INFRARED SYNCHROTRON RADIATION: FROM THE PRODUCTION TO THE USE

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Outline

- Production and Properties of Infrared Synchrotron Radiation;
- Experimental Apparatus: Michelson Interferometry+Infrared Microscopy
- Solid-State Applications:
  - Superconduting Transition (THz and Far-IR Spectroscopy)
  - Gap determination
  - Spectral-Weight and penetration depth
  - Metal-to-Insulator Transitions
- Biology:
  - Cellular absorption and replication
- Geological Applications:
  - Microscopic fluid inclusions
- Chemistry:
  - Adsorption at solid surfaces
- New developments
  - THz non linear Spectroscopy
  - Go beyond the diffraction limit: Infrared Nanoscopy
Electromagnetic Spectrum

The “THz gap”, Collective Excitations in Macromolecules and exotic electronic materials

IR Units: 200 cm⁻¹ = 300 K = 25 meV = 50 μm = 7 THz

FIR MIR NIR

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 F. NICHOLS.

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, 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 Ångström. Ångström 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.

~ 50 IRSR Beamlines in the World

1976  Meyer and Lagarde (LURE, Orsay) publish the first paper on IRSR
1981  Duncan and Yarwood observe at Daresbury the first IRSR emission
1985  The first IRSR spectrum (on N$_2$O) is collected at Bessy (Berlin)
1986  The first beamline becomes operating at UVSOR (Japan)
1987  Beamline at Brookhaven (USA)
1992-94 Beamlines at Orsay (France), Lund (Sweden), Daresbury (GB)
1995  First international workshop on IRSR, Rome (Italy)
2001  First IR beamline in Italy (SINBAD@DAΦNE)
2006  Second beamline in Italy (SISSI@Elettra)
2015  First THz beamline in Italy (TERASPARC@SPARC)
2017  Second THz beamline in Italy (TERAFERMI@Elettra)
Production of IRSR

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

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

- \( I \) 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

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

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

Very large emission angles
SISSI: \( H = 70 \, \text{mrads} \); \( V = 25 \, \text{mrads} \)
**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:

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

- \( I \) is the current in amperes,
- \( \Theta (\text{rads}) \) the emission angle
  - (concentrated in \( \Theta_{\text{max}} \sim 1/\gamma \sim 10 \text{ mrads} \))
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
The most important figure of merit for IRSR is the **Brilliance**

\[ B_{se} = \frac{d^2F}{d\theta d\varphi} \text{ (photons/0.1\%bw/cm}^2/\text{str)} \]

Where the **Actual Source Area** is an estimation of the dimension of the source at the exit port (Hulbert and Weber, 1992; A. Nucara, 1998)

**Limiting Noise**

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

Where: A detector area, D* detectivity, B brilliance, \( \Delta \nu \) bandwidth, \( \varepsilon \) etendue, t measuring time, \( \xi \) optical efficiency
Advantages of IRSR

**ADVANTAGES:**

- FLUX GAIN
- BROAD BAND
- LINEAR & CIRCULAR POLARIZATION
- BRILLIANCE GAIN
  - Diffraction Limited Spatial Resolution
  - Better Signal-to-Noise
  - Faster Data Collection

**SPECTROSCOPY**

**MICROSCOPY**
SISSI (Source for Imaging and Spectroscopy in the Infrared)

- **Figure M1**
  - Plane
  - Dimension: 30X15

- **Figure M2**
  - Ellipsoidal
  - Dimension: 35X18

- **Figure M3**
  - Plane
  - Dimension: 15X8

- **Figure M4**
  - Ellipsoidal
  - Dimension: 16X10

**IRSR Focus**

- 65±5 (H) x 25 (V) mrad
- 20 microns

15.5 m
Brilliance gain at SISSI

Increasing the Far-IR Flux: Coherent vs Incoherent Synchrotron Radiation

Flux:

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

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

Diffraction due to chamber size
Production of Coherent Synchrotron Radiation

Two main methods in a Synchrotron Machine

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

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

Momentum compaction factor \(\alpha\): \(\Delta p/p = \alpha = \sigma/L\)

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

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

SISSI@Elettra: E. Karanzoulis, A. Perucchi and S.L., 2007
A Michelson Interferometer is based on the interference effect among the two electromagnetic waves at the beam-splitter site.

