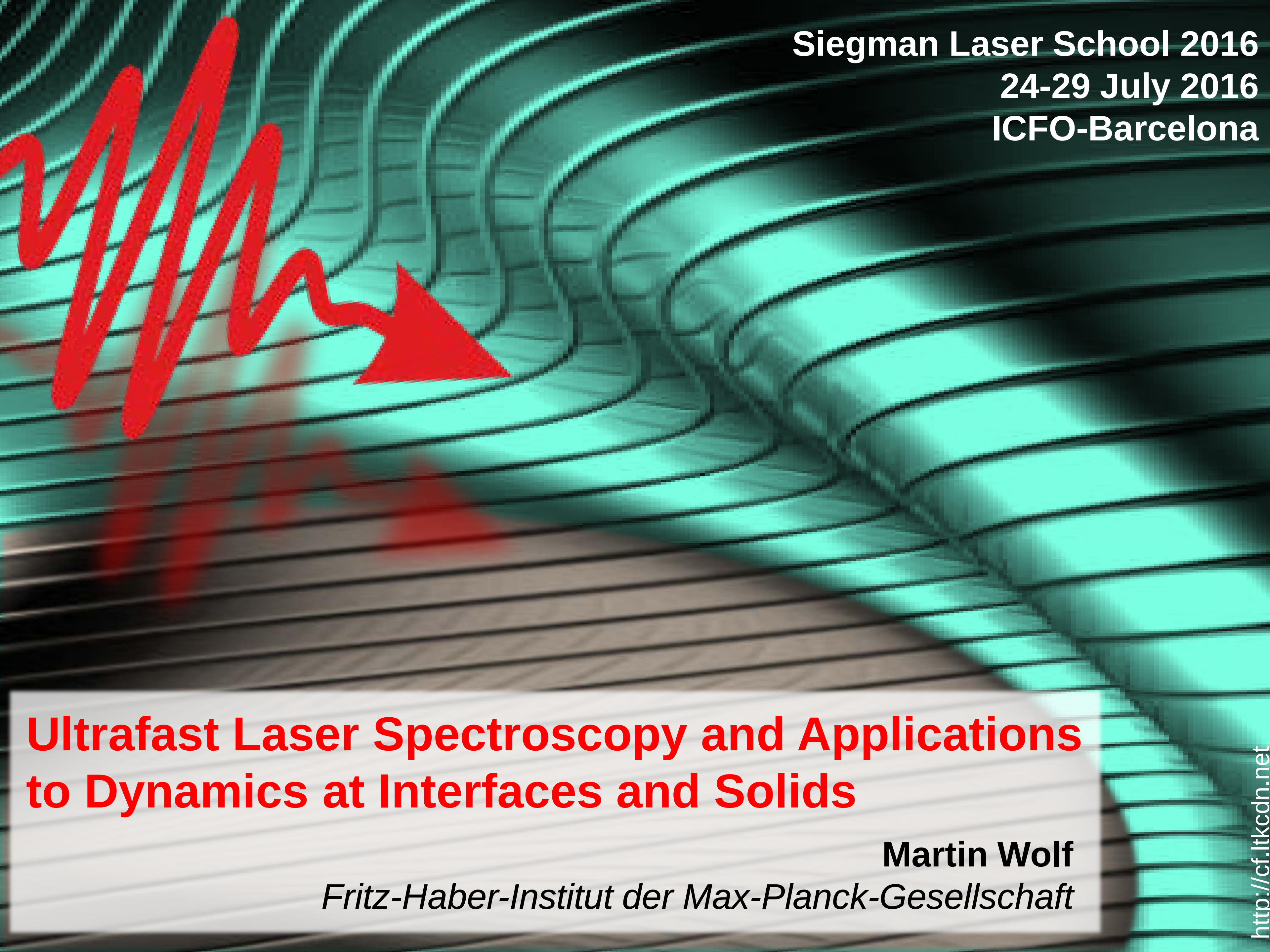
Siegman Laser School 2016
24-29 July 2016
ICFO-Barcelona



