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THz studies with SR and FEL radiation

- The THz spectral range
- THz spectroscopy with Synchrotron Radiation
- THz non-linear studies

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The THz gap

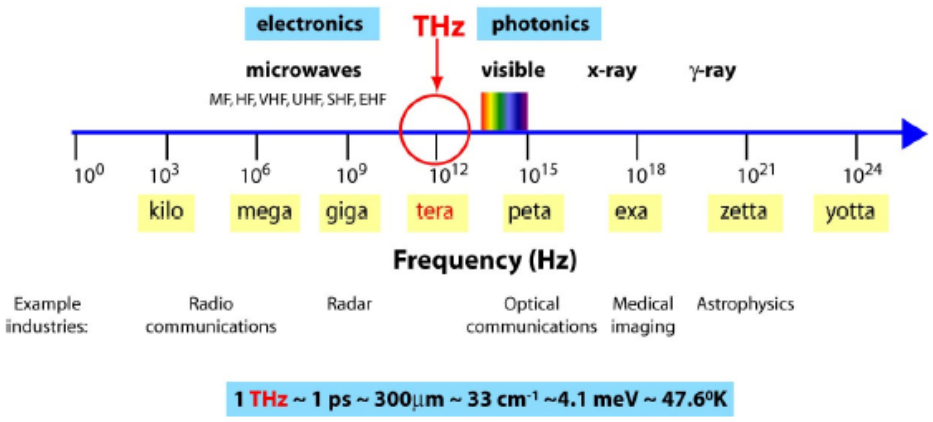
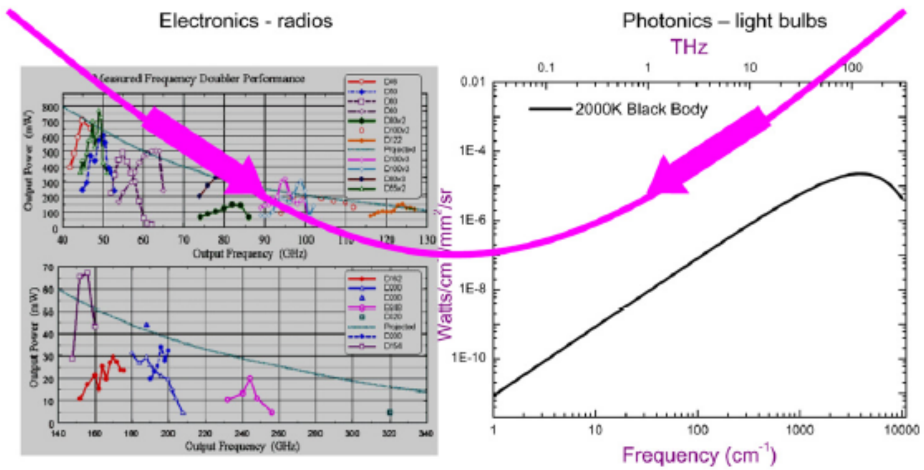


Figure 1. Schematic of the electromagnetic spectrum showing that THz light lies between electronics and photonics.



G. Williams, Rep. Prog. Phys. **2006**

Free electrons (Drude)

Lattice vibrations (phonons)
Rotational modes
Librational/Torsional modes
Intermolecular modes

Hydrogen bonds
Van der Waals interactions

Electro-magnons

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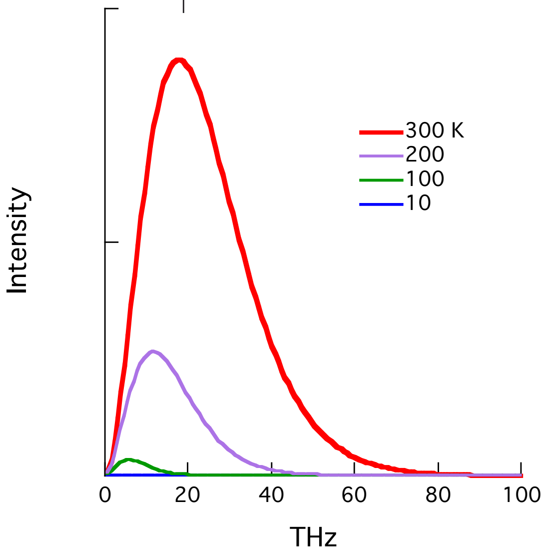
Properties of THz light

- **Non-ionizing**
safe use on living people/animals, non-destructive for biological samples
- **Highly penetrating**
sees through many materials, as packaging, clothing, walls
- **Chemical specificity**
distinguishes between different plastics, drugs, explosives
- **High contrast**
between strong (metals, water) and weak (plastics, tissues) absorbers
- **High-speed communications**
1000 times faster than GHz

…the main drawback is spatial resolution ~ mm

THz light and blackbody radiation



Planck's law

$$I(\nu,T) = \frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}}-1}$$

Wien's law

λ_{max}= b/T   b=2.897 10^{-3} K m

ν_{max}= 0.1035 T   THz K^{-1}

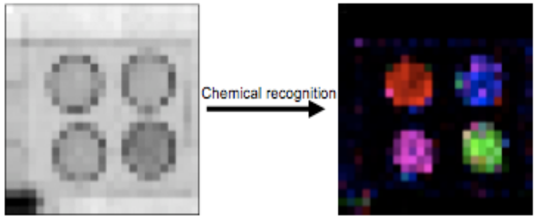
All objects at room temperature are THz radiation emitters

THz modes are normally populated at room T

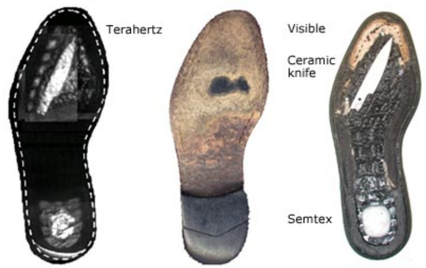
Technological applications

Pharmaceutical

Fig. 8. Visible image of sample with four pellets containing different chemicals: (1) lactose, (2) aspirin, (3) sucrose, and (4) tartaric acid.



Security



TeraView

Quality control

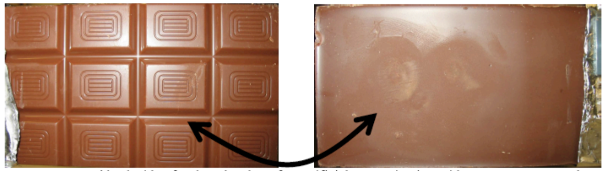
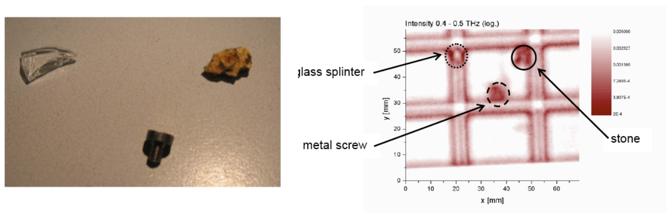
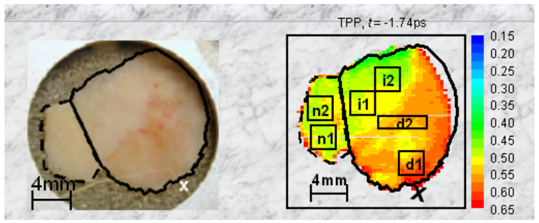


Figure 3. Front and back side of a chocolate bar after artificial contamination with a stone, a M2 metal screw and a glass splinter.



Medical imaging



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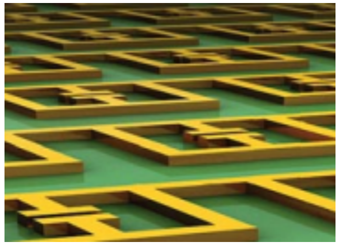
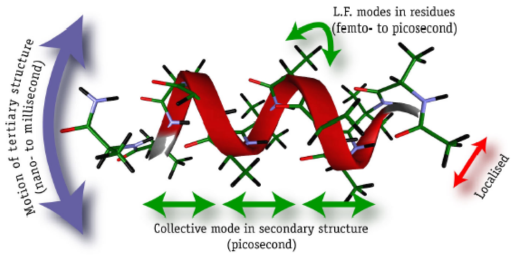
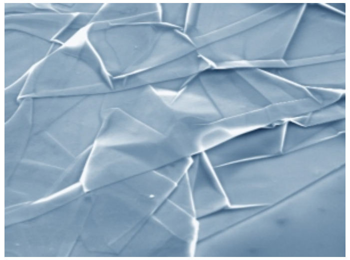
THz Spectroscopy

Superconductivity
Collective excitations
Multiferroics
Heterostructures
Metamaterials
Plasmonics

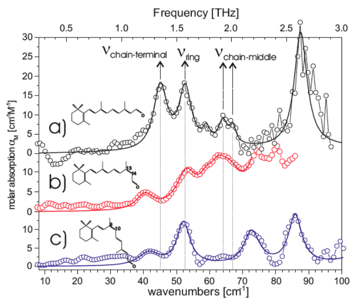




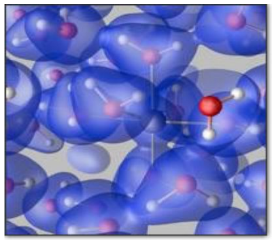


Graphene
2D chalchogenides
Black Phosphorus

Protein Folding
Amyloid fibrils
Isomers



Polar liquids
Hydrogen bonds
Van der Waals interactions
Solutions



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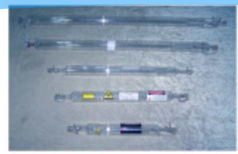
THz sources for spectroscopy and imaging

