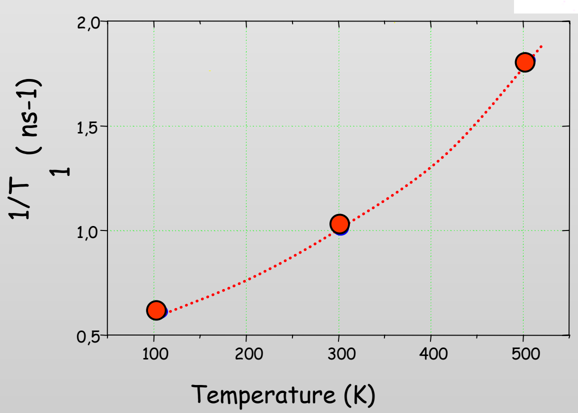
Lifetime= first order process

From P.Guyot-Sionnest, P. Dumas and Y.J. Chabal
Phys. Rev. Lett.64(1990)2156

From T-dependence of the lifetime…



Lifetime H-Si(111)-(1x1)



Multiphonon decay:

$$\frac{1}{T_1} = (1+n_1)(1+n_2)(1+n_3)(1+n_4) - n_1 n_2 n_3 n_4$$

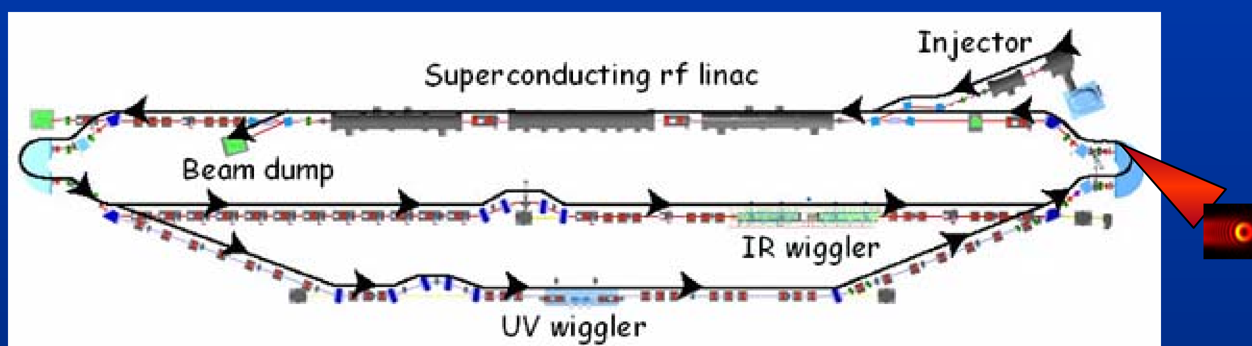
Bose-Einstein factor

$$n = 1 - \exp(\eta\omega_0/kT)$$

P.Guyot-Sionnest, P.Dumas et Y.J.Chabal
J.Electr. Spectr. Related Phenomena 54/55 (1990), 27

Induction decay, photon echo Ph.Guyot-Sionnest

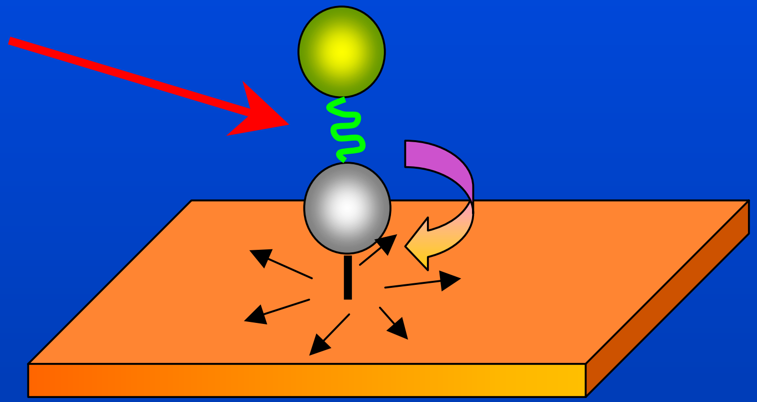
<u>Future directions:</u>
New science at facility such as Jefferson Lab (or future 4GLS in UK)?