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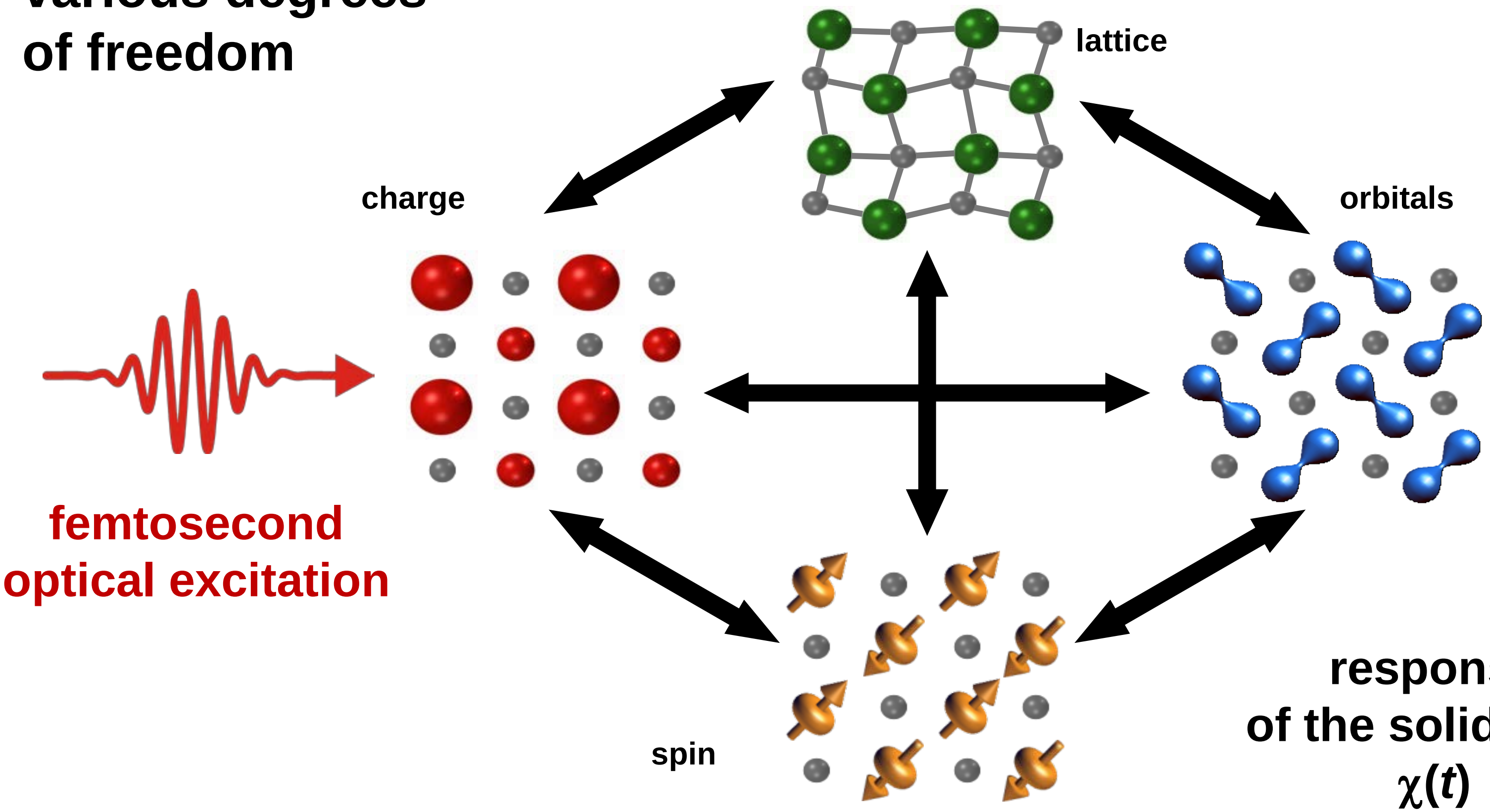
Ultrafast Laser Spectroscopy and Applications to Dynamics at Interfaces and Solids

Martin Wolf
Fritz-Haber-Institut der Max-Planck-Gesellschaft

Motivation: Elementary interactions in solids

Coupling between the various degrees of freedom



femtosecond optical excitation

response of the solid state $\chi(t)$

General: Many elementary processes in physics, chemistry, biology occur on an ultrafast, typically femtosecond, time scale

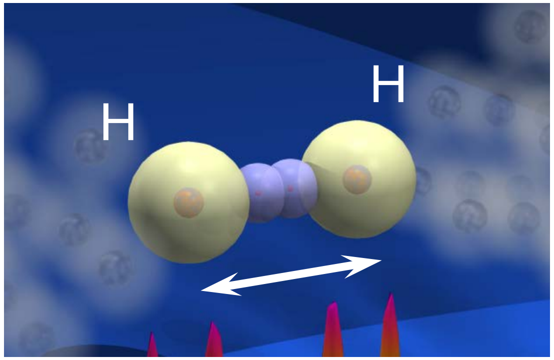
courtesy of A. Föhlisch

Ultrafast elementary processes

Vibrations of molecules and solids (phonons)

8 fs: Vibrational period of the H-H bond in an H_2 molecule

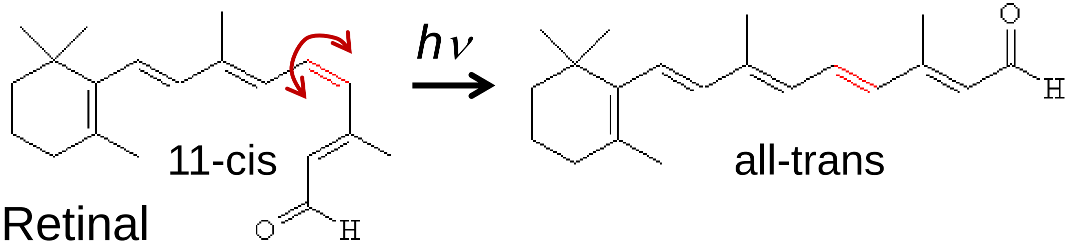
25 fs: Period of lattice vibration in diamond (optical phonon)



Structural changes of molecules and solids

200 fs: Bacteriorhodopsin turns from *cis* into *trans* conformation (following illumination)