Monochromatic Sources

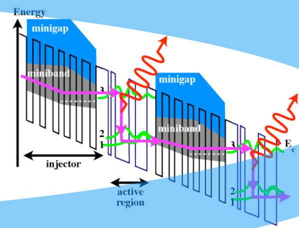
Backward-Wave-Oscillators

Gunn/Impatt-Diodes



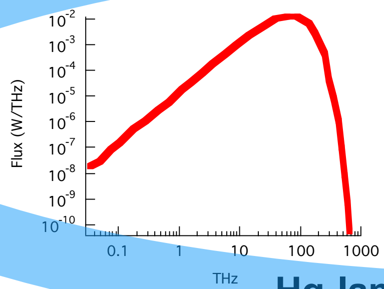
Gas Lasers (CO_2 and CO_2-pumped)
Si/Ge Lasers

Quantum Cascade Lasers



Broadband Sources

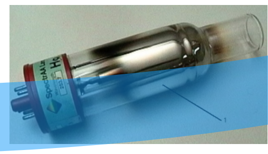
Globar (blackbody source)
silicon carbide rod electrically heated up to 1000 to 1650˚C



Total Flux:
10 μW between 0-1 THz
5 mW between 0-10 THz
1,5 W between 0-100 THz

Because of poor collimation typically one has nW power at sample at THz frequencies

Hg-lamp
Performs slightly better than Globar, below 5 THz



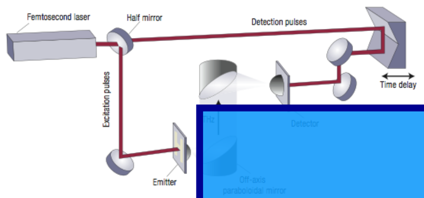
Femtosecond THz sources

0.1 THz

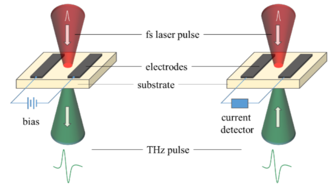
3 THz

15 THz

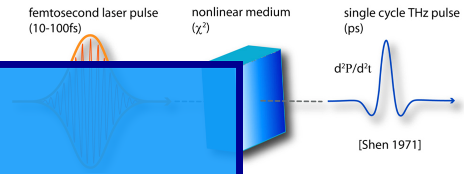
THz
Time Domain Spectroscopy



Photoconductive Antennas
GaAs, TiO_2, …



Optical Rectification
ZnTe, GaP, $LiNbO_3$, etc.



[Shen 1971]

RESTSTRAHLEN BAND GAP

Optical rectification in organic crystals

DAST, OH1, DSTM

$$\eta < 10^{-2}$$

Increasing THz power
---> Increasing Laser power
---> Dealing with radiation damage of the emitter
(losses in brightness/time-structure)

Optical Parametric Amplifiers
Tunable, Narrow-Band

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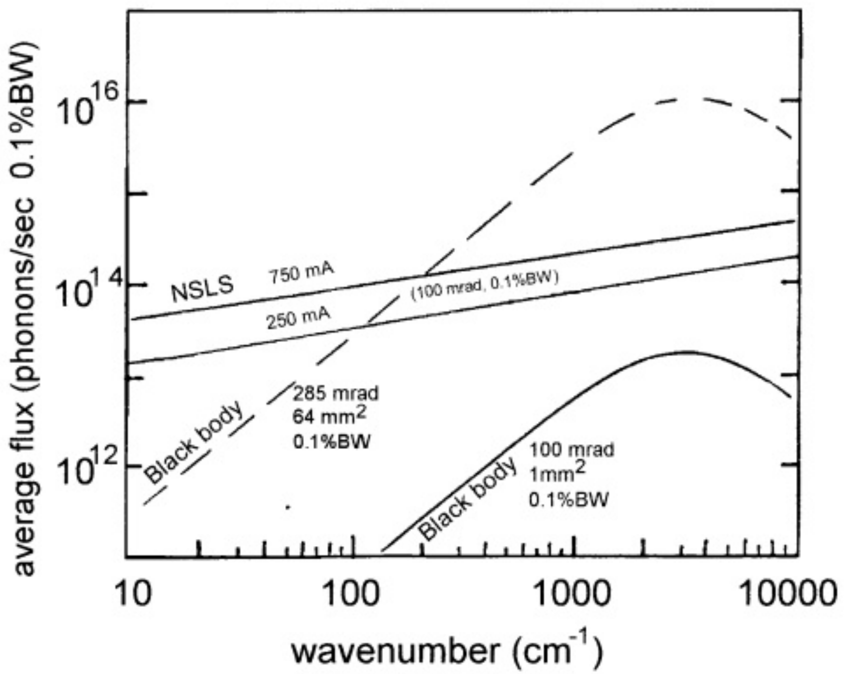
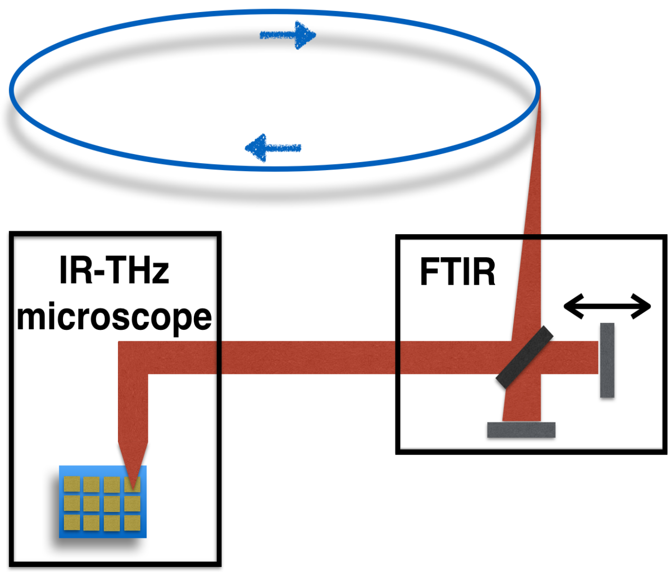
THz studies with SR and FEL radiation

- The THz spectral range
- THz spectroscopy with Synchrotron Radiation
- THz non-linear studies

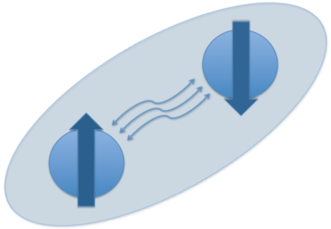
Storage-Rings



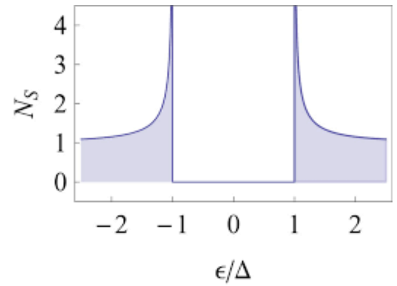
Kircher et al., JOSA B **1997**



Superconducting Gap opening



Cooper pair formation opens up a gap in the density of states

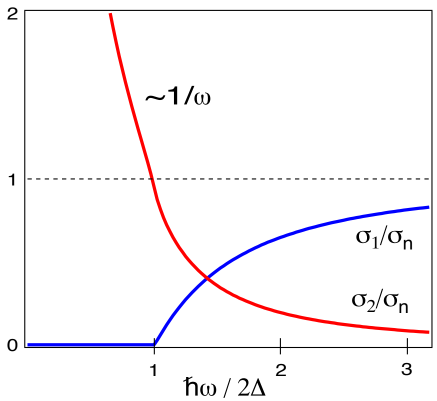


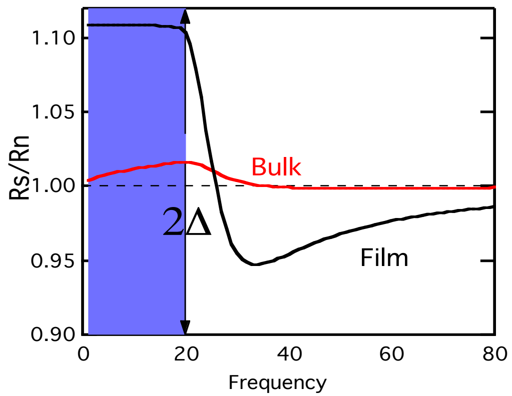
Superconductivity is ruled by *low-energy* electrodynamics:

The Superconducting Gap size and shape provide information on the nature and symmetry of pairing

$$2\Delta / k_B T_C = 3.52$$ → $T_c \approx 10$ K → $2\Delta \approx 1$ THz

The Mattis-Bardeen (MB) relations are derived within the BCS theory, for a s-wave SC in the dirty limit





