INFRARED SYNCHROTRON RADIATION:
SPECTROSCOPY AND MICROSCOPY

Stefano Lupi

Department of Physics
University of Rome La Sapienza,
CNR-INFM COHERENTIA and SISSI@Elettra (EU-Italy)
Outline

Electromagnetic Spectrum;
Infrared Synchrotron Radiation;
Experimental Apparatus: Michelson Interferometry+Infrared Microscopy

Solid-State Applications:
1. Superconducting Transition (THz and Far-IR Spectroscopy)  
   Flux Gain
2. Spectral-Weight and penetration depth
3. Metal-to-Insulator Transitions (from THz to visible)  
   Brilliance Gain
   1. Mott-Hubbard Physics
   2. Peierls and e-\textit{ph} Physics

Geological Applications:
1. Microscopic fluid inclusions  
   Brilliance Gain

Chemistry:
1. Adsorption at solid surfaces  
   Brilliance Gain

Biology:
1. Cellular absorption  
   Brilliance Gain

Cultural Heritage
The “THzgap”, Collective Excitations in Macromolecules and exotic electronic materials

Electromagnetic Spectrum

IR Units: $200 \text{ cm}^{-1} = 300 \text{ K} = 25 \text{ meV} = 50 \mu\text{m} = 7 \text{ THz}$

- Phonons;
- Drude absorption;
- Gaps in superconductors;
- Molecular Rotations;

- Molecular Vibrations
  - Fingerprints for Chemistry, Biology, And Geology

- Molecular Overtones and Combinations bands;
- Excitons;
- Gaps in semiconductors
A STUDY OF THE TRANSMISSION SPECTRA OF CERTAIN SUBSTANCES IN THE INFRA-RED.

By Ernest E. Nicholls.

Within a few years the study of obscure radiation has been greatly advanced by systematic inquiry into the laws of dispersion of the infra-red rays by Langley, Rubens, and Snow, and others. Along with this advancement has come the more extended study of absorption in this region. The absorption of atmospheric gases has been studied by Langley and by Angstrom. Angstrom has made a study of the absorption of certain vapors in relation to the absorption of the same substances in the liquid state, and the absorption of a number of liquids and solids has been investigated by Rubens.

In the present investigation, the object of which was to extend this line of research, the substances studied were: plate glass, hard rubber, quartz, lamp-black, cobalt glass, alcohol, chlorophyll, water, oxyhemoglobin, potassium alum, ammonium alum, and ammonium-iron alum.

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
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<tbody>
<tr>
<td>1976</td>
<td>Meyer &amp; Lagarde (LURE, Orsay) publish the first paper on IRSR</td>
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<tr>
<td>1981</td>
<td>Duncan and Yarwood observe at Daresbury the first IRSR emission</td>
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<tr>
<td>1985</td>
<td>The first IRSR spectrum (on N\textsubscript{2}O) is collected at Bessy (Berlin)</td>
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<tr>
<td>1986</td>
<td>The first beamline becomes operating at UVSOR (Japan)</td>
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<td>1987</td>
<td>Beamline at Brookhaven (USA)</td>
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<td>1992-94</td>
<td>Beamlines at Orsay (France), Lund (Sweden), Daresbury (GB)</td>
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<tr>
<td>1995</td>
<td>First international workshop on IRSR, Rome (Italy)</td>
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IRSR Beamlines in the World
Advantages of IRSR

**ADVANTAGES:**

- **Diffraction Limited Spatial Resolution**
- **Better Signal-to-Noise**
- **Faster Data Collection**

**BROADBAND SOURCE**

**LINEAR & CIRCULAR POLARIZATION**

**FAR-IR SOURCE**

**PULSED EMISSION**

**SPECTROSCOPY**

**BRILLIANCE**

**MICROSCOPY**
Instrumentation I: Michelson Interferometer

A Michelson Interferometer is based on the interference effect among the two electromagnetic waves at the beamsplitter site.