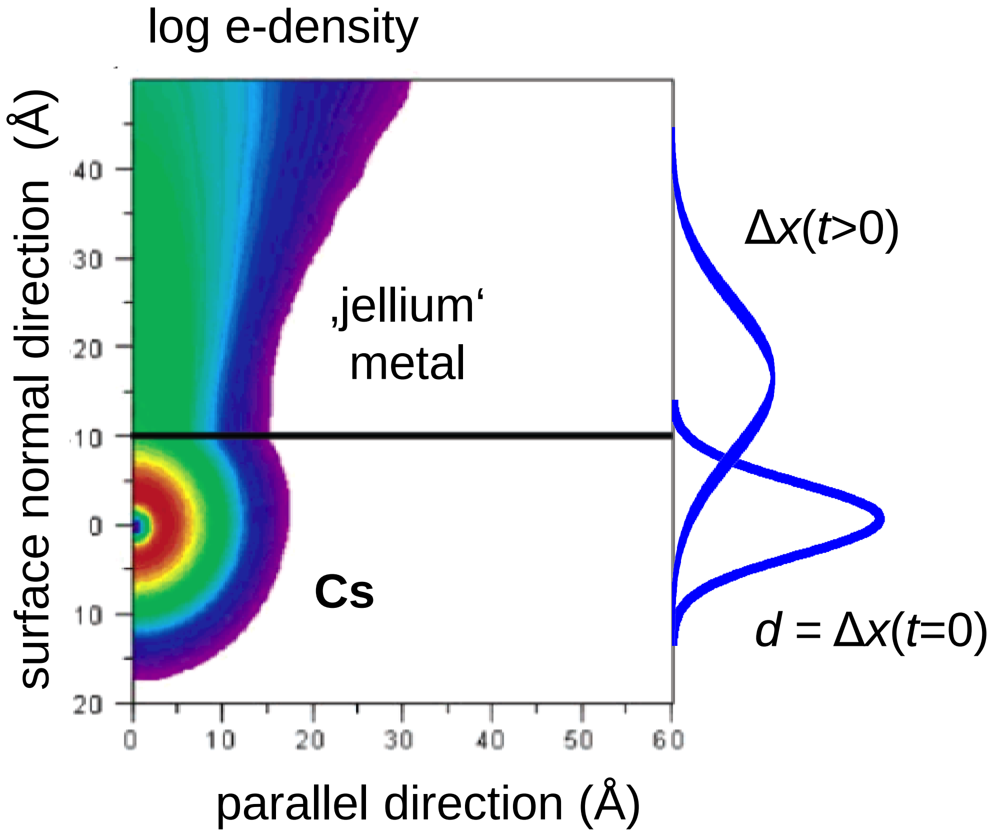
cis-trans isomerization



Ultrafast elementary processes

Spreading of a Gaussian wave packet

Example: alkali atom at metal surface



localized states

⇓

superposition of plane waves

$$\langle \Delta x \rangle^2 = d^2 (1 + \Delta^2)$$

$$\Delta = \frac{\hbar}{2md^2} \cdot t$$

characteristic time
spreading of Gaussian wave packet

$t\,[\mathrm{s}] = 10^4 \cdot (d\,[\mathrm{m}])^2$

$\boldsymbol{d = 5}$ **Å ➨** $\boldsymbol{t = 2.5}$ **fs**

see F. Schwabl, *Quantum Mechanics*

Ultrafast elementary processes

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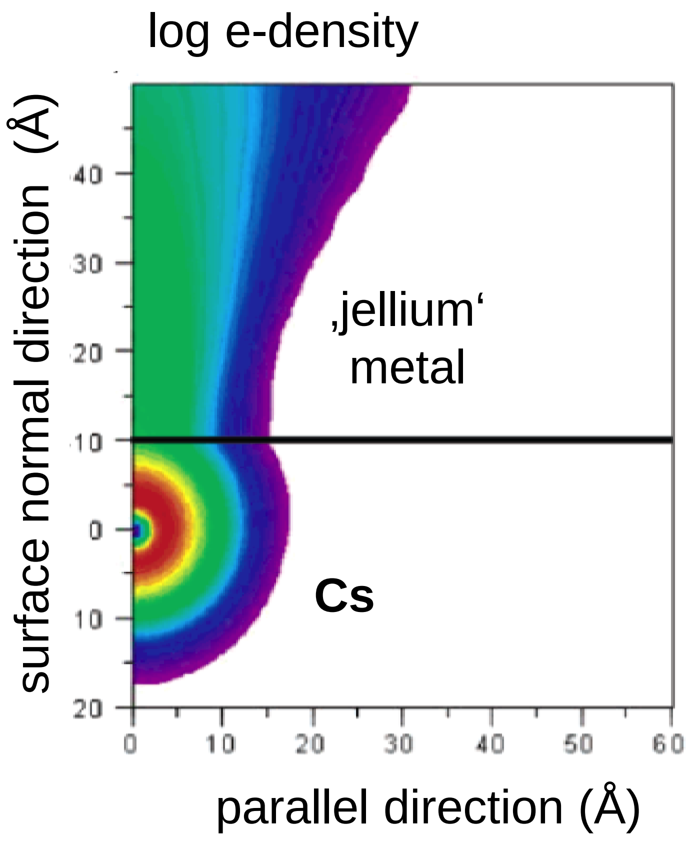
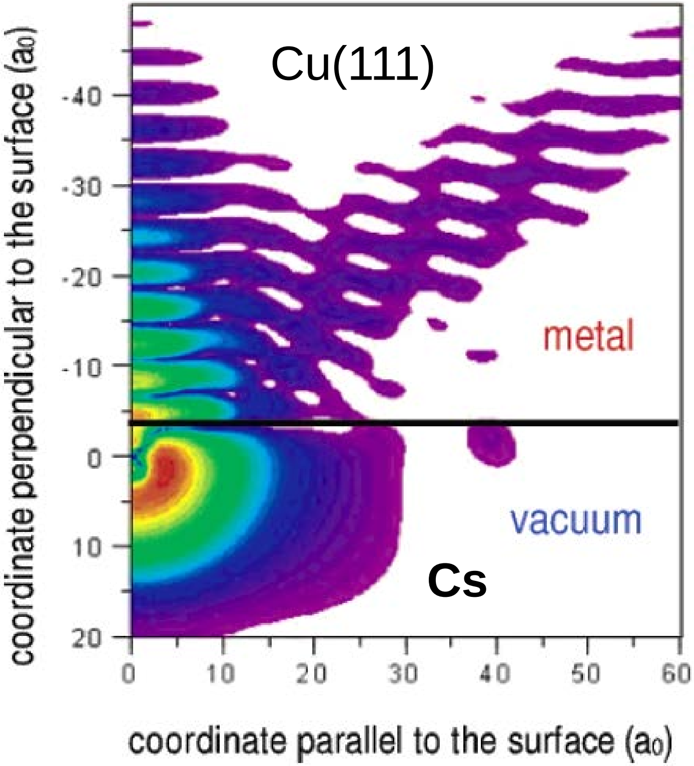