Single vs multi-gap superconductors

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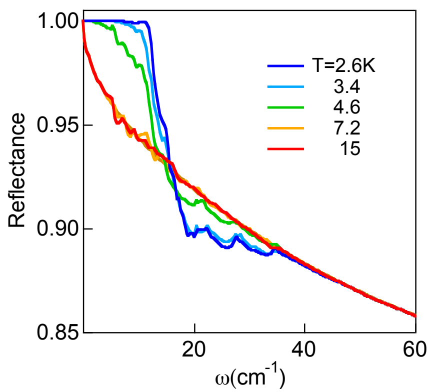
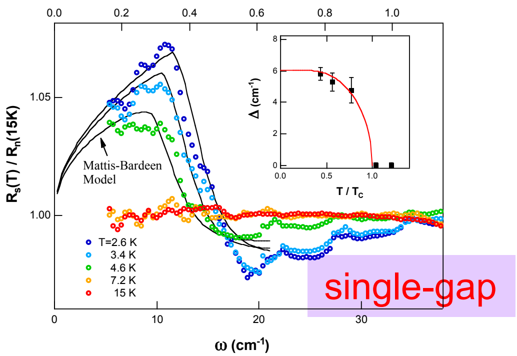
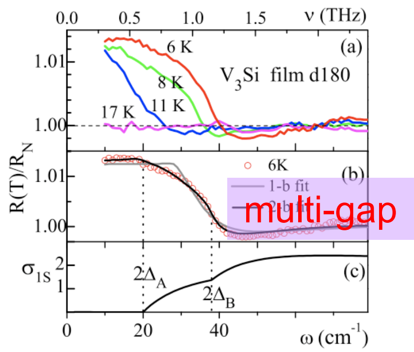
B-doped diamond





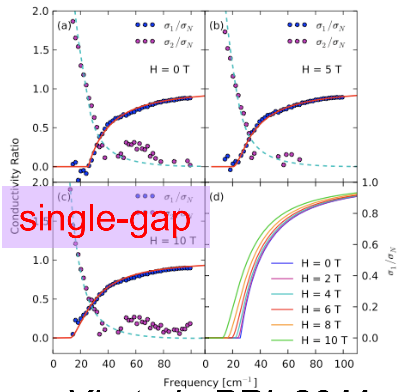
Ortolani et al., PRL **2006**

V_3Si



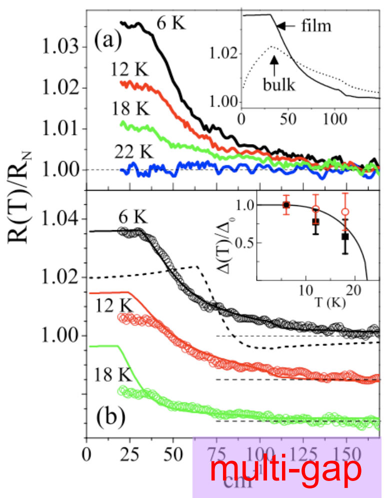
Perucchi et al., PRB **2010**

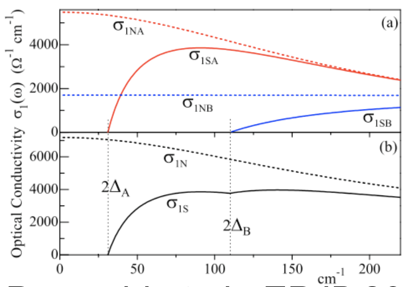
$Nb_{0.5}Ti_{0.5}N$



Xi et al., PRL **2011**

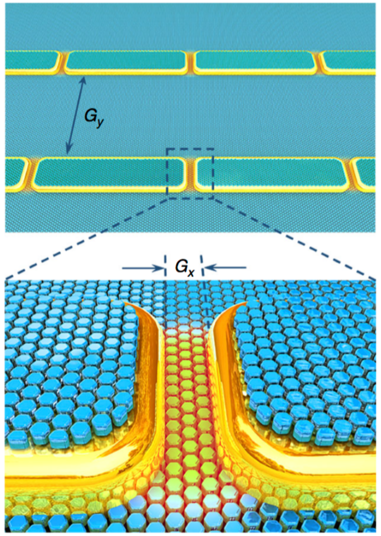
$Ba(Fe,Co)_2As_2$

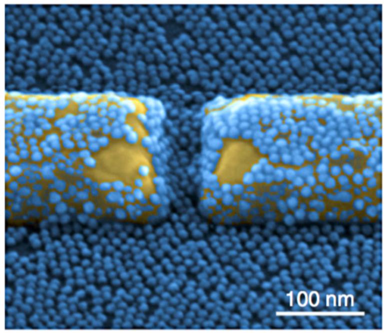


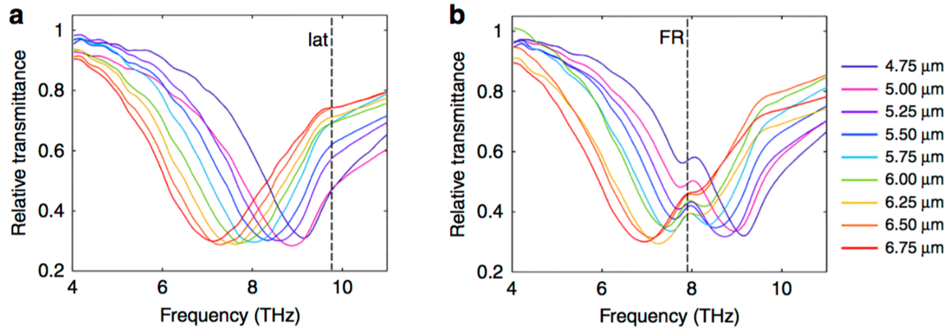


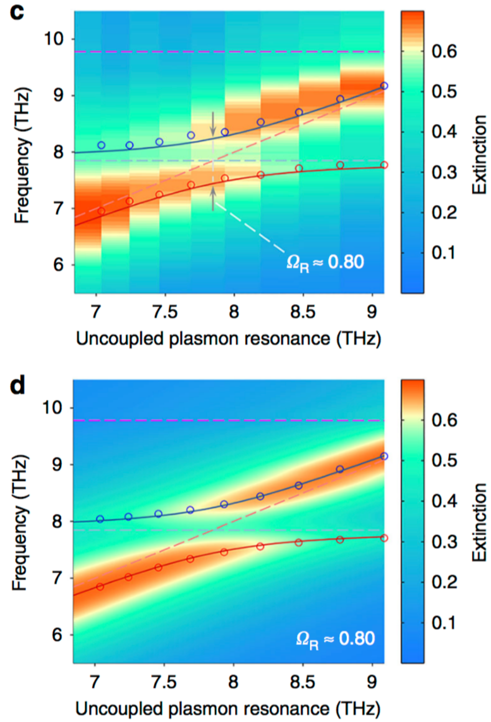
Perucchi et al., EPJB **2010**

THz plasmonics







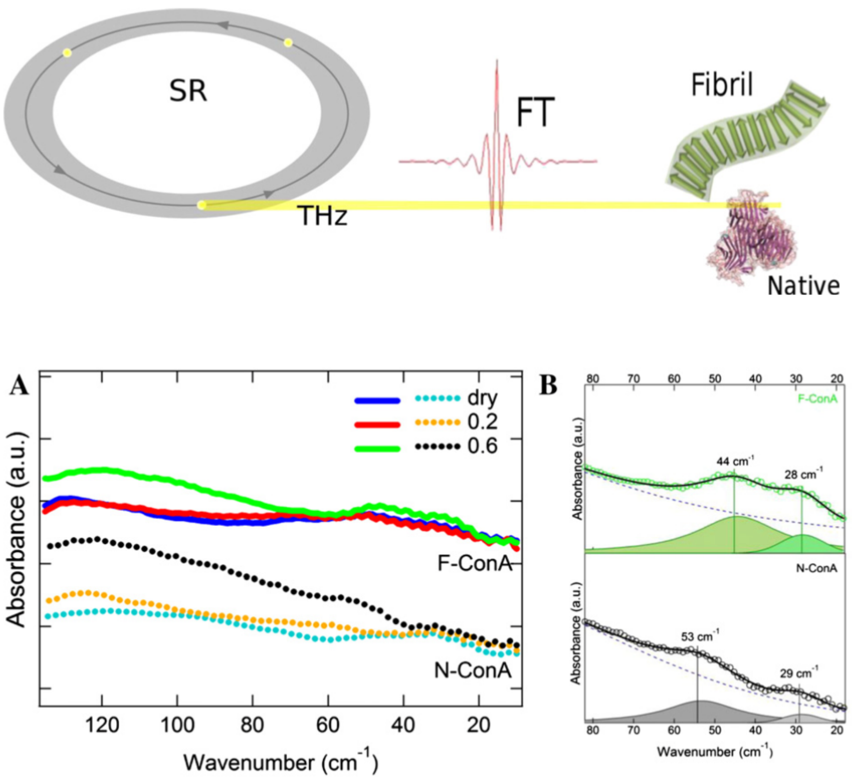


Sub-wavelength confinement (100 nm vs 50 µm)
Electric field enhancement
Increased detection