**Spectral Resolution**

$$\Delta \nu \approx \frac{1}{d} \text{ (cm}^{-1}) \approx 0.001 \text{ cm}^{-1} \approx 1 \mu\text{eV}$$

Detector → Measure of the figure of interference

**Interferogram**
Interferogram

Spectrum

Monochromatic

Fourier Transform

Policromatic

Interferogram

Spectrum

IR Source

Spectrum
**Instrumentation II**

**Infrared Microscopy**

**Infrared Microscope---->Beam Condenser**

Visualize and measure small and/or no-homogenous sample (size<100 μm) with a high spatial resolution

**Bruker-Hyperion**

In the IR spatial Resolution is determined by diffraction

\[ \delta = 0.61 \frac{\lambda}{NA} \approx \lambda \]

For example with a 36x objective with NA=0.5, one obtains:

- at \( \lambda = 10 \text{ μm} \) (1000 cm\(^{-1}\)): 12 μm
- at \( \lambda = 2.5 \text{ μm} \) (4000 cm\(^{-1}\)): 3 μm
Production of IRSR

**Standard Bending radiation**
(emitted during the circular trajectory in the bending due to the constant B field)

QuickTime™ e un decompressore TIFF (LZW) sono necessari per visualizzare quest'immagine.

\[
P(\lambda) = 4.4 \times 10^{14} \times I \times \Theta_H \times bw \times (\rho/\lambda)^{1/3} \text{ photons s}^{-1}
\]

- \(I\) is the current in amperes,
- \(\Theta_H\) (rads) the horizontal collection angle,
- \(bw\) the bandwidth in per cent,
- \(\lambda\) the wavelength, and
- \(\rho\) the radius of the bending.

\[
\Phi_{V-NAT}(\text{mrad}) = 1.66(1000 \times \lambda (\mu\text{m})/ \rho(\text{m}))^{1/3}
\]

at ALS for \(\lambda= 100 \mu\text{m}\) \(\Phi_{V-NAT}= 50 \text{ mrad}\)

**Very large emission angles**
SISSI: \(H=70\text{ mrad}\); \(V=25\text{ mrad}\)
Edge Emission
(emitted at the entrance (exit) of a bending magnet due to the rapid variation of the B field)

In the Far-Field approximation:

\[ P = \alpha \times I \times \gamma^4 \Theta^2/(1 + \gamma^4 \Theta^2)^2 \text{ photons s}^{-1} \]

\( I \) is the current in amperes,
\( \Theta \text{ (rads)} \) the emission angle
(concentrated in \( \Theta_{max} \sim 1/\gamma \sim 10 \text{ mrad} \))
The IRSR flux and Brilliance depend only on:

- beam current
- source size/emittance
- extraction aperture
- transmission optics

Instead scarcely depend on the machine energy

\[ \sim \left( \frac{\lambda_c}{\lambda} \right)^{1/3} \]

Elettra
I= 300 mA
Increasing the Far-IR Flux: Coherent vs Incoherent Synchrotron Radiation

\[ I = I_{\text{incoh}} + I_{\text{coh}} = (N(1 - f_v) + N^2 f_v)I_{\text{incoh}} \]

\[ f_v = \left| \int n(z)e^{i\pi \cos(\theta)z} dz \right|^2 \]

Bunch form factor

Diffraction due to chamber size

QuickTime™ and a decompressor are needed to see this picture.
Production of Coherent Synchrotron Radiation

Two main methods

**Low-\(\alpha\) mode**

- Needed to change the magnetic optics:
- Only dedicated runs

Momentum compaction factor \(\alpha\):
\[ \frac{\Delta p}{p} = \alpha = \sigma / L \]

Where \(\sigma\) is the bunch length and \(L\) is the length of the ideal trajectory inside the machine