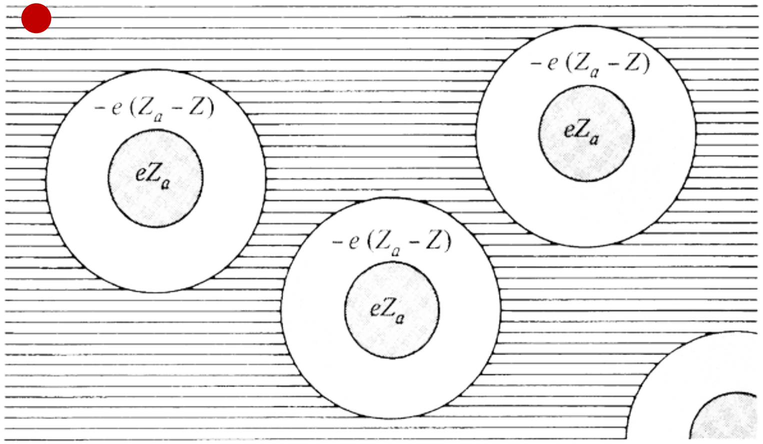


Chulkov et al., Chem. Rev. **106**, 4195 (2006)

Ultrafast elementary processes

Electrons in solids: scattering time between subsequent collisions

Simple picture (Drude 1900)



Ashcroft / Mermin

Electric conductivity of metals:

$$\vec{j} = \sigma \vec{E}, \qquad \sigma = \frac{ne^2\tau}{m_{eff}}$$

with scattering time τ

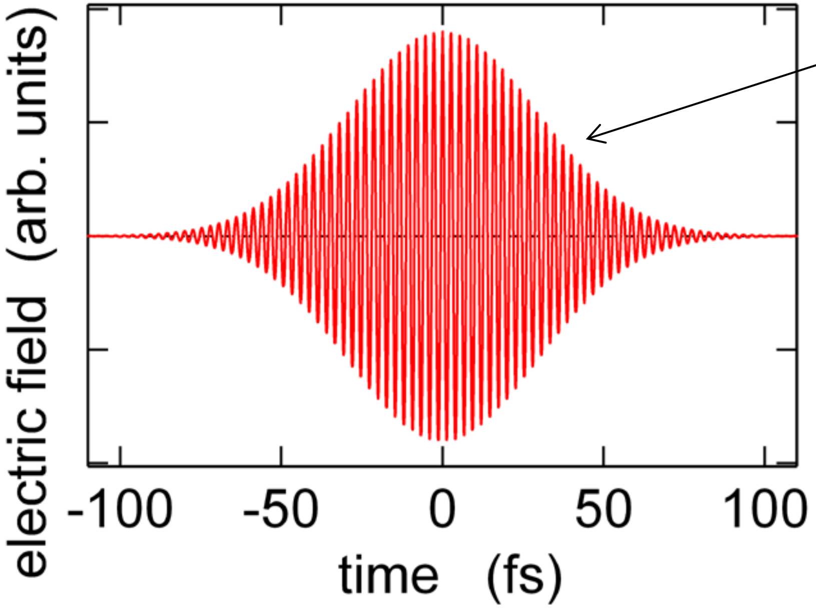
40 fs:	in silver (@ 300K)
3 fs:	in iron
100 fs:	in graphite

Note: Resistivity arises from scattering of Bloch electrons at deviations from the periodic crystal structure (e.g. phonons or defects)

⇒ **Goal:** Use femtosecond laser pulses to study ultrafast processes in matter

What is a femtosecond laser pulse?