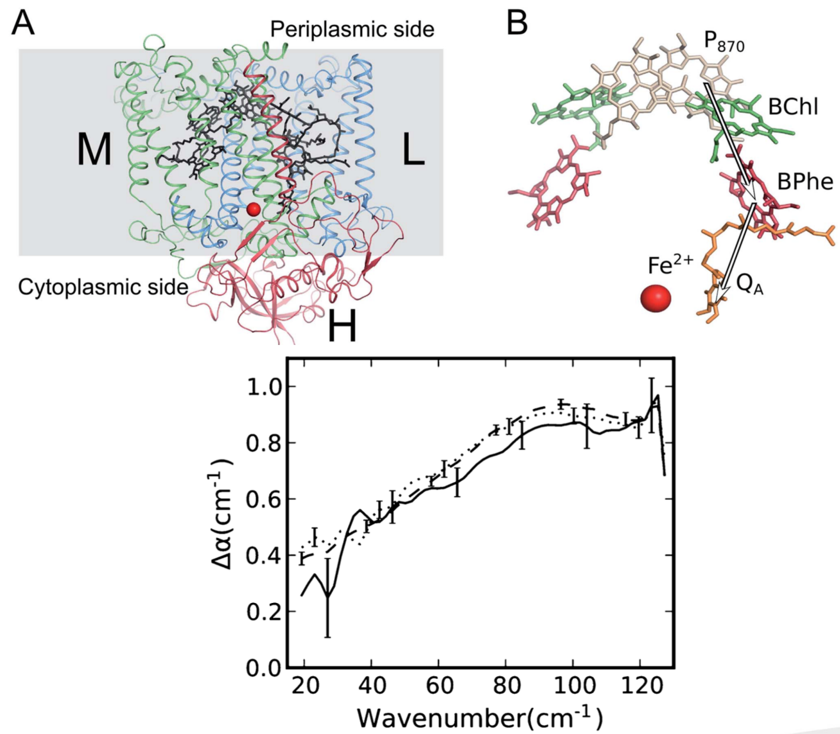
Cavity quantum electrodynamics:
Hybridization, Rabi splitting

Jin et al., Nature Communications **2018**

THz spectroscopy of proteins



F. Piccirilli et al., Biophysical Chemistry **2015**



I. Lundholm et al., RSC Adv. **2014**

THz studies with SR and FEL radiation

- The THz spectral range
- THz spectroscopy with Synchrotron Radiation
- THz non-linear studies

THz Free Electron Lasers

Low-gain FELs with optical cavity

- UCSB (USA)
- Budker Institute (Russia)
- CLIO (France)
- FELIX / FLARE (Netherlands)
- FELBE (Germany)

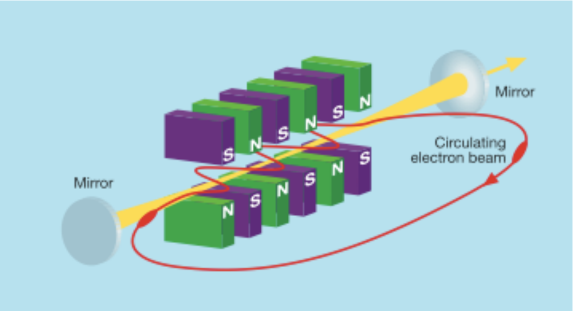
…

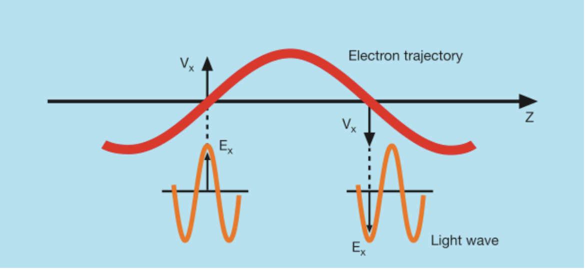
$$\lambda = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2}\right)$$

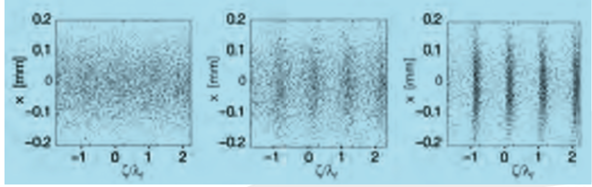
Upon one passage in the undulator, radiation grows by a few percent
$\rightarrow$ Several passages are needed before reaching saturation

λ=100 μm
K~1

E ~10 MeV	E ~ 1 GeV
γ ~ 20	γ ~ 2000
λ_U ~ 50 mm	λ_U ~ 500 m !!!

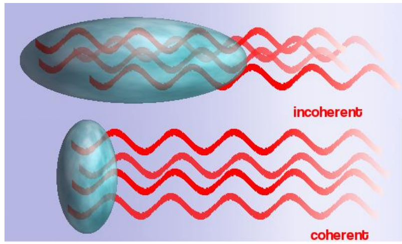






From DESY-FLASH brochure

Superradiant emission

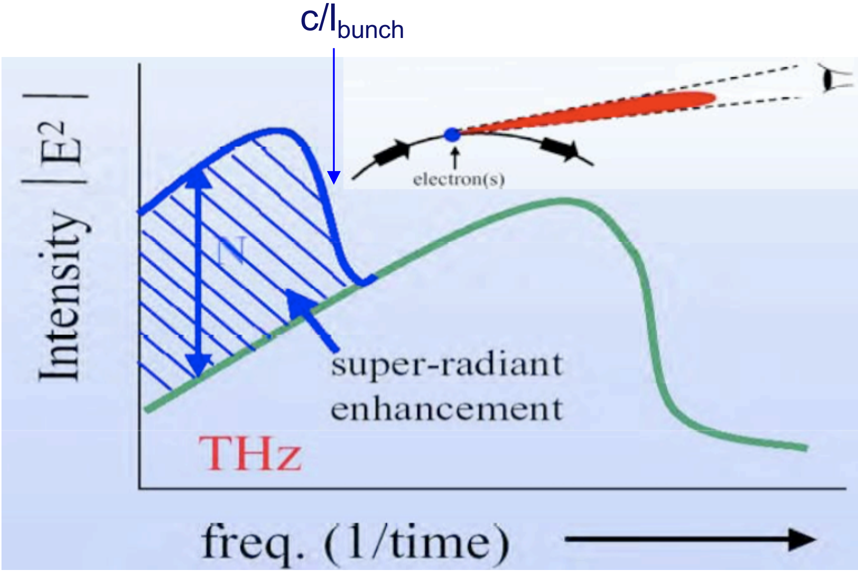


Coherent enhancement factor

$$N[1 + Nf(\omega)]$$

Form factor

$$f(\omega) = \int_{-\infty}^{+\infty} \rho(t)\exp(-i\omega t)dt$$



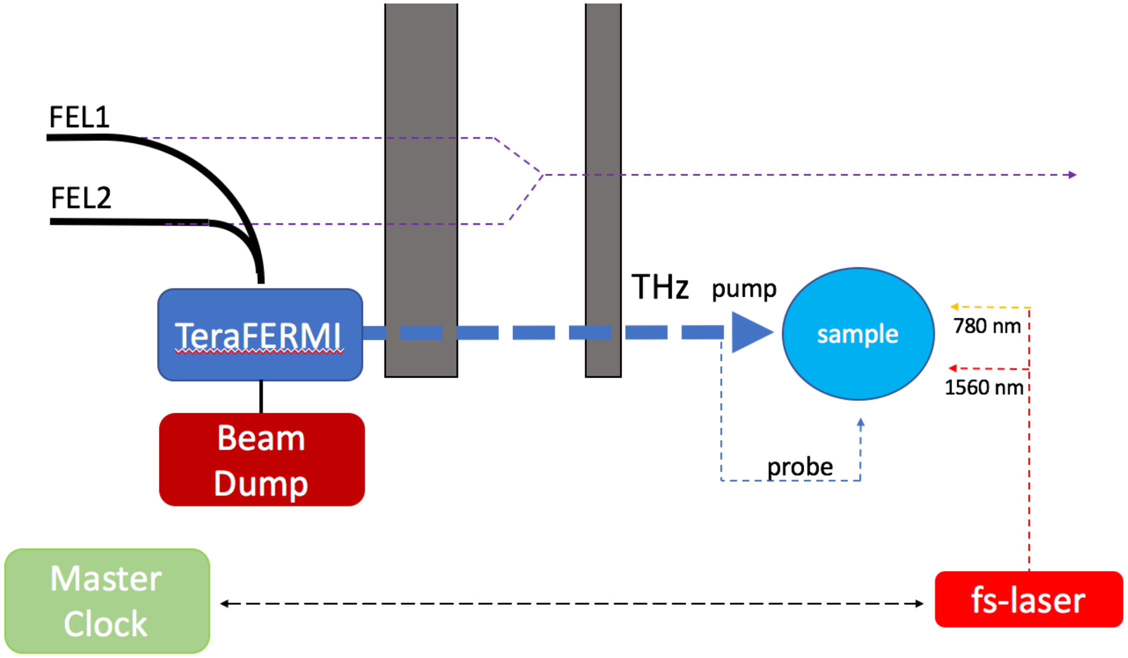
N ~ 6.24*10^7 @ 1pC
Storage-Rings in low-α
Bessy II, Soleil, Diamond, Anka, CLS, ...
Elettra (*bursting mode*)