**Instrumentation**

Measuring a source power spectrum: Michelson Interferometer

**Spectral Resolution**

\[ \Delta \nu \sim \frac{1}{d} \text{ (cm}^{-1}) \sim 0.001 \text{ cm}^{-1} \sim 1 \mu\text{eV} \]
Interferogram

Spectrum

Monocromatic

Policromatic

IR Source

Fourier Transform

\[ \text{Interferogram} \]

\[ \text{Spectrum} \]

\[ v_0 \]

\[ v_1 \]

\[ v_n \]

\[ \text{Spectrum} \]

\[ \text{Interferogram} \]

\[ \text{IR Source} \]

\[ \text{Spectrum} \]
In the IR spatial Resolution is determined by diffraction

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

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
Experimental Techniques

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

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

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

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

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

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

Reference: gold evaporated in situ

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

\( R \) \( \downarrow \)
Kramers-Kronig transf.
\( \downarrow \)
optical conductivity \( \sigma(\omega) \)

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

(FLUX GAIN)
Superconductivity today

... because

Superconductivity is ruled by low-energy electrodynamics:

- Superconducting gap: THz range
- Spectral weight of condensate and penetration depth: THz
- Mediators of pairing (phonons, etc.): THz
- Range of sum rules: THz, Mid, or Near Infrared
- Free-carrier conductivity above $T_c$: Infrared

Infrared and THz spectroscopy plays a fundamental role
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

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

Ferrel-Glover-Tinkham Rule

Drude absorption

Drude reflectance

\[
\sigma_1^{\text{sup}}(\omega) = \frac{\omega^2_{ps}}{8} \delta(\omega) + \sigma_1^{\text{reg}}(\omega)
\]
THz Reflectivity of Superconducting Diamond

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

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

Peak at 2\(\Delta\) in Rs/Rn

\[ s\text{-wave Dirty-Limit Regime; } 2\Delta (2.6 \text{ K}) = 12 \pm 1 \text{ cm}^{-1} \rightarrow 2\Delta / k_B T_C = 3.2 \pm 0.5 \]

M. Ortolani, S. L. et al, PRL 2006
Solid-State Applications II
Metal-to-Insulator Transition (MIT)

(BRILLIANCE GAIN)
Insulator to Metal Transitions
Many materials are insulating although band theory suggests a metallic ground state: V$_2$O$_3$, VO$_2$, NiO, NiSe$_2$, La$_2$CuO$_4$, Cs$_3$C$_{60}$ → Strong Electronic Correlations → Hubbard Model

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

$U$ Coulomb repulsion
$t$ Bandwidth

$U$ prevents double on-site occupancy → a gap in the spectra of excitations is induced

How to transform an Insulator in a Metal

Bandwidth-Controlled MIT

Filling-Controlled MIT

$F_c$ Fermi level

$\epsilon_F$ large gap

$U$
IRSR Microscopy at high pressures

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

\[ \text{Op.D.} = -\ln(T) = \alpha d \]

\[ R_{\text{diam/sam}} = \frac{I_R}{I_0} \]
THz Reflectivity of Superconducting H3S

P=155 GPa

F. Capitani et al., Nature Physics 2017
**Generalities on Vanadium dioxides VO$_2$**

Strong Interplay between electron-lattice and electron-electron interactions

**Driving MIT mechanism Hubbard or Peierls?**

High Pressure may disentangle the two mechanisms
P-dependent infrared measurements on VO$_2$

Simultaneous measurements of reflectance and transmittance at 300 K in the M1 monoclinic insulating phase on a thin VO$_2$ sample

Pressure induces a metallization process in a new monoclinic structure Mx

This indicates a concomitant role of lattice (V-V) phonons and electronic excitations in the MIT

Pressure Induced Polymerization of Polyacetylene in Zeolite

D. Scelta et al, Chemistry of Mat. 2014
How look the IR spectrum of a cell?

Vibration Frequencies correspond to finger-print for the molecule
Infrared Group frequency region

- O-H, N-H
- C-H
- C=O
- C-N, O
- C-C, C-O, C-N

Wavelength (microns) vs. Frequency (cm⁻¹)
IRSR spectrum of a single cell during mitosis

The cell physiology is not altered under IRSR illumination

Fig. 1. Infrared spectrum of a mouse UN2 hybridoma B living cell, recorded with an aperture of 3×3 μm². The instrumental resolution was set at 4 cm⁻¹, and the spectrum displayed is the result of 128 co-added scans (the total recording time is 55 sec).
Studying hair by IRSR microscopy

Medulla (about 10 μm)
Cuticle (about 5 μm)
Cortex (about 40-50 μm)