- ➢ Flash of light with duration of ~ 1 to ~1000 fs
- ➢ Description by the electric field $\boldsymbol{E}(\boldsymbol{x},t)$
- ➢ Peak field can be > 10 V/Å



Electric field envelope $|A(t)|$

Complex-valued phase

$$E(t) = \mathrm{Re}\,[A(t)exp(-\mathrm{i}\omega_{\mathrm{c}}t + \varphi)]$$

Complex-valued carrier envelope

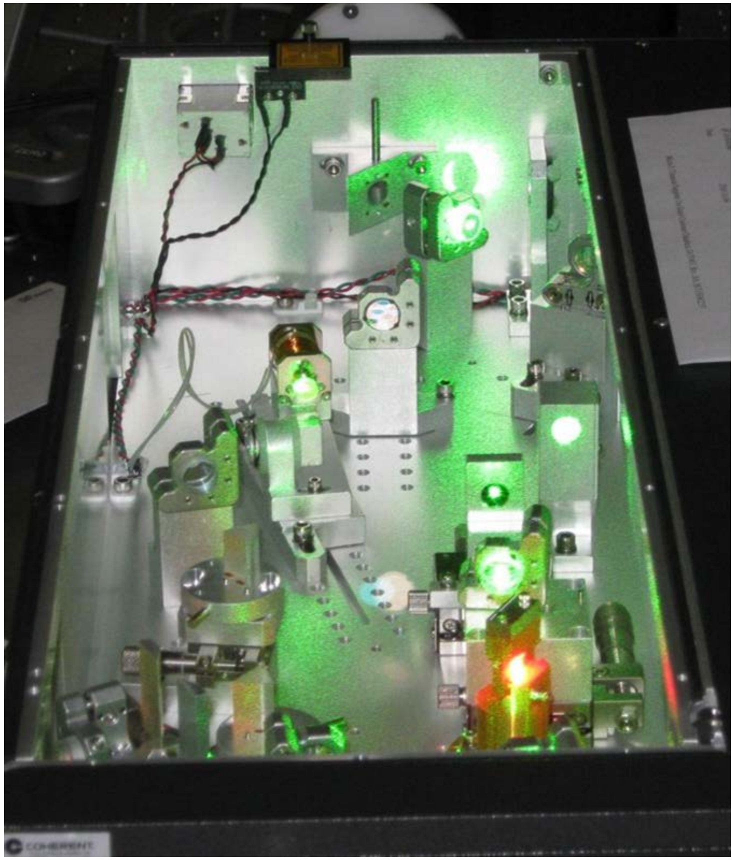
chirped pulse: $\omega_c = \omega_c(t)$

Shown here:

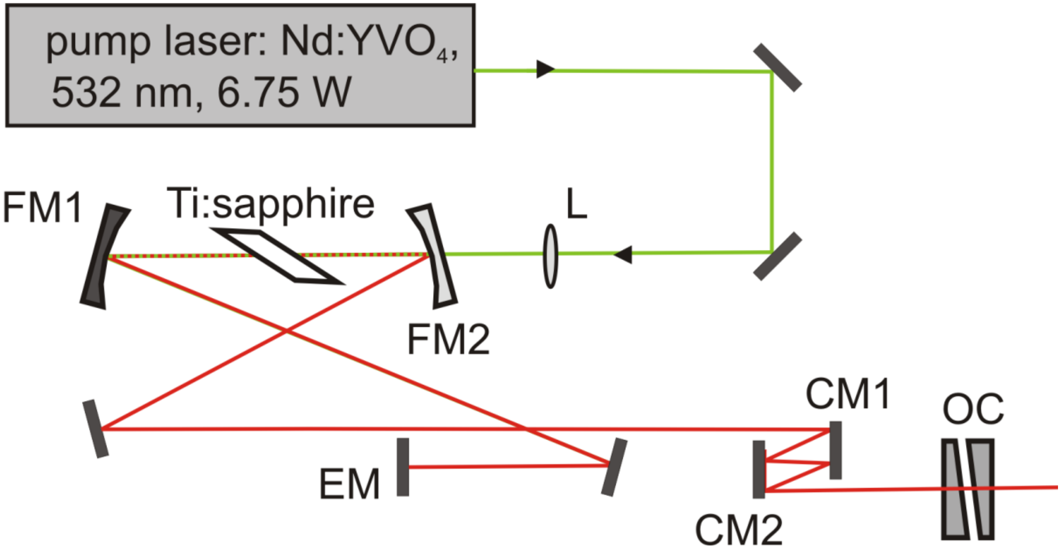
- ➢ 100-fs pulse, centered at 800 nm
  (frequency ~400 THz, 2.5 fs per cycle)
- ➢ Bandwidth-limited (ω_c = const)

How to generate such fs pulses?

Typical femtosecond laser



- Most popular gain medium: Ti:sapphire
- Typically 1 to 10 W average laser power