N ~ 6.24*10^{10} @ 1nC
Single-pass accelerators
TeraFERMI, TELBE, FLASH

Phase Stable

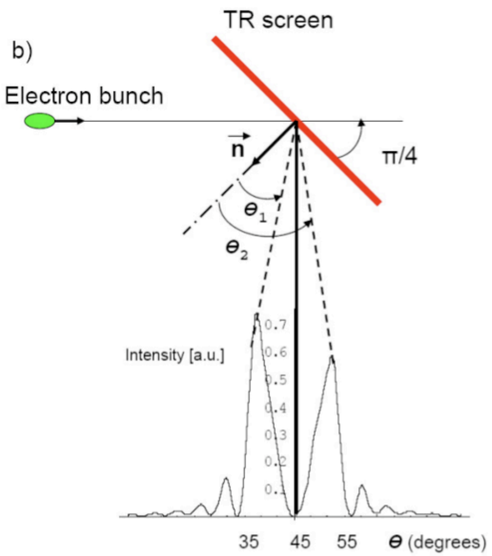
The TeraFERMI project

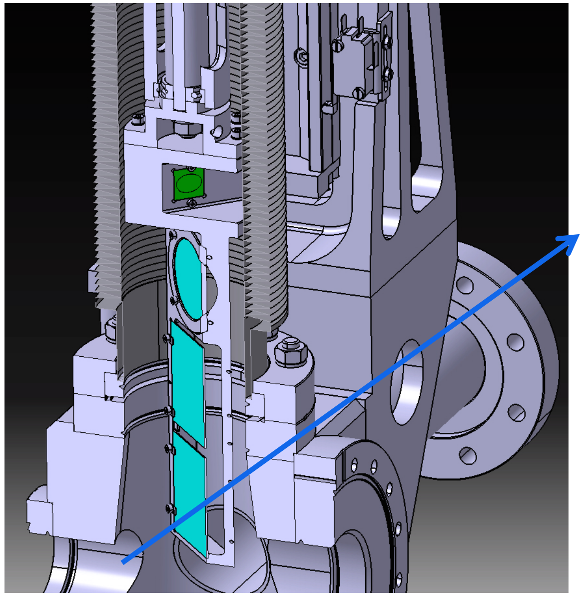
Exploiting the properties of the FERMI-FEL electron beam to produce
Short (sub-ps), Powerful (>MV/cm), Broadband (0.1-10 THz)
THz pulses to be used as a **Pump** beam for ultrafast nonlinear spectroscopies



Coherent Transition Radiation

Transition Radiation occurs when relativistic electrons cross the boundary between two media of different dielectric constant





The Ginzburg-Frank equation:

$$\frac{d^2U}{d\omega d\Omega} = \frac{e^2}{4\pi^3\varepsilon_0 c}\frac{\beta^2\sin^2\theta}{(1-\beta^2\cos^2\theta)^2}$$

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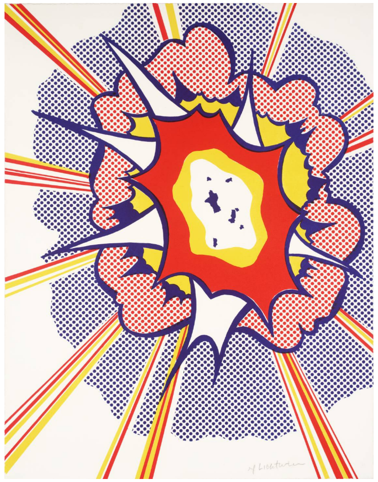
Why THz?

THz light couples to electronic, vibrational and magnetic excitations



Optical pump

THz pump

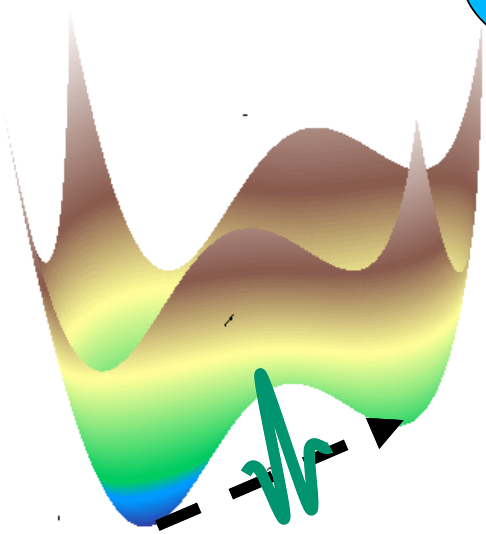
THz control of matter

Nonlinear Phononics

Superconductivity
Metal-insulator transitions
Ferroelectrics

Macromolecules

Protein folding
RNA/DNA



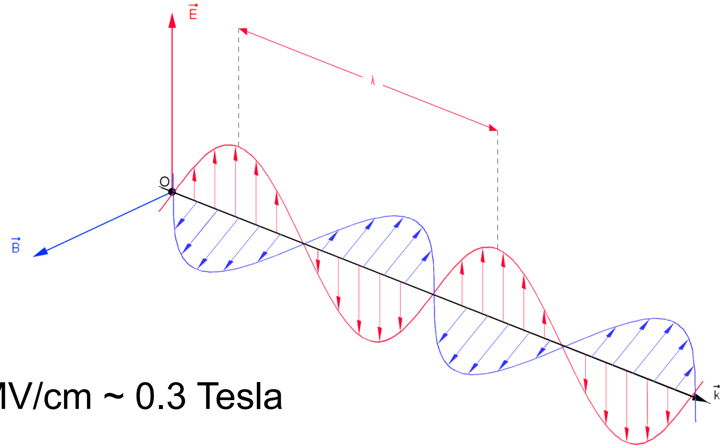
Molecular alignment

Polar liquids

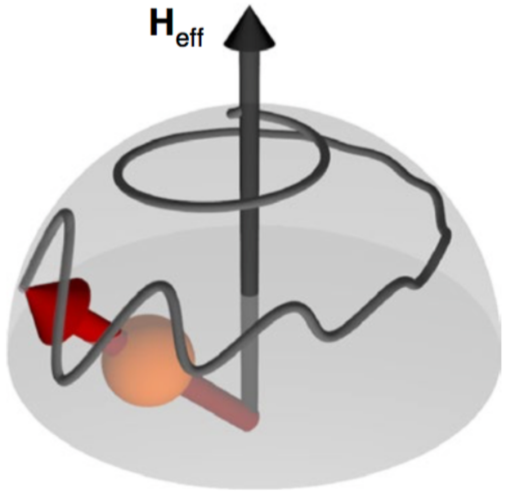
Reaction pathways

catalysis

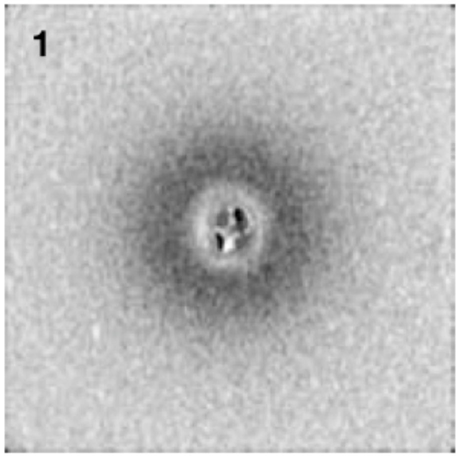
Magnetic excitations



1 MV/cm ~ 0.3 Tesla



Neeraj, 2021



Tudosa, 2004

Ultrafast magnetic switching

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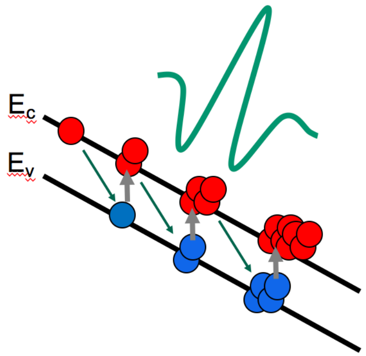
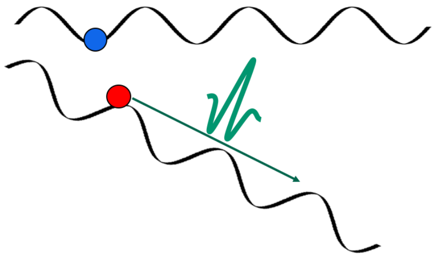
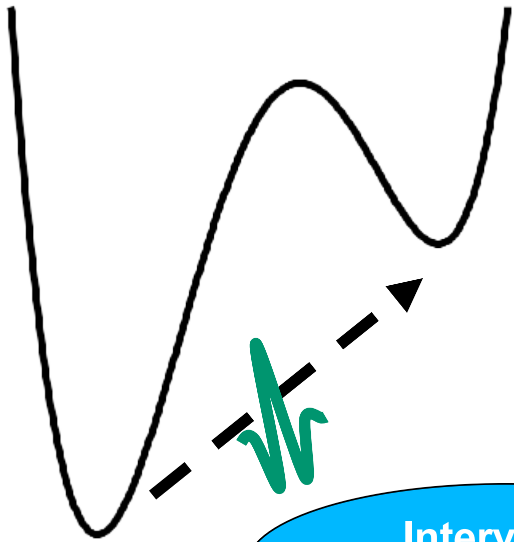
Electronic excitations

Impact Ionization



Zener tunneling





Intervalley scattering

Franz-Keldish

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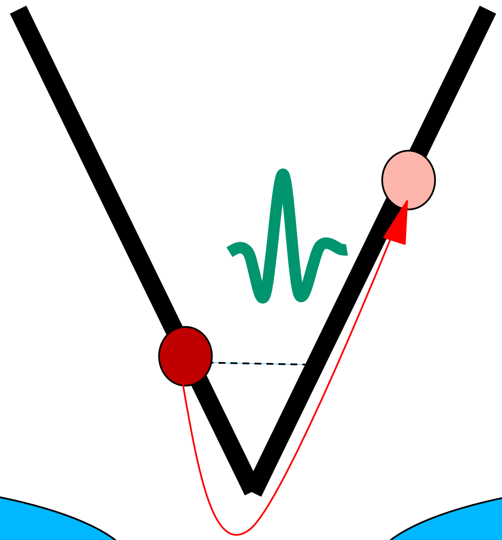
Dirac materials

Graphene

Topological Insulators



TMDs

Black phosphorus

Saturable Absorption

Harmonics Generation

Optically-active plasmonics

Nonlinear susceptibility

THz pump can resonantly excite electrons or lattice modes

linear *Pockels* *Kerr*

$$P_i = \varepsilon_0(\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \cdots)$$

THz pump-IR probe

THz pump can resonantly excite electrons or lattice modes

linear *Pockels* *Kerr*

$$P_i = \varepsilon_0(\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j {E_k}^2 + \cdots)$$

E_j= Probe (780 nm)

E_k= Pump (THz)

Pockels effect:

An external electric field induces linear variation of the refractive index on a material
Centro-symmetric crystals can not exhibit this effect (no preferred direction)

Kerr effect:

The change of the refractive index is proportional to the square of the applied electric field.