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

Lipid profile
Protein profile

P. Dumas et al, 2004
Geological Applications: liquid inclusion in minerals

Brilliance gain

Liquid Inclusion in quartzite

Mapping with 3μm x 3μm (diffraction limited)

Infrared Spectra

Water Distribution

CO₂ Distribution

A. Perucchi, S.L. et al, 2006
Interstellar micron size dust analysis

comparison SRS-Black body:
3 micron Particles from asteroid “Orgueil”

Molecular water
Aliphatic CH
OH- silicates

Absorbance

Wavenumber (cm⁻¹)

Particles collected from the MIR shuttle
Recent Developments

1. THz IV generation sources: Non linear and time-resolved spectroscopy;

2. Beating the diffraction limit → IRSR Nanoscopy
Linear vs. Non Linear Spectroscopy

**Linear Spectroscopy**

- Low Power Source
- Small Perturbation → Sample retains its equilibrium properties

**Non linear and Time-Resolved Spectroscopy**

- High Power/Pulse
- Strong Perturbation → out of equilibrium states → manipulation of matter through em fields
Linear versus Non-Linear Optical Response

Actually the linear/non-linear electrodynamics regimes can be estimated through the ratio

\[ Q = \left[ \frac{eE}{\omega} \right] / p_F \]

Electromagnetic Momentum

Fermi Momentum

Linear regime \( E_{\text{THz}} \approx 10-100 \text{ V/cm} \) → \( Q<<1 \) \( \leftarrow \rightarrow T=T(\omega) \) \( \leftarrow \rightarrow \sigma=\sigma(\omega) \)

Non linear regime → \( Q=1 \)

Putting \( \omega/2\pi=1 \) THz and \( p_F \), \( Q=1 \) for \( E_{\text{THz}} \approx 50 \text{ kV/cm} \) → then the optical functions start to be dependent on the applied electric field.

For instance: \( T=T(\omega,E_0) \) \( \leftarrow \rightarrow \sigma=\sigma(\omega,E_0) \)
THz Sources for Non Linear and Pump-Probe Spectroscopy

Figures of merit of a pump source:

1) Energy per pulse ≈ 1 μJ-10 mJ;
2) Pulse duration → sub-ps scale (more relaxed than in VIS-Near-IR) → an excitation starts to exist after half a cycle (T≈100 fs-10 ps);
3) Rep rate tens of Hz to MHz;
4) Frequency tunability;
5) Associate electric field 100 KV/cm (1 mV/Å) to 100 MV/cm (1V/Å) → Atomic field;
6) Associate magnetic field ≈ 1 T
Coherent Radiation from sub-ps electron bunches

\[
\frac{d^2I}{d\omega d\Omega} = \frac{d^2I_{sp}}{d\omega d\Omega} \left[ N + N(N - 1)F(\omega) \right]
\]

Long bunch emits incoherently
\( \sigma_z > \lambda \)

Short bunch emits coherently
\( \sigma_z \leq \lambda \)

Diffraction Radiation

Undulator Radiation
SPARC LAB: Linear accelerator at 250 MeV
Achieved THz Performances

<table>
<thead>
<tr>
<th>Electron beam parameters</th>
<th>Single bunch (VB mode: max compression)</th>
<th>4-bunches per train (VB mode + laser comb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge/bunch (pC)</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>Energy (MeV)</td>
<td>130</td>
<td>100</td>
</tr>
<tr>
<td>Bunch length (fs)</td>
<td>160</td>
<td>200</td>
</tr>
<tr>
<td>Rep. Rate (Hz)</td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Radiation parameters</th>
<th>SPARC (single bunch)</th>
<th>SPARC (4-bunches/train)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy per pulse (μJ)</td>
<td>40</td>
<td>0.6 10^{-6} (@ 1 THz)</td>
</tr>
<tr>
<td>Peak power (MW)</td>
<td>&gt; 100</td>
<td>3 (@ 1 THz)</td>
</tr>
<tr>
<td>Electric field (MV/cm)</td>
<td>1.5</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Pulse duration (fs)</td>
<td>120</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>50 GHz-5 THz</td>
<td>50 GHz-5 THz</td>
</tr>
</tbody>
</table>

E.Chiadroni et al, APL 2013
3D Topological Insulators

Dirac Metallic Surface

Insulating state in the bulk due to Spin-Orbit
Non-Linear THz response of TI Dirac Fermions

