Principles and applications of ultrafast terahertz spectroscopy

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www.turchinovich-lab.de

Current topics of AG Turchinovich

THz cond-matt physics: charge, lattice and spin dynamics in…

Graphene and Co

Nature Commun (2015)
Nature Nanotech (2018)
Science Adv. (2018)
Nature (2018)
*Science Adv. (2021)**

Spintronics

Nature Phys (2015)
Nature Photon (2016)
Science (2018)
Nature Commun (2020)

Semiconductors

PRB (2012)
APL (2013), PRB (2015)
OE (2016), Nano Lett (2016)
APL (2017)

Ultrafast NLO and lasers

JPhysD (2016)
Nature Photon (2016)
Photon. Res. (2017)

Organic / PV / Phys Chem

JPCL (2014,2015)
Nature Commun (2017)
Nature Commun (2018)

Open PhD position

EU FET Project on **THz nonlinear optoelectronics**
PhD position starting from September 2021

Prerequisites: accomplished Master‘s project within

- ultrafast / THz optics
  and/or
- experimental condensed matter physics / optoelectronics

If interested, please contact Prof. Dmitry Turchinovich by email dmtu@physik.uni-bielefeld.de with the Subject line: *PhD THz NLO*

Terahertz range ca 0.1 – 20 THz

Frequency $f = \omega/2\pi$ = 1 THz = 10^{12} Hz

Oscillation period $T = 1/f$ = 1 ps

Wavelength $cT = \lambda$ = 300 μm

Wavenumbers $1/\lambda$ = 33 cm^{-1}

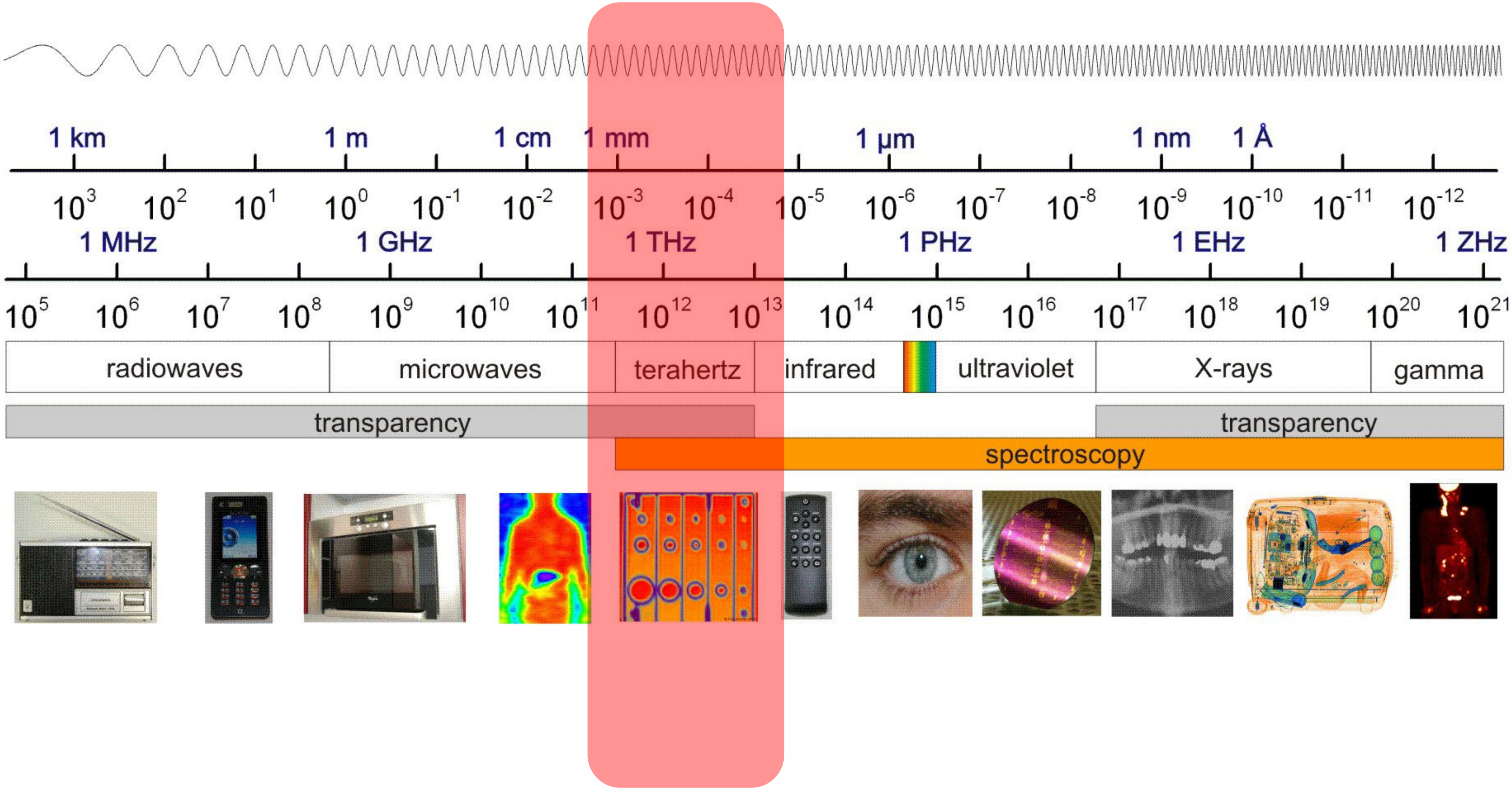
Photon energy $\hbar\omega$ = 4.1 meV

Temperature equivalent T = 48 K

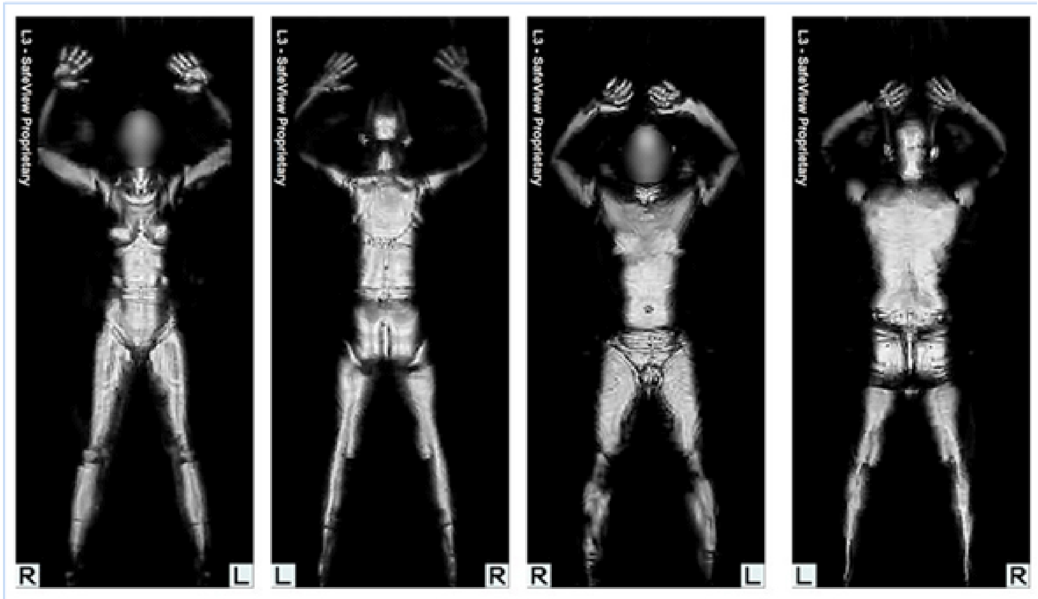
Compare to NIR light: 800 nm = 1/ 2.66 fs = 380 THz

Where is THz in the spectrum?

THz is ***light*** *: electromagnetic waves / photons*

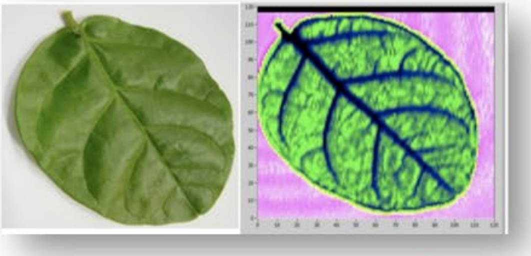


Probably the most famous daily-life application of THz

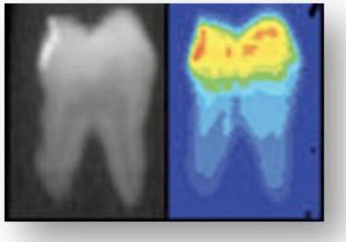


thznetwork.org

(Other) applications of THz radiation



Bio-imaging

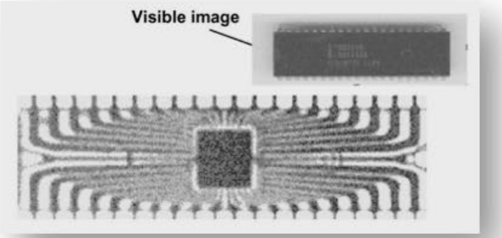


Medical Diagnoses

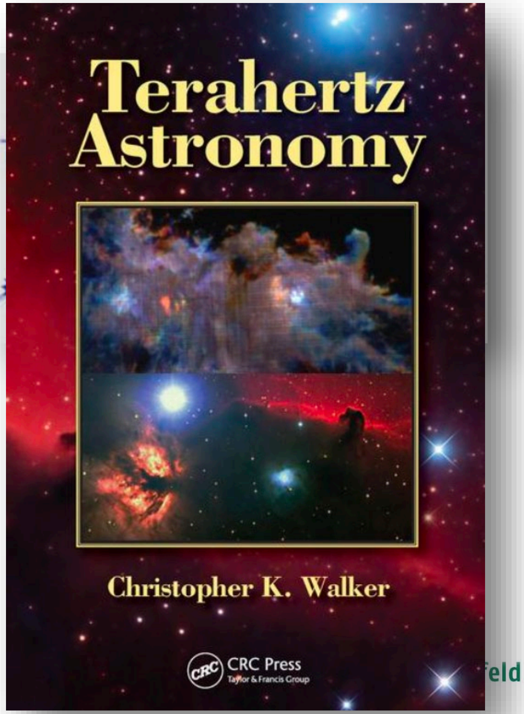
Communication

THz Applications

Security Camera

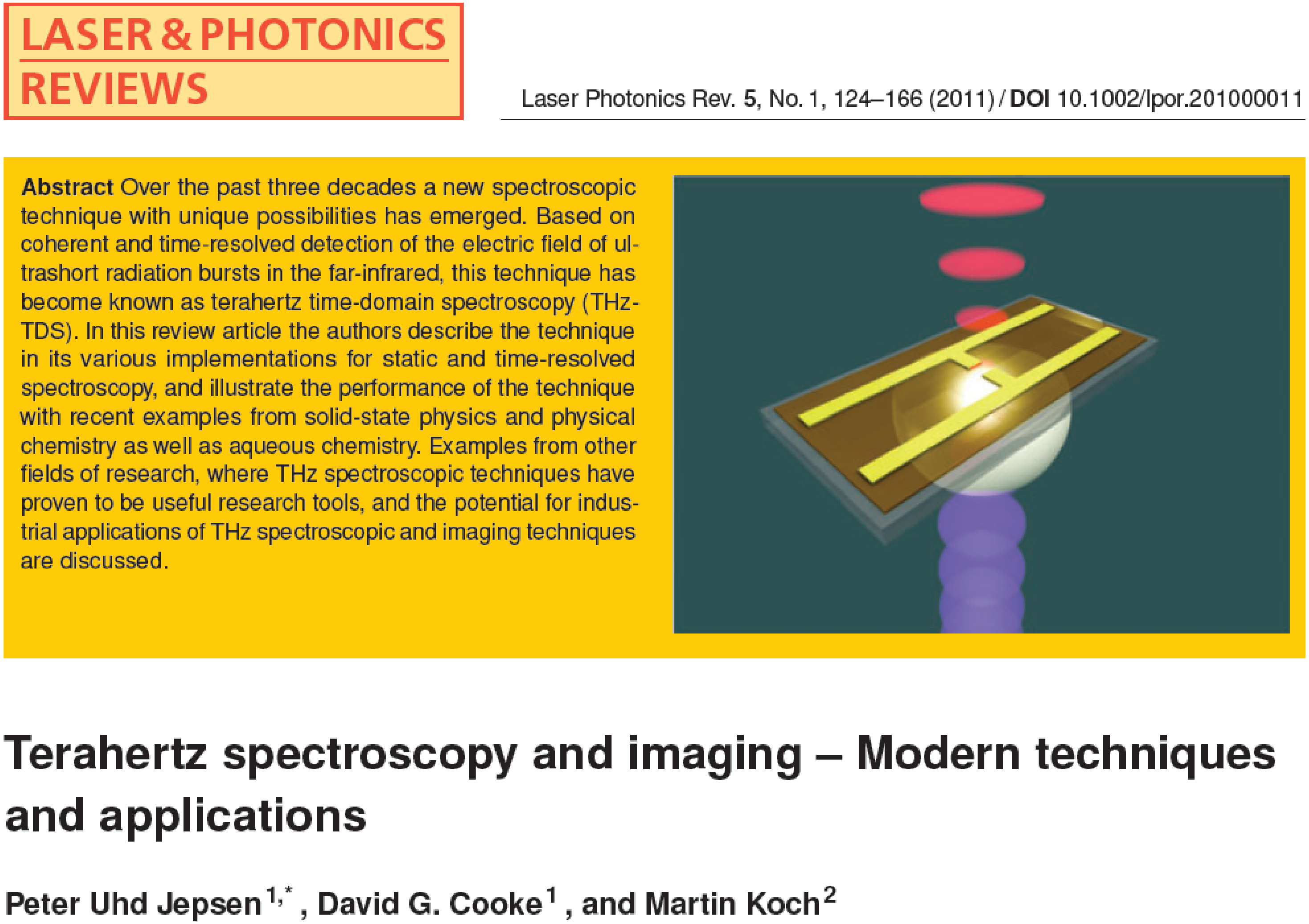


Industrial Inspections



https://www.imp.tu-darmstadt.de/forschung_imp/ont_imp/ntt.de.jsp

Good reviews



LASER & PHOTONICS REVIEWS

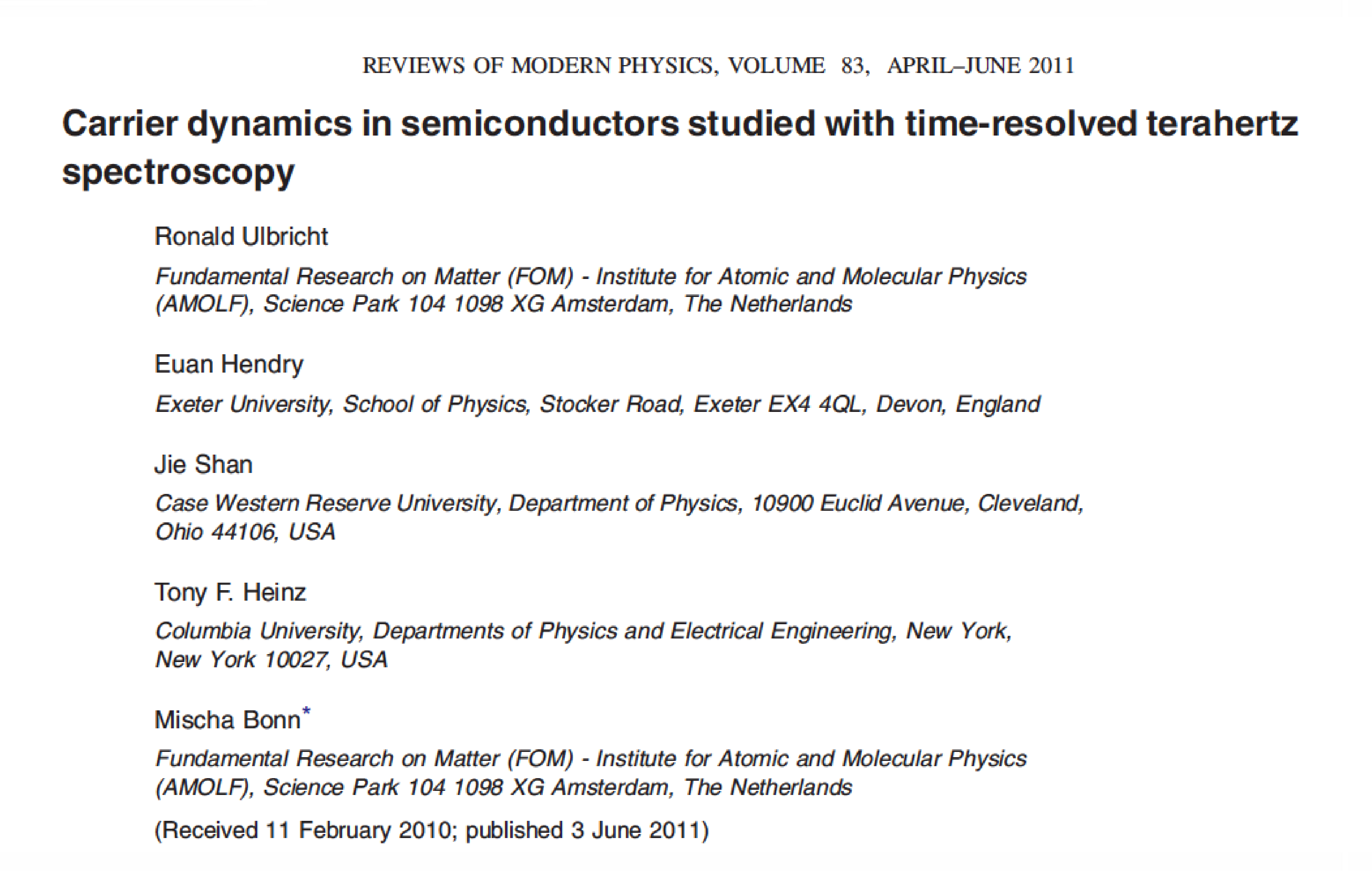
Laser Photonics Rev. **5**, No. 1, 124–166 (2011) / **DOI** 10.1002/lpor.201000011

Abstract Over the past three decades a new spectroscopic technique with unique possibilities has emerged. Based on coherent and time-resolved detection of the electric field of ultrashort radiation bursts in the far-infrared, this technique has become known as terahertz time-domain spectroscopy (THz-TDS). In this review article the authors describe the technique in its various implementations for static and time-resolved spectroscopy, and illustrate the performance of the technique with recent examples from solid-state physics and physical chemistry as well as aqueous chemistry. Examples from other fields of research, where THz spectroscopic techniques have proven to be useful research tools, and the potential for industrial applications of THz spectroscopic and imaging techniques are discussed.

Terahertz spectroscopy and imaging – Modern techniques and applications

Peter Uhd Jepsen[1,*], David G. Cooke[1], and Martin Koch[2]

Good reviews



REVIEWS OF MODERN PHYSICS, VOLUME 83, APRIL–JUNE 2011

Carrier dynamics in semiconductors studied with time-resolved terahertz spectroscopy

Ronald Ulbricht

Fundamental Research on Matter (FOM) - Institute for Atomic and Molecular Physics (AMOLF), Science Park 104 1098 XG Amsterdam, The Netherlands

Euan Hendry

Exeter University, School of Physics, Stocker Road, Exeter EX4 4QL, Devon, England

Jie Shan

Case Western Reserve University, Department of Physics, 10900 Euclid Avenue, Cleveland, Ohio 44106, USA

Tony F. Heinz

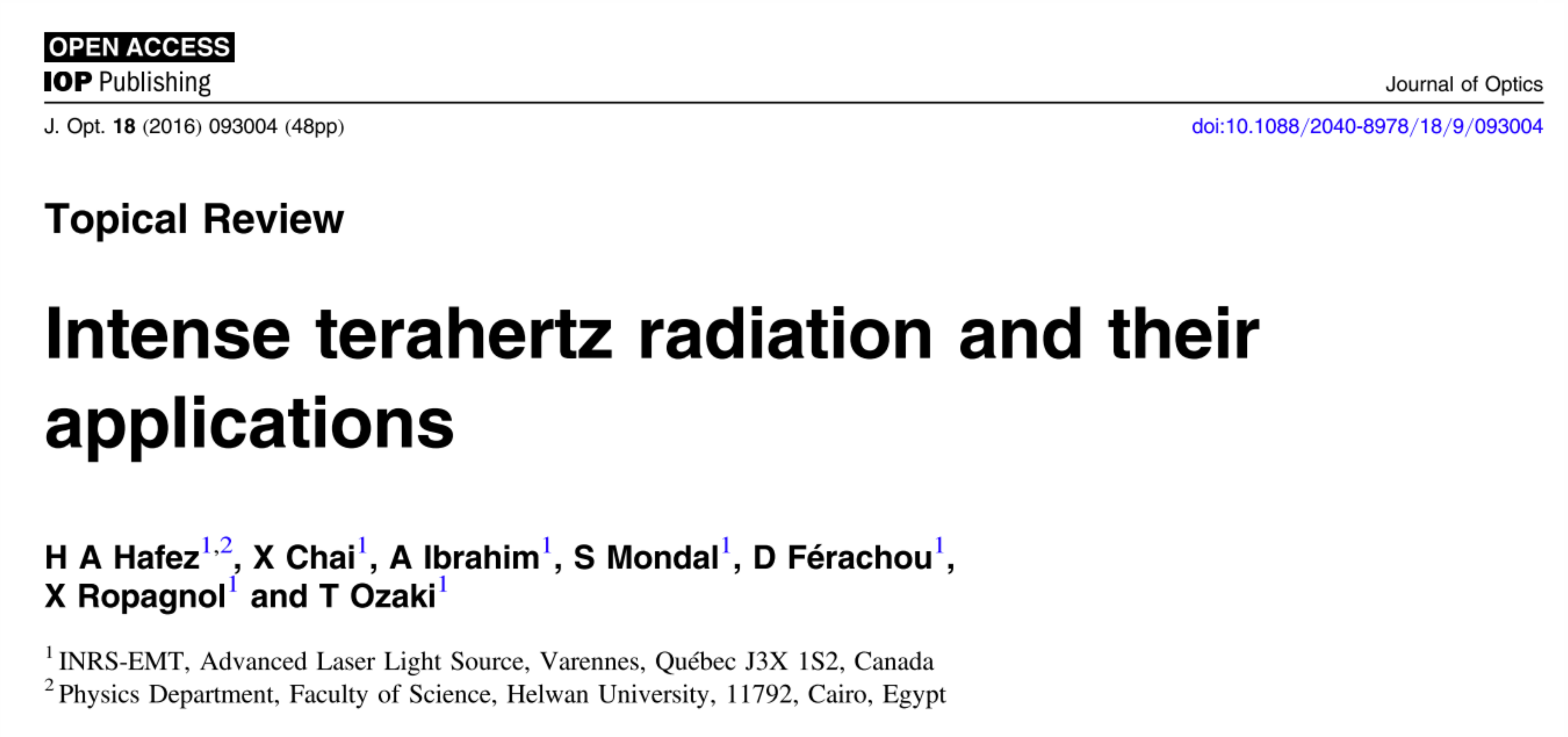
Columbia University, Departments of Physics and Electrical Engineering, New York, New York 10027, USA

Mischa Bonn*

Fundamental Research on Matter (FOM) - Institute for Atomic and Molecular Physics (AMOLF), Science Park 104 1098 XG Amsterdam, The Netherlands

(Received 11 February 2010; published 3 June 2011)

Good reviews



OPEN ACCESS
IOP Publishing

Journal of Optics

J. Opt. **18** (2016) 093004 (48pp)

doi:10.1088/2040-8978/18/9/093004

Topical Review

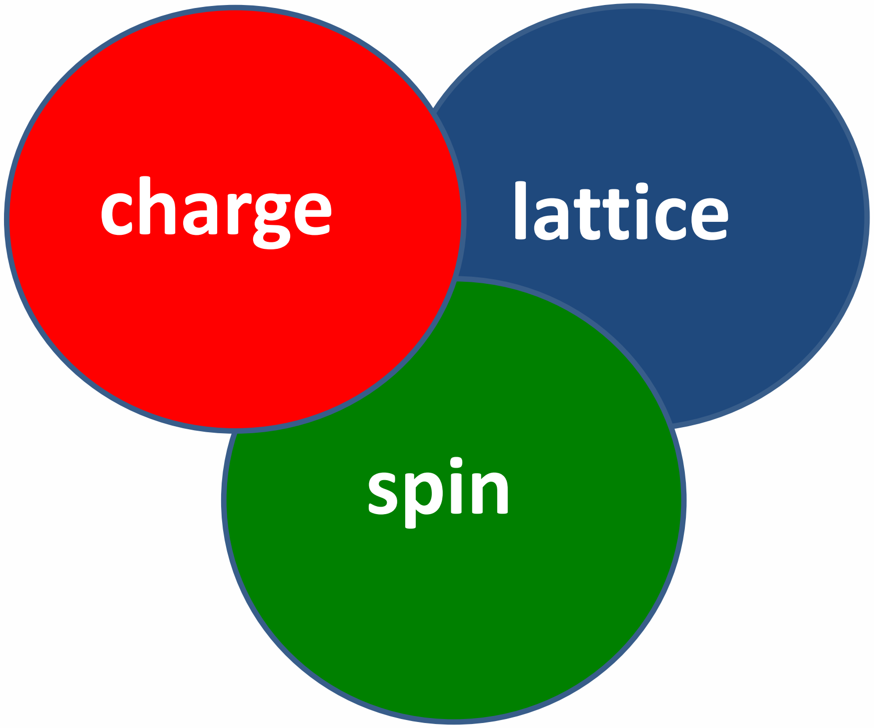
Intense terahertz radiation and their applications

H A Hafez[1,2], **X Chai**[1], **A Ibrahim**[1], **S Mondal**[1], **D Férachou**[1], **X Ropagnol**[1] **and T Ozaki**[1]

[1] INRS-EMT, Advanced Laser Light Source, Varennes, Québec J3X 1S2, Canada
[2] Physics Department, Faculty of Science, Helwan University, 11792, Cairo, Egypt

THz radiation and cond-matt physics

Typical timescales for elementary processes:
10s – 100s of femtoseconds to a **few picoseconds**



Relevant timescales for elementary excitations in condensed matter

- **Lattice** vibration and **spin** precession periods, **electron** momentum scattering time, …

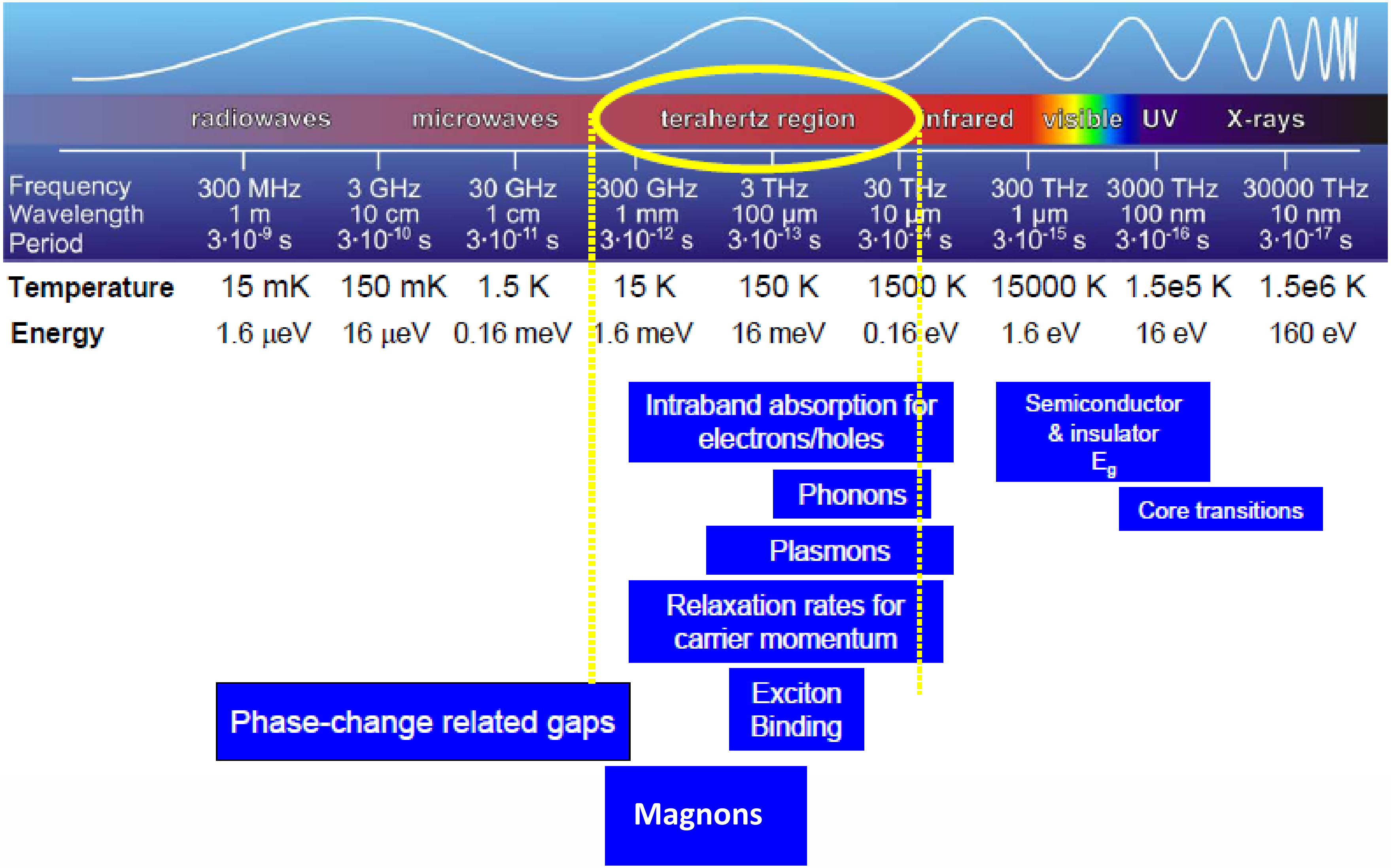
have **characteristic time** τ of

10s-100s of **femtoseconds** to a few **picoseconds**

In the THz frequency range $\omega\tau \sim 1$

➔ **direct observation of dynamics in materials**

THz phenomena in solids



Frequency	300 MHz	3 GHz	30 GHz	300 GHz	3 THz	30 THz	300 THz	3000 THz	30000 THz
Wavelength	1 m	10 cm	1 cm	1 mm	100 μm	10 μm	1 μm	100 nm	10 nm
Period	$3 \cdot 10^{-9}$ s	$3 \cdot 10^{-10}$ s	$3 \cdot 10^{-11}$ s	$3 \cdot 10^{-12}$ s	$3 \cdot 10^{-13}$ s	$3 \cdot 10^{-14}$ s	$3 \cdot 10^{-15}$ s	$3 \cdot 10^{-16}$ s	$3 \cdot 10^{-17}$ s
Temperature	15 mK	150 mK	1.5 K	15 K	150 K	1500 K	15000 K	1.5e5 K	1.5e6 K
Energy	1.6 μeV	16 μeV	0.16 meV	1.6 meV	16 meV	0.16 eV	1.6 eV	16 eV	160 eV

Intraband absorption for electrons/holes

Phonons

Plasmons

Relaxation rates for carrier momentum

Exciton Binding

Phase-change related gaps

Magnons

Semiconductor & insulator E_g

Core transitions

Ultrafast THz spectroscopy

Ultrafast, complex-valued optical spectroscopy with **single-cycle pulses** of THz light.