- ✓ Vibrational dynamics at surfaces: understanding the energy transfer between intra- and inter-molecular modes

- ✓ Double resonant SFG – Imaging?

- ✓ Pump-probe experiments (UV-IR) in short time scale



✓ If IR-FEL and IR-synchrotron (from the same ERL) are used , easier is the synchronisation

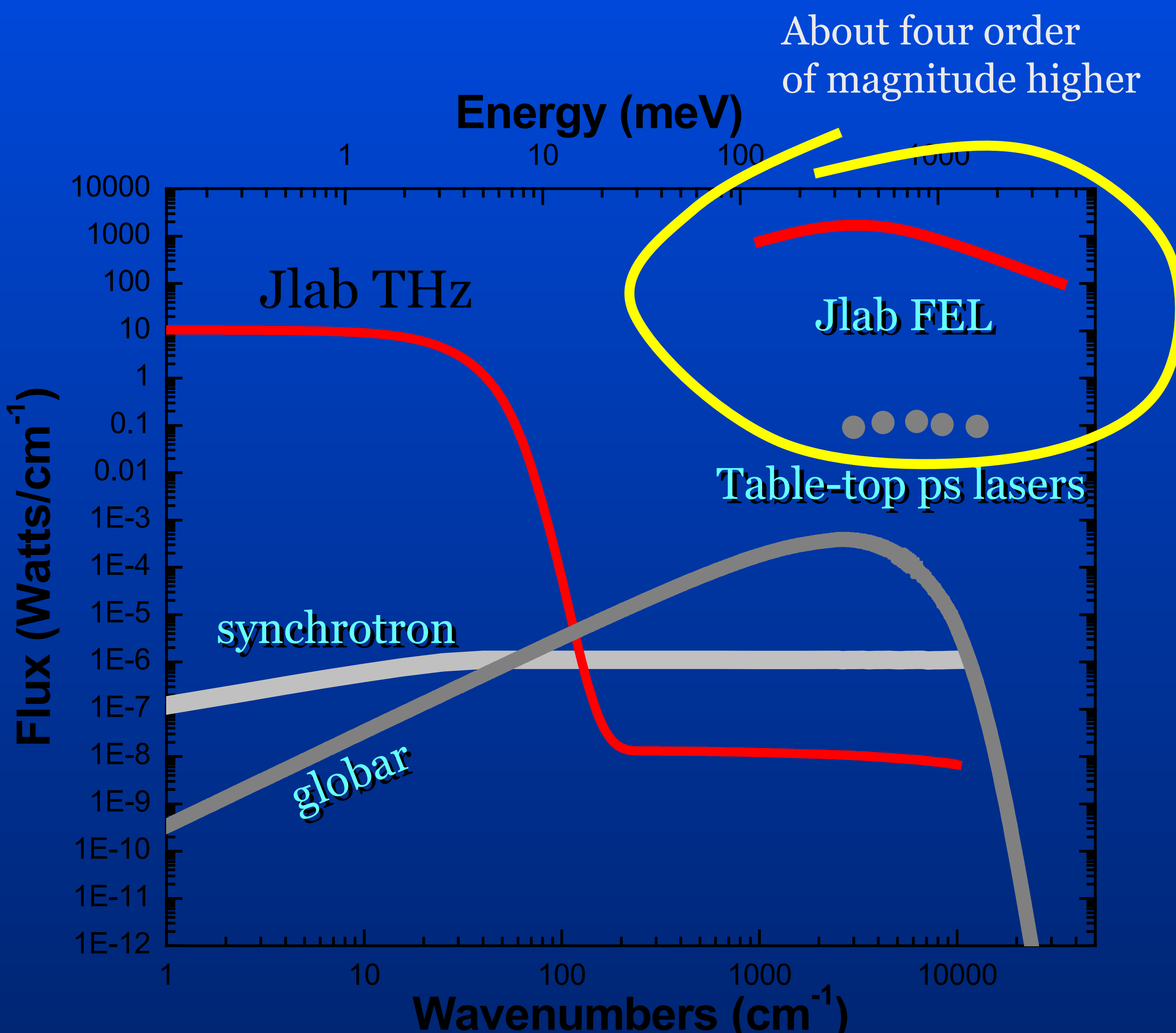
✓ Modifying the adsorbate substrate -mode will be detectable in the far-IR range using synchrotron (intensity, frequency change)