THz fluence-dependent spectroscopy

THz pump can resonantly excite electrons or lattice modes

linear *Pockels* *Kerr*

$$P_i = \varepsilon_0(\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j{}^2 + \chi_{ijkl}^{(3)} E_j{}^3 + \cdots)$$

E_j = THz field

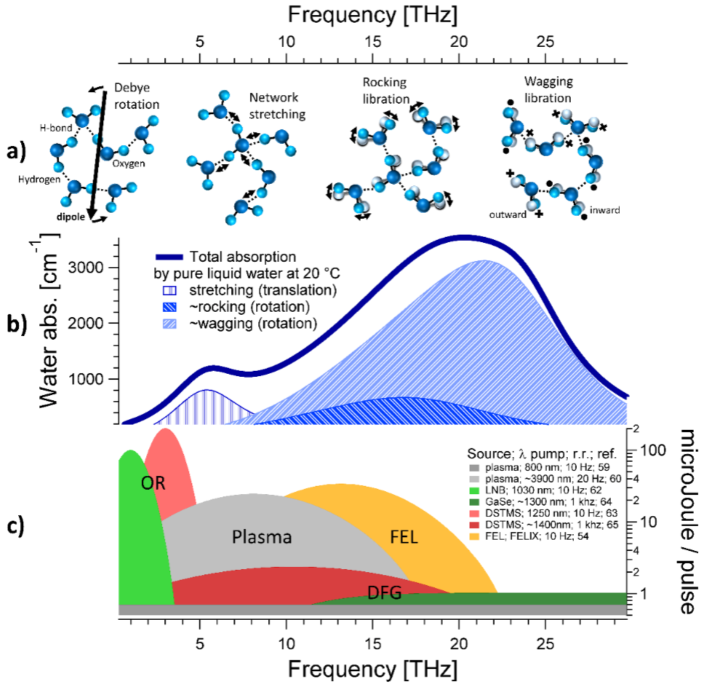
Pockels effect:

An external electric field induces linear variation of the refractive index on a material
Centro-symmetric crystals can not exhibit this effect (no preferred direction)

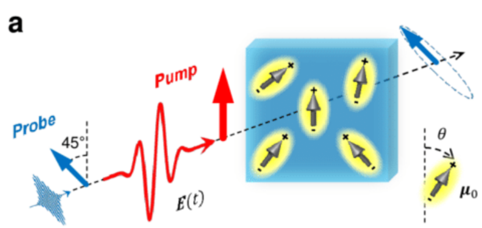
Kerr effect:

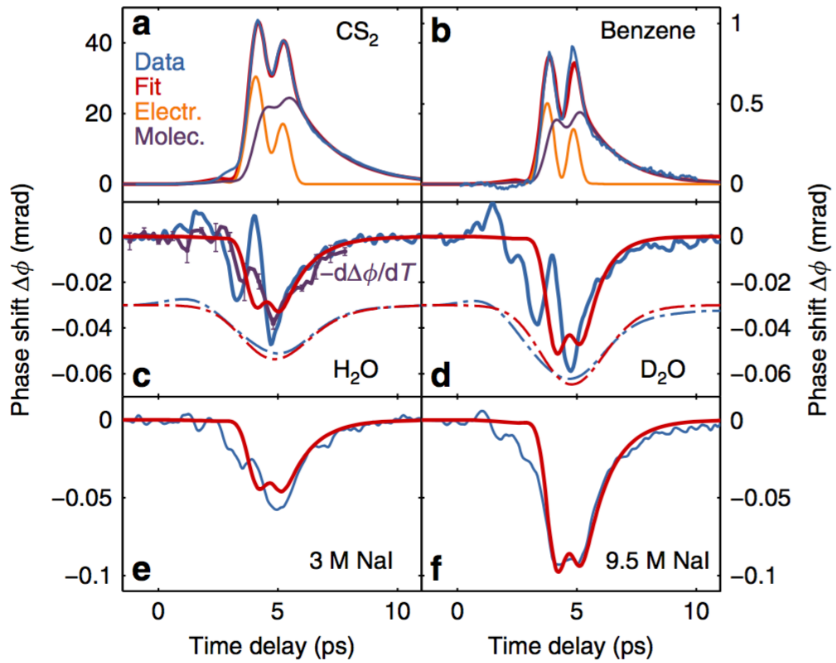
The change of the refractive index is proportional to the square of the applied electric field.

THz Kerr effect in water



F. Novelli et al., *Materials* **2020**





P. Zalden et al., Nat. Comm. **2018**

Single-cycle electromagnetic pulses in the THz regime orient the dipole moments of liquid water along their electric field. Given the resulting negative sign of $\Delta n = n_{//}-n_{\perp}<0$, the polarizability of water molecules in the liquid state is lower parallel to their dipole moment than perpendicular, i.e., $\alpha_{//}<\alpha_{\perp}$

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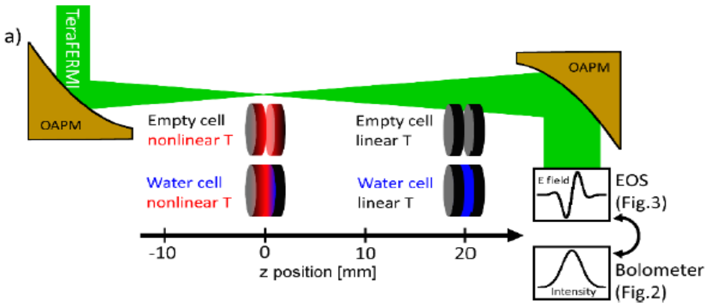
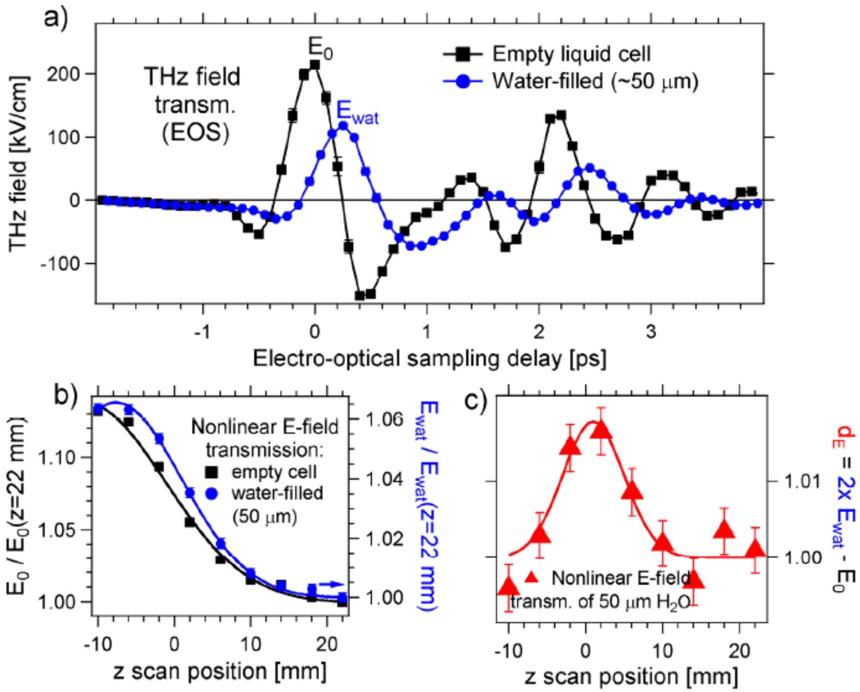
THz-fluence dependent measurements

Nonlinear THz transmission by liquid water



By open aperture z-scan transmission experiments on static liquid cells we detect the THz fields with electro-optical techniques.

We show that it is possible to quantify the **nonlinear response of liquid water at ~1 THz** even when large signals originate from the sample holder windows.



$$\alpha(P) = \alpha + \alpha^{NL} \times P,$$

$$\alpha^{NL} \approx (1 - d_I(0)) \frac{\alpha}{P \times (1 - e^{-\alpha L})},$$