In THz spectroscopy, **electric field of light-waves** is **measured directly** in the time domain.

→ THz time-domain spectroscopy (THz-TDS)

THz physics is multi-physics

Ingredients of a THz experiment:

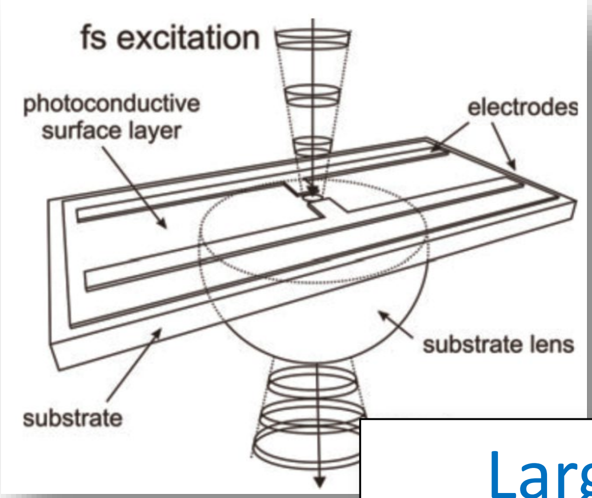
- Electrodynamics
- Optics / Nonlinear optics / Ultrafast optics
- Laser physics
- Solid state physics
- (Strong-field atom optics / Plasma physics)
- (Spintronics)
- ....

↓↓↓↓

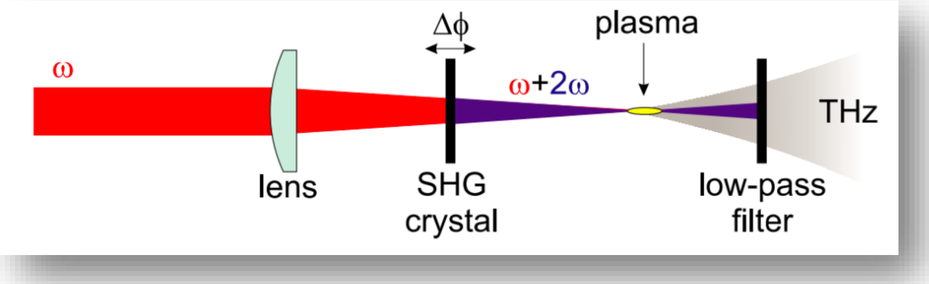
Photonics and Materials science

Methods of THz generation and detection

Jepsen et al, LPR 2011

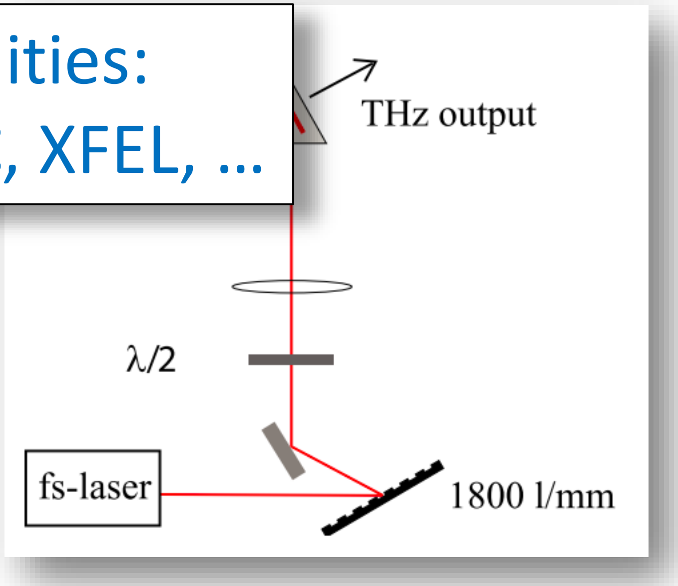


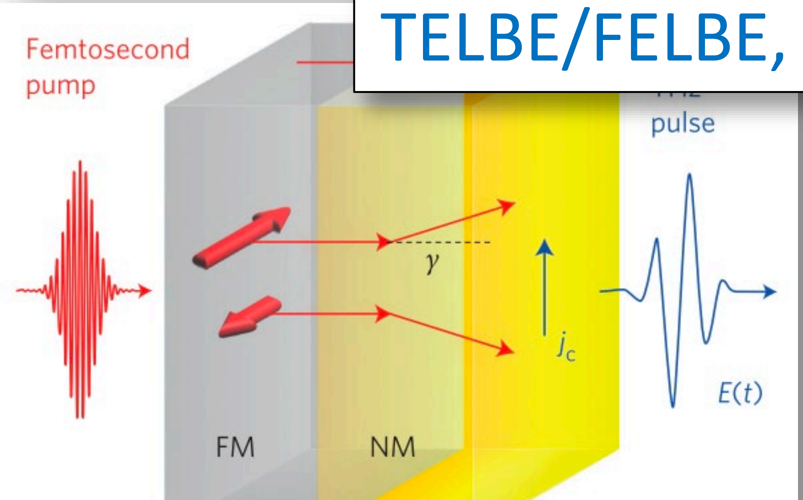
Hoffmann and Fülop, JPhysD 2011



Large-scale facilities:
TELBE/FELBE, SLAC, XFEL, …

Hoffmann and Fülop, JPhysD 2011

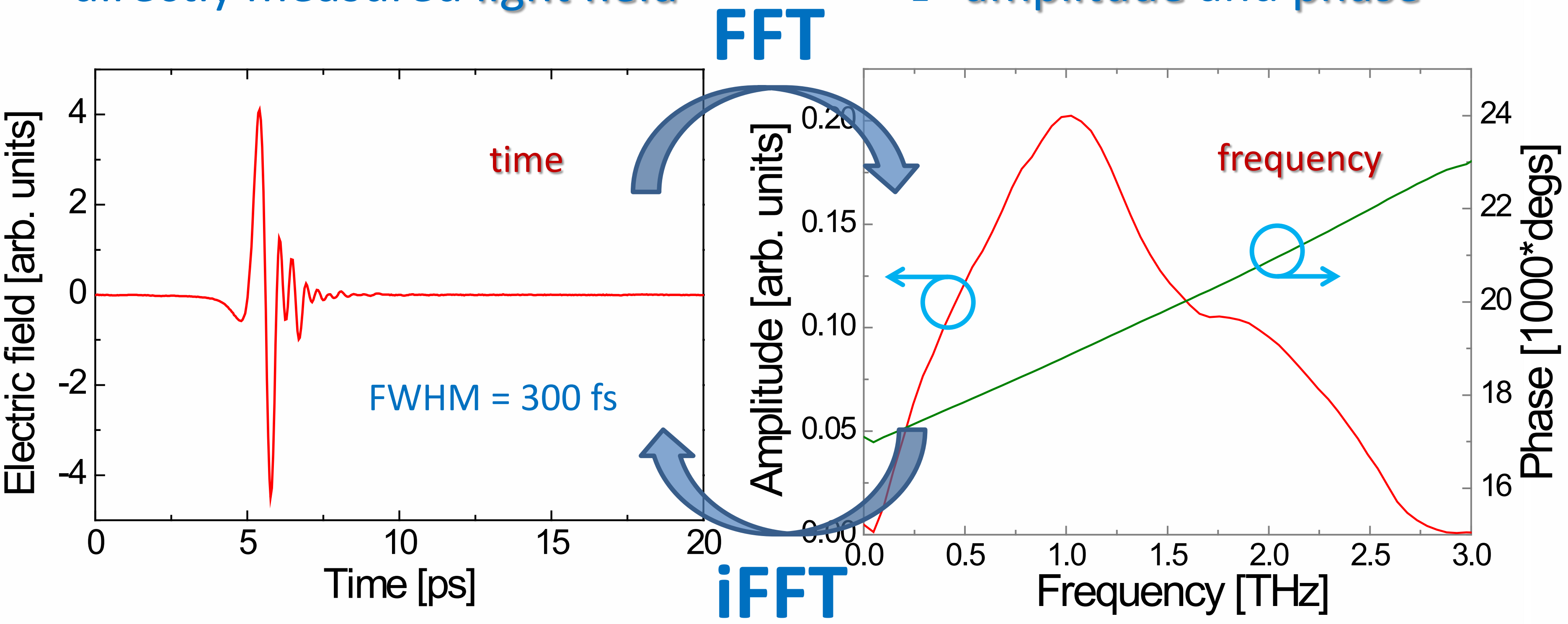




Seifert et al, Nature Photon 2016

THz pulse: ideal tool for ultrafast spectroscopy

directly measured light field → amplitude and phase

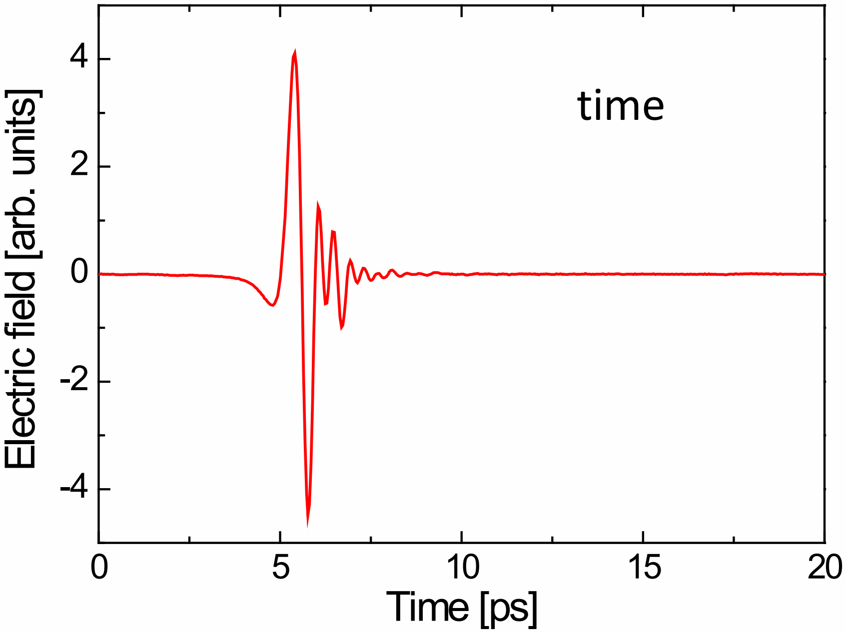


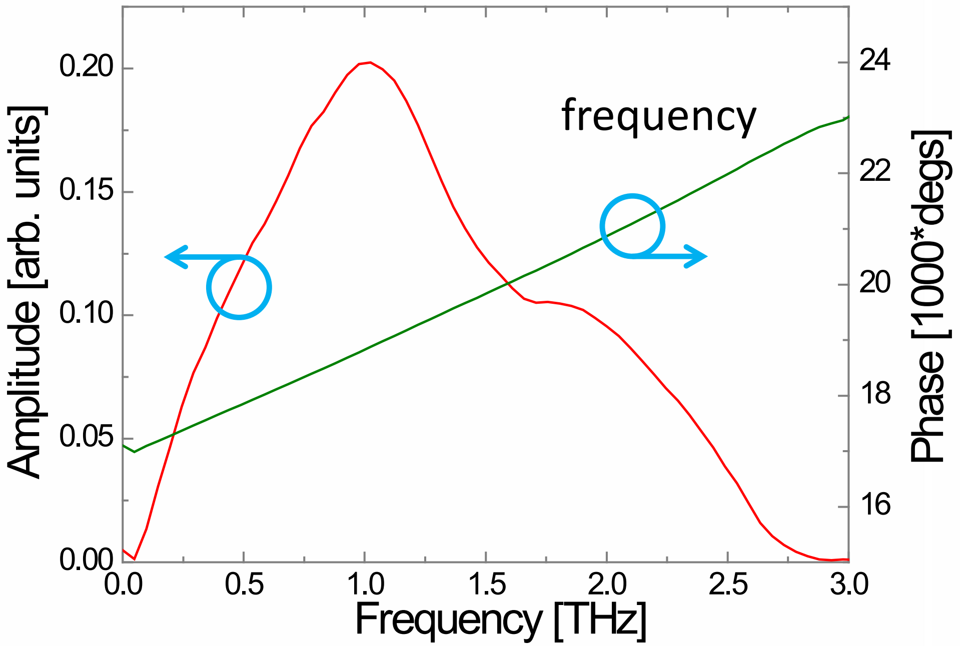
Ultrafast time resolution Broad bandwidth Complex-valued spectrum

THz pulse: ideal tool for ultrafast spectroscopy

$$E(t)=\frac{1}{2}\sqrt{\mathrm{I(t)}}\exp[i\varphi(t)]+c.c.$$

$$\hat{E}(\omega)=\int_{-\infty}^{+\infty}\mathrm{E(t)}\exp(-i\omega t)\,dt=$$
$$=E(\omega)\exp\left[i\varphi(\omega)\right]$$



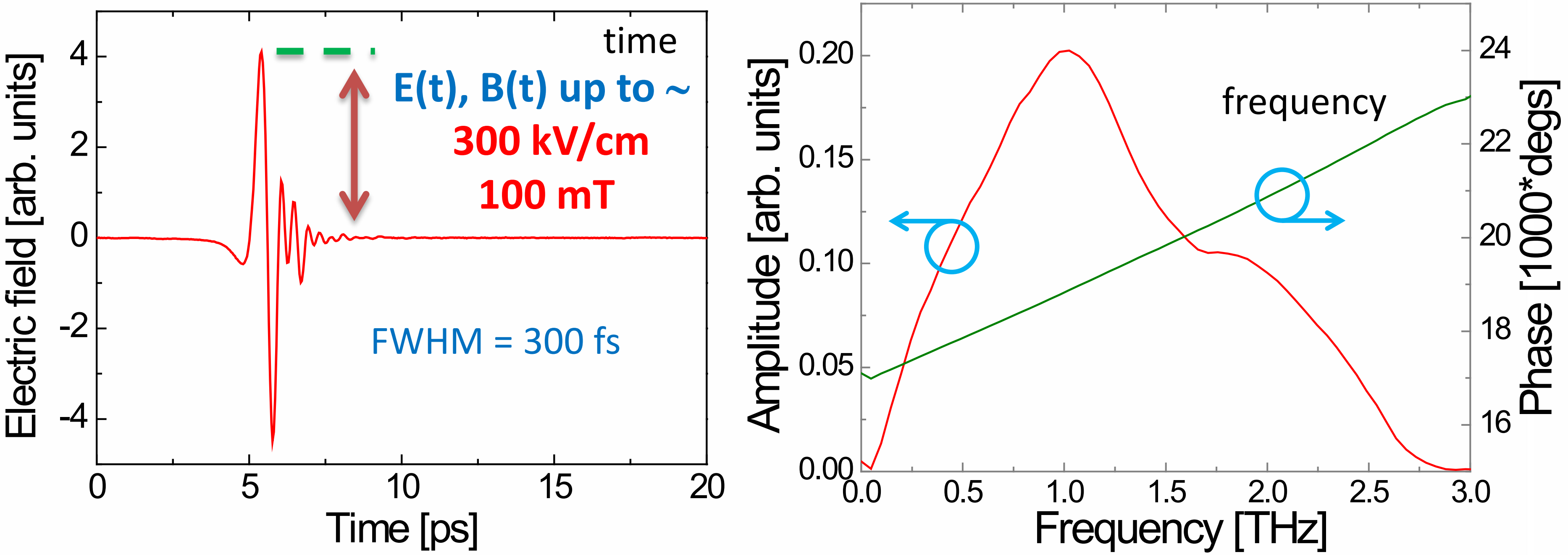


$$\varphi(t)=\omega t+\varphi_0(t)$$

$$\varphi(\omega)=kr+\varphi_0(\omega)=\frac{\omega r}{c}+\varphi_0(\omega)$$

φ_0 – arbitrary initial phase

Ideal tool for spectroscopy



THz pulse is ultrafast and contact-free:

Ohm-meter (dielectric spectroscopy)

Volt-, Amp-, Magnetometer (emission spectroscopy)

E or B – field switch / ctrl pulse (nonlinear spectroscopy)

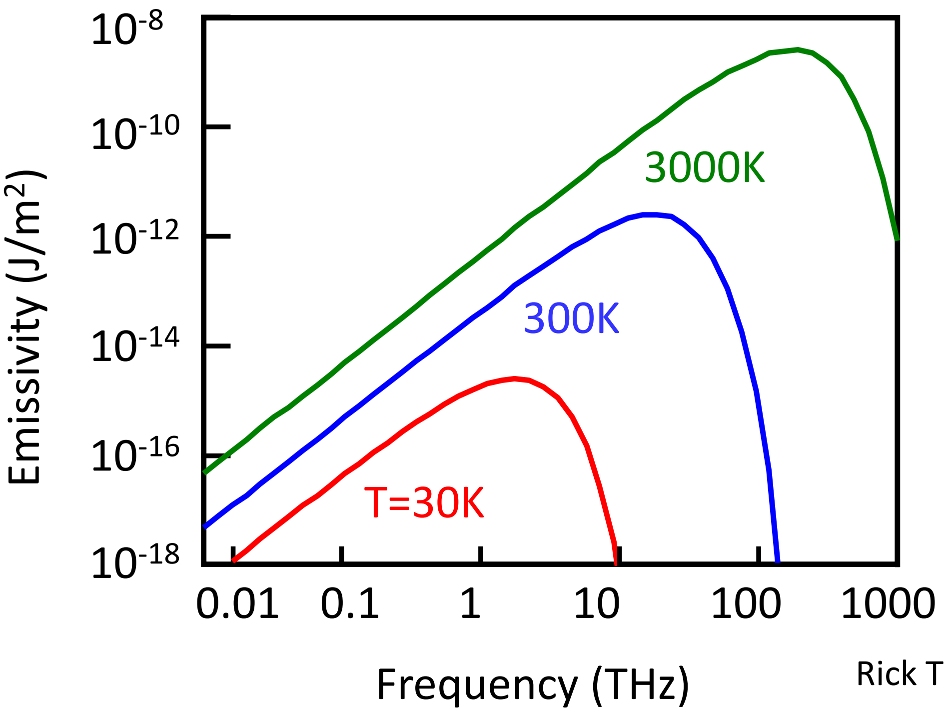
Sources and detectors of THz radiation

…. have long been a challenge

Blackbody spectra roll off very rapidly in the THz special range

Planck's law of blackbody emission

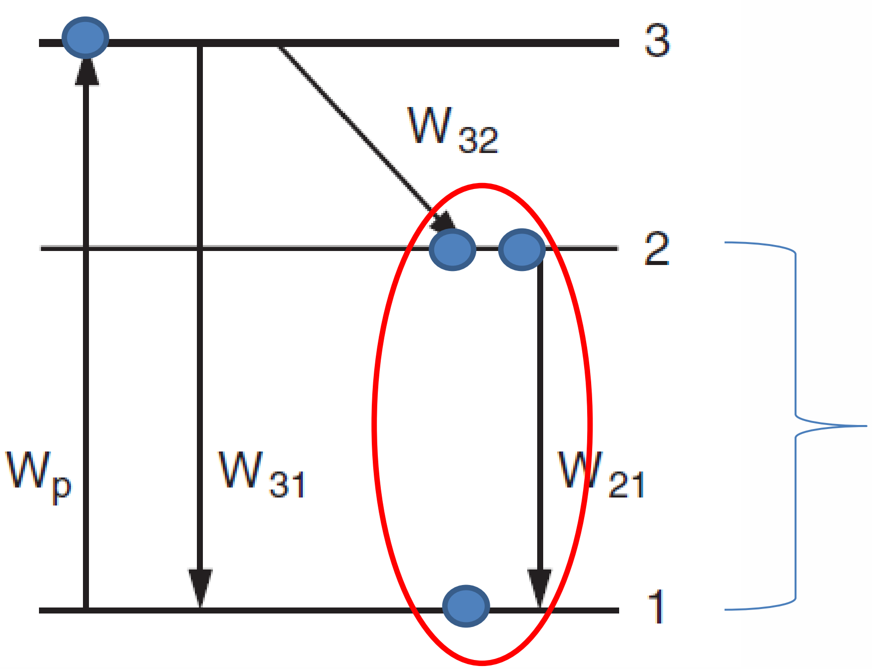
$$I(\nu,T)=\frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}}-1}.$$



Rick Trebino's lectures

Natural (thermal) THz sources are very weak.

THz laser at room temperature is a challenge



At 1 THz, $\hbar\omega$ = 4.1 meV

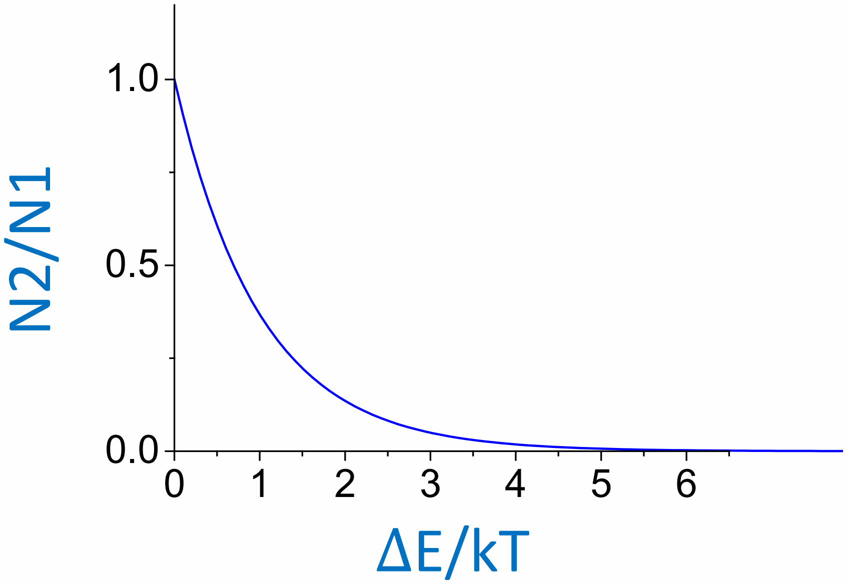
At 300 K
kT = 26 meV = 6.3 THz

Two-level system thermal population

Maxwell-Boltzmann distribution:

$$N_2/N_1 = exp(-\Delta E/kT)$$

At **low energies ≈ kT,** thermal population of upper level is high



Electronics ↔ Optics

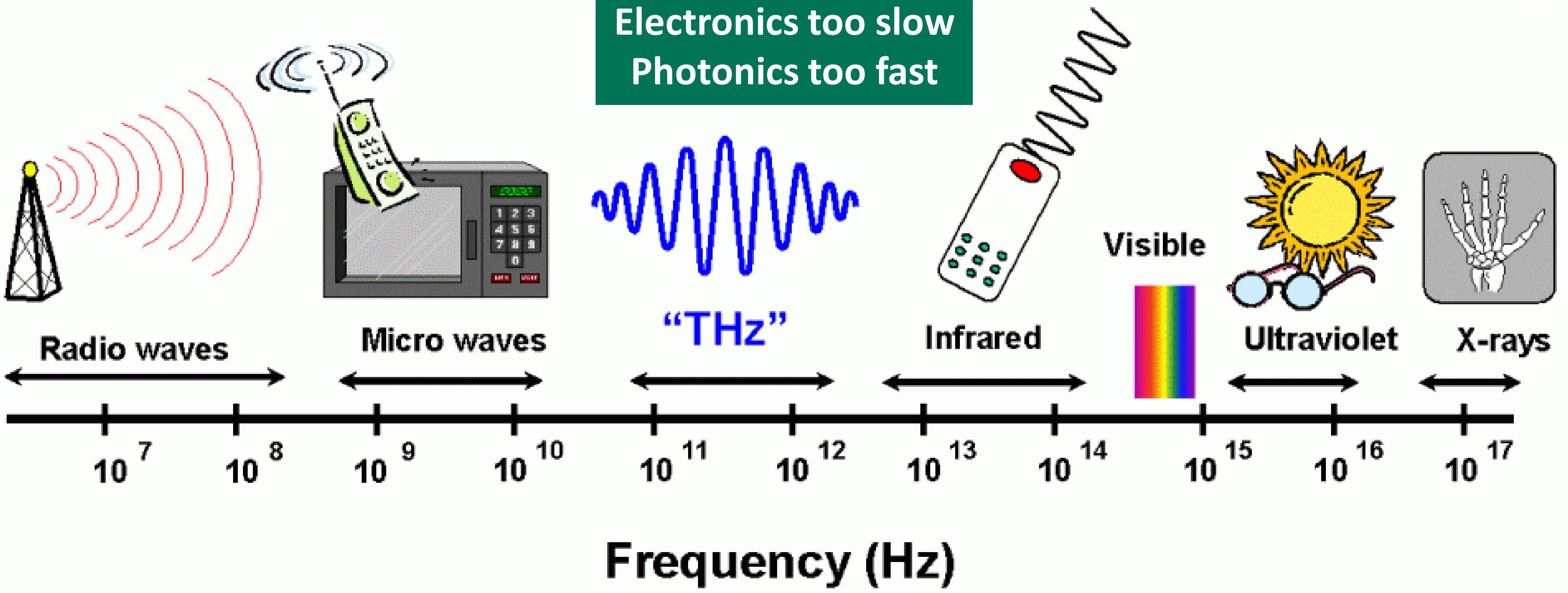
CLASSICAL TRANSPORT

ELECTRONIC DEVICES

QUANTUM TRANSITIONS

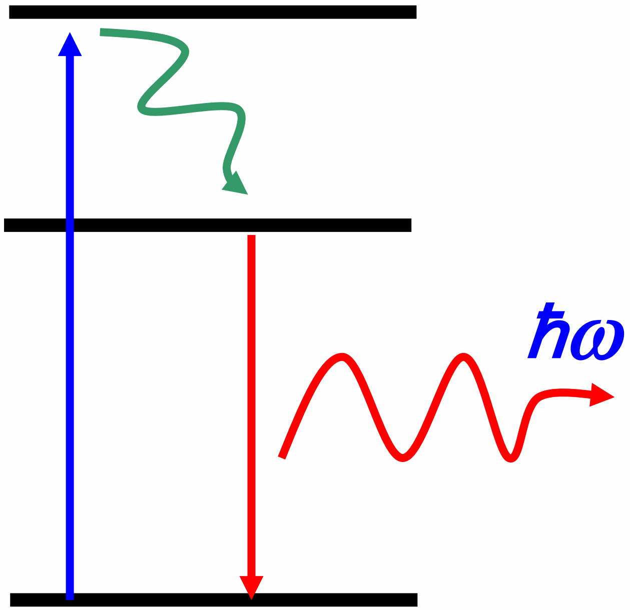
PHOTONIC DEVICES

”THz gap”
Electronics too slow
Photonics too fast

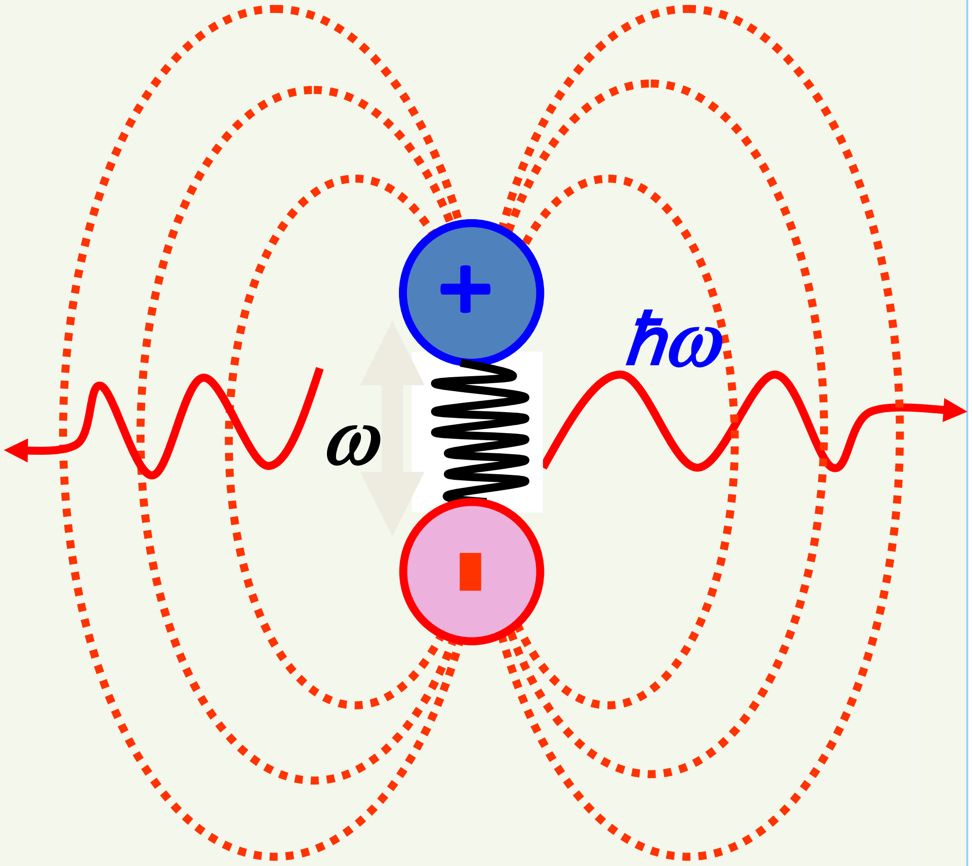


Combine classical and photonic approaches: ”lightwave electronics”

What drives the radiation?



Quantum representation



Classical representation
(Hertz dipole)

Maxwell's equations

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0},$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},$$

$$\nabla \cdot \mathbf{B} = 0,$$

$$\nabla \times \mathbf{B} = \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \mu_0 \mathbf{J},$$

$$\Downarrow$$

can be combined to…

Wave equation and its solution

FORCED WAVE EQUATION:

$$\nabla^2 E - \frac{n^2}{c^2}\frac{\partial^2 E}{\partial t^2} = \frac{1}{\varepsilon_0 c^2}\frac{\partial^2 P}{\partial t^2}$$

$$\boxed{J = \frac{dP}{dt}}$$

time-dependent source terms: current density ***J*** or polarization ***P***

FAR FIELD SOLUTION:

$$E_{rad}(t) \propto \frac{\partial^2 P}{\partial t^2} = \frac{\partial J}{\partial t}$$

Current and polarization instabilities cause electromagnetic radiation

Practical examples: radio antennas, radiation from 50 Hz electric grid

Why is this solution important?

$$J(t), P(t) \Leftrightarrow E(t)$$

J = [A/m^2] = [C/m^{2}s];

P = ∫ Jdt = dipole moment/volume = [Cm/m^3] = [C/m^2]

If you know current density and/or polarization dynamics,

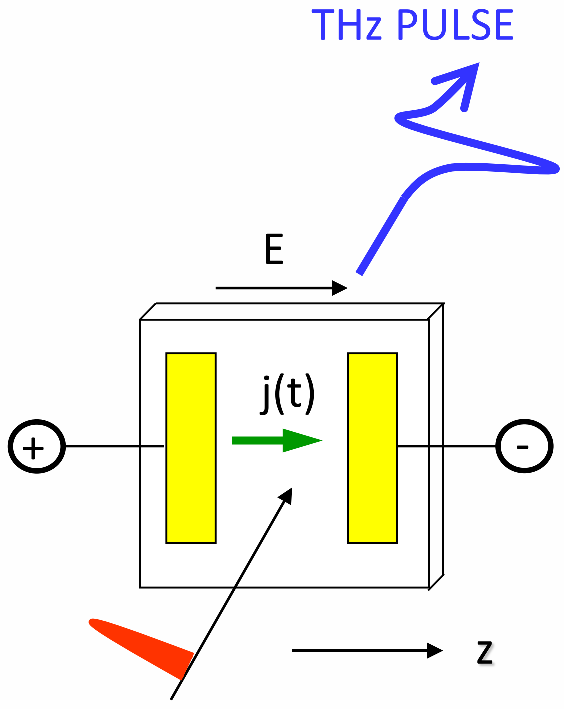
you can predict your emitted electric field.

And vice versa.

Generation and detection of THz pulses - photoconductive

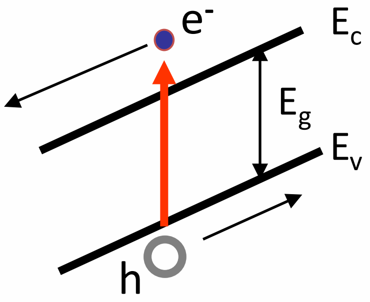
Bulk semiconductor (GaAs)

PHOTOCURRENT



100 fs laser pulse

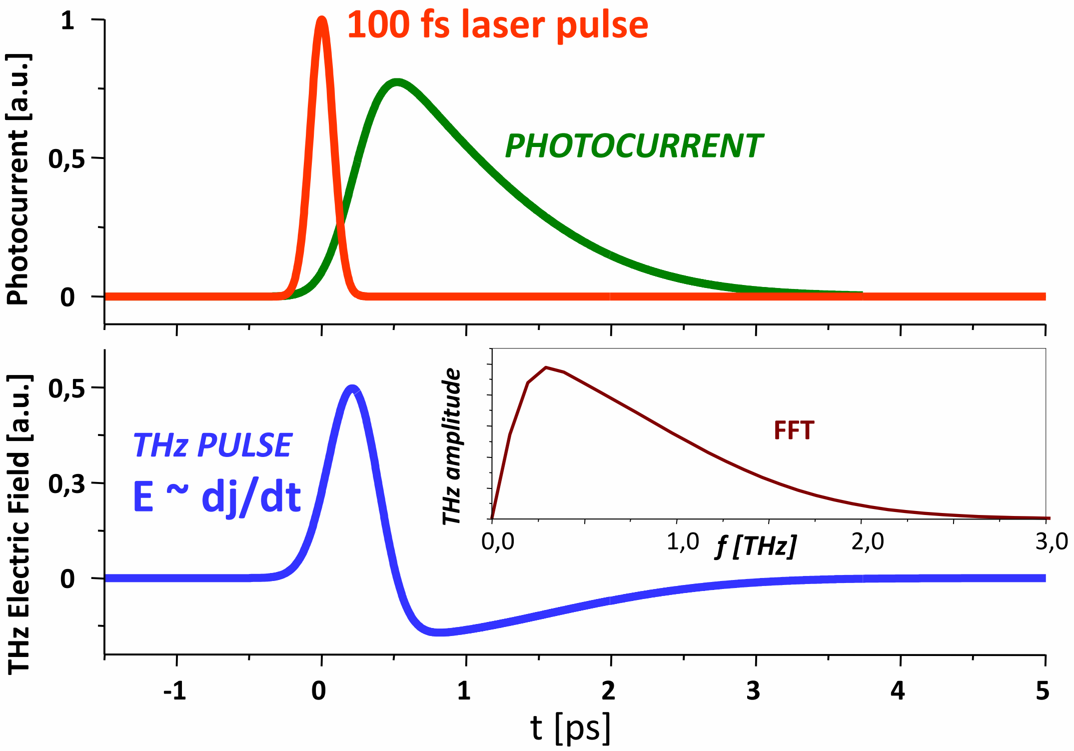
$\hbar\omega > E_g(\text{GaAs})$



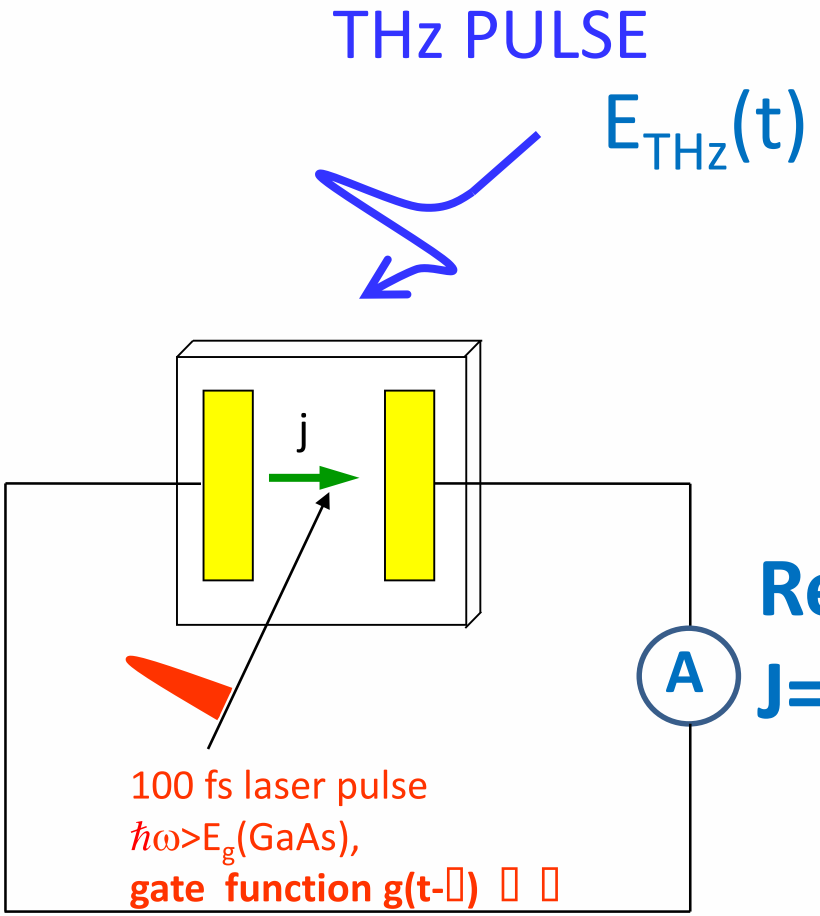
$$j(t) = |e|\, \mu(t)\, n(t)\, E(t)$$

$$E_{THz} \sim dj/dt = d^2P/dt^2$$

in the far field



Photoconductive detection: reversed emitter antenna



100 fs laser pulse
$\hbar\omega > E_g$(GaAs),
gate function g(t-□) □ □

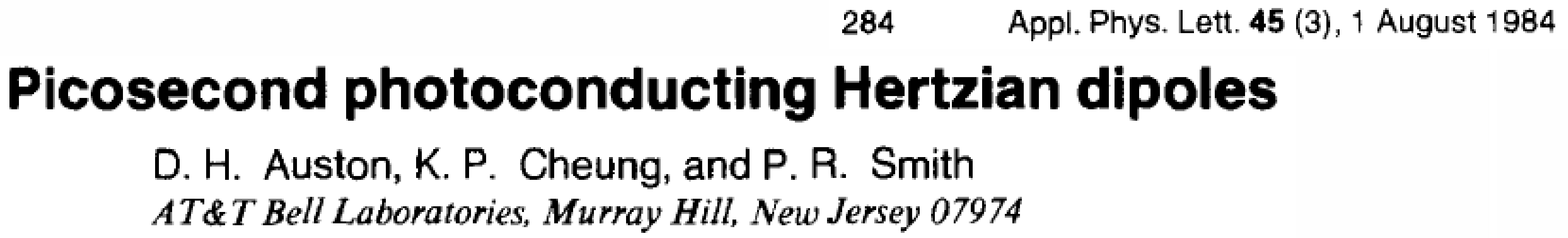
Current in the circuit:
$J = \square\, g(t-\square)E_{THz}(t)dt$

Read
$J = \square E_{THz}$

Gating f-n is laser-induced conductivity in semiconductor:

□ = e□N(t - □),
□- carrier mobility
and **N – laser induced carrier density**

Pioneering work: David Auston et al



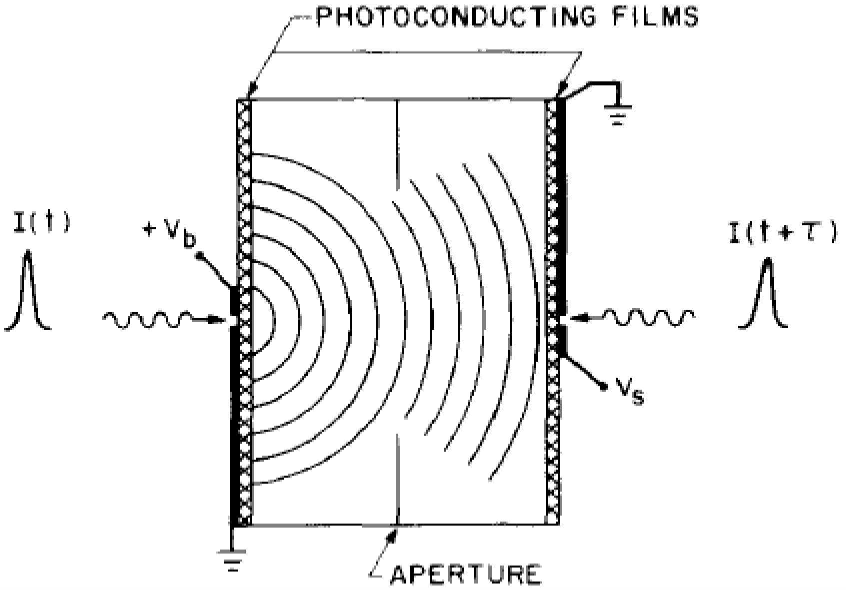
284 Appl. Phys. Lett. **45** (3), 1 August 1984

Picosecond photoconducting Hertzian dipoles

D. H. Auston, K. P. Cheung, and P. R. Smith

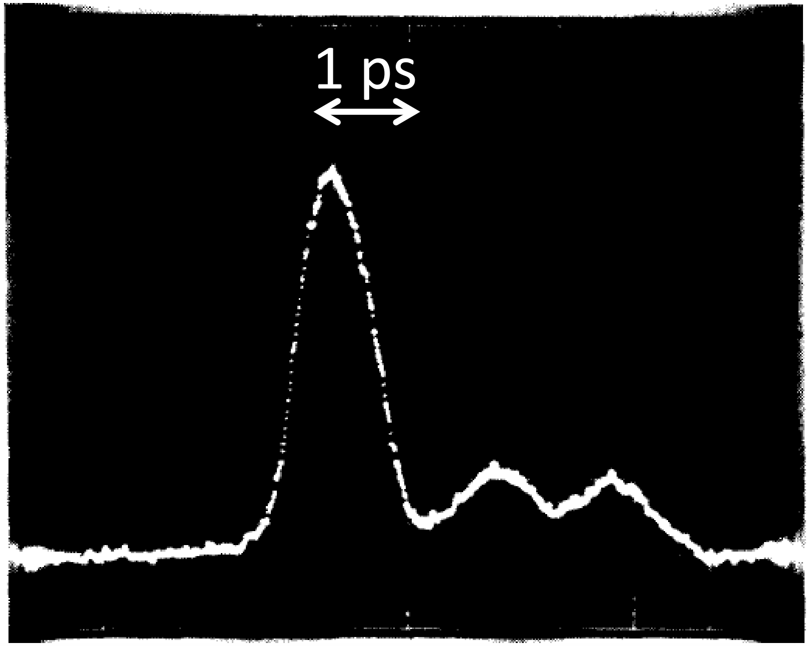
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Two laser-gated photoconductive antennas:



One for emission, one for detection

Cross-corrleation measurement of a sub-ps EM waveform



Sampling the THz lightwave

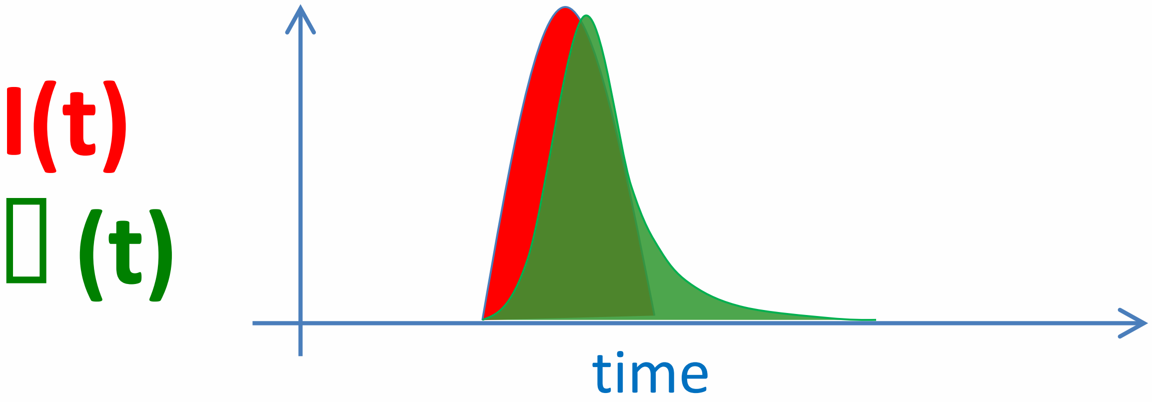
- Using such a gated detection, one measures a **time-dependent signal** (e.g. current) which is proporional to the **electric field of the THz pulse**

- The detection is **sensitive to the sign of the field**

- **Phase-resolved** detection, a **direct measurement of a lightwave**!

Photoconductive detection:

For measuring fast THz fields, the **photo-conductivity** in semiconductor must have the **lifetime** comparable to the **laser pulse duration**.

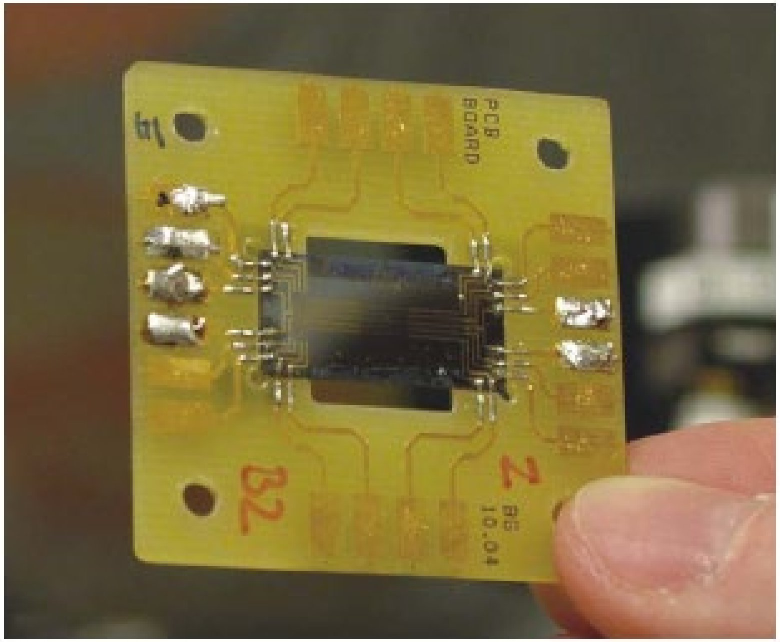


Carrier lifetime in direct-gap semiconductors (eg GaAs) is 100s of picoseconds to nanoseconds. In indirect-gap materials (e.g. Si) it is milliseconds. **We need sub-ps → Use materials with defects for shorter free-carrier lifetime**

Photoconductive antenna, aka Auston switch or PC-switch

GaAs is best material for PC switches
Matched with Ti:Sapphire lasers:
800 nm = 1.55 eV
E_g(GaAs) = 1.44 eV

For detectors one usually uses LT-GaAs, RD-SOS, Er:GaAs, etc



Jepsen, Jacobsen and Keiding, J. Opt. Soc. Am. B **13**, 2424 (1996)

Photoconductive antenna, aka Auston switch or PC-switch

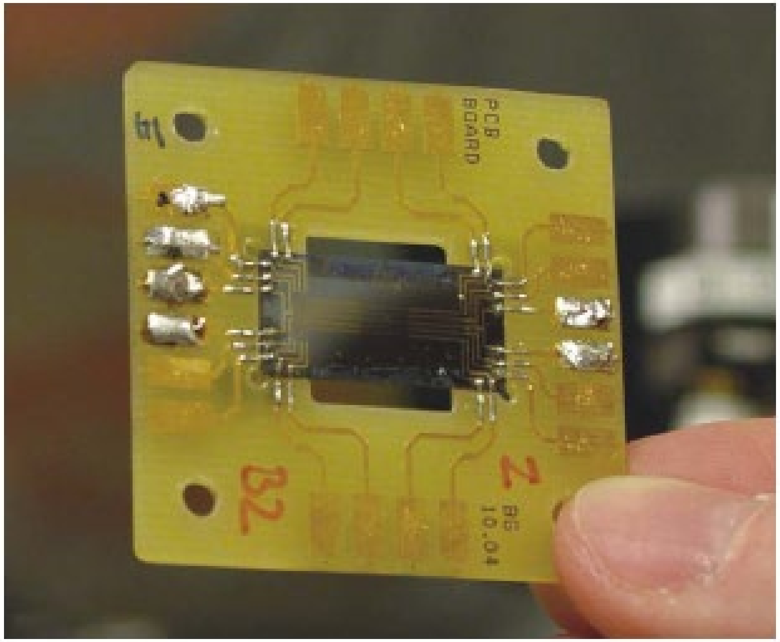
GaAs is best material for PC switches

Matched with Ti:Sapphire lasers:

800 nm = 1.55 eV

E_g(GaAs) = 1.44 eV

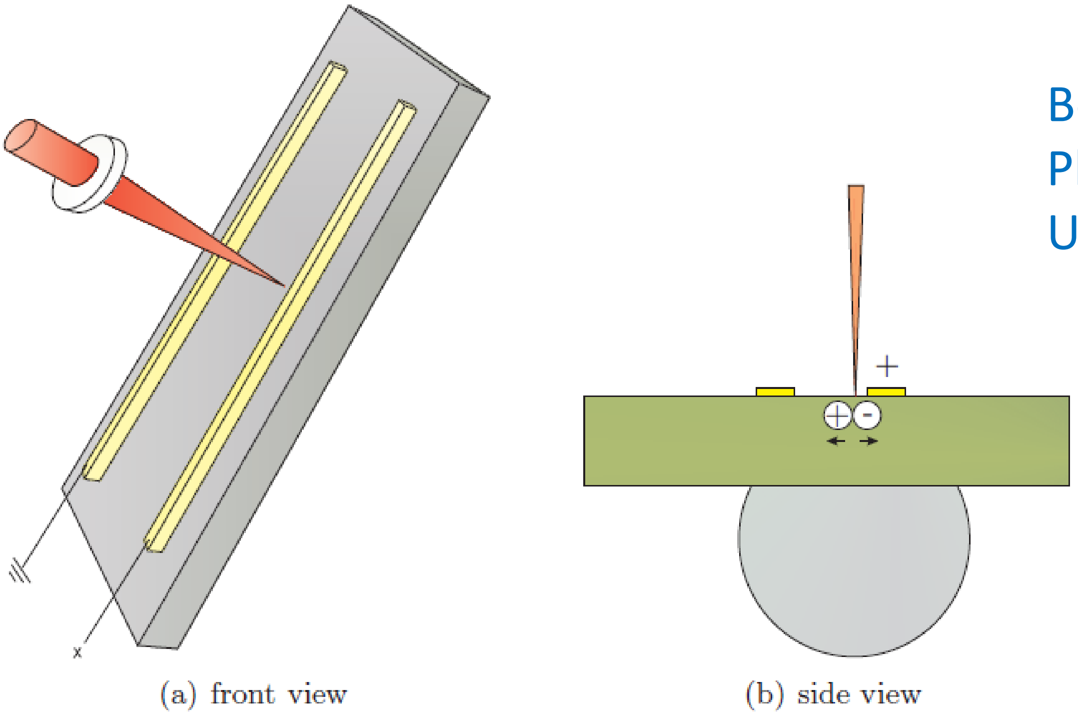
For emitter antennas, one can use normal GaAs with long free-carrier lifetime. **Why?**



Jepsen, Jacobsen and Keiding, J. Opt. Soc. Am. B **13**, 2424 (1996)

Silicon lens - coupled antennas

Usually the photocoductive gap in PC-switches is 10-100 um, i.e. sub-wavelength for THz radiation ➔ Large diffraction angle for THz, also TIR in substrate. For outcoupling and collimation, PC-antennas are typically coupled to index-matched Silicon hyper-hemispherical lenses

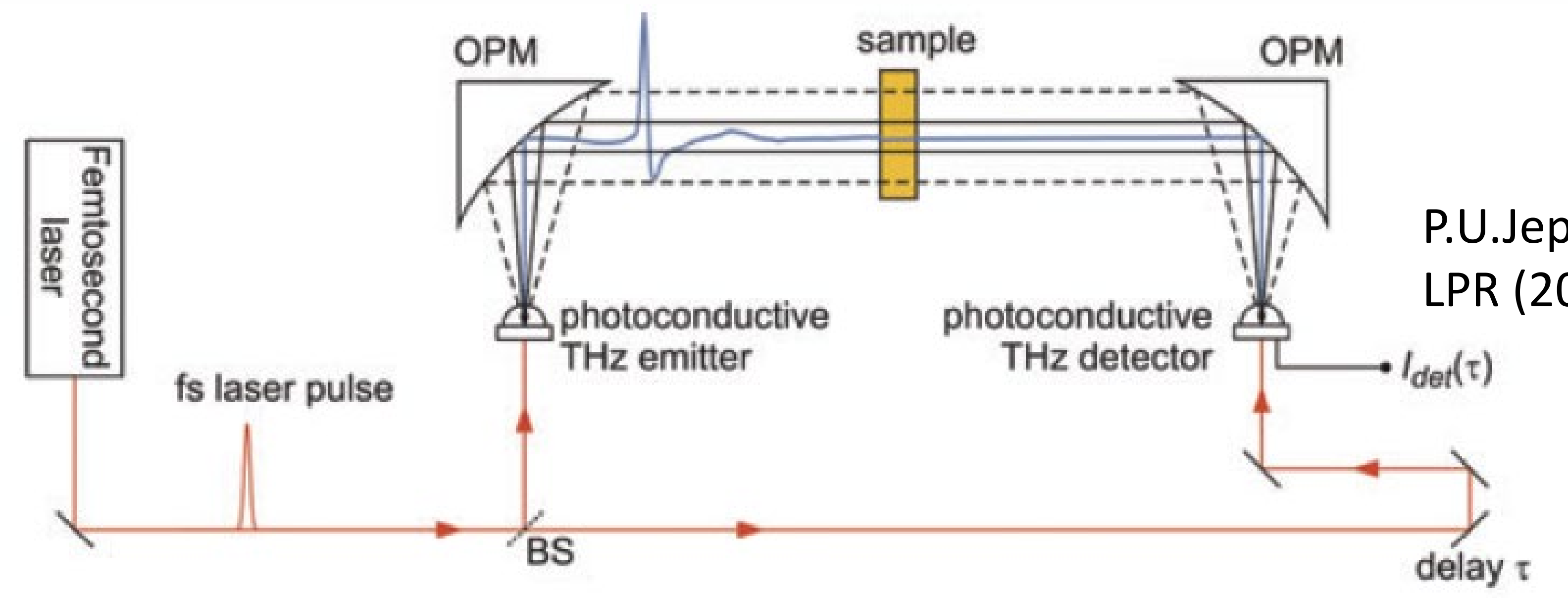


(a) front view (b) side view

Bernd Fischer
PhD thesis,
Uni Freiburg (2005)

THz Time-Domain Spectroscopy

Allows to measure the **lightwaves as E(t)**, rather than I(t).
The **most direct way of detecting the light**.
The lightwave transmitted through the sample carries **full information on the dielectric function** of the material.