F. Giorgianni et al., Nature Communications (2016)
Non-Linear THz response of TI Dirac carriers

According to the classical equation of motion one electron in an electric field $E$ is accelerated with a momentum variation $dp/dt = -eE$. 

$$E = E_0 \cos \omega t \Rightarrow p = (-eE_0/\omega) \sin \omega t$$

**Massive Electrons**

$$\varepsilon(p) = \frac{\bar{p}^2}{2m}$$

$$v_x = \frac{d\varepsilon}{dp_x} = \frac{p_x}{m} = \frac{-eE_0}{m\omega} \sin \omega t$$

For $n$ electrons one has an electric current

$$J_x(t) = -env_x = \frac{ne^2E_0}{m\omega} \sin \omega t$$

**Dirac Electrons**

$$\varepsilon(p) = v_F \sqrt{p_x^2 + p_y^2}$$

$$v_x = \frac{d\varepsilon}{dp_x} = \frac{v_F p_x}{\sqrt{p_x^2 + p_y^2}} = -v_F \text{sgn} \omega t$$

For $n$ electrons one has an electric current

$$J_x(t) = -env_x(t) = e^2nv_F \frac{4}{\pi} \left[ \sin \omega t + \frac{1}{3} \sin 3\omega t + \ldots \right]$$

Linear current vs. $E$

Unlinear current vs. $E$
Dirac THz Non-Linearity in Bi$_2$Se$_3$ Topological Insulator

Harmonic Generation

Terahertz saturable absorber

F. Giorgianni et al., Nature Communications (2016)
The resolving capability of an optical component is ultimately limited by the diffraction (Abbe’s theory, 1873). The minimum resolution ($\delta$) for the optical component are thus limited by its aperture size, and expressed by:

$$\delta = 0.61 \frac{\lambda}{NA} \approx \lambda$$

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

- at $\lambda = 10 \, \mu m$ (1000 cm$^{-1}$): 12 $\mu m$
- at $\lambda = 2.5 \, \mu m$ (4000 cm$^{-1}$): 3 $\mu m$

The fine spatial structure is contained in the near-field which exponentially decreases far from the focal point.

Need to capture the near-field signal.
Beyond the Diffraction Limit: The use of Evanescent waves

In order to enhance the spatial resolution one should increase the wavevector \(k_x\) bandwidth \(\Delta k_x\):

**For propagating light the ultimate limit of** \(k_x = \frac{2\pi}{\lambda}\)

Being \(k = \sqrt{k_x^2 + k_y^2 + k_z^2}\), \(k_x >> k = \frac{2\pi}{\lambda}\) if \(k_z\) is imaginary

An evanescent wave (along a direction) has along this direction an exponentially decreasing amplitude:

\[
E(r,t) = E_0 e^{ik_xx} e^{ik_yy} e^{-kzz}
\]

Due to the evanescent nature, this wave which maximizes the spatial resolution should be analyzed at distances on the order of \(k_z^{-1} \approx \lambda\) from the source
The metallic AFM-Tip acts as an antenna transforming far-field light in a plasmon which propagates to the apex localizing energy on nanoscale dimension comparable to apex-size.

**Spatial resolution ~ AFM tip radius**

**SPATIAL RESOLUTION INDEPENDENT OF λ**

Comparison among different Spatially Resolved Spectroscopies

X. F. De Abajo 2010
Visualizing Plasmon Propagation and Scattering in Single Carbon Nanotube (Optics at Finite q)

Figure 1 | Infrared s-SNOM of one-dimensional plasmons in carbon nanotubes. a, Illustration of s-SNOM. Infrared (IR) light is focused onto the apex of a metal-coated AFM tip, the large near-field momentum of which enables optical excitation of plasmons in the carbon nanotube (CNT) on a hBN substrate. Interference between the tip-excited plasmon wave and its reflection from the nanotube end leads to periodic modulation of tip-scattered infrared radiation measured by an HgCdTe detector in the far field. b, Three-dimensional plot of the near-field scattering intensity (height) along a representative SWNT. Prominent modulation of the infrared scattering intensity from the one-dimensional plasmon can be observed over the whole nanotube. Inset: AFM topography image of the same SWNT. Scale bars, 100 nm.

Z. Shi, Nature Photonics 2015, IRSR from ALS IR Beamline
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FREQUENCY AND TIME-RESOLVED
TERAHERTZ SPECTROSCOPY

The SISSI/TERAFERMI-ELETTRA group:
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P. Di Pietro
L. Vaccari

The LNF-INFN SPARC Lab group:
E. Chiadroni