**Low-e beam energy**

- Injected the machine at low-E:
- Reducing life-time and stability

\[ \sigma \approx E^{2/3} \]

IRIS@Bessy-II: U. Schade et al, PRL 2003

SISSI@Elettra: E. Karanzoulis, A. Perucchi and S.L., 2007
IRSR Brilliance

The most important figure of merit for IRSR is the Brilliance

$$B_{sx} = \frac{d^2F/\,d\theta\,d\phi}{ASA}$$ (photons/0.1%bw/cm²/str)

Where the Actual Source Area is an estimation of the dimension of the source at the exit port (Hulbert and Weber, 92; A. Nucara, 1998)

Limiting Noise

$$\%N = \frac{100A^{1/2}D^*}{B(\nu)\Delta \nu e t^{1/2} \xi}$$

Where: A detector area, D* detectivity, B brilliance, Δν bandwidth, ε etendue, t measuring time, ξ optical efficiency
Brilliance gain at SISSI

S. Lupi et al, 2007
Brilliance gain at SISSI

QuickTime™ e un decompressore TIFF (LZW)
sono necessari per visualizzare quest'immagine.
Experimental Techniques III

Reflectivity, Transmittance, and Absorption $R + T + A = 1$

\[ R(\omega) = \frac{I_R(\omega)}{I_0(\omega)} \]

\[ R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]

Via Kramers-Kronig
Transformation
real and imaginary part
of the optical response
functions ($n, \varepsilon, \sigma$) can be
obtained

\[ \bar{n} = \sqrt{\varepsilon} \]

\[ \varepsilon_1 = n^2 - k^2 = \varepsilon_{\infty} - \frac{4\pi}{\omega} \sigma_2 \]

\[ \varepsilon_2 = 2nk = \frac{4\pi}{\omega} \sigma_1 \]
Reflectivity experiments

Reference: gold evaporated *in situ*

Reflectivity:
\[ R = \frac{I_R^{\text{crys}}}{I_R^{\text{gold}}} \]

Kramers-Kronig transf.

optical conductivity \( \sigma(\omega) \)

Single crystals may be very small:
Solid-State Applications I
Superconductivity

(FLUX GAIN)
Superconductivity today:

1. Looking for new materials
   • 1986: High-$T_c$ cuprates
   • 1990: $C_{60}$ fullerene
   • 2000: MgB$_2$
   • 2003: Na$_x$CoO$_2$·3H$_2$O
   • 2004: B-doped diamond

2. Understanding new materials

Infrared spectroscopy plays a role...
... because

Superconductivity is ruled by low-energy electrodynamics:

- Superconducting gap: THz-range
- Spectral weight of condensate and penetration depth: THz-range
  - Mediators of pairing (phonons, etc.): Far-infrared
  - Free-carrier conductivity above $T_c$: Infrared
Basic optics of Superconductors

Minimum excitation energy: Cooper-pair breaking $2\Delta$

Superconducting gap observed if:
- sample in the dirty-limit ($2\Delta < \Gamma$)
- Cooper pairs in s-wave symmetry

\[ \int [\sigma_1(\omega, T>Tc) - \sigma_1(\omega, T<Tc)] d\omega = \frac{\omega_{ps}^2}{8} = n_s e^2/m^* \rightarrow \lambda = c/\omega_{ps} \]

Ferrel-Glover-Tinkham Rule
Diamond: the “silicon” of the future?

A diamond-based electronics?