✓ If there is energy transfer between absorbate-substrate mode and frustrated translation/rotation, then reflectivity will change, anti-absorption band modified (can also be checked by resistance measurement on thin film)

✓ Energy exchange in complex molecules (biology) adsorbed on substrate

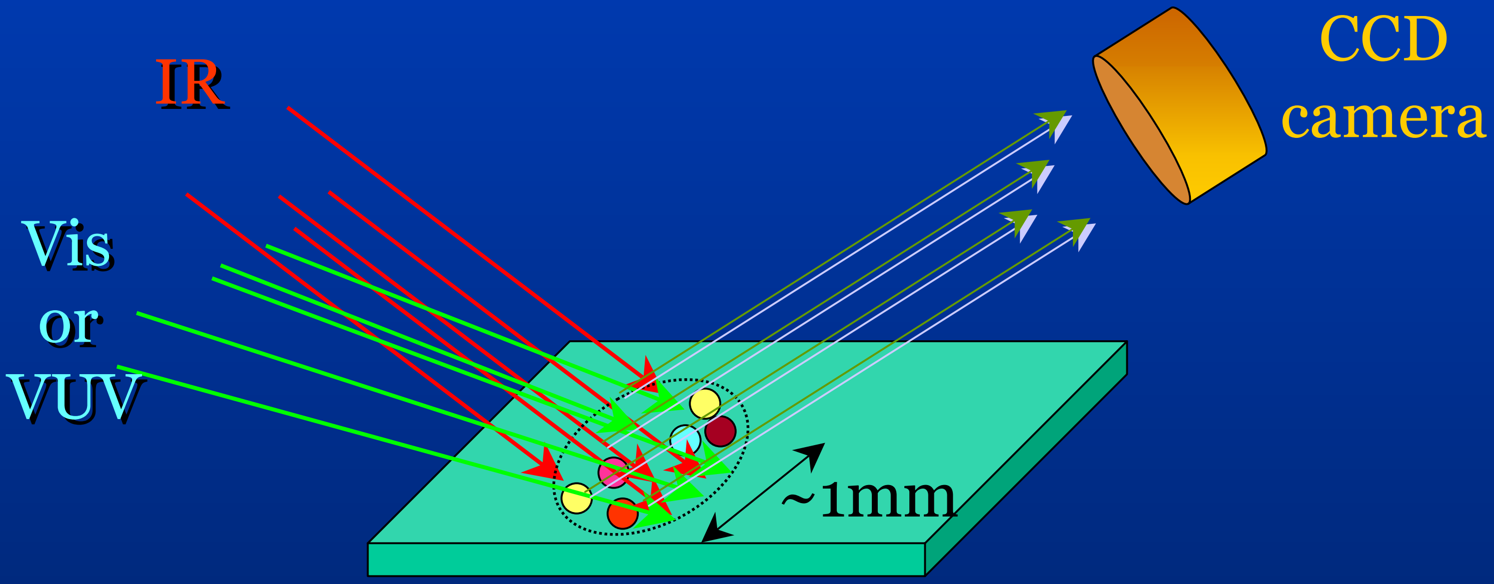
Double resonant SFG, especially going to the VUV
(-Resonance Raman
and λ^4 dependency of Raman Cross sections)

and imaging adsorbate?