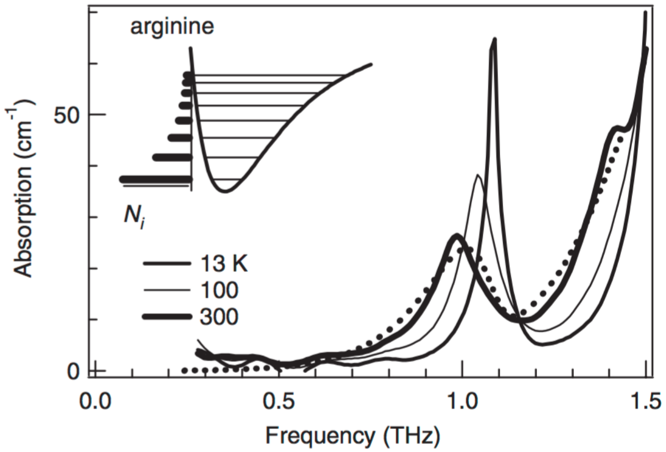
$$n(P) = n + n^{NL} \times P,$$

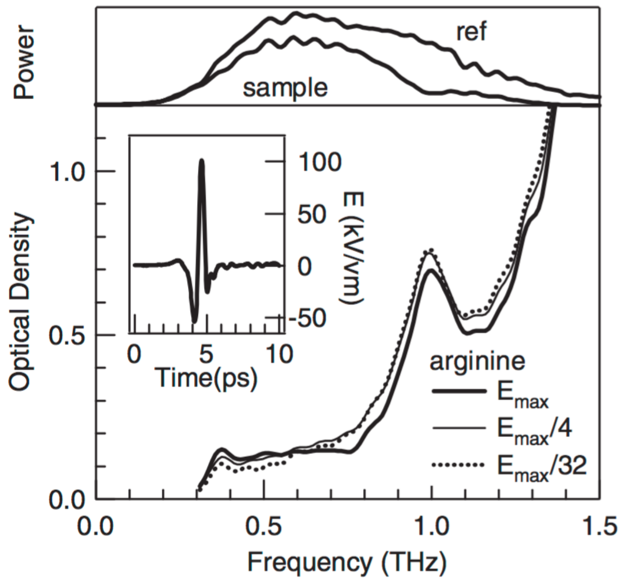
$$n^{NL} = \Delta T \frac{\alpha}{P \times (1 - e^{-\alpha L})} \frac{\lambda}{1.8 \times (1 - S)^{0.25}},$$

F. Novelli et al., Appl. Sci. **2020**

THz-fluence dependent measurements

Ladder climbing of the anharmomic intermolecular potential in aminoacids





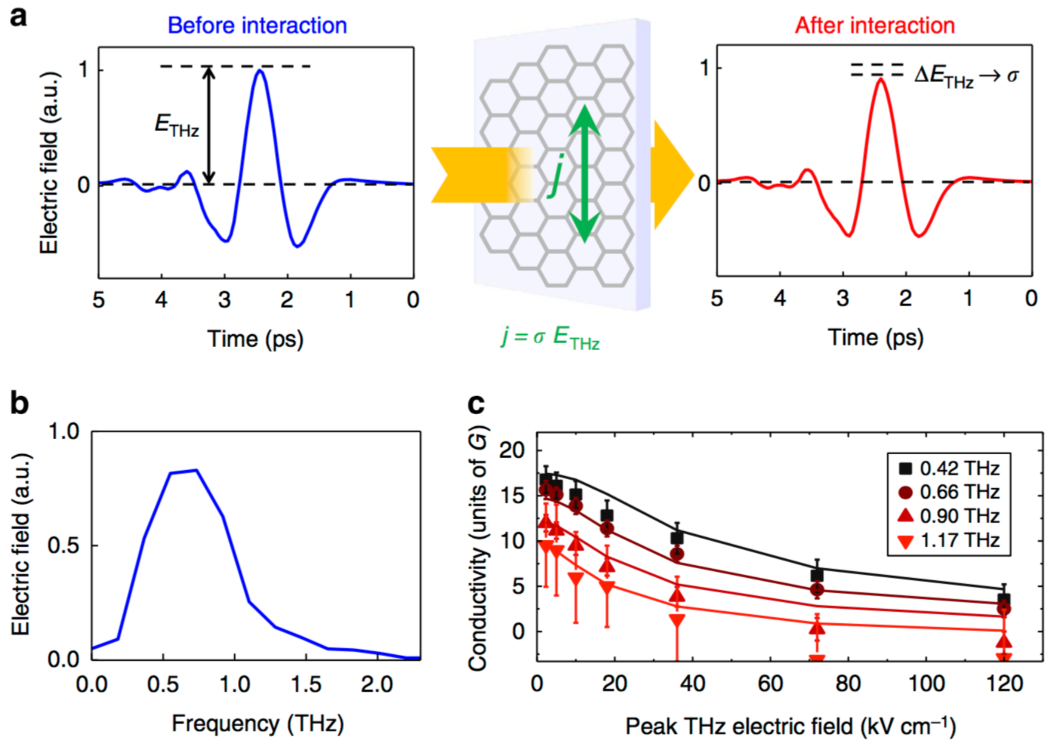
$$\frac{d\rho_{i,i}(t)}{dt} = -\gamma_1(\rho_{i,i} - \rho_{i+1,i+1}) - i\frac{E(t)}{\hbar}(\mu_{i-1,i}\rho_{i,i-1} - \mu^*_{i-1,i}\rho^*_{i,i-1}) + i\frac{E(t)}{\hbar}(\mu_{i,i+1}\rho_{i+1,i} - \mu^*_{i,i+1}\rho^*_{i+1,i}), \quad (1)$$

$$\frac{d\rho_{i+1,i}(t)}{dt} = \frac{d\rho^*_{i,i+1}(t)}{dt} = -\left(i2\pi\nu_{i,i+1} + i(\mu_{i+1,i+1} - \mu_{i,i})\frac{E(t)}{\hbar} + \gamma_2\right) \times \rho_{i+1,i} - i\frac{E(t)}{\hbar}\mu_{i+1,i}(\rho_{i+1,i+1} - \rho_{i,i}), \quad (2)$$

“The mode population around the levels with <n>=2.2 rises to a higher level with <n>=22.2, indicating ladder climbing of 20 steps. This is far from thermal equilibrium.”

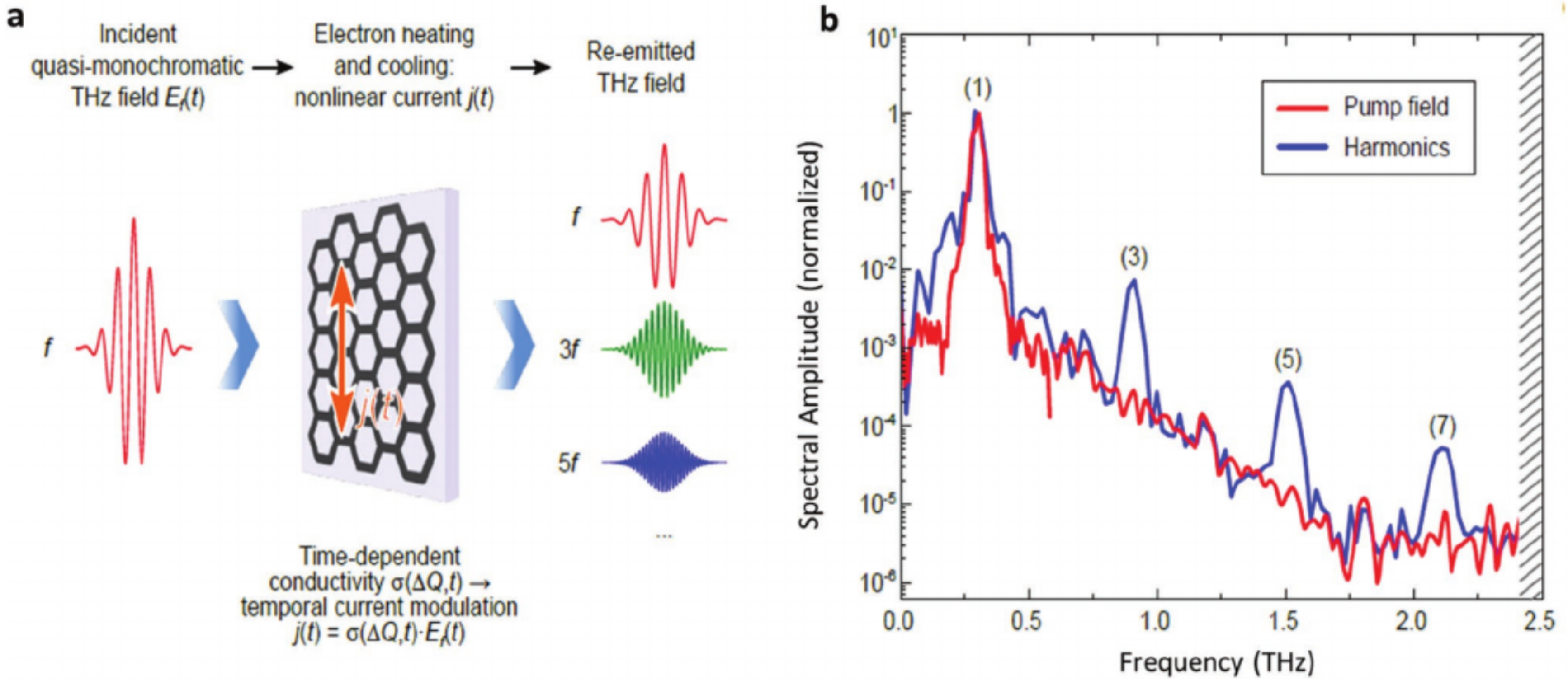
M. Jewariya et al., PRL **2010**

THz field induced transparency in graphene



Mics et al., Nature Communication (2015)