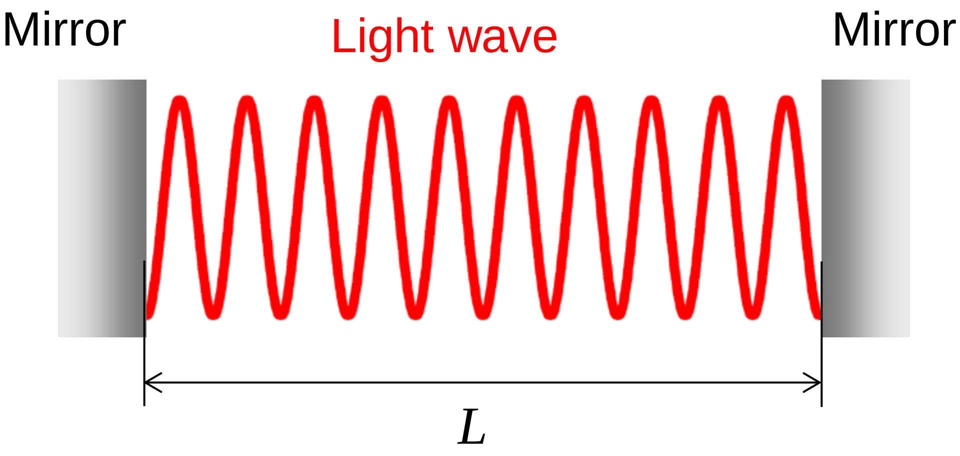


Laser oscillator: $f_{rep} \sim$ 100 MHz

$\Rightarrow$ pulse energy ~ 10 nJ

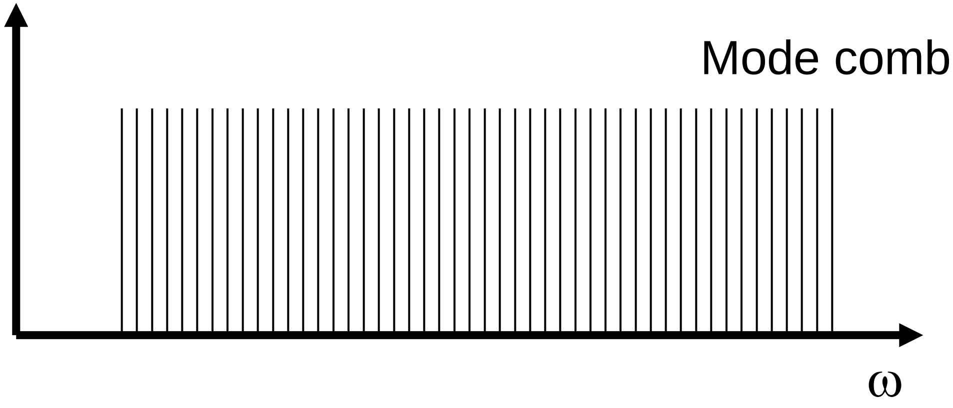
What is the underlying principle for generation of femtosecond laser pulses ?

Fabry-Perot laser resonator



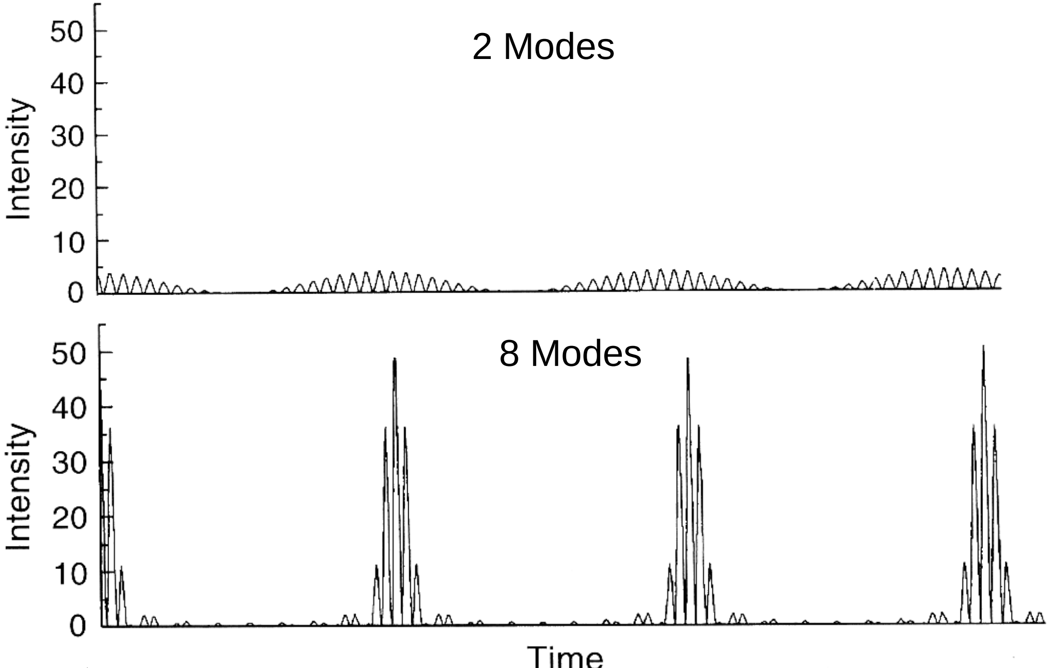
Only wavelengths $\lambda_j = 2L/j$ survive

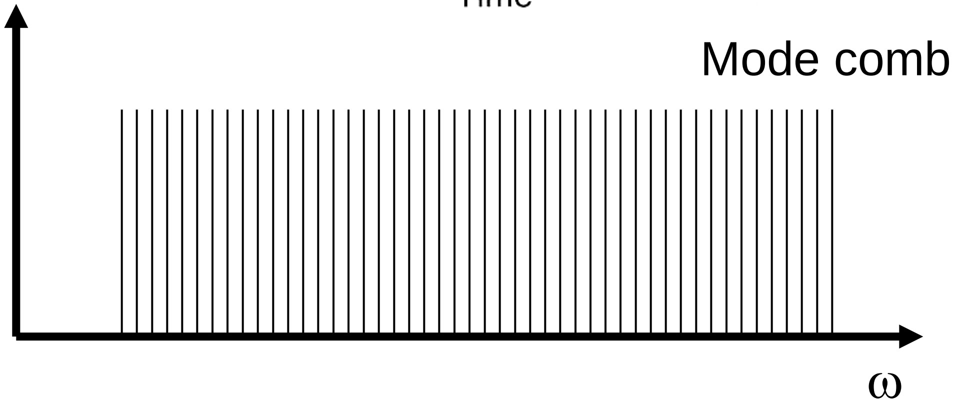
$\Rightarrow$ frequency comb of modes,
$\omega_j = j\Delta\omega = j\pi c/L$