Courtoisy of G.P. Williams

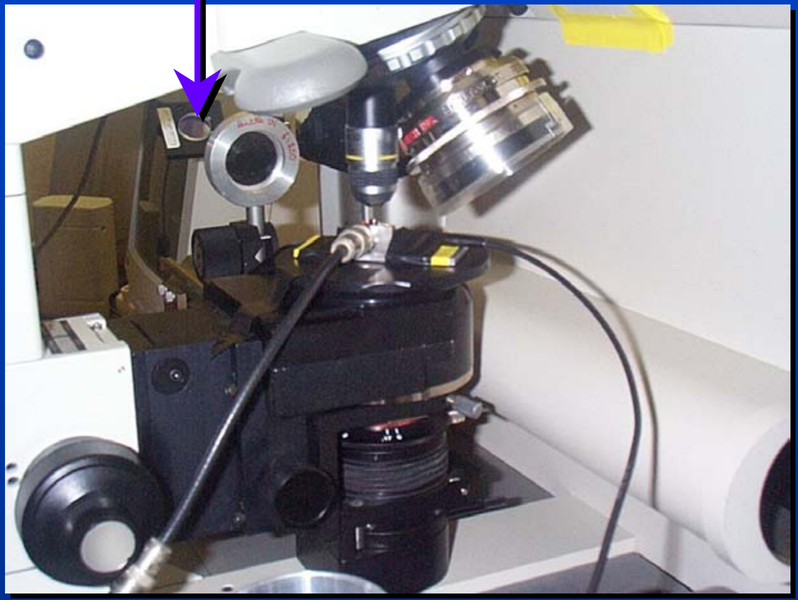
Typically, in SFG, the beam sizes are about 100 μm
By increasing the spot size to 1 mm, JLAB FEL will deliver the same SFG intensity