P.U.Jepsen
LPR (2011)

More details later in this lecture.

Photoconductive THz-TDS systems

- Usually used with nJ-level femtosecond oscillators at 80-100 MHz reprare, no laser amplifier needed (THz energy supplied by bias circuit)
- Difficult to align, but have very high sensitivity. Dynamic range (power) > 50-60 dB
- Typical frequency range up to 4-5 THz
- Modern, commerially-available systems are based on fiber lasers, and use fiber-coupled PC-switches for easier alignment

Nonlinear-optical THz generation and detection

- Usually used with mJ-level femtosecond amplifiers at kHz reprates. THz energy supplied solely by the laser pulse.
- Easy to align, but not very sensitive. Dynamic range (power) > 20-30 dB
- Typical frequency range with 50-100 fs laser pulses up to 3 THz
- Typically home-built, and are used for pump-probe experiments

Wave equation and its solution

FORCED WAVE EQUATION:

$$\nabla^2 E - \frac{n^2}{c^2}\frac{\partial^2 E}{\partial t^2} = \frac{1}{\varepsilon_0 c^2}\frac{\partial^2 P}{\partial t^2} \longleftarrow \boxed{J = \frac{dP}{dt}}$$

time-dependent source terms: current density ***J*** or polarization ***P***

FAR FIELD SOLUTION:

$$E_{rad}(t) \propto \frac{\partial^2 P}{\partial t^2} = \frac{\partial J}{\partial t}$$

Current and polarization instabilities cause electromagnetic radiation

Nonlinear polarization:
frequency mixing in non-centrosymmetric material

Let the field **E(t)=E$_1$cos(□ $_1$t) + E$_2$cos(□ $_2$t)** – *two-color field*

Using Euler's formula **cos(x) = [exp(ix) + exp(-ix)]/2,**

we derive the 2nd-order polarization **P$^{(2)}$(t) = □$_0$ □$^{(2)}$ E(t)^2** :

$$P^{(2)}(t)=\varepsilon_0\chi^{(2)}E(t)^2=$$

$$=\frac{1}{2}\varepsilon_0\chi^{(2)}\left[\begin{array}{l} E_1^2[\cos(2\omega_1 t)+\cos((\omega_1-\omega_1)t)]+ \\ +E_2^2[\cos(2\omega_2 t)+\cos((\omega_2-\omega_2)t)]+ \\ +2E_1E_2\cos[(\omega_1+\omega_2)t]+2E_1E_2\cos[(\omega_1-\omega_2)t] \end{array}\right]$$

P$^{(2)}$ (□)= P(2□ $_1$) + P(2□ $_2$) + P(0□ t)+ P(□ $_1$ +□ $_2$) + P(□ $_1$ -□ $_2$)

P$^{(2)}$ (□) □ E^2 = I

2nd order nonlinear terms:

$P^{(2)}(\omega) = P(2\omega_{1,2}) + P(0\omega t) + P(\omega_1 + \omega_2) + P(\omega_1 - \omega_2)$

$$P^{(2)}(2\omega_{1,2}) = \frac{1}{2}\varepsilon_0\chi^{(2)}E_{1,2}^2\cos(2\omega_{1,2}t)$$

second-harmonic seneration **(SHG)**

$$P^{(2)}(0\omega) = \frac{1}{2}\varepsilon_0\chi^{(2)}E_{1,2}^2$$

optical rectification **(OR)**, only depends on amplitude, free from carrier frequency

$$P^{(2)}(\omega_1 + \omega_2) = \varepsilon_0\chi^{(2)}E_1E_2\cos[(\omega_1 + \omega_2)t]$$

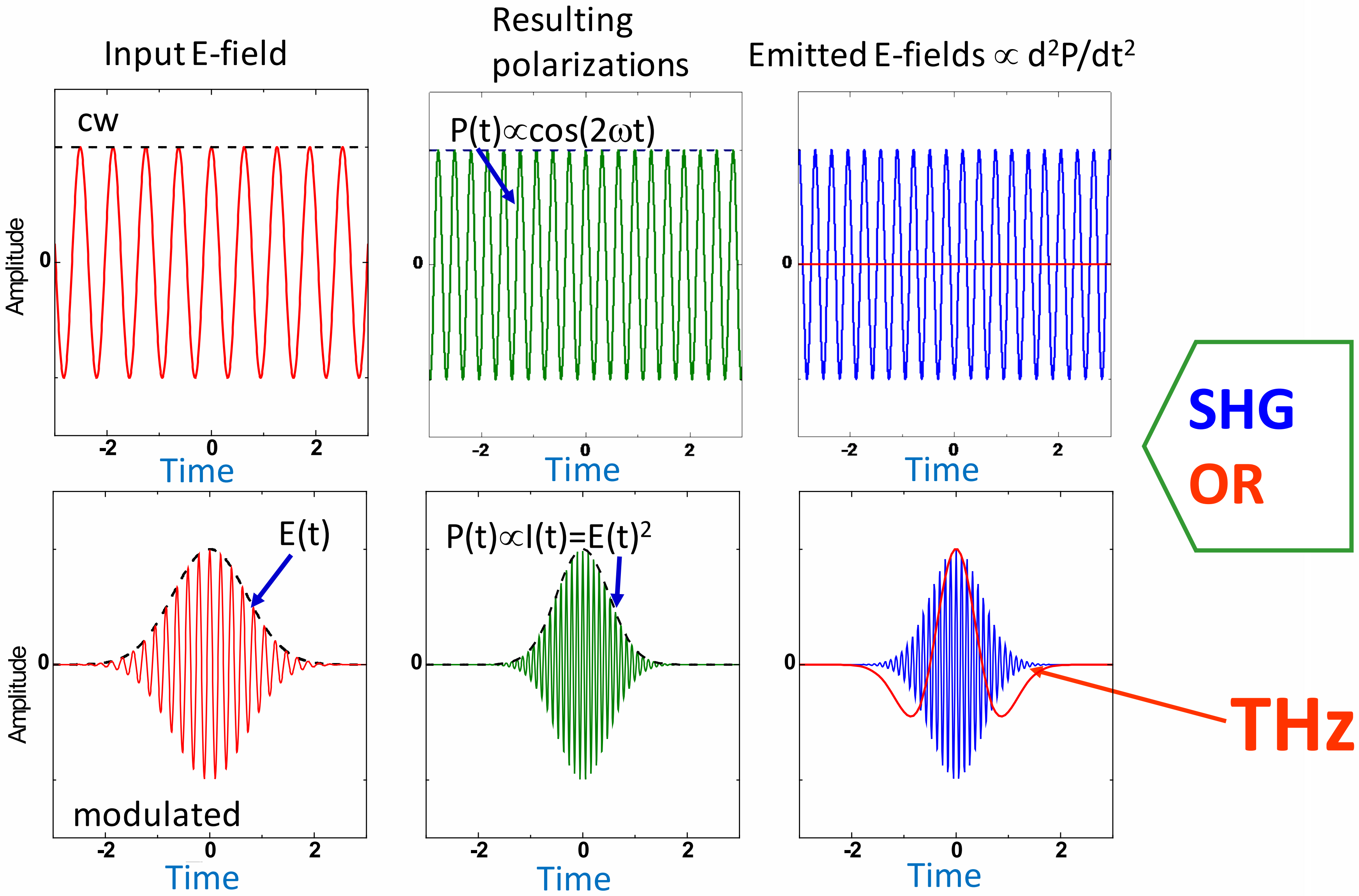
sum-frequency generation **(SFG)**

$$P^{(2)}(\omega_1 - \omega_2) = \varepsilon_0\chi^{(2)}E_1E_2\cos[(\omega_1 - \omega_2)t]$$

difference-frequency generation **(DFG)**

If $\omega_1 = \omega_2$ ➔ SFG ≡ SHG and DFG ≡ OR

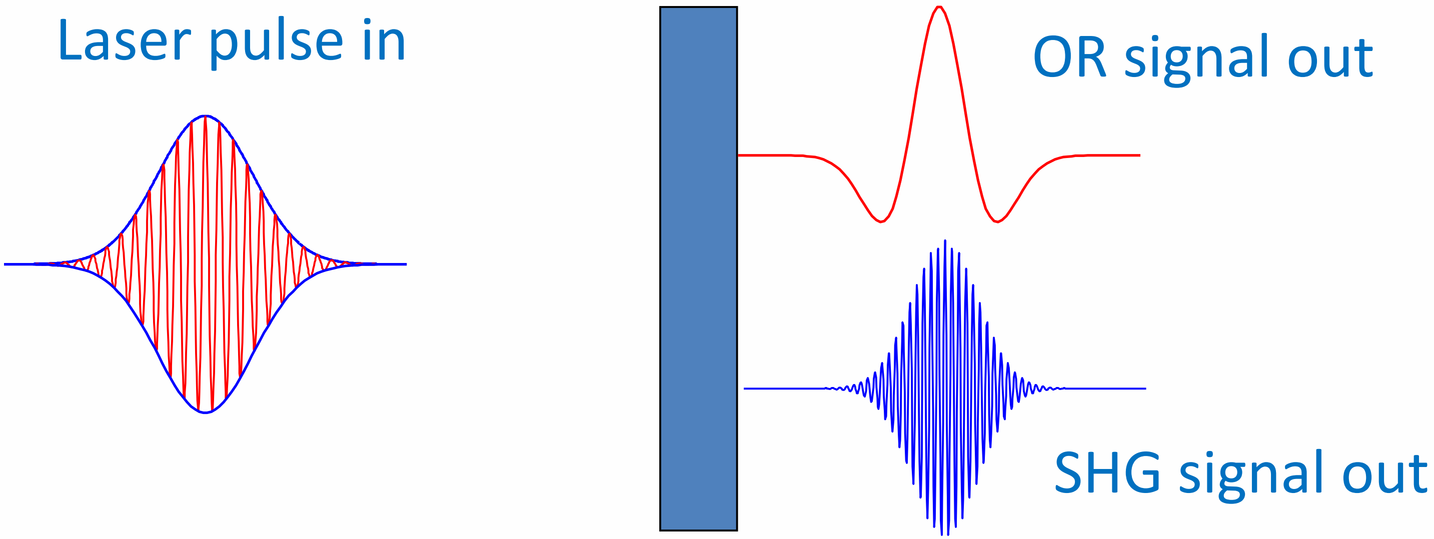
Radiation by 2nd order nonlinear terms: Modulated vs unmodulated input


Input E-field

Resulting polarizations

Emitted E-fields ∝ d^2P/dt^2

Idealistic picture of pulsed NL generation by $\chi^{(2)}$ process



Nonlinear crystal

Laser pulse in

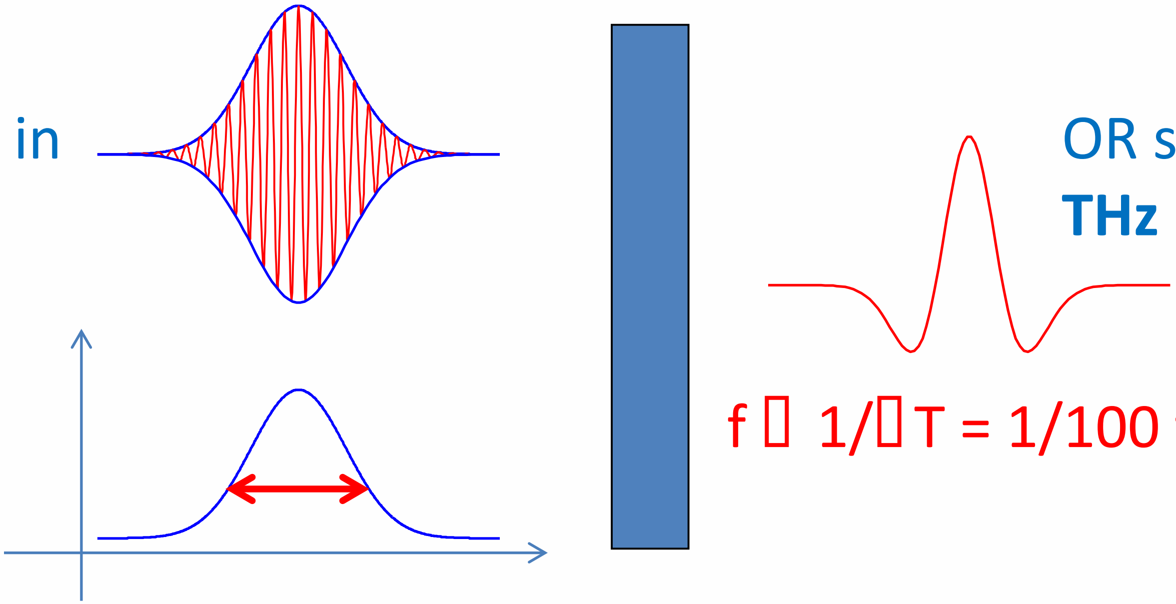
OR signal out

SHG signal out

In reality, nonlinear crystals are optimized **either** for SHG, **or** for OR. The optimization is by **phase-matching**

THz generation by optical rectification of femtosecond laser pulses

Laser pulse in



OR signal out:

THz pulse

f □ 1/□T = 1/100 fs □ 10 THz

$P^{(2)}$ (OR) □ envelope^2,

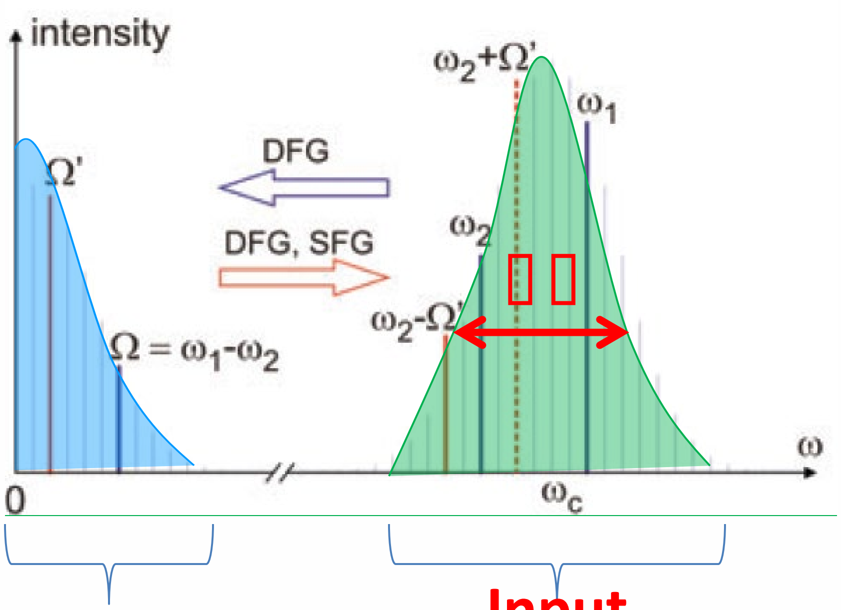
FWHM □T □ 100 fs

In OR process the oscillation of the ENVELOPE of the input translates into the oscillation of the CARRIER WAVE of the resulting signal

OR allows for very efficient **down-conversion** of optical signals, e.g. from $□_0$ = 380 THz (800 nm) to □ = 1 THz (0.3 mm), i.e. by a factor of 10^2 - 10^3

Frequency-domain representation of optical rectification

Translation of the **bandwidth** of the laser pulse to DC

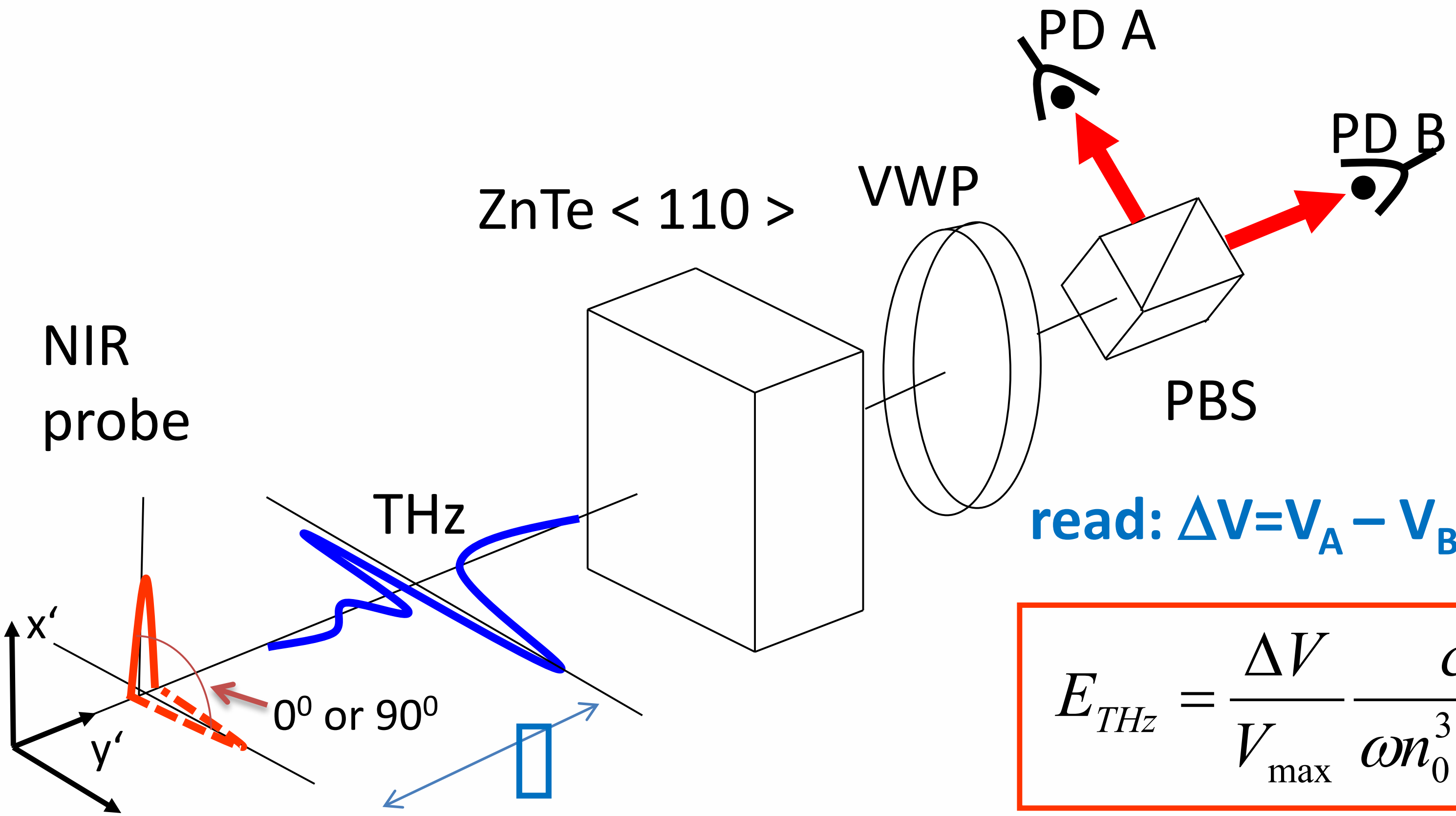


OR polarization (THz around dc)

Input polarization (laser around □$_0$)

P. U. Jepsen et al, LPR (2011)

THz detection in nonlinear crystals: Free-Space Electroooptic Sampling (FEOS)



read: $\Delta V = V_A - V_B \propto E_{THz}$

$$\boxed{E_{THz} = \frac{\Delta V}{V_{\max}} \frac{c}{\omega n_0^3 r_{41} d}}$$

- **THz field induces birefringence** in the eo crystal (e.g. ZnTe)
- A delayed **gating laser pulse experiences this birefringence**, and acquires the phase retardation **proportional to the instantaneous THz field**, which is analyzed.

FEOS is time-resolved THz-induced Pockels effect

Application of external electric field ***E*** to an electrooptic crystal in a chosen direction leads to (quasi-)instantaneous modification of its refractive index in several directions **(Pockels effect).**
This leads to induced birefringence of the crystal, proportional to electric field strength of ***E (including its sign!)***.

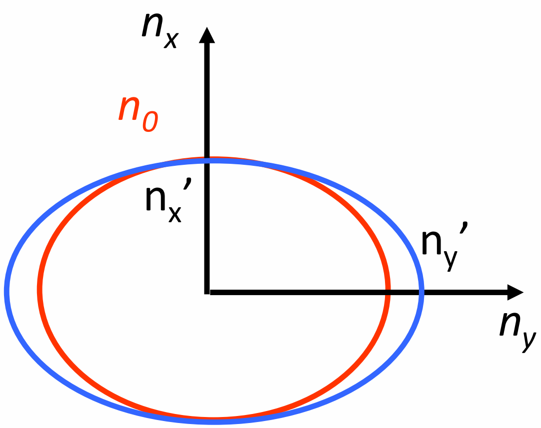
E.g.: cubic crystals, such as GaAs or ZnTe, with <110> axes orientation:

$$\Delta n = n_0{}^3 r_{41} E$$

$\boldsymbol{n_0}$ is a background refractive index,
$\boldsymbol{r_{41}}$ is electrooptic coefficient, ***E*** – external field

With and without external field:

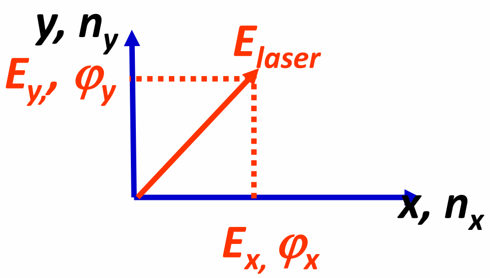
$$n_y{}'-n_x{}'=\Delta n$$



THz detection in nonlinear crystals: Free-Space Electroooptic Sampling (FEOS)

Pre-polarized light, when propagating through such a crystal, will experience phase retardation, depending on the strength of ***E***

$$\Delta\varphi = \frac{\omega \Delta n d}{c} = \frac{\omega n_0^{3} r_{41} \boxed{E} d}{c}$$



Δφ is a phase retardation between orthogonal polarization states of light

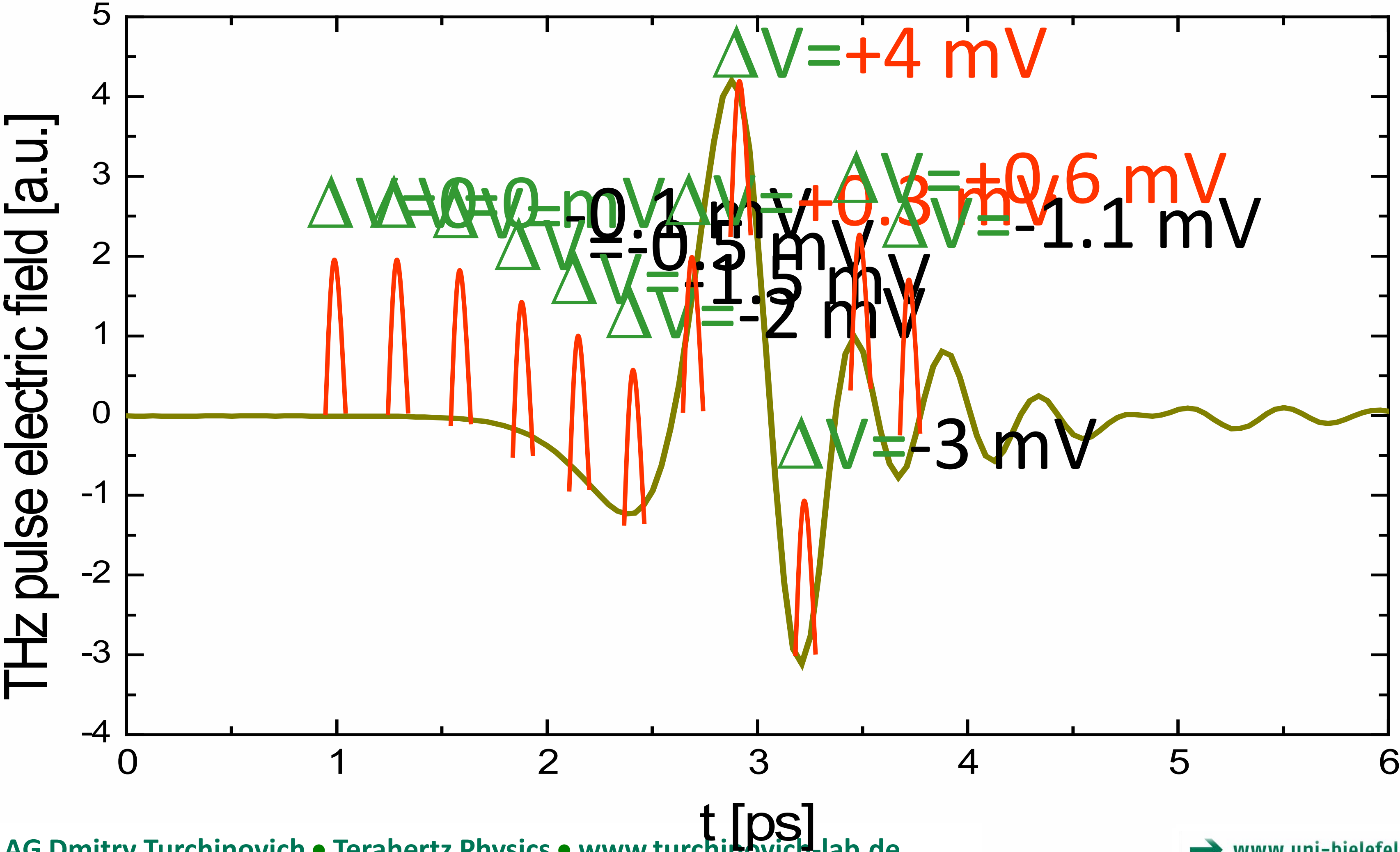
ω is an optical frequency

d is a crystal thickness

FEOS allows for **accurate calibration of THz field strength**, if the electrooptic coefficient of the crystal is known

FEOS sampling of THz field

Cross-correlation of THz field and gating laser pulse. Read the eo signal – the voltage difference on the photodiodes. Background-free!

