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 Fourth Generation Light Source?
Synchrotron radiation: a bright source of Infrared photons

Edge emission:

Bending magnet emission:

$B = \text{const}$

$0^\circ$ port

$4^\circ$ port
Flux comparison between various facilities

- DIAMOND (3 GeV, 400 mA, BM, 30x35 mrad)
- U4IR (0.8 GeV, 700 mA, BM, 90x90 mrad)
- U10B (0.8 GeV, 700 mA, BM, 40x40 mrad)
- NSLS II (3 GeV, 500 mA, ER+BM, 15x40 mrad)
- ESRF (6 GeV, 200 mA, ER, 8.5x16 mrad)
- SOLEIL (2.75 GeV, 500 mA, ER+BM, 20x78 mrad)
Infrared emission is well accounted for theoretically the SRW software (Oleg Chubar) (both flux and intensity profile)

**NSLS U4IR 90x90 mrad 700 mA**

- 10 microns @ U4IR: $1.5769e+14$ Photons/s/0.1%bw
- 100 microns @ U4IR: $7.3359e+13$ Photons/s/0.1%bw
- 300 microns @ U4IR: $4.9233e+13$ Photons/s/0.1%bw

**JLAB (G. Williams) 170x146 mrad 10 mA**

- 100 microns @ JLAB: $1.83021e+12$ Phot/s/0.1%bw
- 300 microns @ JLAB: $1.53084e+12$ Phot/s/0.1%bw
- 1000 microns @ JLAB: $1.13926e+12$ Phot/s/0.1%bw
Flux comparison between various facilities

Photons/s/0.1%bw

Wavelength (µm)

DIAMOND (3 GeV, 400 mA, BM, 30x35 mrad)
U4IR (0.8 GeV, 700 mA, BM, 90x90 mrad)
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JLAB, 0.1 GeV, 10 mA
Uncoherent emission
IR beamline @ ESRF

Calculated intensity profile at 6.2 meters from source
\( \lambda = 0.52 \) microns

Recorded with a CCD camera at 6.2 meters from source
\( \lambda = 0.52 \) 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: $1.67 \times 10^{14}$ 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) + BRODBAND

- 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»

Lipids profile
Protein profile (Amide I)

Fuzzy-c-means clustering

β-dominant
α-dominant

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

FEL & LPC 2004
Spectra recorded with a 3x3 μm² aperture in the nucleus

![Graph showing spectral changes over time](image)

- Before PMA
- After 48 hours
- After 72 hours

Absorbance

Wavenumbers (cm⁻¹)

Absorbance units
48 Hours after PMA...

Intensity profile of lipids

Nucleus (Amide I)

Absorbance unit

Wavenumbers (cm⁻¹)

J.L. Teillaud, N. Jamin, L. Miller and P. Dumas
Skin and hair structures

Stratum Corneum: 10-20 µm

Epidermis: 60-80 µm

Dermis: >100 µm

Cuticle: ~5-8 µm

Cortex: ~40-80 µm

Medulla: ~10-20 µm

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

Apt. Size= 6x6 μm^2

Absorbance units

Wavenumbers (cm\(^{-1}\))

Medulla
Cortex
Cuticle

Wavenumbers (cm\(^{-1}\))

1800 1700 1600 1500

1 2 3

1 2 3

FEL & LPC 2004
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

FEL & LPC 2004
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-substrate motion

Frequency smaller for external modes than for internal modes

Blackbody 300K

Blackbody 1200K

Blackbody 300K

Synchrotron

Far-IR

Mid-IR
Cu-O modes: isotopic effect

Wavenumbers (cm⁻¹)

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

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:

\[ (\sqrt{3} \times \sqrt{3}) \text{R}30^\circ \text{ CO/CU(111)} \]

IR reflectance change

\( R_{\text{CO}} / R_{\text{Clean}} \) (\%)

CO Stretch

Anti-absorption
Dipole-forbidden

Frequency (cm\(^{-1}\))

G.P. Williams, C. Hirschmugl et al.
To make the story short...
Anomalous skin effect

For copper skin depth = 27 nm at 90K

Reflectivity

Frequency (cm⁻¹)
\( \omega = \omega_0 \)

Friction force

\( \mathbf{f} = M \eta \mathbf{v}_1 \)

\( \omega \neq \omega_0 \)

No Friction!!
\[ |r_s|^2 \]

**Cu**

**CO + Cu**

**Frequency (cm\(^{-1}\))**

- 0.94
- 0.95
- 0.96
- 0.97
- 0.98
- 0.99

**Reflectance**

**Resulting IR spectrum**

\[ \Delta R_p = -\frac{4}{c n m \cos \theta} \frac{n_a M \eta}{(ned)^2} \]

**Resistance change!**
Persson defines:

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


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 $E_F$

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

\[
\rho_a (\varepsilon_F) 
\]

\[
\eta \omega_F = \varepsilon_F 
\]

\[
k_{\parallel} = k_F \sin \Theta 
\]