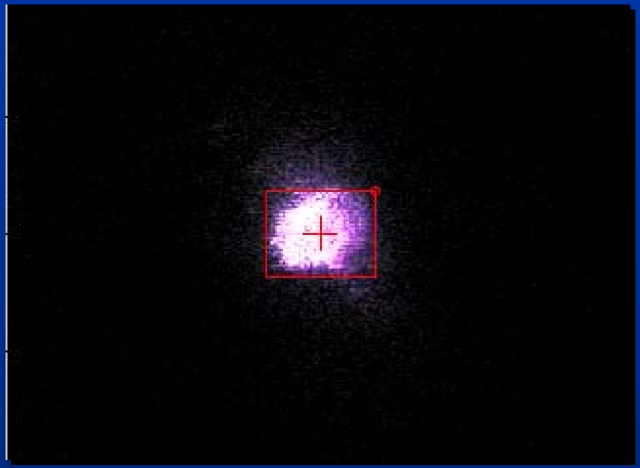


Projected spot size ~IR wavelength

Two colours experiments

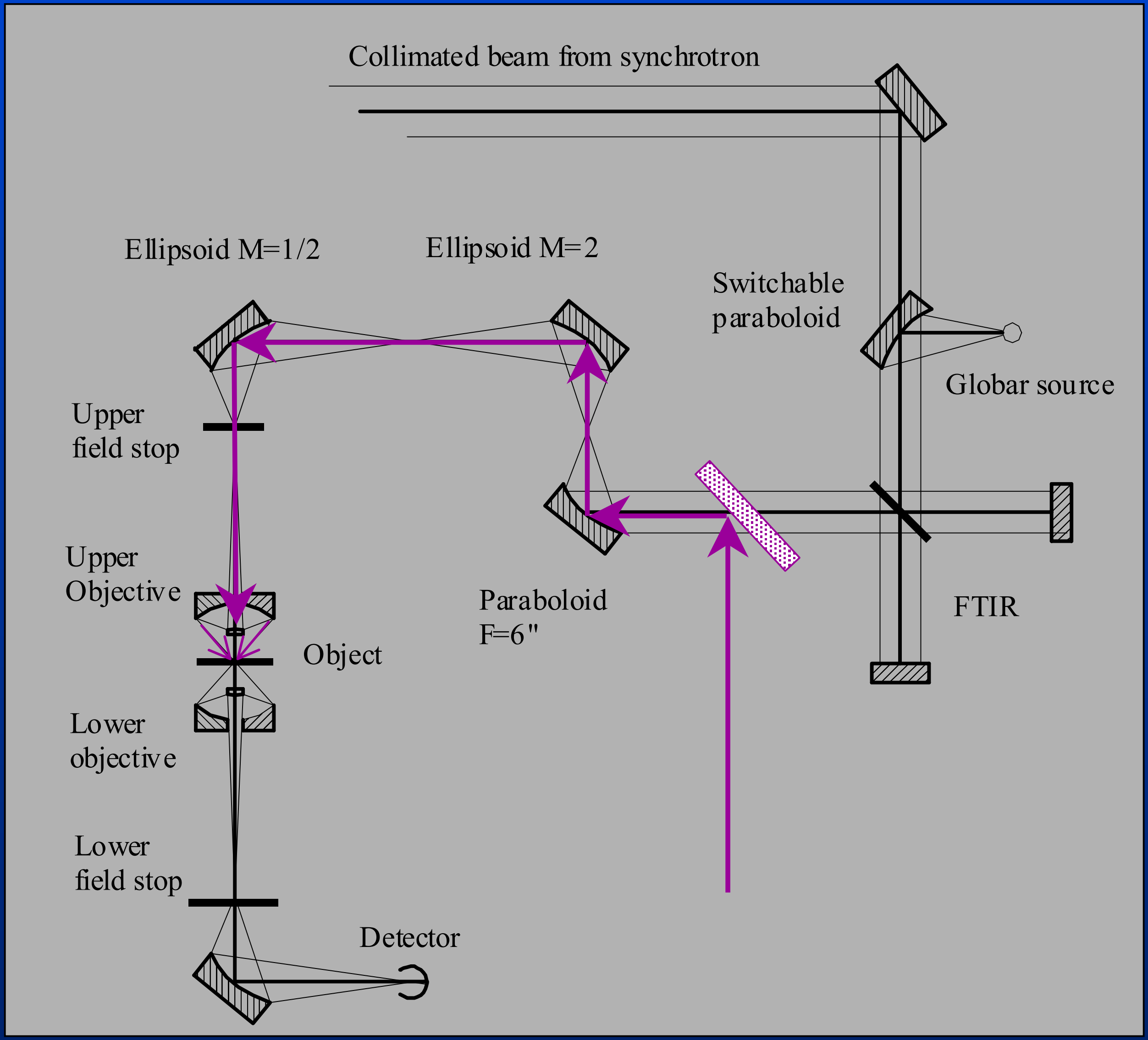
FEL-VUV

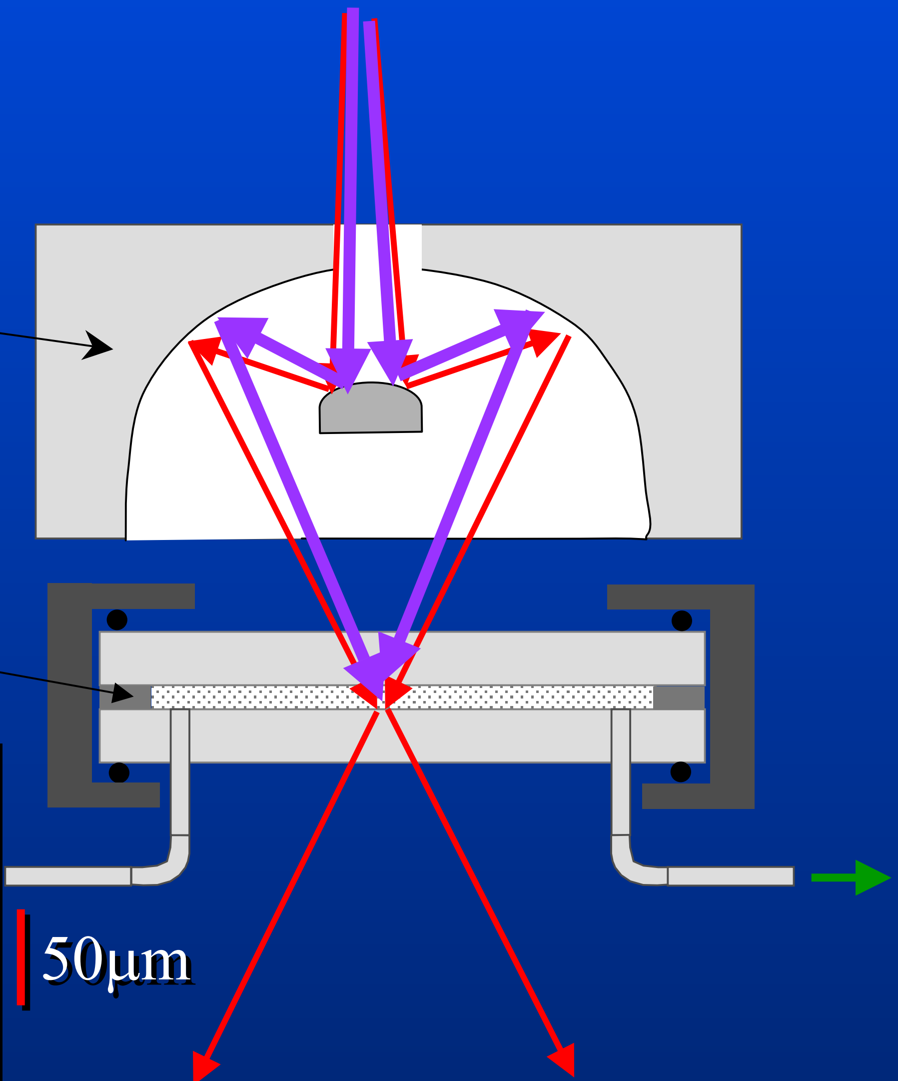