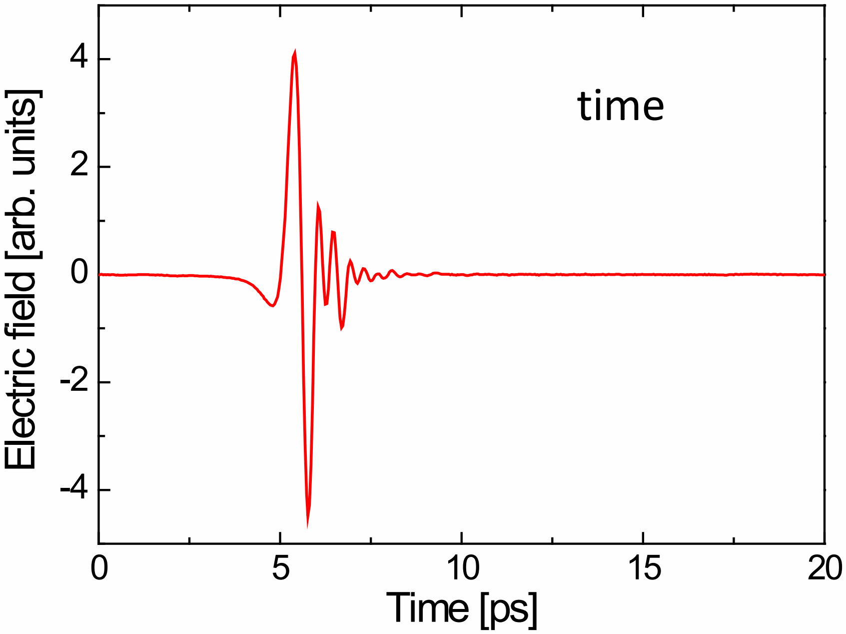


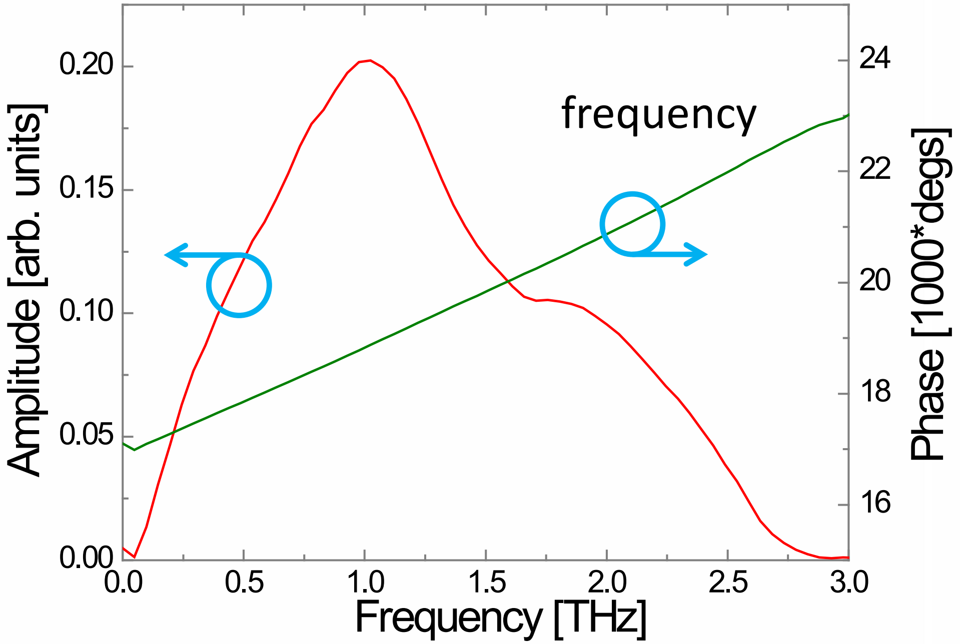
THz time-domain spectroscopy

THz pulse: ideal tool for ultrafast spectroscopy

$$E(t) = \frac{1}{2}\sqrt{\mathrm{I(t)}}\,\exp[i\varphi(t)] + c.c.$$

$$\hat{E}(\omega) = \int_{-\infty}^{+\infty} \mathrm{E(t)}\exp(-i\omega t)\,dt = $$
$$= E(\omega)\exp[i\varphi(\omega)]$$





$$\varphi(t) = \omega t + \varphi_0(t)$$

$$\varphi(\omega) = kr + \varphi_0(\omega) = \frac{\omega r}{c} + \varphi_0(\omega)$$

$\square_0$ – arbitrary initial phase

(Frequency-dependent) dielectric function and its equivalents

$$\hat{\varepsilon} = (1+\hat{\chi}) = \overbrace{(n + i\,\kappa)}^{\hat{n}}{}^{2} = \varepsilon_{\infty} + \frac{i\,\hat{\sigma}}{\varepsilon_{0}\,\omega}$$

What the material feels: microscopic response to the oscillating light field

ε(ω): **dielectric function** ➔ **D = $\varepsilon_0\varepsilon$E**

χ(ω): **optical susceptibility** ➔ **P =$\varepsilon_0\chi$E**

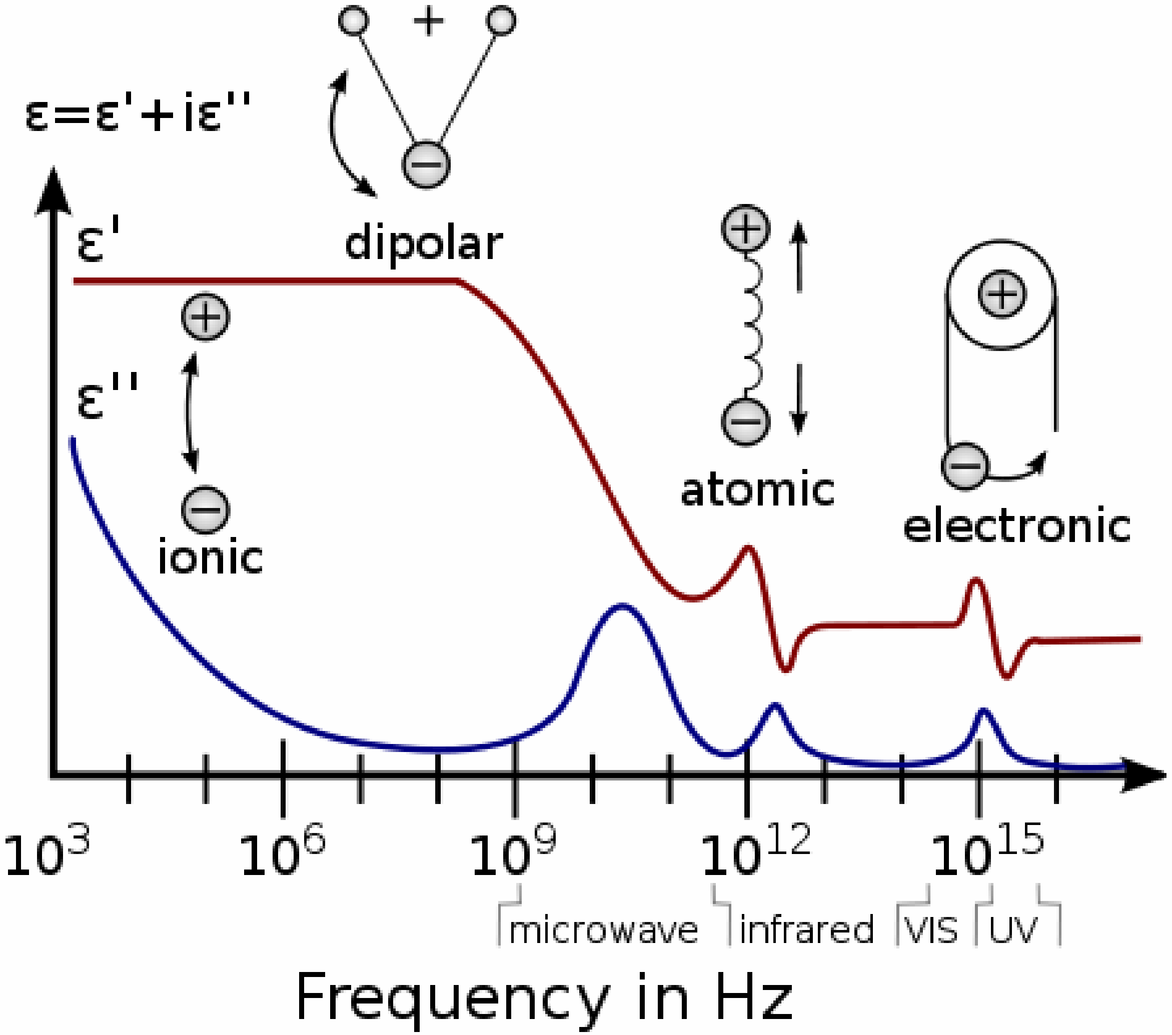
□ (ω): **optical conductivity** ➔ **j =σE**

n(ω): **(phase) refractive index, Re(n)**

κ(ω): **extinction coefficient, Im(n)**

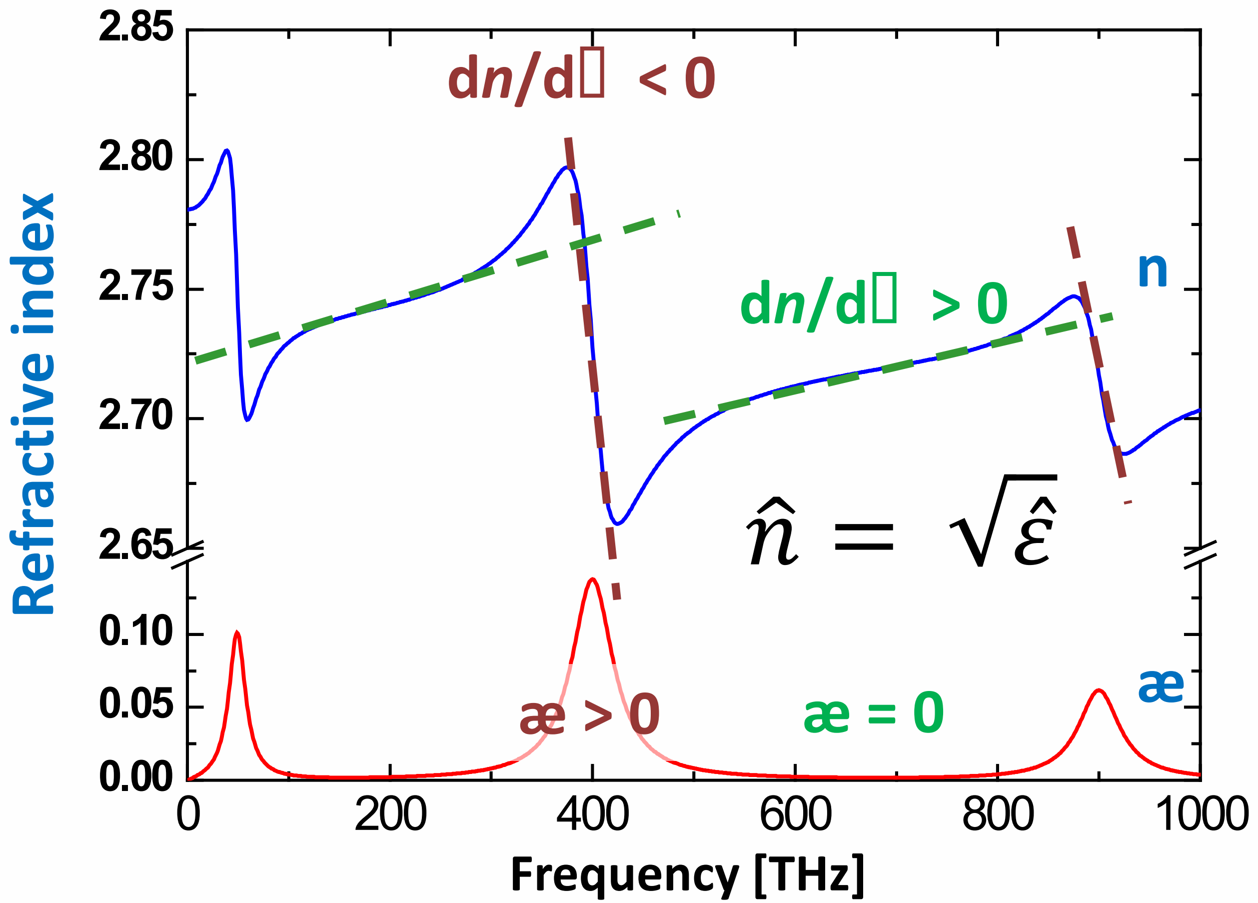
What the light feels: determine the propagation of the light wave

Dielectric function of materials depends on frequency



Wikipedia

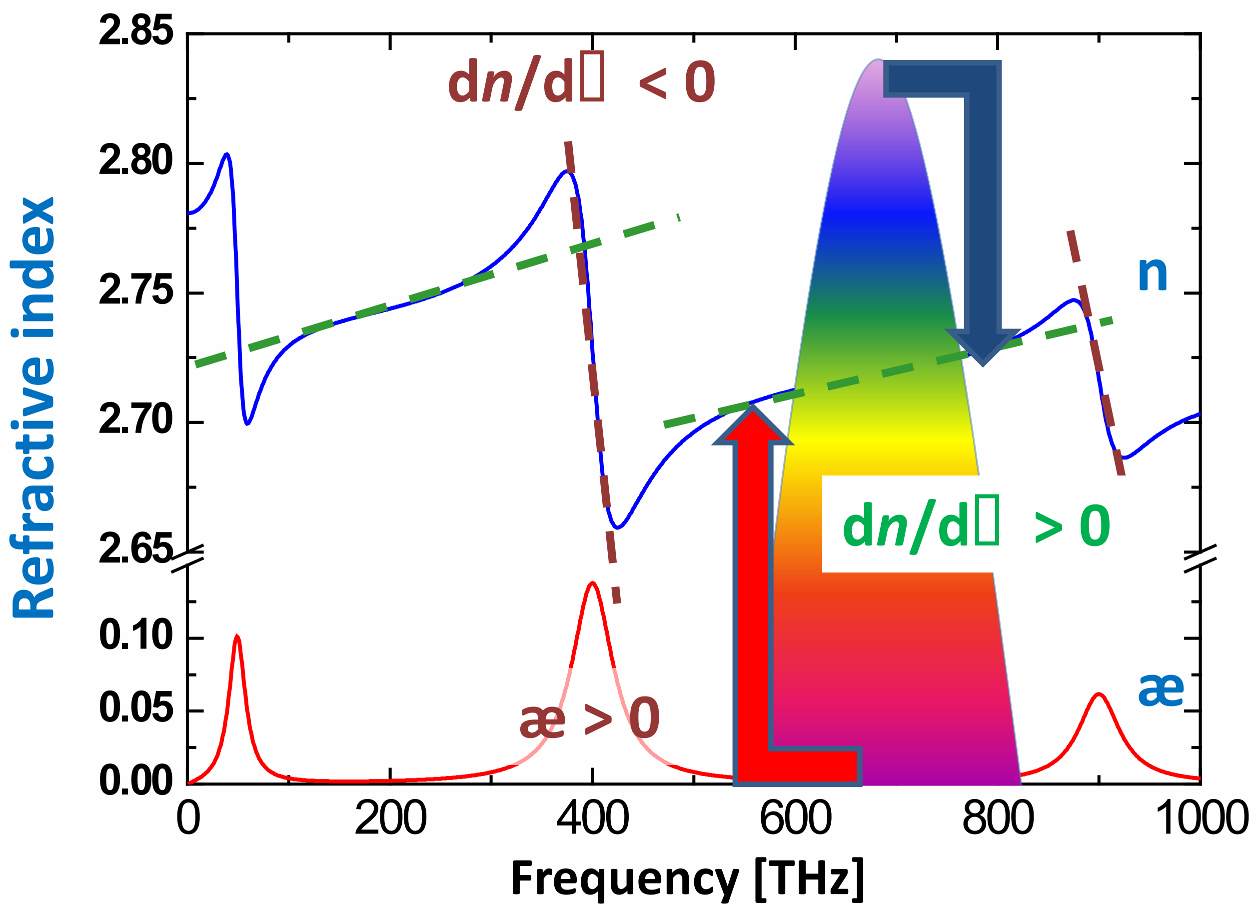
Dispersion of refractive index



Typically, in <u>transparent</u> spectral regions **d*n*/d > 0 – normal dispersion**

Around the <u>absorption</u> peaks, **d*n*/d < 0 – anomalous dispersion**

Dispersion of a wavepacket



Different frequencies in the pulse will experience differen values of ***n*** ➔
will propagate with different phase *(*) = r n(*) /c* ➔
pulse reshaping in time

Optical phase in a dielectric in frequency domain

How to measure the dielectric f-n with propagating light field:

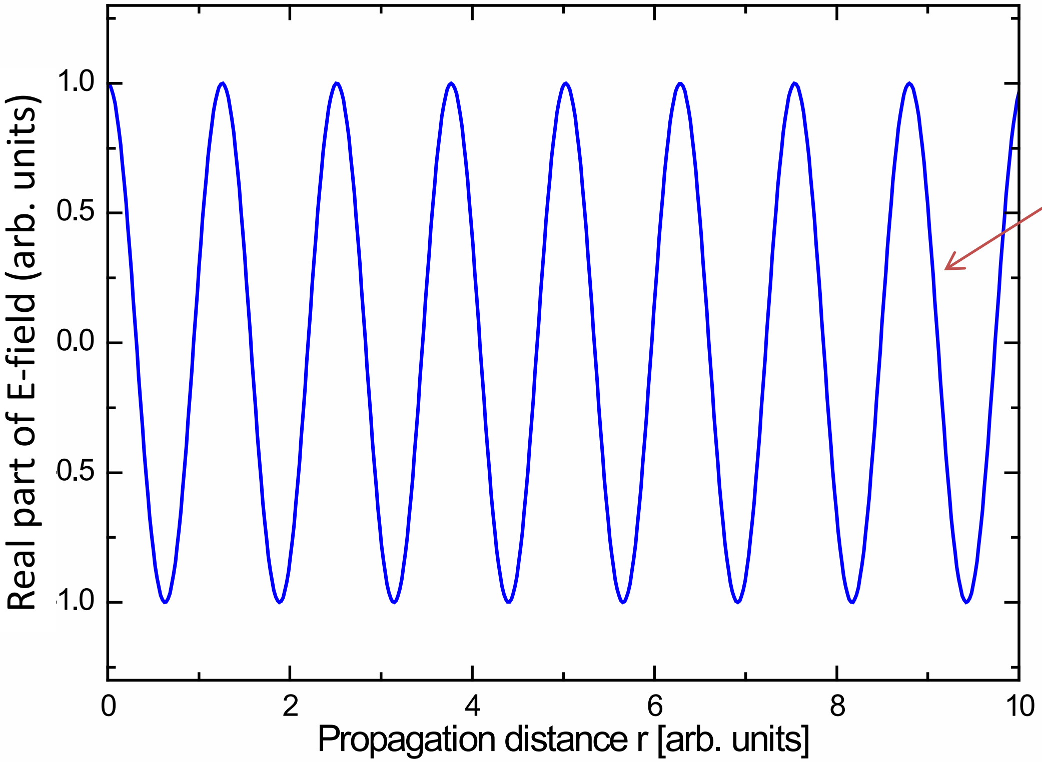
$$\hat{E}(\omega) = E(\omega)e^{i\varphi} = E(\omega)e^{i\hat{k}r} = E(\omega)exp[\frac{i\omega\hat{n}(\omega)r}{c}]$$

In the frequency domain the optical phase is □ **= k̂r,** where **r** is the propagation distance, and **k̂** is the complex-valued propagation constant, dependent on the frequency and on complex-valued refractive index **n̂**.

Propagation of an electromagnetic wave through the dielectric

$$\hat{E}(\omega) = E_0 \exp(i\varphi) = E_0 \exp(i\hat{k}r) = E_0 \exp\left(i\frac{\omega\hat{n}(\omega)}{c}r\right)$$

In air, **n = 1**.

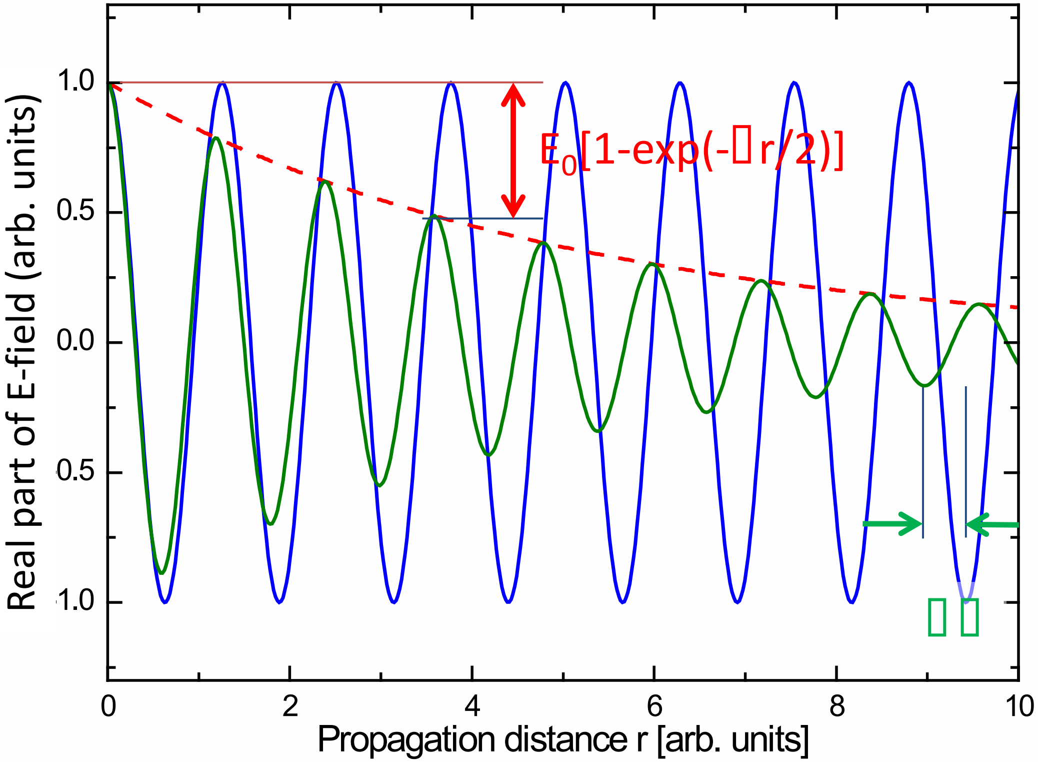


Wave in air.

Propagation of an electromagnetic wave through the dielectric

$$\hat{E}(\omega) = E_0 \exp(i\varphi) = E_0 \exp(i\hat{k}r) = E_0 \exp(i\frac{\omega\hat{n}(\omega)}{c}r)$$

In air, **n = 1**. In dielectric ***n̂ = n + iæ***



$$\hat{E} =$$

$$= E_0 \exp(i\hat{k}r)$$

$$= E_0 \exp\left(\frac{i\omega[n + iæ]}{c}r\right) =$$

$$= E_0 \exp\left(-\frac{\omega æ}{c}r\right)\exp\left(\frac{i\omega n}{c}r\right)$$

$$= \boxed{E_0 \exp(-\alpha r/2)}\boxed{\exp(i\varphi')}$$

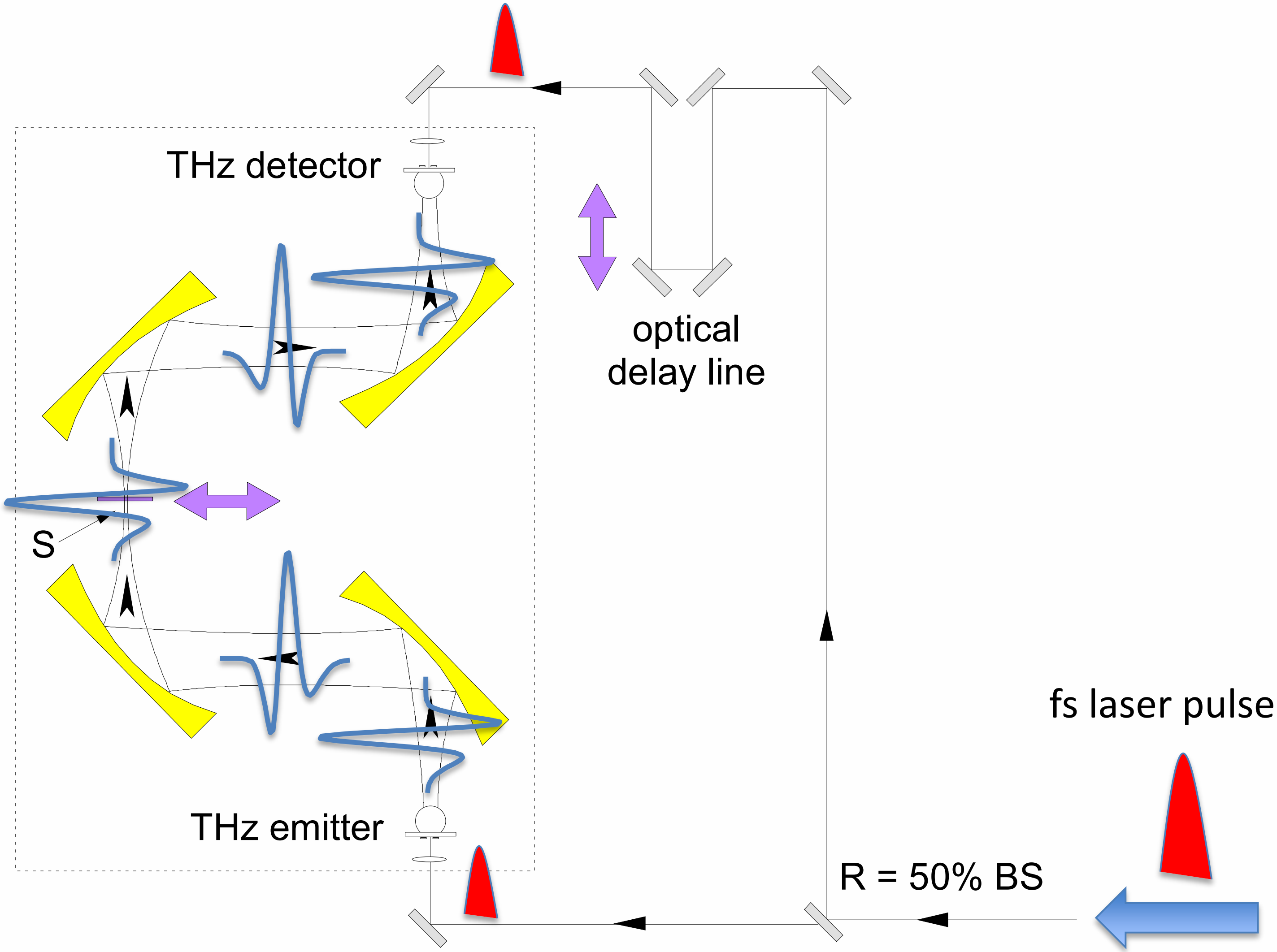
***α =2□ æ/c** – power absorption coefficient of the wave*