- Chemical Vapor Deposition films: less expensive and suitable for devices
- Mechanically stable
- Large-gap insulator (5.5 eV)
- Excellent thermal conductivity (2 to 4 times that of Cu)
- Strong hole-doping already obtained \( (n_h > 10^{22} e_h/cm^3) \)
- Electron-doping coming
- …and superconducting!
  (E.A. Ekimov et al., *Nature* 428, 542 (2004)).
THz Reflectivity of Superconducting Diamond

\[ \omega \leq \Gamma (T) : R_n (\omega) = 1 - \left( \frac{8\omega \Gamma(T)}{\omega_p^2} \right)^{1/2} \]

\[ \omega \leq 2\Delta(T) : R_s (\omega) = 1 \]

Peak at 2\Delta in Rs/Rn

\[
\begin{align*}
\text{s-wave Dirty-Limit Regime; } & 2\Delta(2.6 \text{ K}) = 12 \pm 1 \text{ cm}^{-1} \\
& \Rightarrow 2\Delta/k_B T_c = 3.2 \pm 0.5
\end{align*}
\]

M. Ortolani, S. L. et al, PRL 2006
Absolute reflectivity and conductivity of Superconducting Diamond

$2\Delta(0) = 12.5 \text{ cm}^{-1} = 3 k_B T_c$ [BCS: 3.53]

$\lambda(0) = 1 \mu\text{m}$ (dirty limit)

M. Ortolani, S. L. et al, PRL 2007)
Which interaction is responsible for pairing?

Electron-phonon coupling

Anomalous-Drude model:

\[ \Gamma(\omega) = \frac{(\omega_p^2/\omega)\epsilon_2(\omega)}{\left[(\epsilon_1(\omega) - \epsilon_{\infty})^2 + \epsilon_2^2(\omega)\right]^2}. \]

\[ \Gamma(\omega) = \frac{2\pi}{\omega} \int_0^\omega (\omega - \Omega)\alpha^2 F(\omega) d\Omega \]

\[ \alpha^2 F(\omega) \propto W(\omega) = \frac{1}{2\pi} \frac{d^2}{d\omega^2} [\omega \Gamma(\omega)] \]

A phonon branch appears at 70 meV with B-doping, which also interacts with the charges.

The only optical phonons in diamond (~1300 cm\(^{-1}\)=160 meV) is not IR-active, but Raman-active. The peak in \(\alpha^2 F(\omega)\) indicates hole-phonon interaction.

Holes interact with a broad phonon branch centered around 140 meV:

M. Ortolani, S. L. et al, PRL 2007
Superconducting CCA$_6$

c-axis oriented policrystals $T_c=11.4$ K (G. Loupia et al, 2005)

Clean-limit regime $\rightarrow$ Ca-Doped Graphite

-----$\rightarrow$ No Optical Information (Gap, Penetration depth, …) about Superconducting State

M. Ortolani, S.L. et al, unpublished
CaAlSi (anisotropic superconductor)
polarized gap measurements

s-wave Dirty-Limit Regime both along the exagonal plane and along the c-axis:

\[ 2\Delta_{ab}(0 \text{ K}) = 19 \pm 1 \text{ cm}^{-1} \]
\[ 2\Delta_{c}(0 \text{ K}) = 23 \pm 1 \text{ cm}^{-1} \]

\[ 2\Delta_{ab}/k_B T_C = 3.9 \pm 0.2 \]
\[ 2\Delta_{c}/k_B T_C = 4.5 \pm 0.2 \]

S. Lupi et al, PRL 2007
Josephson Plasma Resonance along the c-axis of a High-$T_c$ SC: La-Ba-Sr-Cu-O

$T_c = 36$ K

$T_c = 10$ K

$\omega (\text{cm}^{-1})$

$R_c(\omega)$

$\text{La}_{1.875}\text{Ba}_y\text{Sr}_{0.125-y}\text{Cu}_4$

JPR Edge at 14 cm$^{-1} = 0.4$ THz

Solid-State Applications II
Metal-to-Insulator Transition

(BRILLIANCE GAIN)
Metal-to-Insulator Transition (MIT)

Theory of Metal to Insulator Transitions
High-Pressure IRSR Spectroscopy
Electron-Electron interaction and insulator-to-metal transition (MIT)

Electronic correlation: failure of band model

Hubbard model

\[ H = -t \sum_{<ij>\sigma} (c^+_{i\sigma}c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow}n_{i\downarrow} \]

\( t \): hopping integral

(\text{strongly dependent on atomic distances})

\( U \): coulomb repulsion

\( U \) prevents double on-site occupancy

the opening of a gap in the spectra of excitations is induced

Pressure may increase \( t \) and therefore the \( t/U \) ratio inducing a MIT
Electron-Lattice interaction
Peierls MIT

A charge density wave (CDW) ground state develops in low-dimensional metals as a consequence of electron-phonon interaction.