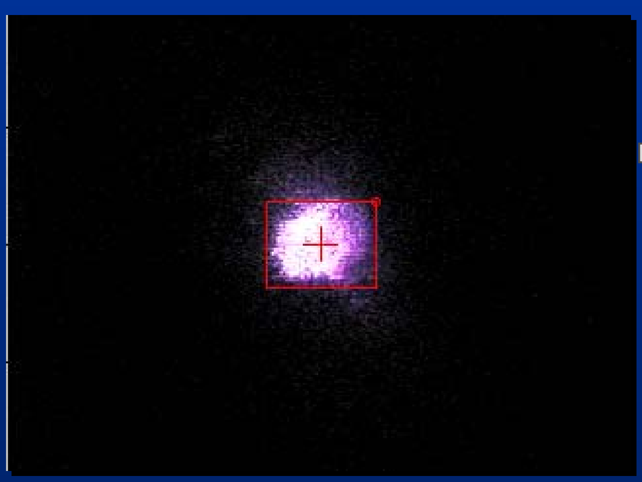


50µm

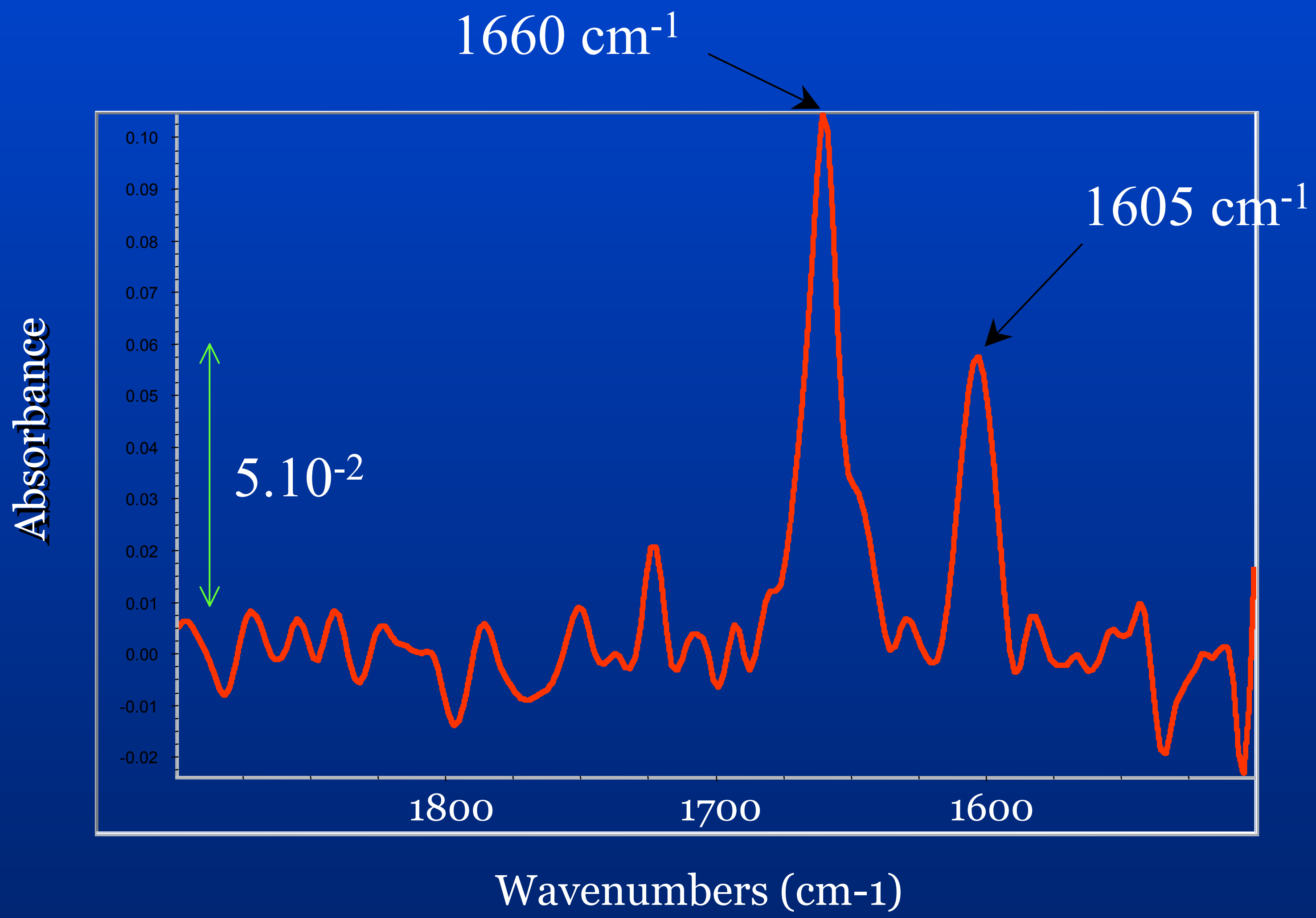
Using the focusing optics of the microscope for both IR and FEL-UV