***□φ = □ (n-1)r/c** - phase shift in a dielectric compared to air (n=1)*

THz time-domain spectroscopy principle

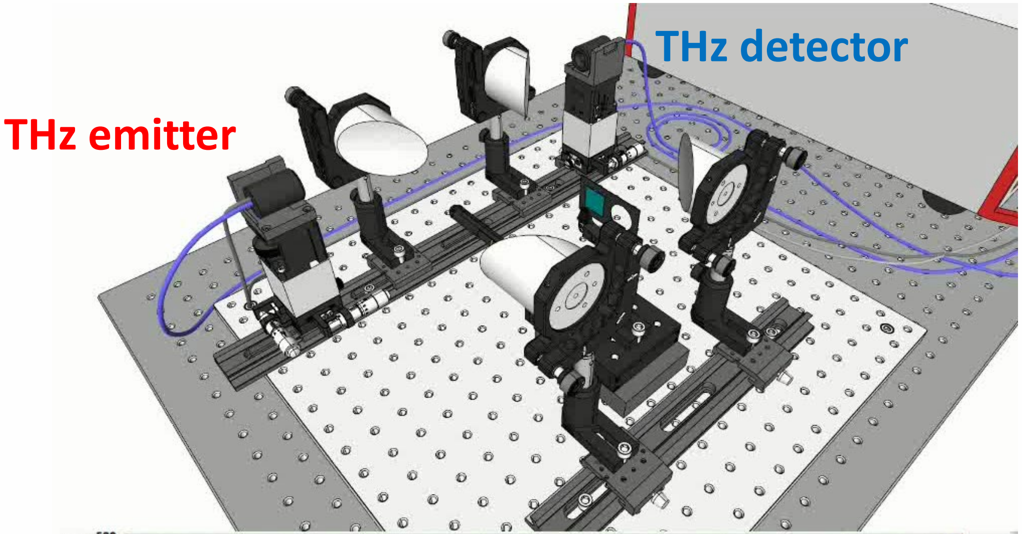
- THz TDS is based on the **directly-measured frequency-dependent amplitude and phase change** of the THz field transmitted through the sample (as compared to some reference)
- **Phase change** at each frequency directly yields **refractive index** at each frequency
- **Amplitude change**, combined with the **knowledge of refractive index**, gives the **absorption coefficient** at each frequency

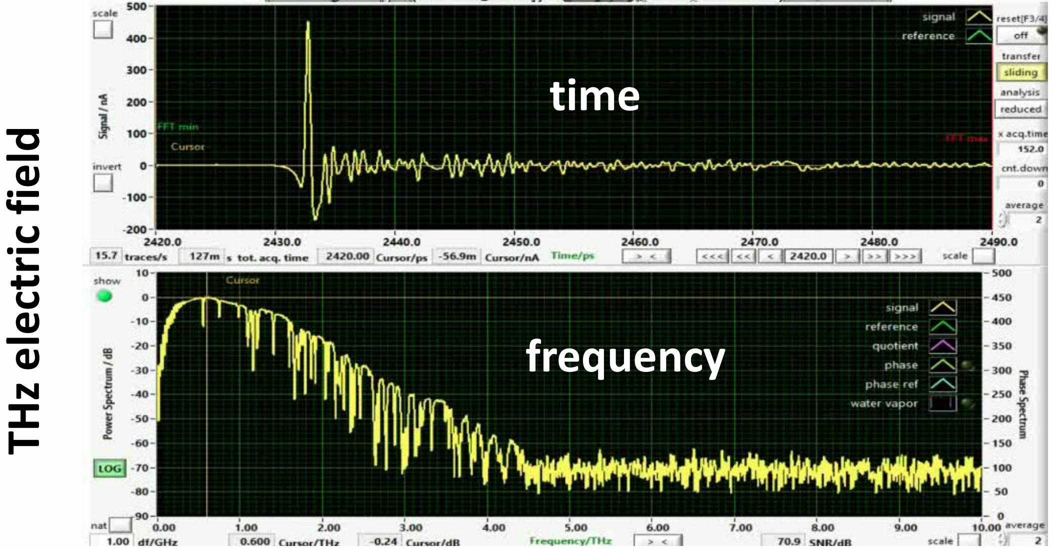
Principle of THz time-domain spectroscopy



THz time-domain spectrometer

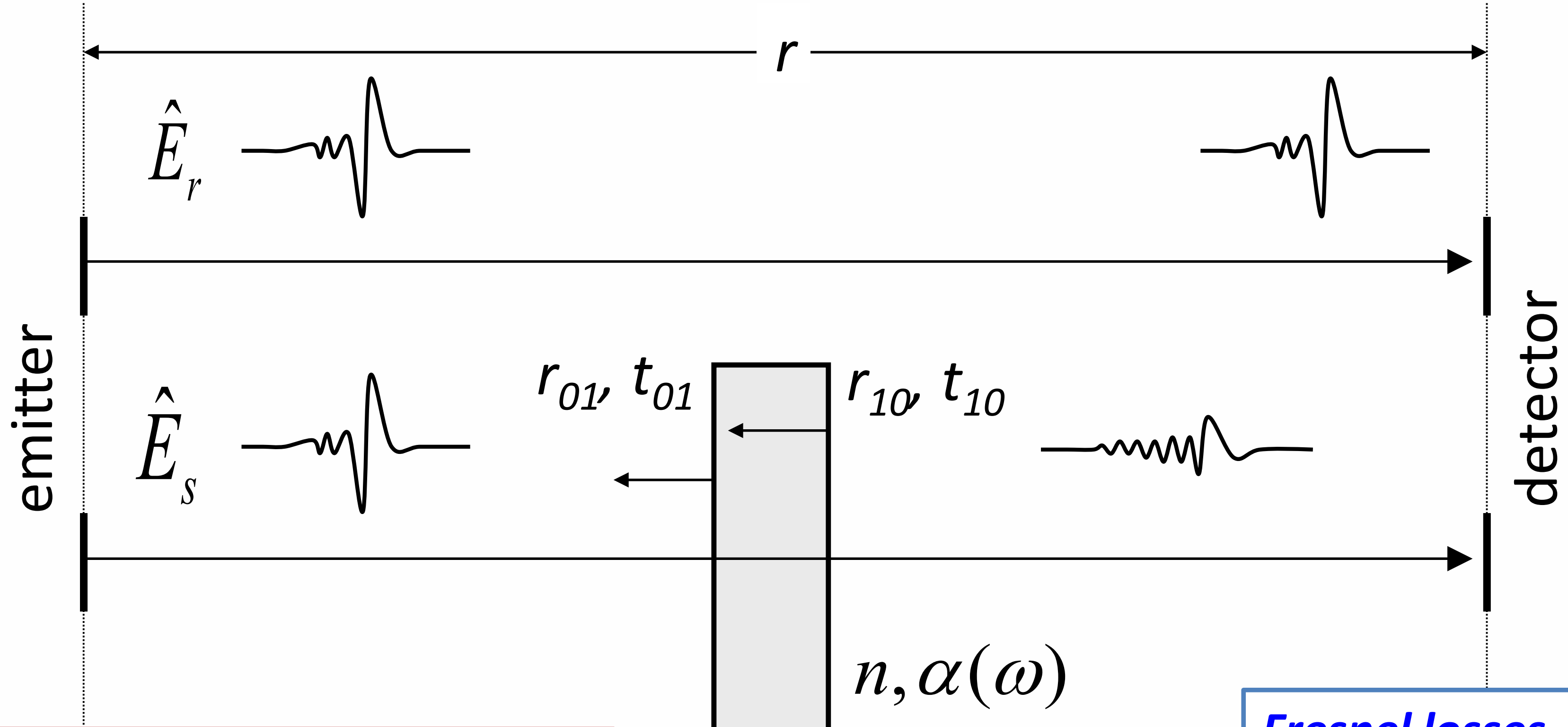
video by Wentao Zhang





THz time-domain spectroscopy

Reference and sample THz fields E(t) and E‘(t)



Phase shift due to *n*

Attenuation due to ▯ and *t(n)*

(consider æ<<*n*)

Fresnel losses

$r_{01} = (1-n)/(1+n)$

$r_{10} = (n-1)/(1+n)$

$t = 1+r$

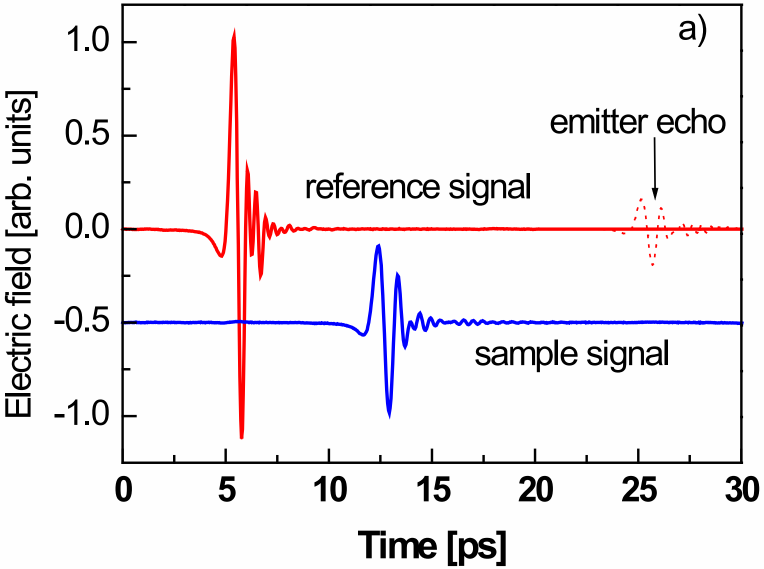
THz time-domain spectroscopy of CdTe at 300 K

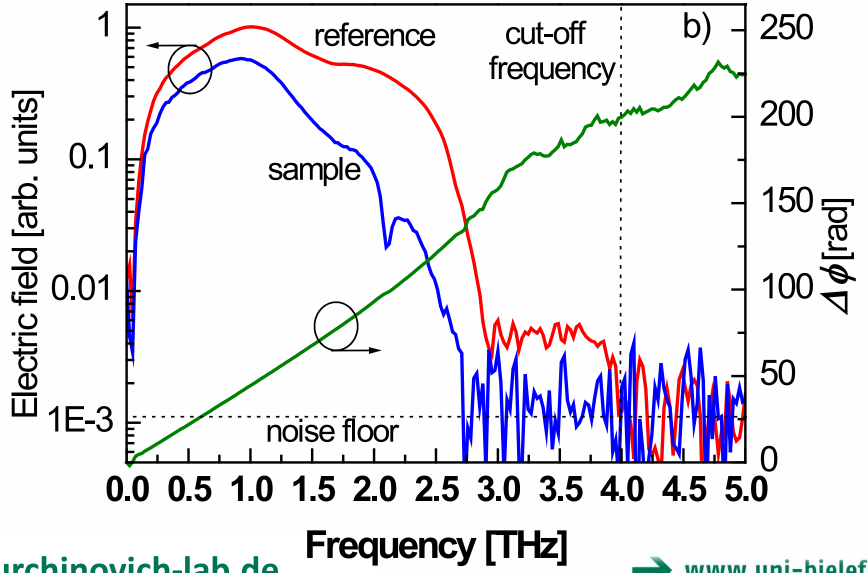
$$\frac{\hat{E}_s}{\hat{E}_r} = \frac{4n}{(1+n)^2} e^{-\frac{\alpha}{2}d} e^{i(n-1)kd} =$$

$$= \frac{E_s}{E_r}\exp[i(\phi_s - \phi_r)]$$

$$n = \frac{\phi_s - \phi_r}{kd} + 1$$

$$\alpha = -\frac{2}{d}\ln\left[\frac{E_s}{E_r}\frac{(1+n)^2}{4n}\right]$$





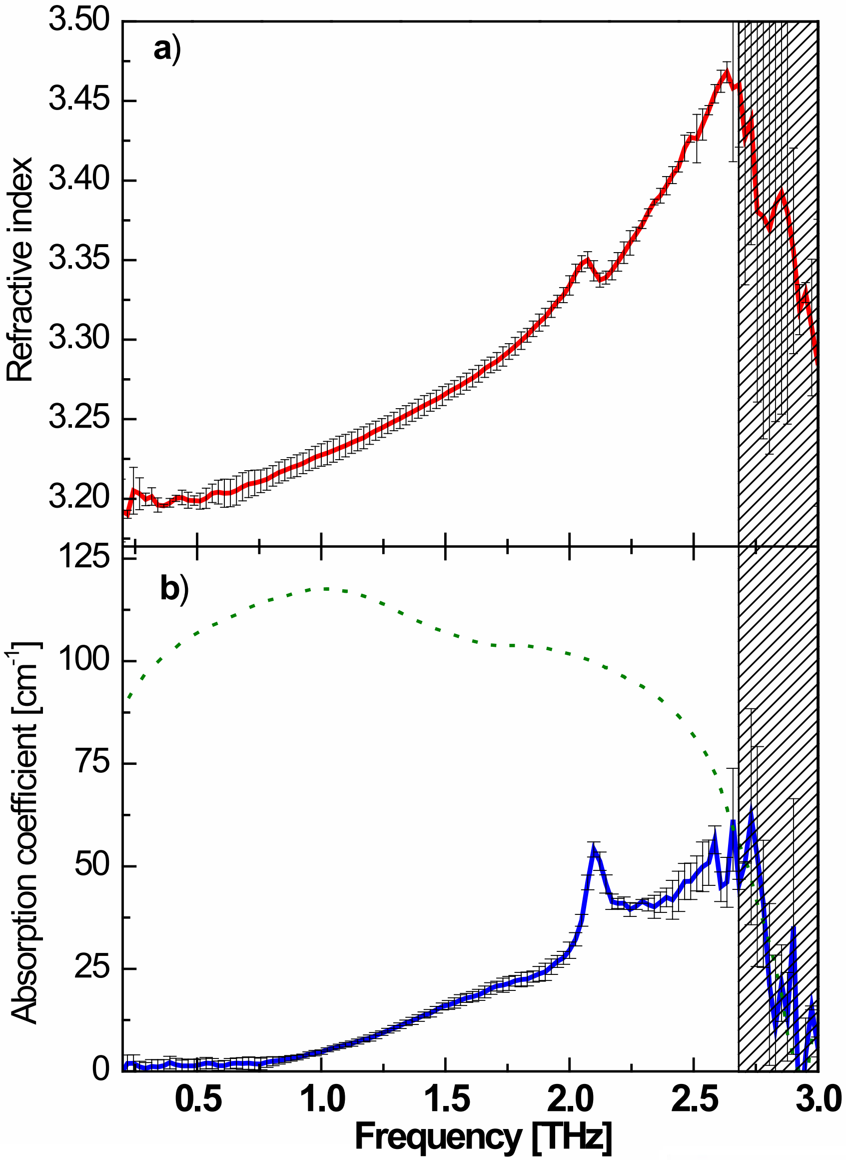
THz time-domain spectroscopy of CdTe at 300 K

strong TO-phonon

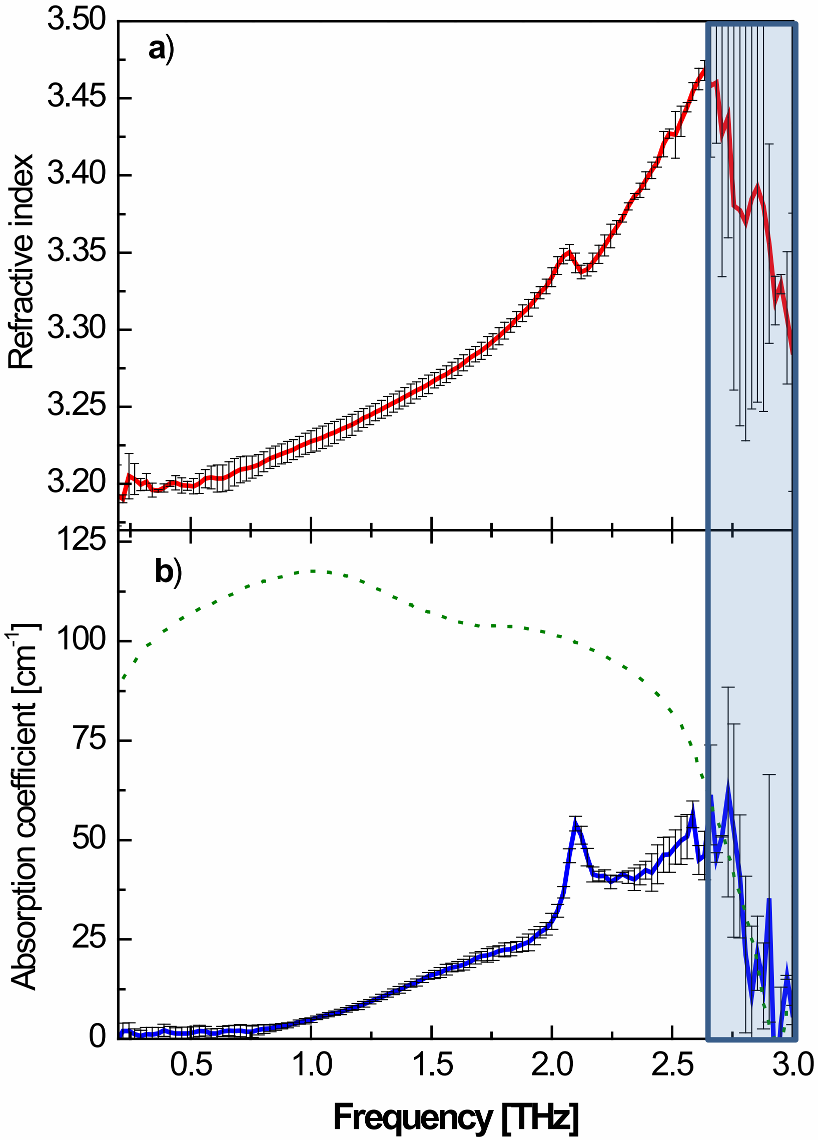
4.3 THz

2TA(X) mode

2.07 THz



Signal to noise is important



$$n(f) = \frac{\varphi_{sam}(f) - \varphi_{ref}(f)}{\frac{2\pi f}{c} d} + 1$$

$$\alpha(f) = -\frac{2}{d} \ln \left[\frac{E_{sam}(f)}{E_{ref}(f)} \frac{[1+n(f)]^2}{4n(f)} \right]$$

Caution:

Signal to noise (S/N) ratio is important, it defines the dynamic range of spectroscopy.

If S/N = 1, then calculated α=0. ➔

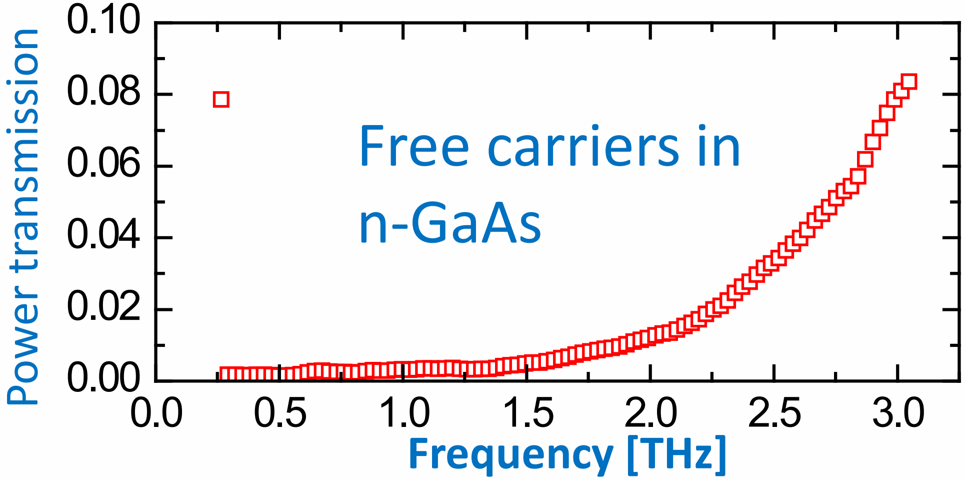
$$\alpha_{max} = \frac{2}{d} \ln \left[S/N \frac{4n}{[1+n]^2} \right]$$

Ref: P. Jepsen and B. Fischer, Opt. Lett. **30**, 29 (2005)

Field vs power measurement

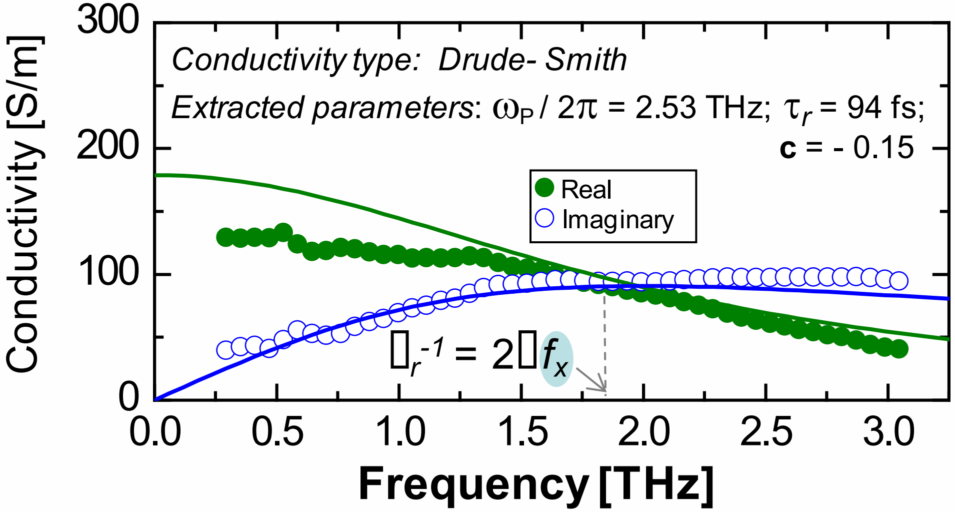
Power transmission:
Extraction of meaningful parameters is difficult and is based on assumption of valid dielectric function

FTIR measures power transmission



Phase resolved field transmission:
Transmitted waveform carries full information about light-matter interaction, i.e. full info on complex dielectric function

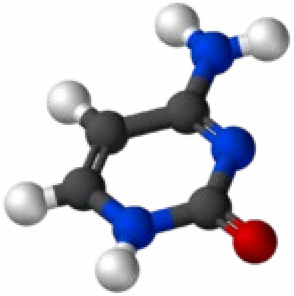
THz TDS measures complex dielectric function



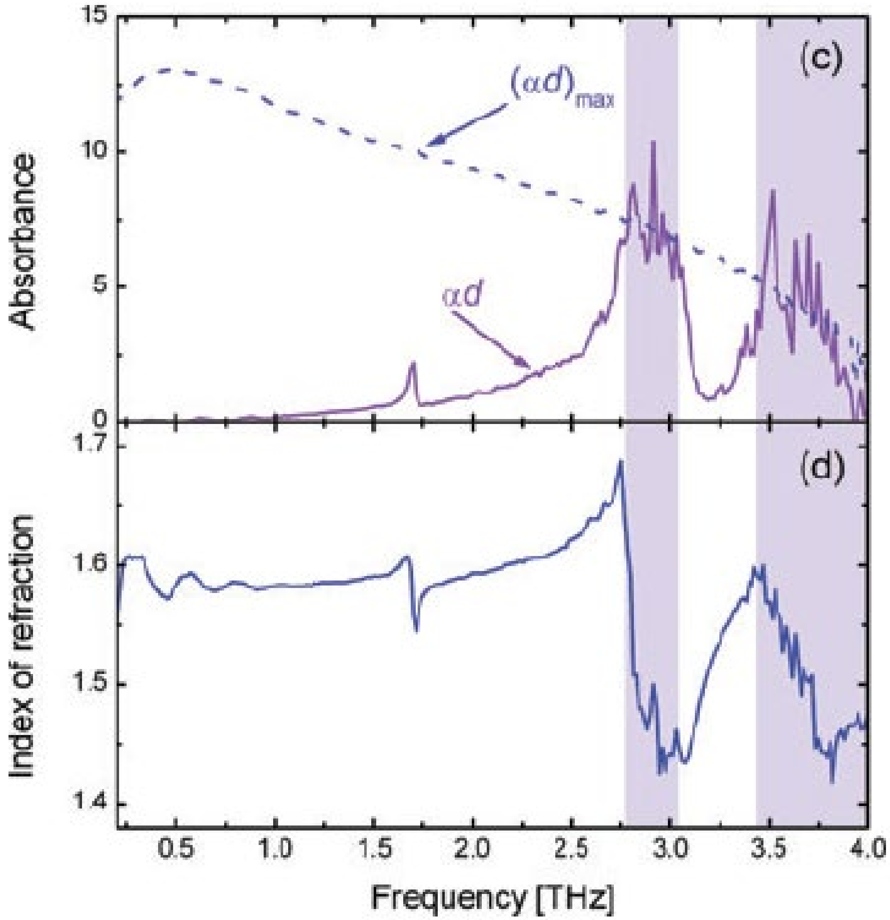
Some examples of THz spectroscopy

Example: vibrational modes in polar molecules

Cytosine at 10 K



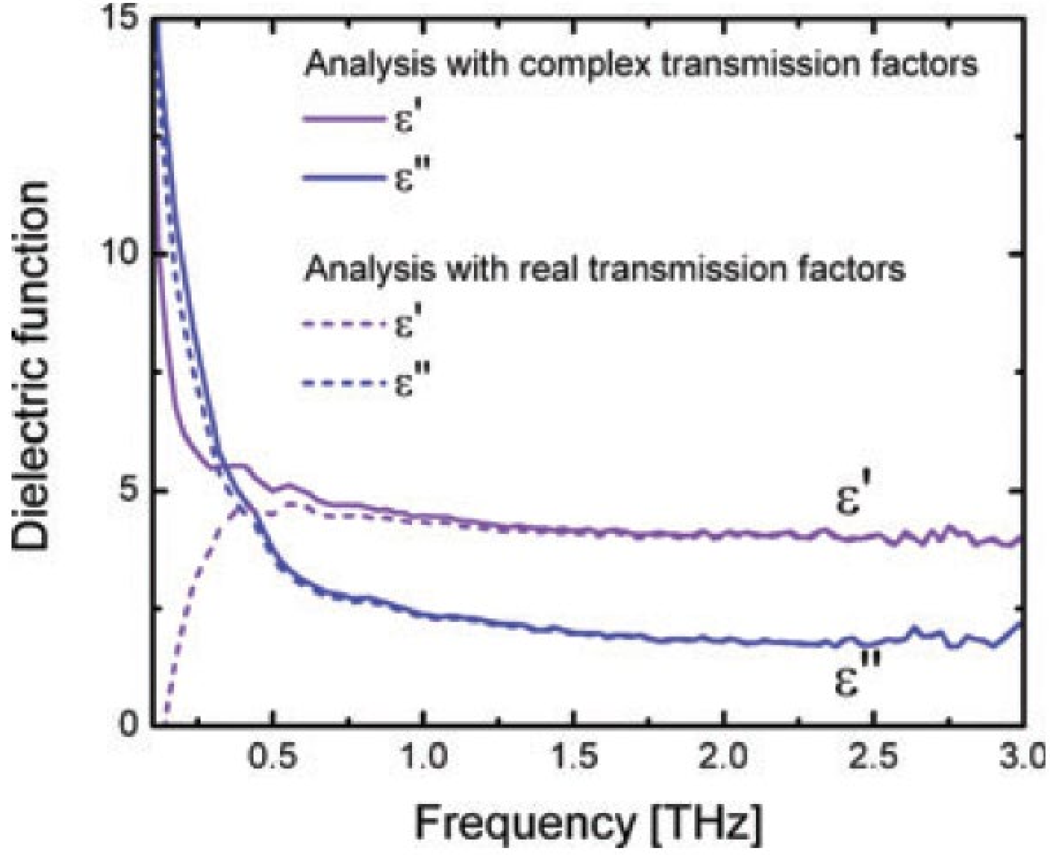
DNA base



P. U. Jepsen et al, LPR (2011)

Example: polar liquids

Water at 300K

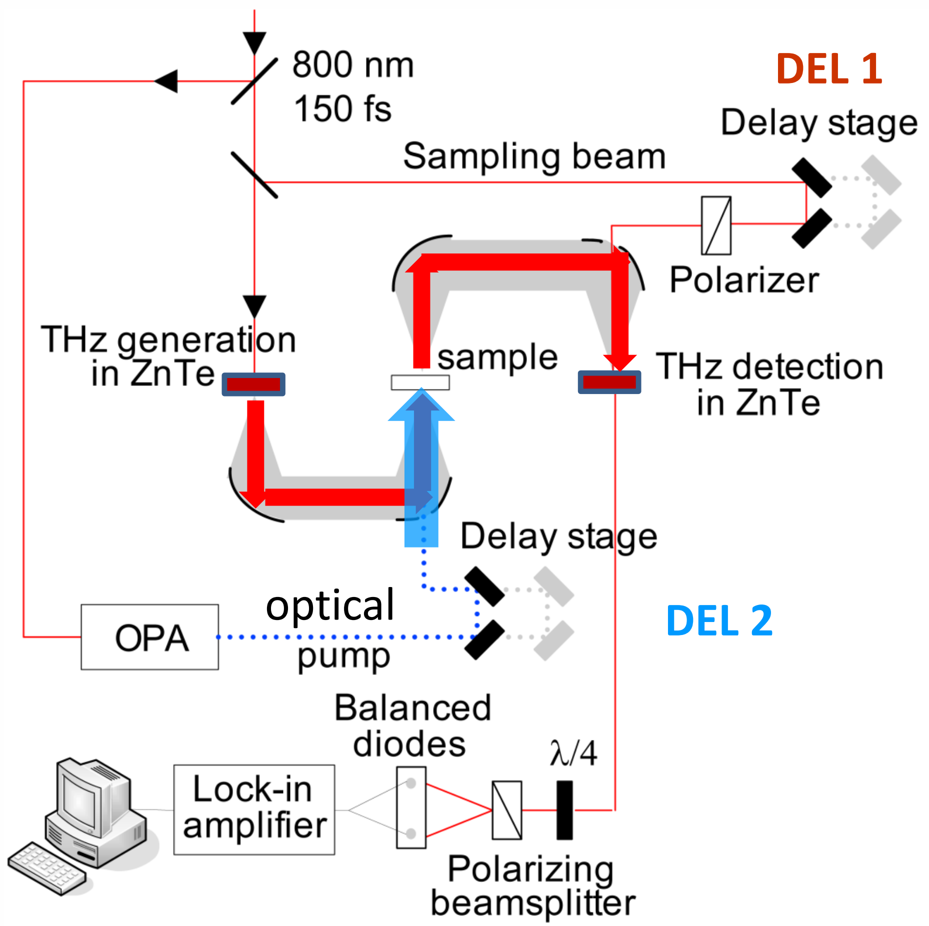


P. U. Jepsen et al, LPR (2011)

THz – TDS summary

- In linear regime, it is essentially a **quasi-static measurement.** We use the ultrafast time resolution to **sample the field of a THz pulse**, to get access to its **complex frequency spectum**.
- In this sense it is similar to FTIR, although the **spectroscopic info provided by TDS** is comprehensive (**complex dielectric f-n** vs just a power transmission spectrum)
- For the **THz mesurements of dynamic processes**, the sample must be stimulated – e.g. using **pump-probe arrangement .** Here, we profit from a short duration of a THz pulse.