Idea:
superposition of modes should yield a wavepacket or pulse

Mode locking





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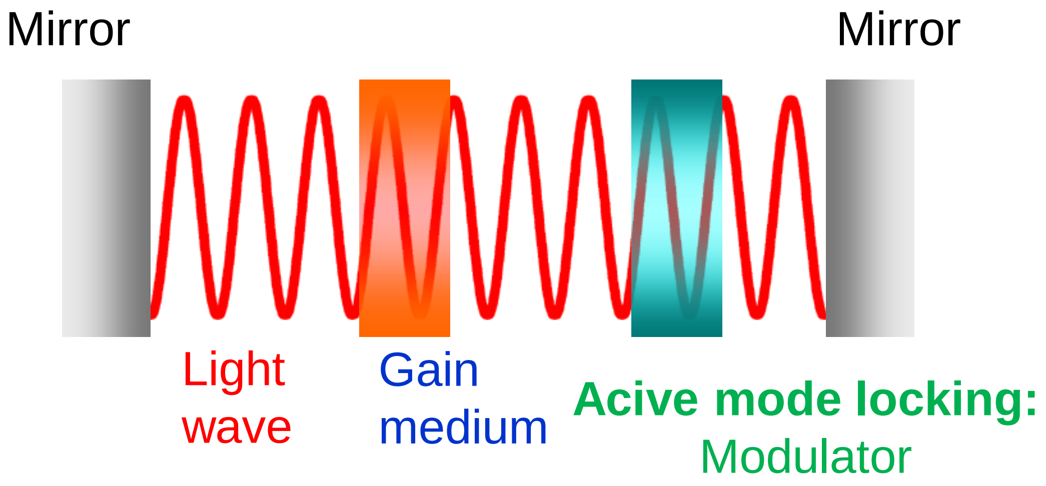
$$\omega_j = j\Delta\omega = j\pi c/L$$

Idea:
superposition of modes should yield a wavepacket or pulse
➡ **mode locking**

Mode locking

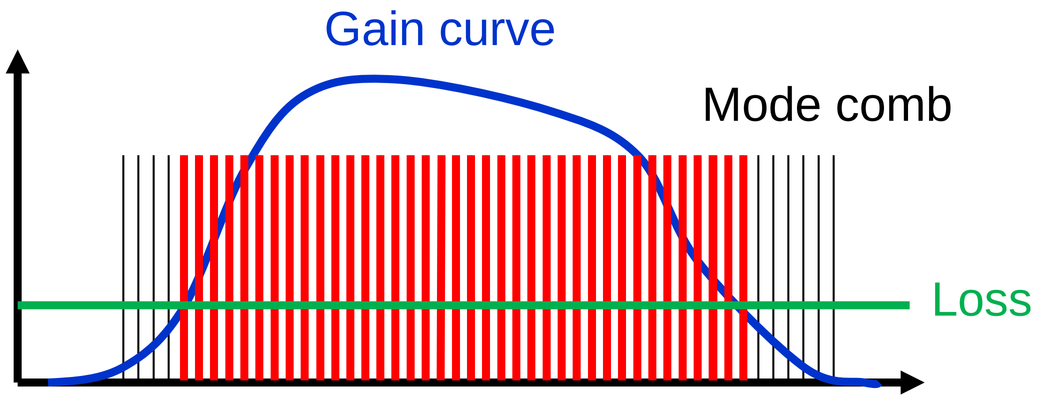
How can we excite and phase-couple all modes within gain profile?



Acive mode locking:
Modulator

Modulate cavity:

sidebands appear at modulation frequency ω_{mod}



Choose $\omega_{mod} = \Delta\omega = \pi c/L$:

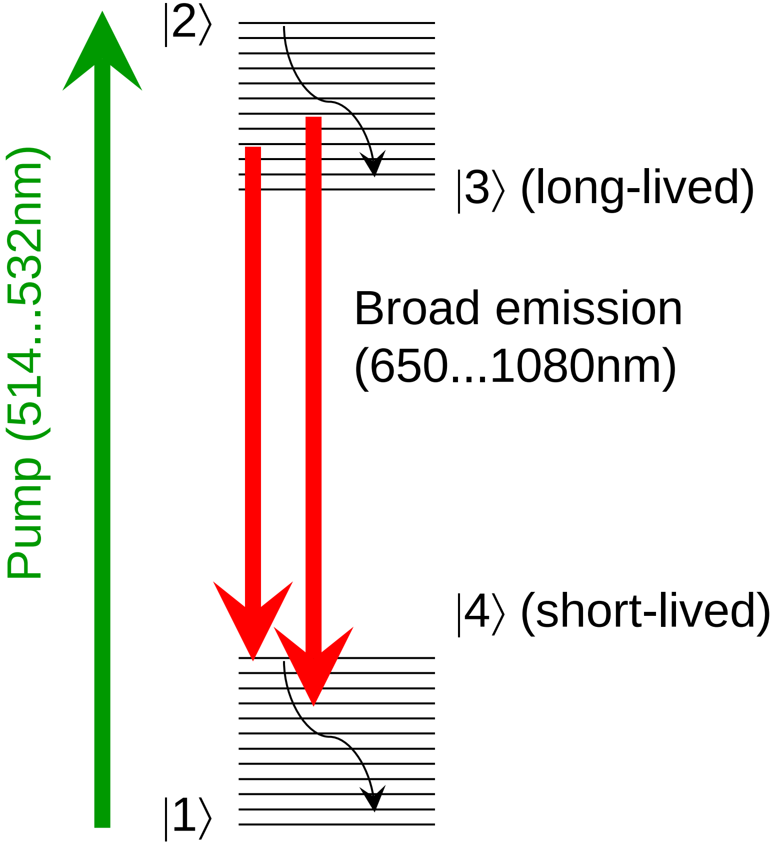
Sidebands are amplified, new sidebands etc.