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

\[
\rho_a (\varepsilon_F) \approx \frac{1}{\Pi (\varepsilon_a - \varepsilon)^2 + (\Gamma/2)^2} \frac{\Gamma/2}{\Pi} 
\]
Cu(111) films

\[ W = \frac{\rho}{d} = \frac{15 \text{ mm} \ U}{6 \text{ mm} \ I} \]
\[ \frac{-\Delta R}{R_0} (\%) \]

\[ d^2 \Delta W (10^{-17} \text{ ohm.m}^2) \]

- CO
- \( 0.02 \text{L C}_2\text{H}_4 \) then CO
- \( 0.5 \text{L CO} \) then \( \text{C}_2\text{H}_4 \)
- \( 0.1 \text{ML Cs} \)
- \( 0.1 \text{ML Cs} \) Then CO
Electronic damping can be determined using either resistance change (when possible) or by reflectivity change (thick crystal..)

<table>
<thead>
<tr>
<th>System</th>
<th>From resistance $\tau_{e-h}(x10^{12} s.)$</th>
<th>From IR $\tau_{e-h}(x10^{12} s.)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO/Cu(111) bulk</td>
<td>-</td>
<td>46</td>
</tr>
<tr>
<td>NO/Cu(111) bulk</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>CO/Cu(111) 40 nm</td>
<td>36</td>
<td>45</td>
</tr>
<tr>
<td>CO/Cu(111) 50 nm</td>
<td>32</td>
<td>35</td>
</tr>
<tr>
<td>O/Cu(111) 50 nm</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>$C_2H_4$/Cu(111) 33 nm</td>
<td>213</td>
<td>235</td>
</tr>
</tbody>
</table>
Non linear spectroscopy with lasers
Surface and Interfaces studies
Sum Frequency Generation

Non linear process generated strickly at interfaces

\[ \propto N_S L_{IR} L_{Vis} L_{SFG} \left( \frac{\partial \mu}{\partial \xi} \right)^2 \left( \frac{\partial \alpha}{\partial \xi} \right)^2 \frac{U_{IR}}{AT} \]
SFG experimental set-up

**Tunable infrared laser sources**

**CLIO FEL**
- 6-20 µm
- 5 ps

**OPO**
- 2.5-10 µm
- 11 ps

\[ \omega_f(\theta) = \omega_{\text{Pump}} - \omega_S(\theta) \]

- YAG \(\times 2\)
  - 532 nm
  - 200 ps

- AgGaS\(_2\)
- CaF\(_2\)
- ZnSe
- Undulator
- Mono
- PM
- Signal
- Pump
- Idler
- Ref. SFG
- Sample
- Ref. SFG

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
The band which appears is not an IR active mode? To understand why, SFG has been carried out, since Band should be Raman and IR active.

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
Interfacial dynamic charge transfer

$A_g(2)$ mode

Vibrational ground state

$C_{60}^{-n}$

$t_{1u}$

$\varepsilon_f = \varepsilon_a |_0$

Metal

$C_{60}^{-n}\downarrow|dn\rangle$

Metal

$C_{60}^{-n+|dn\rangle}$

Metal
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:

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

SFG experimental set-up

IR: 2.5 to 4 µm, 4 to 10 µm  Vis: 410 to 710 nm
DR-SFG of C$_{60}$/Ag(111) interfaces: multilayer

The pentagonal pinch couples to the t$_{1u}$ LUMO!
Vibrational dynamics with SFG

H-Si(111)-(1x1)

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

Lifetime = first order process

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

\[
n = 1 - \exp \left( \frac{\eta \omega_0}{kT} \right)
\]

From T-dependence of the lifetime...

P. Guyot-Sionnest, P. Dumas et Y. J. Chabal
J. Electr. Spectr. Related Phenomena 54/55 (1990), 27
Future directions:
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 $\lambda^4$ dependency of Raman Cross sections)

and imaging adsorbate?
About four order of magnitude higher

Flux (Watts/cm$^{-2}$)

Jlab THz

Jlab FEL

Table-top ps lasers

synchrotron

globar

Courtoisy of G.P. Williams

FEL & LPC 2004
Typically, in SFG, the beam sizes are about 100 \( \mu \text{m} \). By increasing the spot size to 1 mm, JLAB FEL will deliver the same SFG intensity.
Two colours experiments

FEL-VUV

50µm
Using the focusing optics of the microscope for both IR and FEL-UV
Schwarzschild objective

Spacer 10 µm

50 µm
Triplet state of 4-phenylbenzophenone in acetonitrile (CH$_3$CN) (ground state concentration 10^-3 mol/l),
2.10^{-2}

![FT-IR and TR-IR spectrum](image)

**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\(_3\)CN.
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
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and more others.....