Optical pump – THz probe spectoscopy



Joep Pijpers, PhD thesis, AMOLF

The setup consists of:

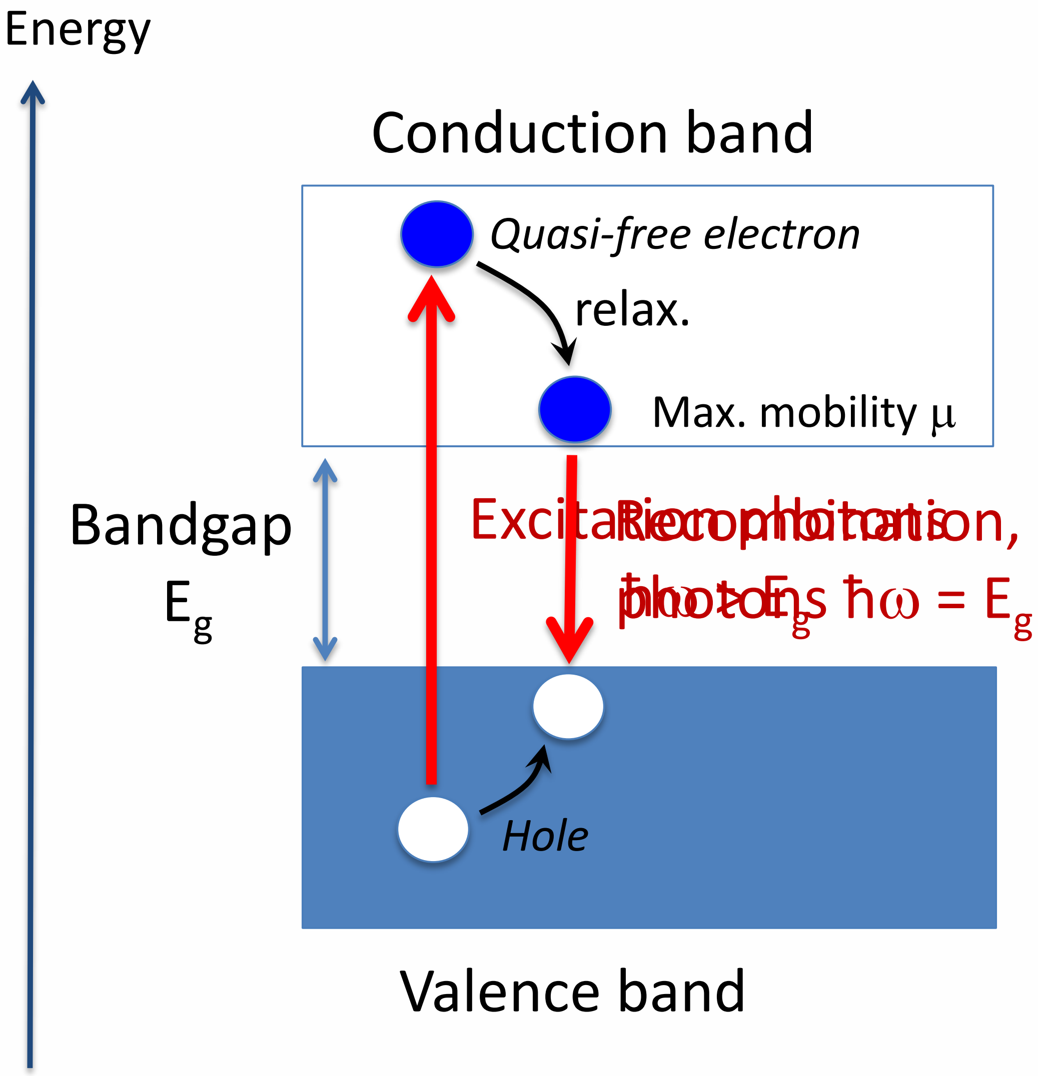
1) **THz TDS**
2) **Optical pump arm**

It has 2 delays:

DEL1 – scanning the gating beam for sampling of a THz waveform (gives THz probe spectrum)

DEL2 – for scanning the optical pump delay

Optical pump – THz probe on a semicondcuctor: what info



Energy

Conduction band

Quasi-free electron

relax.

Max. mobility μ

Bandgap E_g

Excitation photons $\hbar\omega > E_g$

Recombination, photons $\hbar\omega = E_g$

Hole

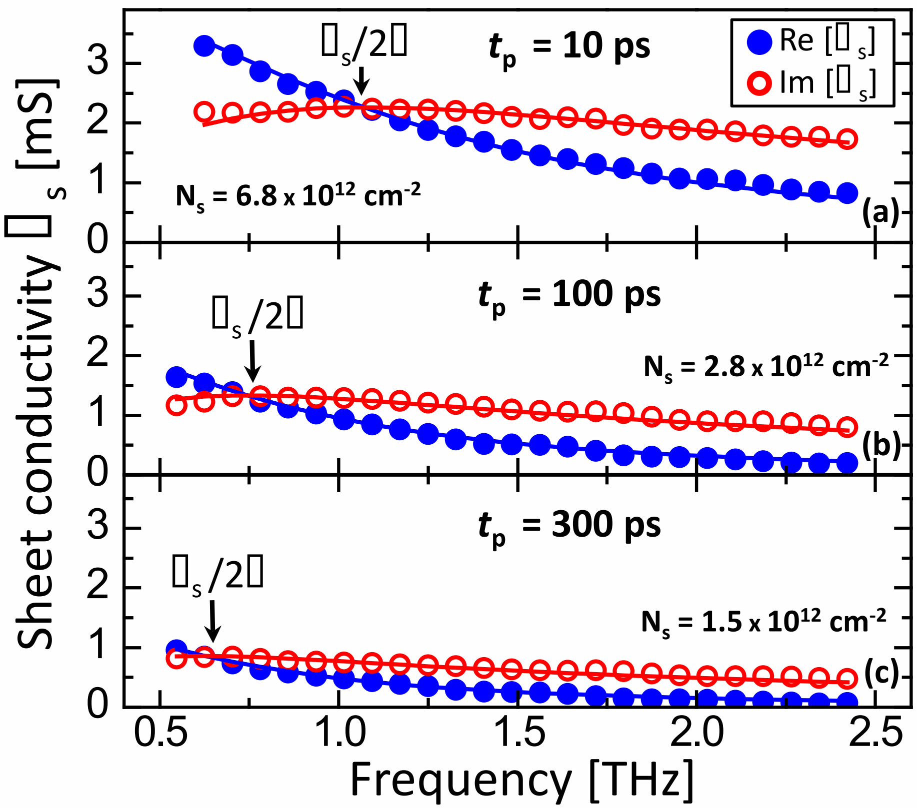
Valence band

What info:

Time-dependent conductivity
$\sigma(t) = \mu(t)N(t)e$

Mobility **$\mu = e\tau/m^*$**
τ - electron momentum scattering time
N – (quasi-free) carrier density

Electron transport: THz (photo-)conductivity



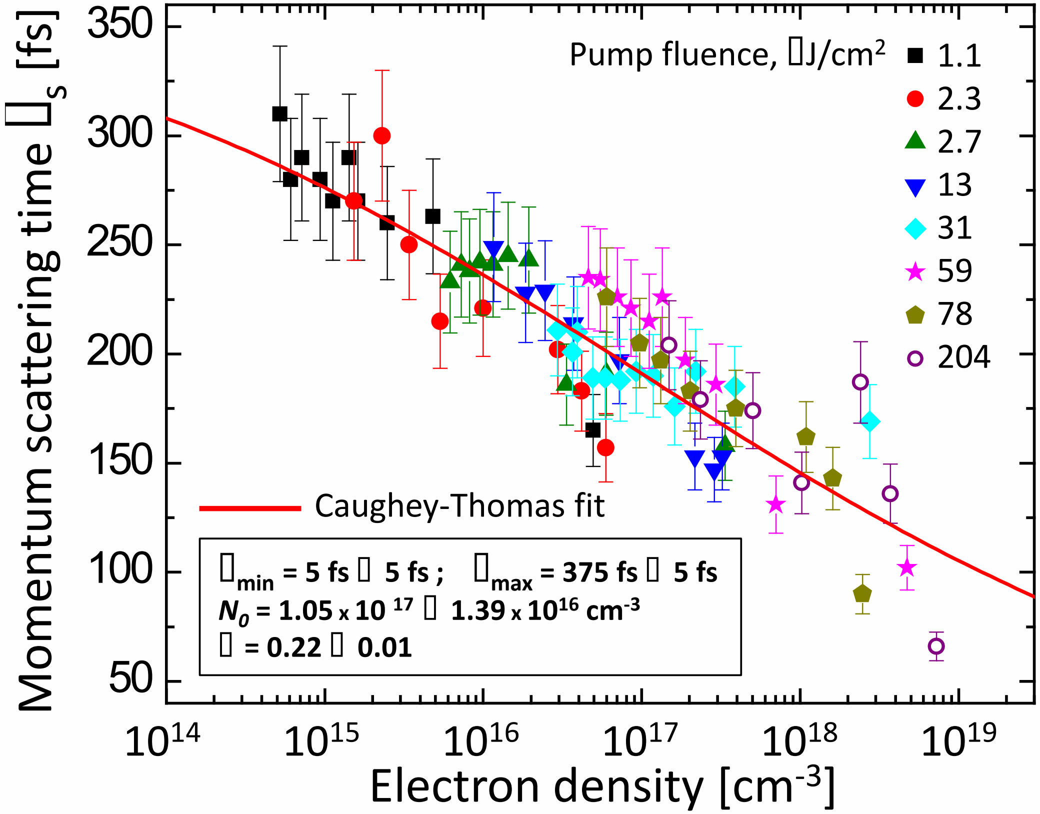
Optical pump – THz probe on GaAs:

Taking conductivity snapshot, at any pump-probe delay.

Directly measure *carrier density N* and electron momentum *relaxation time τ*

$$\hat{\sigma}_{Drude} = \frac{\sigma_{dc}}{1-i\omega\tau}; \quad \sigma_{dc} = e^2 N \tau / m$$

Fine details of transport dynamics



sub-ps time tag for all data points

Photoexcited GaAs:

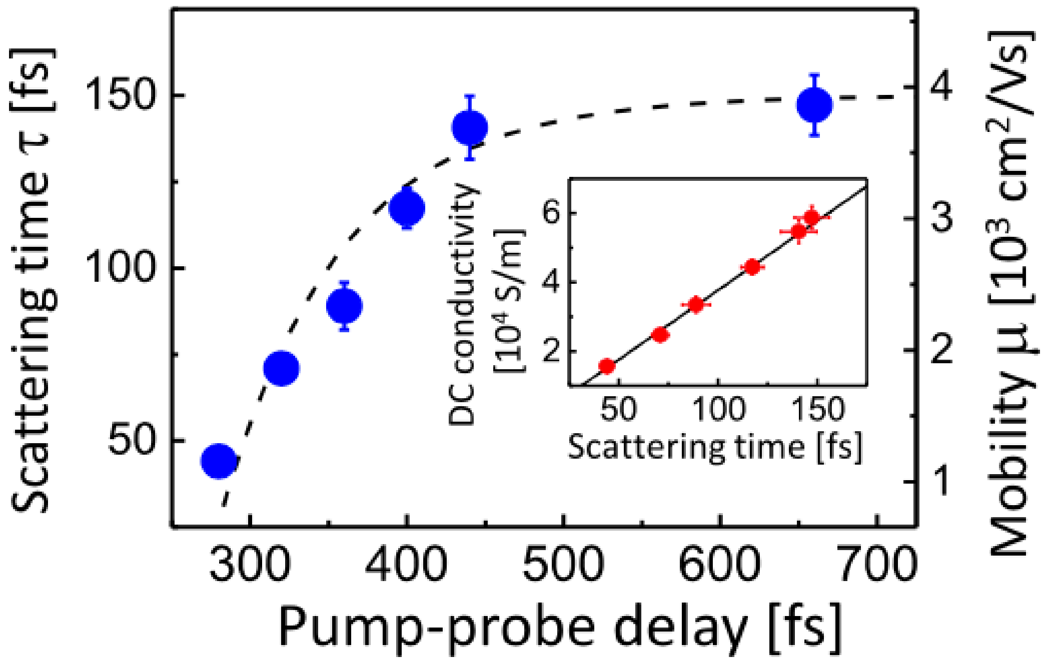
Density-dependent electron scattering time measured over 4 decades of carrier density.

e-h, e-ph, and e-defect scattering enhanced via phase-space filling

Mics, DT et al., APL **102**, 231120 (2013)

Observing the initial buildup of electron mobility with sub-40 fs time resolution

First instants of electronic conduction in GaAs right after the photoexcitation

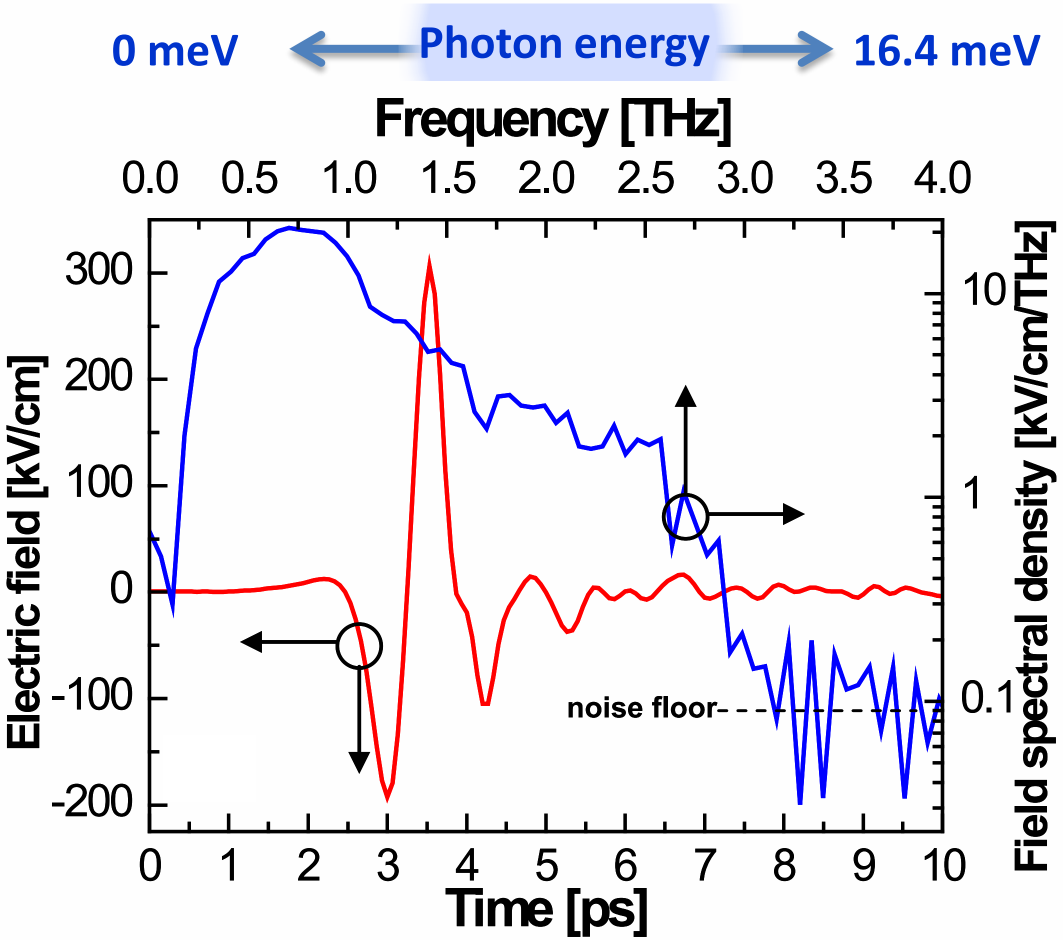


Current becomes time-dependent because of time-dependent mobility

$$j(t) = \sigma(t)E = \mu(t)N(t)eE$$

DT, D'Angelo and Bonn, APL **110**, 121102 (2017)

THz single-cycle nonlinear optics



TPFP optical rectification in lithium niobate

Inherently CEO stable

Small photon energy:

1 THz = 4.1 meV

Large ponderomotive potential

$$U_p = \frac{e^2 E^2}{4 m \omega^2}$$

E.g.: **GaAs, *m* = 0.063 m_0**

1 THz, 100 kV/cm, **U_p = 1.8 eV**

Semiconductor with free carriers at THz frequencies: Drude plasma model

$$\hat{\varepsilon}(\omega) = (n + i\alpha c/2\omega)^2 = \varepsilon_\infty - \omega_p^2/(\omega^2 - i\omega/\tau_r)$$

$$\boxed{\omega_p = (Ne^2/\epsilon_0 m)^{1/2}}$$

$$\hat{\varepsilon} = \varepsilon_\infty + \frac{i\,\hat{\sigma}}{\varepsilon_0\,\omega}$$

Route to THz NLO: change in **plasma frequency** will lead to change in **absorption** and **index:** $\omega_p = 0$ ➔ $\alpha = 0$, $n = \varepsilon_\infty^{1/2}$

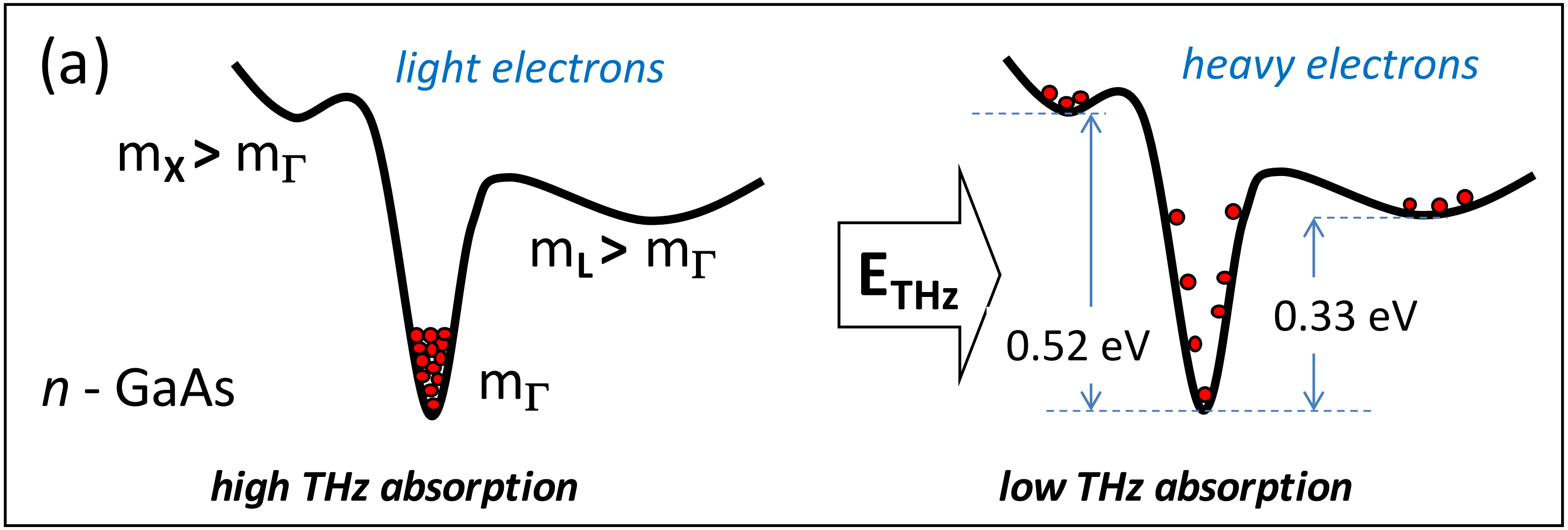
One can manipulate the density **N** and/or effective mass **m**

Mechanism of THz NLO in semiconductors

Side valley population

in the **ponderomotive potential** of a THz pulse:

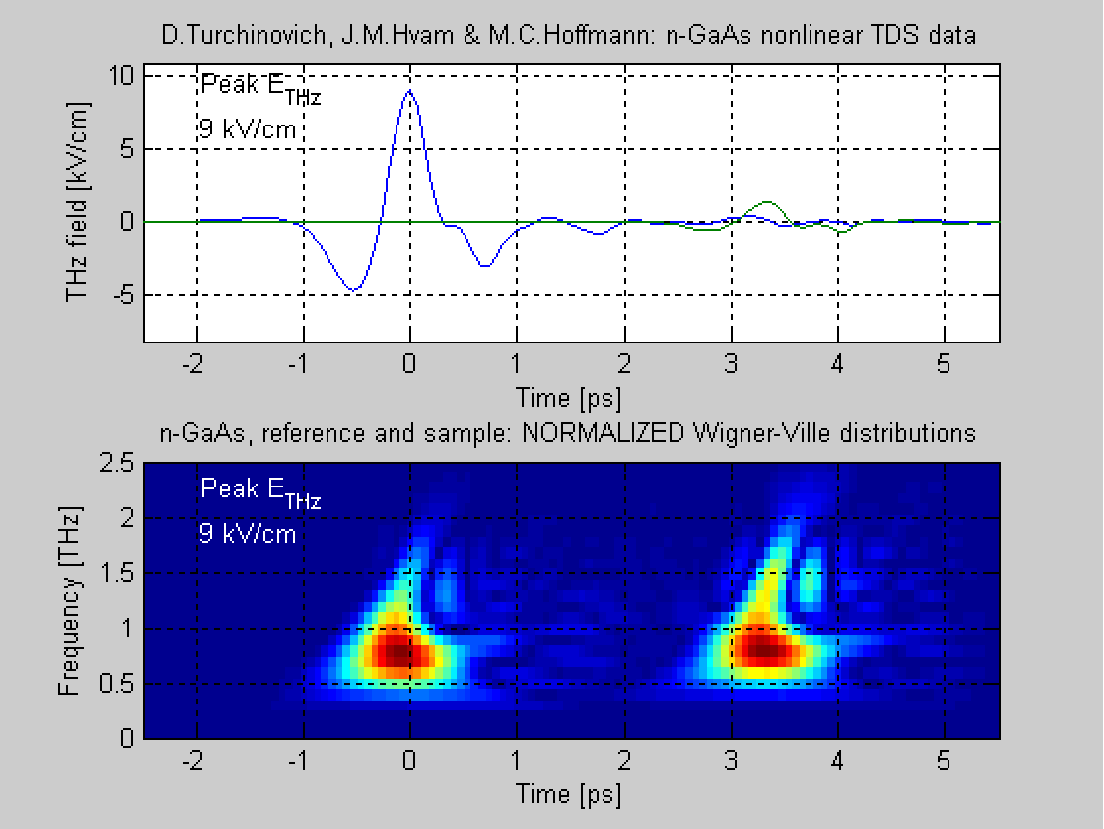
increase of effective mass ➔ change of dielectric function



Turchinovich, Hvam, and Hoffmann, PRB **85**, 201304R (2012)

Single-cycle nonlinear optics live

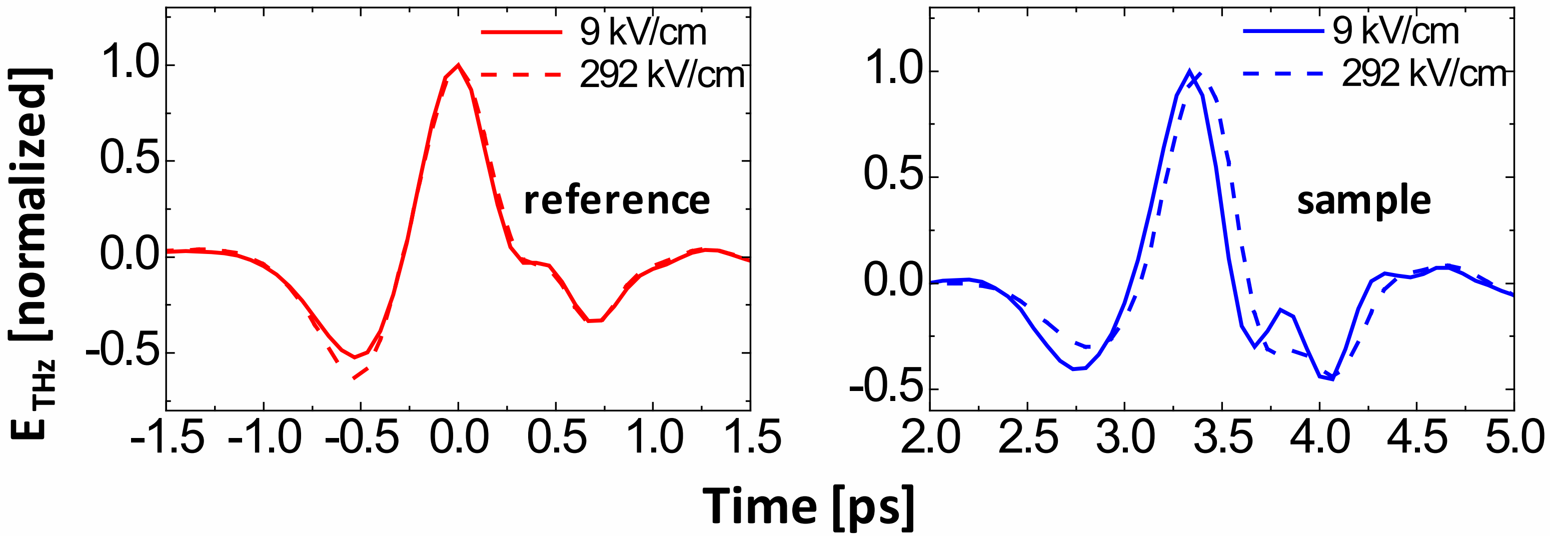
Time-domain THz signals



Time- and frequency- domain spectrograms

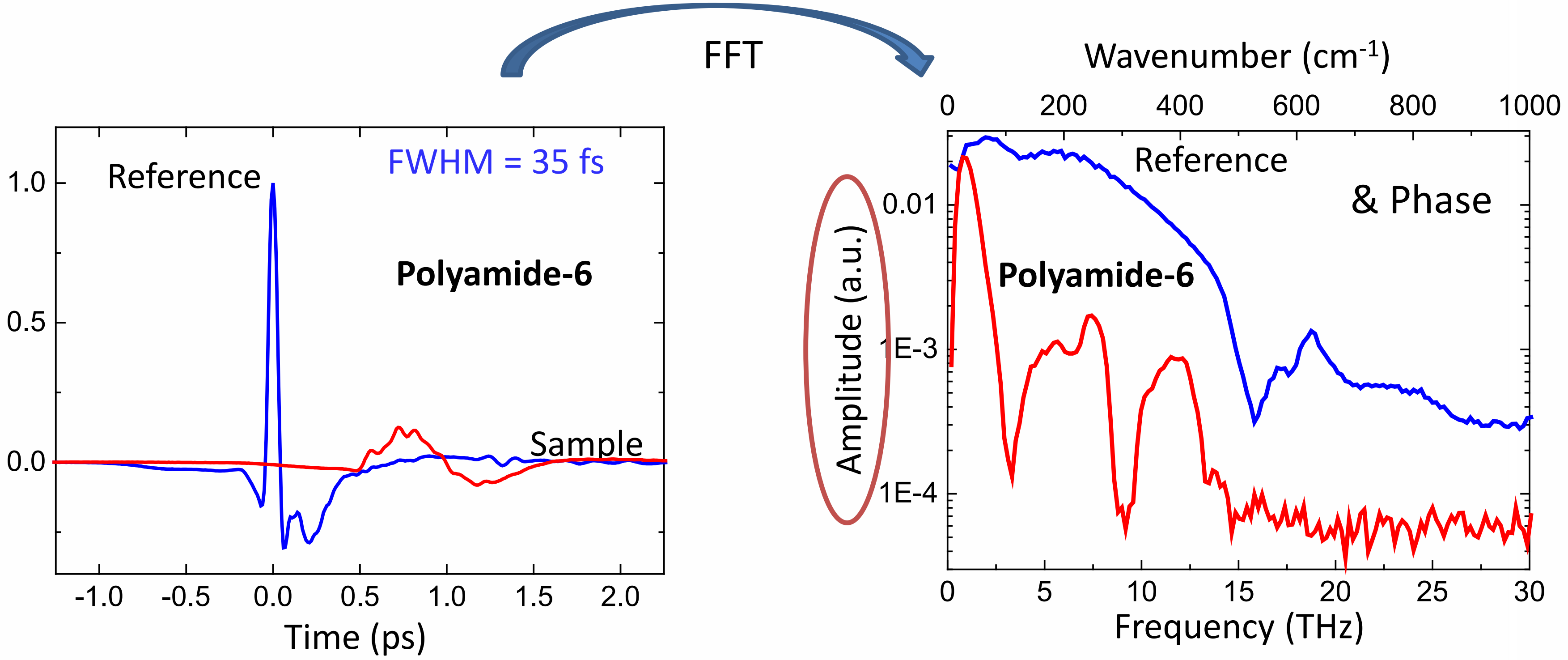
Turchinovich, Hvam, and Hoffmann, PRB **85**, 201304R (2012)