Schwarzschild objective
Spacer 10 µm


50µm

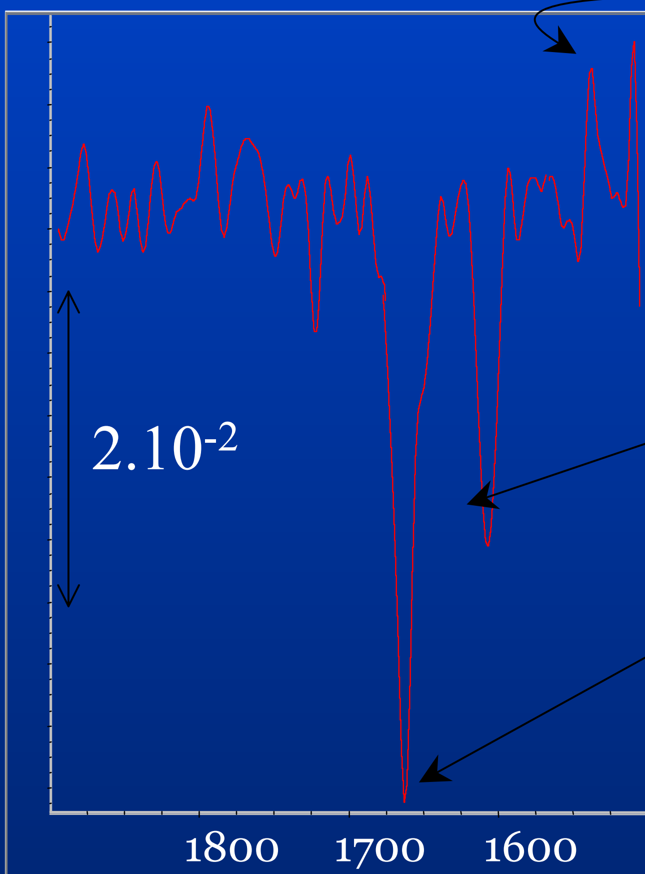
Triplet state of 4-phenylbenzophenone in acetonitrile (CH3CN) (ground state concentration 10^-3 mol/l),



L. Nahon, F. Brouwer, D. Garzella , M.E. Couprie and P. Dumas

Z.X.Sun, S.M.Nikiforov,J.Yang,C.S.Colley, M.W.George
*Appl.Spect.***56**(1)(2002)31

?