Electron density, lattice distortion and single particle band in (a) the metallic state for $T > T_{CDW}$ and (b) in the CDW state at $T = 0$.

The figure is for a one-dimensional, half-filled system. In this case a gap (D) opens in the single-particle spectra of excitations.

Pressure may increase t and reduce lattice distortion inducing a MIT

IRSR Microscopy at high pressures

\[ T = \frac{I_T}{I_0} \]

Opt. D. = \(-ln(T)\) = \(\alpha d\)

\[ R_{\text{diam/sam}} = \frac{I_R}{I_0} \]
Vanadium di-oxide VO$_2$

T-dependent MIT ($T_{MIT} = 340$ K) concomitant with a lattice modification from a low-T monoclinic (M1) to a high-T rutile (R) phase.

MIT Hubbard or Peierls mechanism?

Pressure dependent measurements may provide useful information

Simultaneous measurements of reflected and transmitted intensity on a slab of VO$_2$, 5 microns thick.

Iteratively from T and R the optical conductivity of VO$_2$ has been obtained.

A sudden increase is visible in the optical conductivity (especially in the MIR region) above 10 GPa. A delocalized electronic state is therefore achieved in the monoclinic Peierls state.

Spectral Weight (SW), obtained at low and high frequency shows a different behavior below and above this pressure.

MIT transition of a manganite in the FIR

Pressure-induced MIT at 300 K

In manganite high pressure measurements have shown that the MIT and the Curie transition are intrinsically coupled

A. Sacchetti et al., Phys. Rev. Lett. 2006 (sinbad@frascati)
Geological Applications: liquid inclusion in minerals
Brilliance gain

Liquid Inclusion in quartzite
Mapping with 3µm x 3µm (diffraction limited)

Infrared Spectra

CO₂ Distribution
Water Distribution

A. Perucchi, S.L. et al, 2006
Chemistry

CO adsorbed molecules on Cu metallic surface

Hindered rotation

Vibration

Noise less than 0.01%

G. Williams et al, PRL 1998
Medical and Biological Application of IR Microscopy

Brilliance gain

How look the IR spectrum of a cell?

Proteins

Lipids

Vibration Frequencies correspond to finger-print for the molecule
IRSR spectrum of a single cell during mitosis

QuickTime™ e un decompressore TIFF (LZW) sono necessari per visualizzare quest'immagine.

P. Dumas et al, 2004
Studying hair by IRSR microscopy
Collective (conformational) modes of macromolecules

Organic macro-molecules must be in an aqueous environment to function, i.e. to undergo their conformational switching at THz frequencies needed for high power THz intensity
**THz Single Strand and double strands DNA spectra**

The coupling with sugar skeleton and with the complementary base induce a splitting of the conformational modes and the appearing of low-frequency (<1.5 THz) collective vibrations.

**Possibility to detect conformational changing**
Application to Cultural Heritage

Study of the aging of an ancient paper

A. Perucchi, S.L. et al, 2005
Perspectives

1. Mid-IR and Far-IR imaging coupled with x-ray imaging for biomedical applications;
2. THz Imaging and spectroscopy at III° Generation machines;
3. Circular polarization and dichroism in the Far-IR coupled with High-Magnetic fields
4. fs pulsed THz radiation from IV° generation machine for no-linear time-resolved spectroscopy FERMI@ELETTRA.ppt
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and many others…….