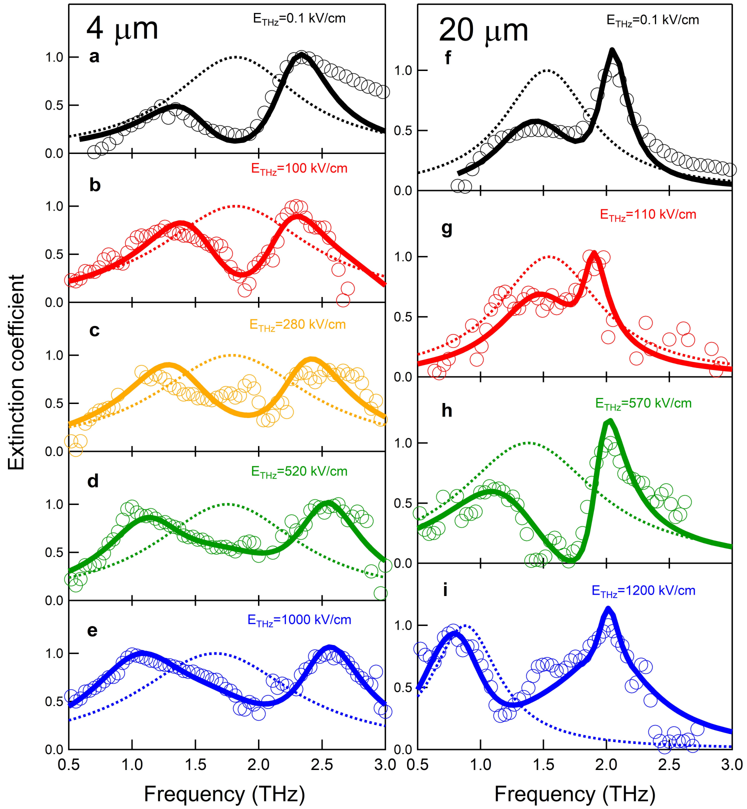
THz Harmonics generation in graphene

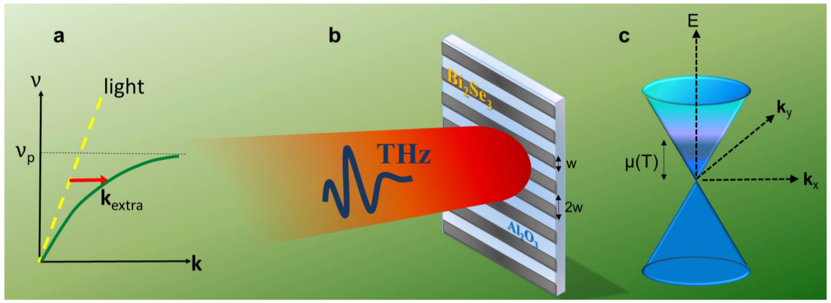


Hafez et al., Nature (2018)

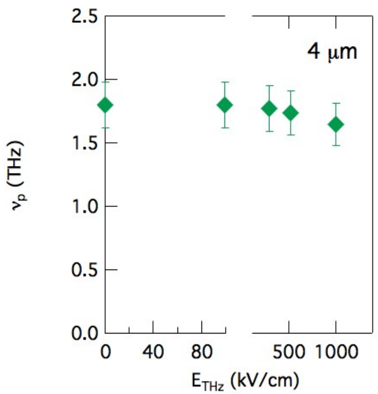
THz-fluence dependent measurements

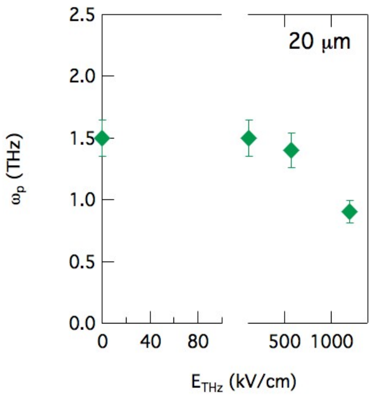
Tuning plasmons in Bi2Se3





$$\nu_p = \sqrt{\frac{\pi}{w}}\left(\frac{e^2}{4\pi\epsilon_0\bar{\epsilon}\hbar}v_F\sqrt{2\pi n g_s g_v}\right)^{1/2},$$

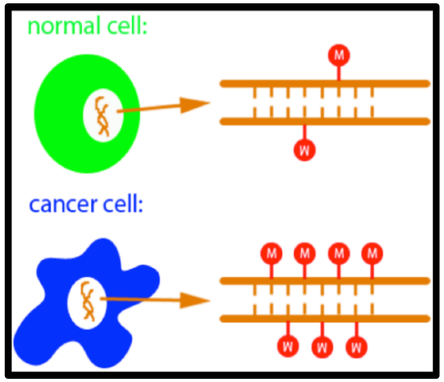




P. Di Pietro et al., Phys. Rev. Lett. (2020)

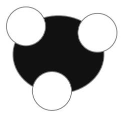
THz irradiation

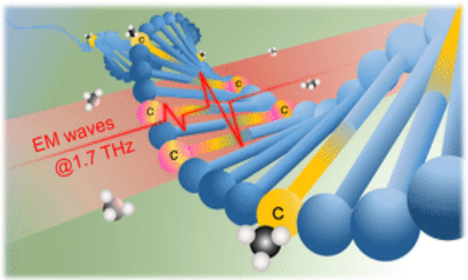
THz induced demethylation



Cancer cells can show enhanced
DNA Methylation

Methyl groups

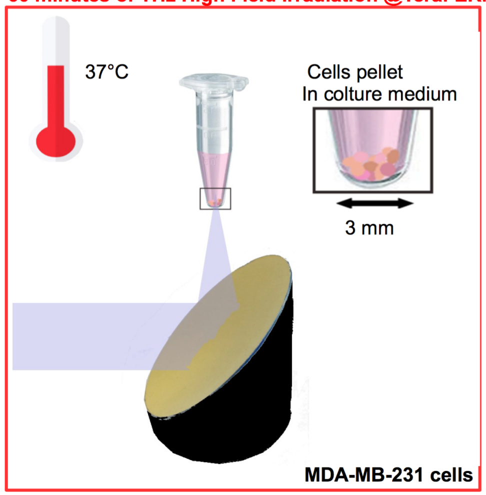




Intense resonant THz radiation induces DNA demethylation

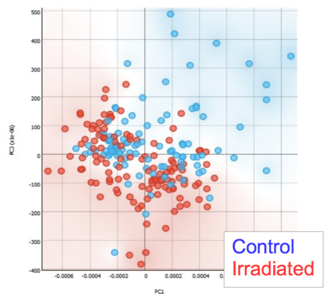
Treatment

60 minutes of THz High Field Irradiation @TeraFERMI



Probe

SR-IR @SISSI on single cells



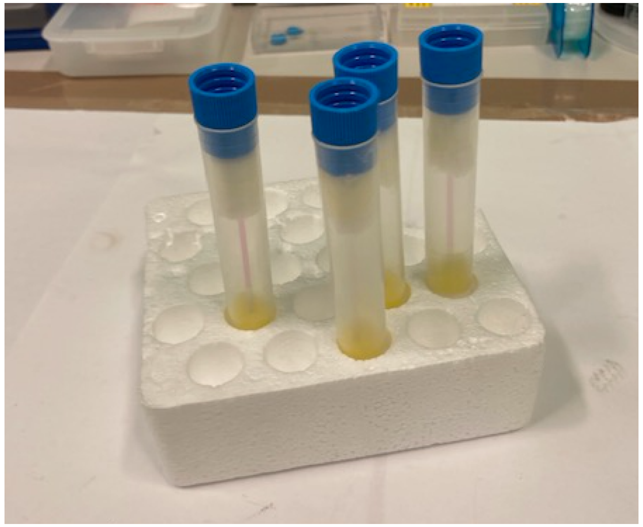
F. Piccirilli, M. Pachetti et al. (2021)

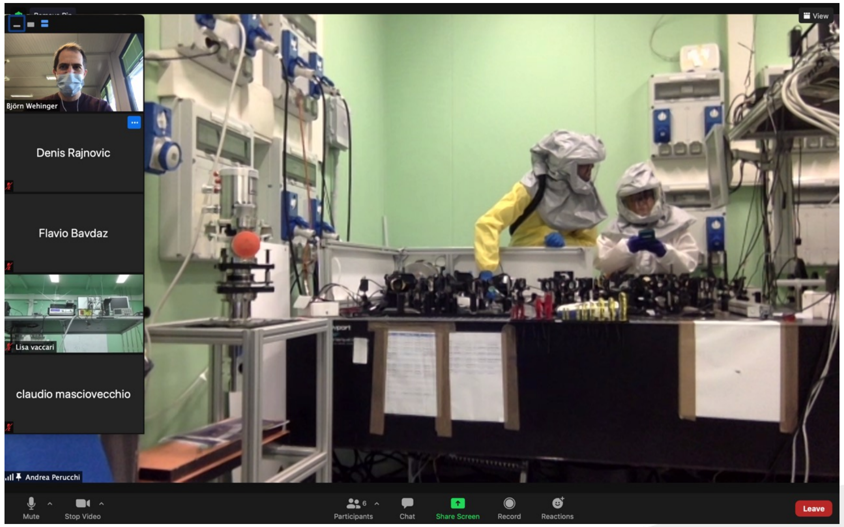
THz irradiation

Covid inactivation through THz irradiation
Elettra - Università di Venezia Cà Foscari - ICGEB

RNA modes resonate at THz frequencies → Inducing RNA damage while keeping the capsid intact → vaccines

Most plastics are transparent to THz radiation.
Unbreakable sample holders can be used.
Virus is sealed within 2 plastic containers.





Experiments are still ongoing...

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Conclusions

THz gap is nowadays filled and THz spectroscopy can be performed with several different conventional equipments

Storage Rings provide bright sources of THz radiation for steady state studies

Small samples, Microscopy, Extreme conditions, etc.

THz control of matter requires short/powerful pulses

(sub-ps duration / >MW peak power / ~MV/cm electric fields)

FEL-based THz beamlines can produce THz pulses for non-linear studies in the whole THz range

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