Zoom-in: single-cycle SPM



Turchinovich, Hvam, and Hoffmann, PRB **85**, 201304R (2012)

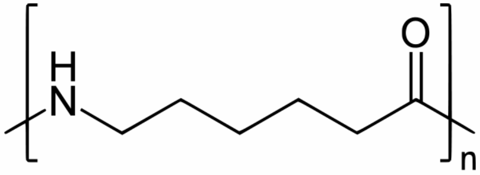
THz probing of polar phonons: coupling of lightwaves to lattice ions

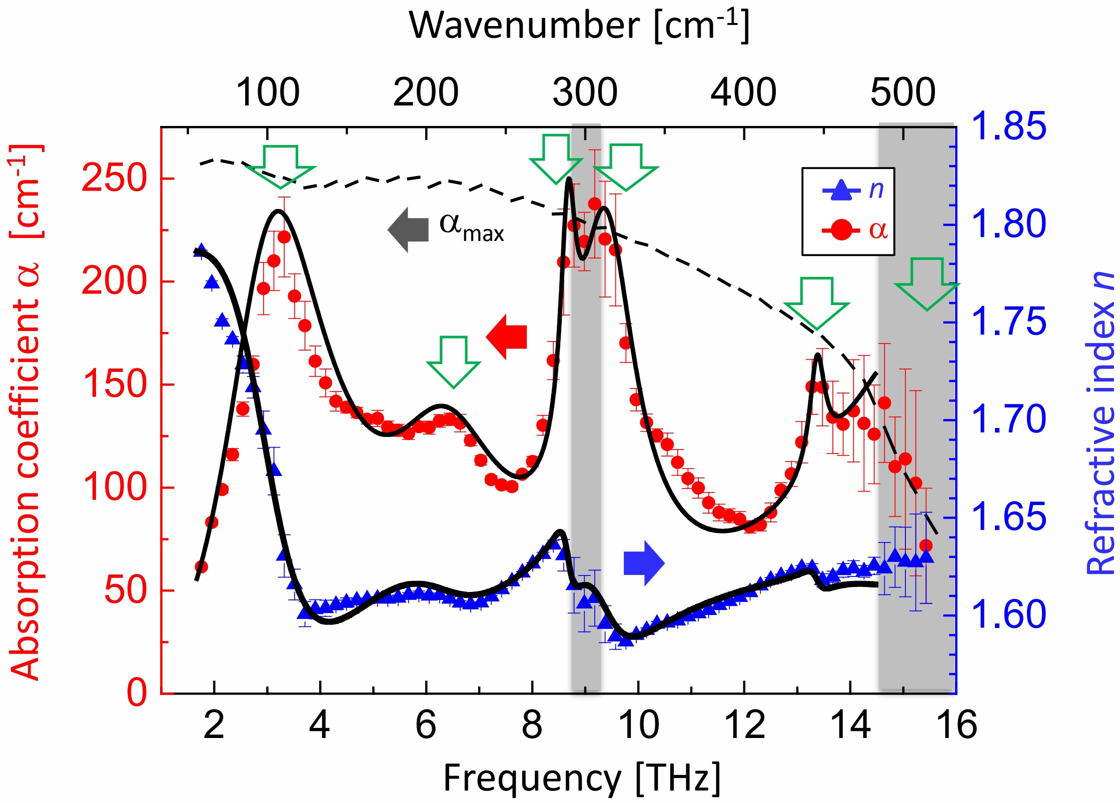


Absorption coefficient $\alpha(\omega)$ & Refractive index $n(\omega)$

Polar lattice vibration in Polyamide-6

Polyamide-6 = Nylon-6

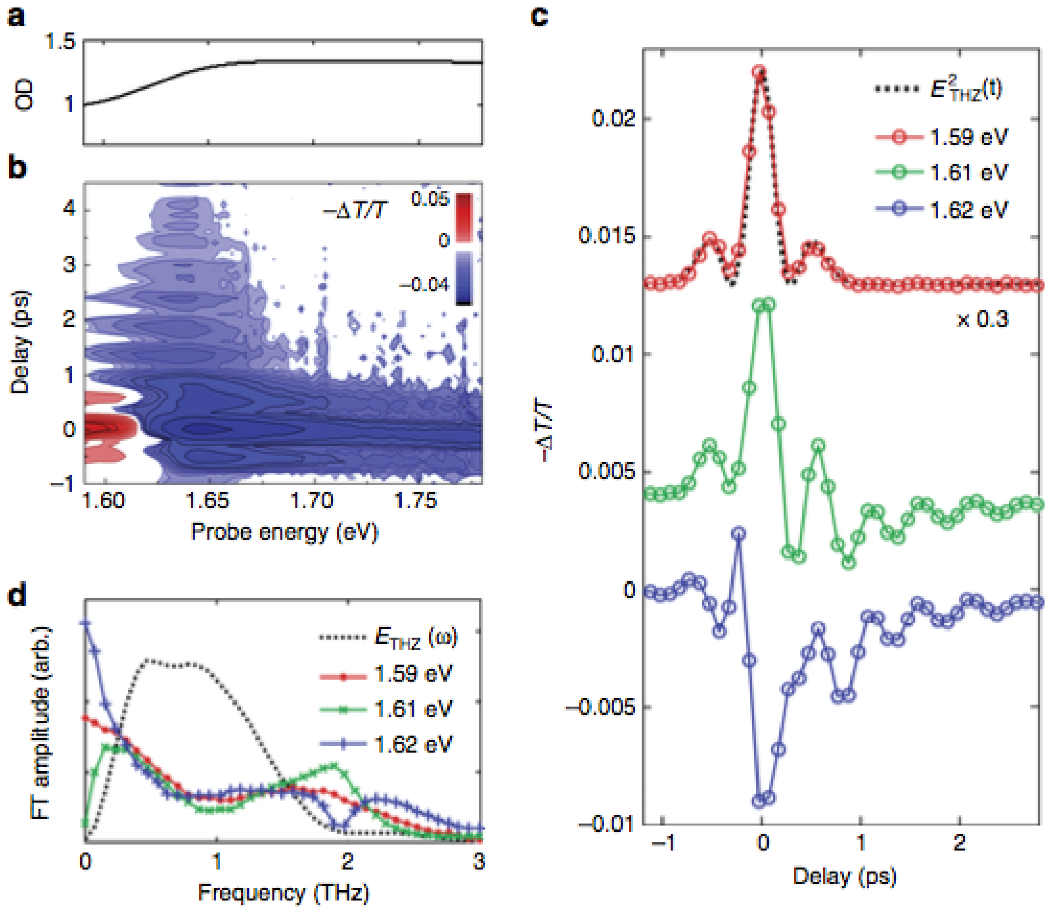




D'Angelo, DT et al., Opt. Express **22**, 12475 (2014)

THz pump – white light optical probe: mode-specific phonon-bandgap coupling in MAPI perovskite

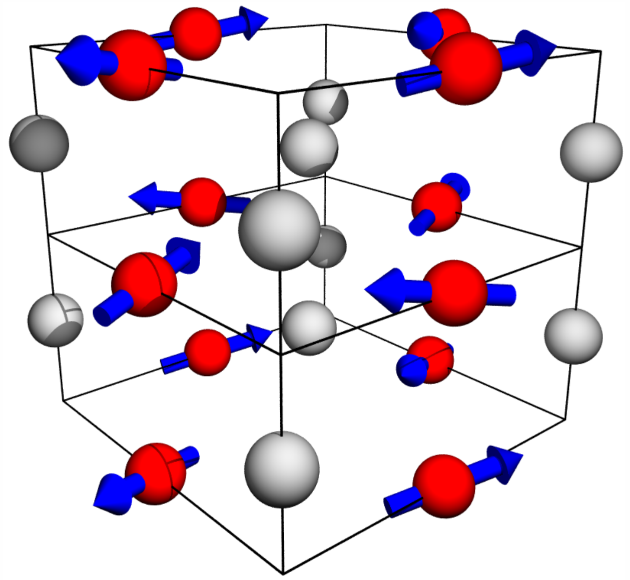
Direct **THz excitation of polar lattice** results in the **oscillations of bandgap energy** at the **phonon frequency**



H. Kim, DT et al., Nature Commun **8**, 687 (2017)

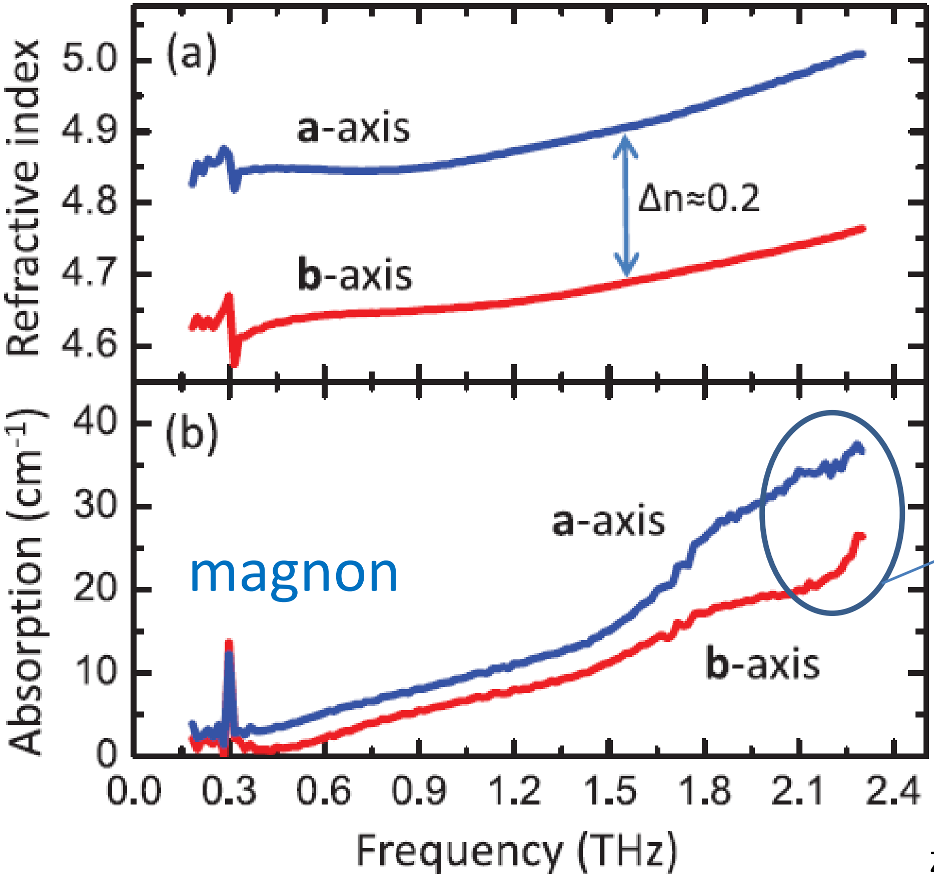
THz spin effects

THz spin waves in $RFeO_3$



Two Fe sublattices result in **canted antiferromagnetic structure**, with two spin modes: **quasi-ferromagnetic** (FM) and **quasi-antiferromagnetic** (AFM) with frequencies in **sub-THz** range

Magnons and phonons in one spectrum (via coupling of the B- and E-fields of a THz pulse)



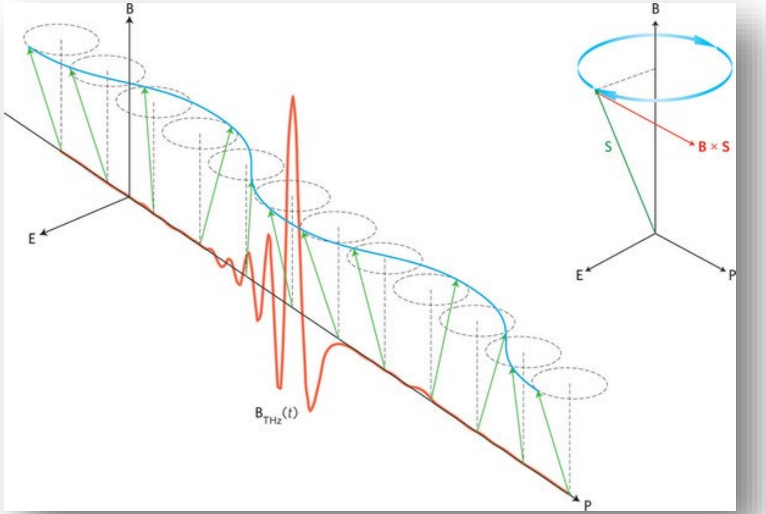
magnon

Wing of a high-frequency phonon

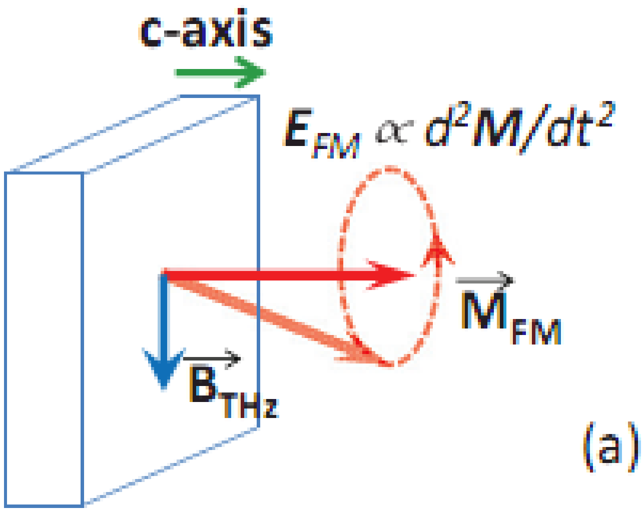
Z. Jin et al, PRB **87**, 094422 (2013)

Transmitted THz field carries all info on the dielectric function

Impulsive excitation of spin waves with the B-field component of a THz pulse



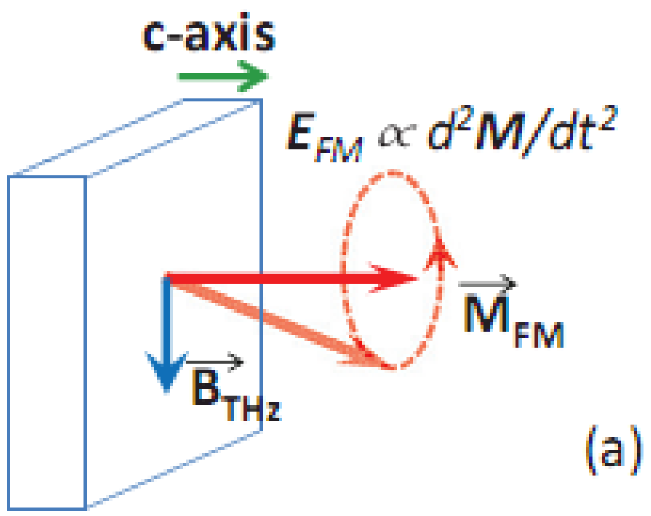
$$T \propto M \times B_{THz}$$

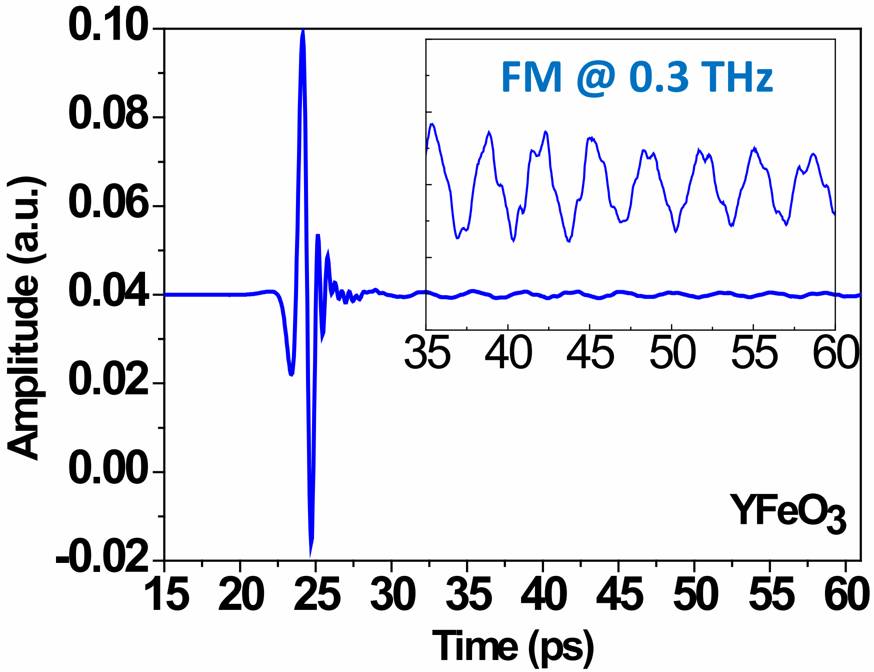


T. Kampfrath et al, Nature Photon. **5**, 31 (2011)
J. Kono, Nature Photon. **5**, 5 (2011)

THz spin waves in $RFe0_3$

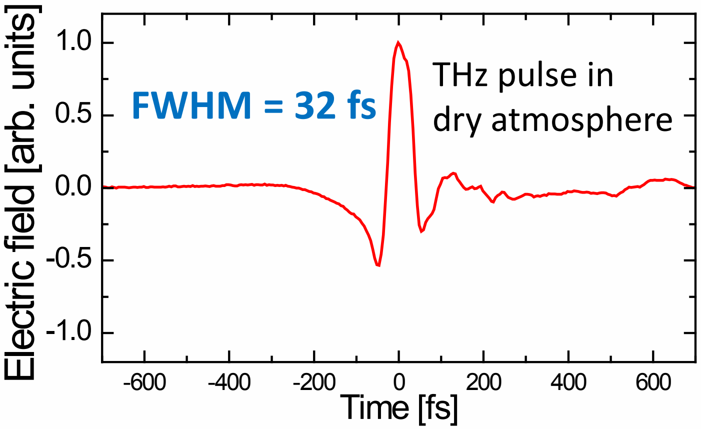
Precessing magnetization **re-emits** circularly-polarized electromagnetic **radiation at Larmor frequency** via free-induction decay

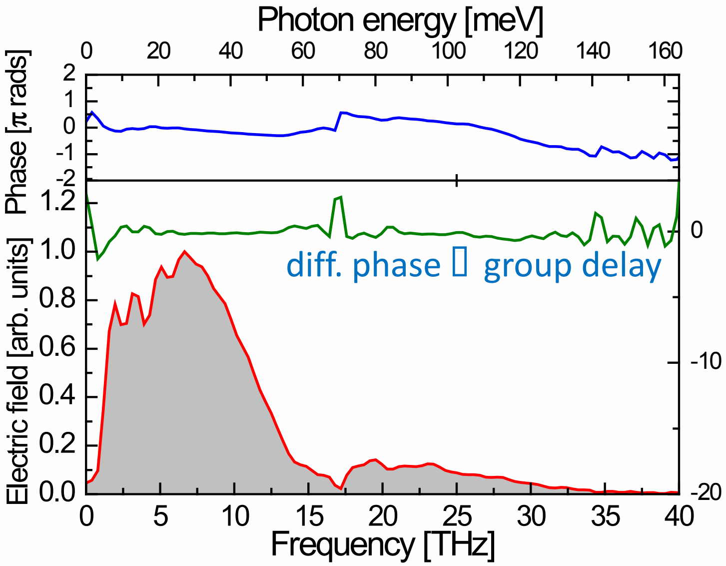




Jin, DT et al., PRB **87**, 094422 (2013)

Ultrabroadband THz spectroscopy





THz air-photonics:

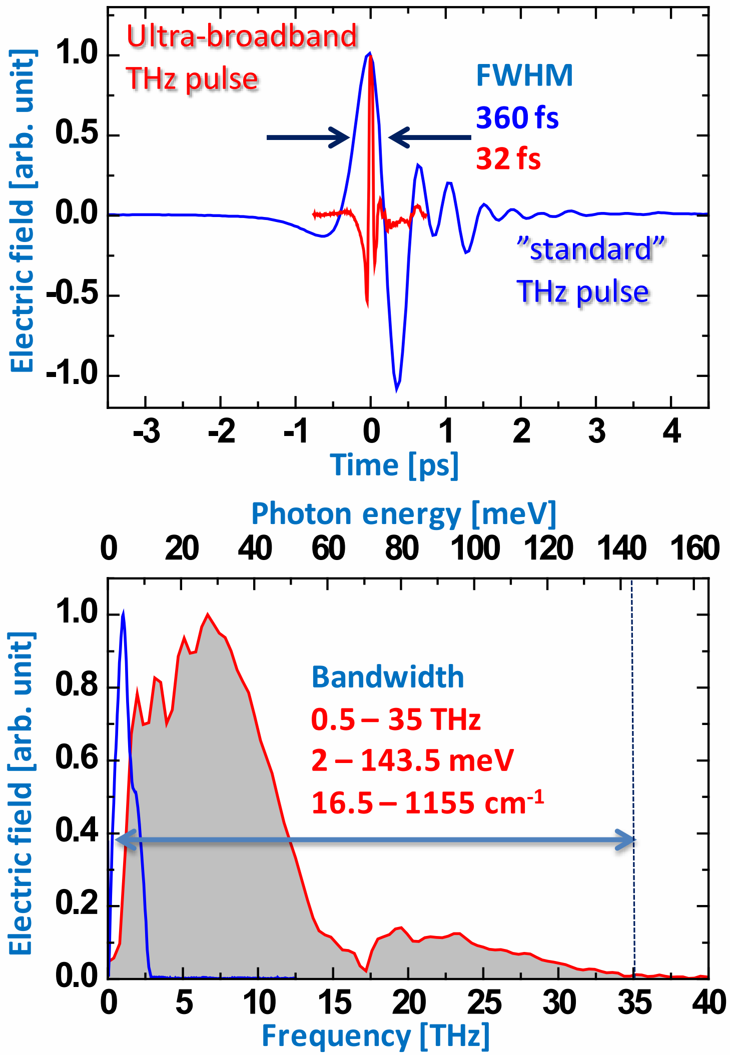
no NL crystals, no phasematching problems

THz generation in air via nonlinear mixing of shaped laser fields in ionized air plasma.

Detection in air via mixing of THz and laser fields.

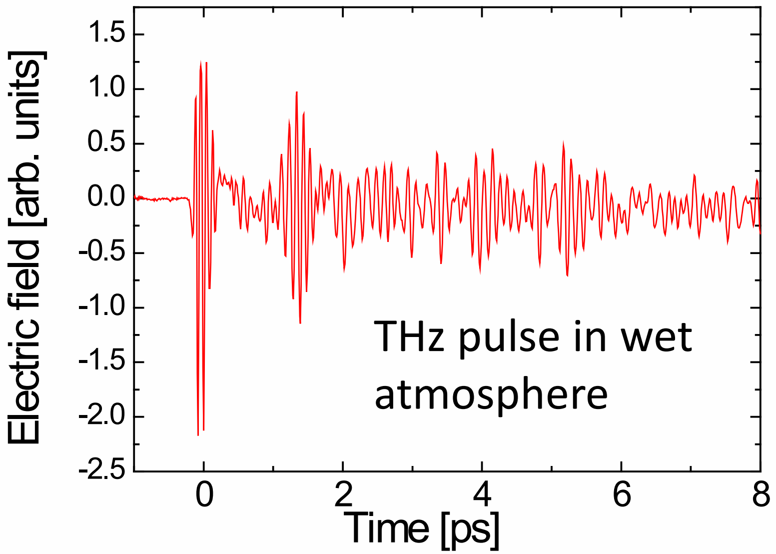
F. D'Angelo and D. Turchinovich

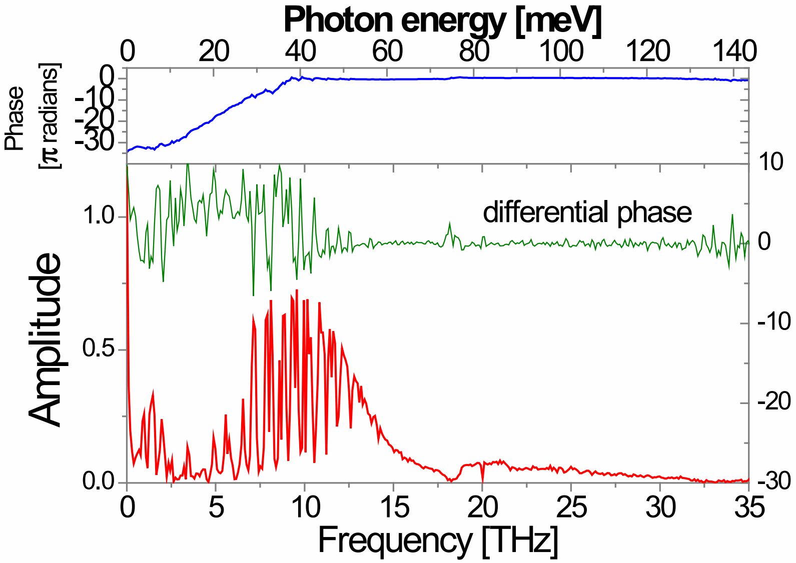
Spectroscopy beyond conventional bandwidth



F. D'Angelo and D. Turchinovich

THz interaction with atmospheric water: rotational lines spectroscopy





F. D’Angelo and D. Turchinovich

Thank you