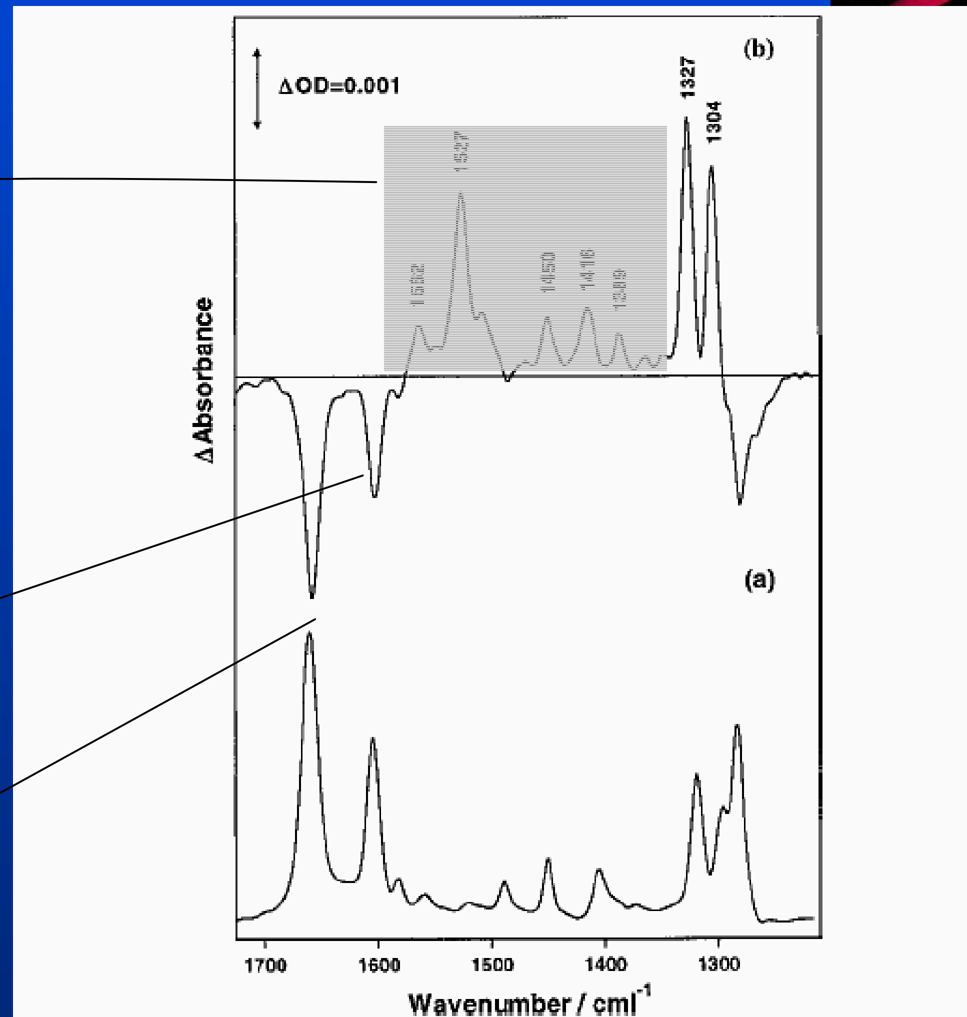


FIG. 10. (**a**) FT-IR and (**b**) TR-IR spectrum (16 scans, 8 cm^{-1} resolution) obtained 1 μs following photolysis (355 nm) of 4-phenylbenzophenone in CD_3CN.

Summary

✓Synchrotron-based IR experiments, as well as laser-based IR experiments have, on themself, their own « niche »

✓Combination of laser and synchrotron based IR experiments is very exciting, especially if both sources exists on the same facility

✓Jlab, as well as the future 4GLS facility will be centers of excellence for new Science involving , among others:

- microscopic studies on materials – including biology
- on surface science – from simple to complex environments

Special thanks to my long –term collaborator
Gwyn P. Williams(Jefferson Lab.)

A. Otto(Duesseldorf)
M.Hein (IBM)
L. Miller (NSLS)
G.L. Carr (NSLS)
P. Guyot-Sionnest'(Chicago University)
Y.J. Chabal (Rutgers University)
A. Peremans, Y. Caudano (Namur-Belgium)
O. Chubar (SOLEIL)
and more others.....