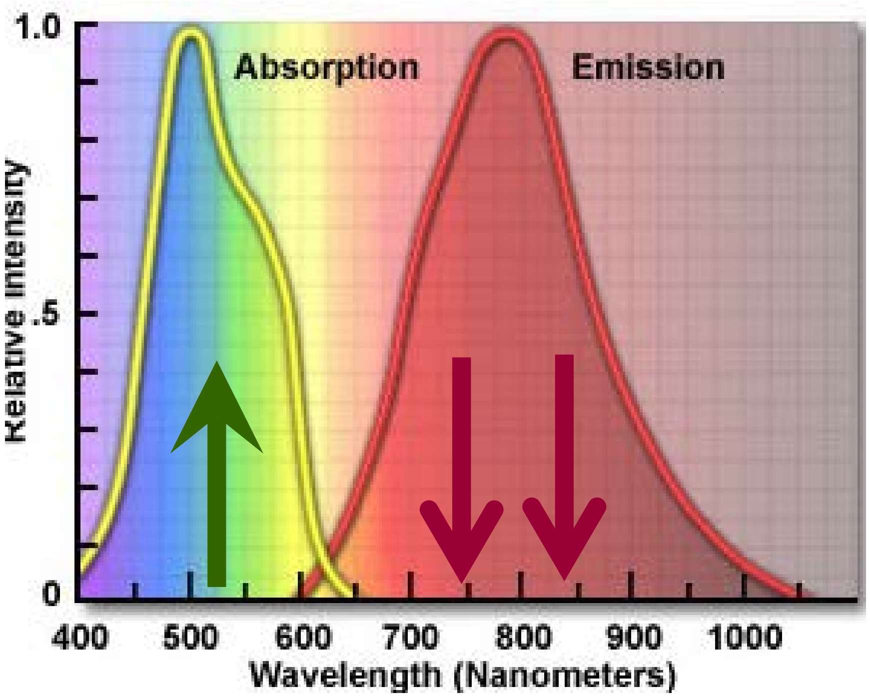
Mode locking
$\Rightarrow$ fs pulse

What is a typical gain metium ?

Gain by laser-pumped Ti:sapphire

Ti^{3+} level scheme:
levels split by coupling to phonons
(vibronic laser)





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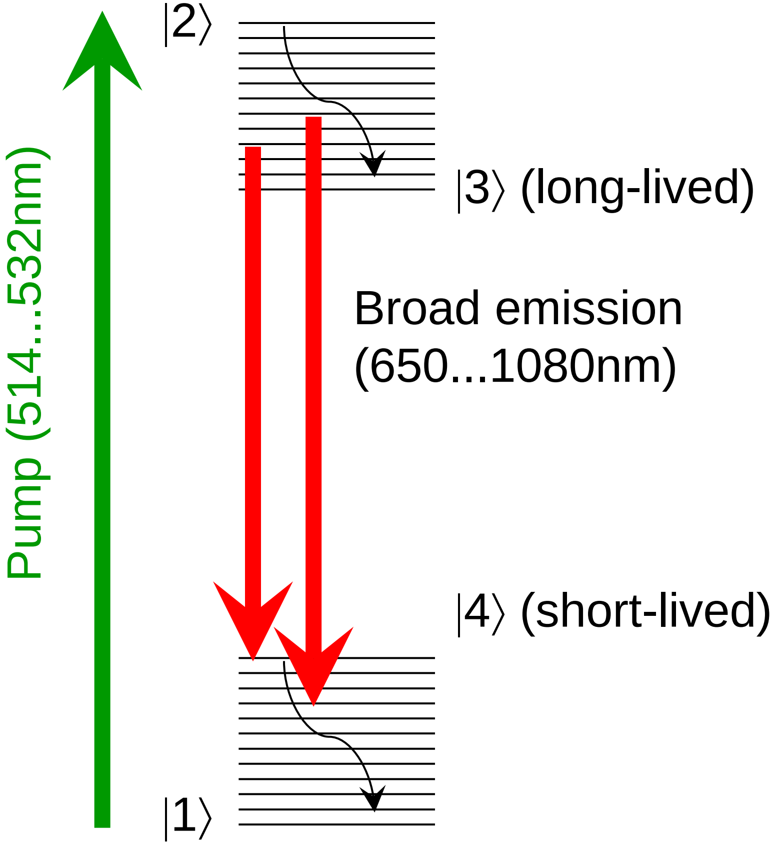


Pump (514...532nm)

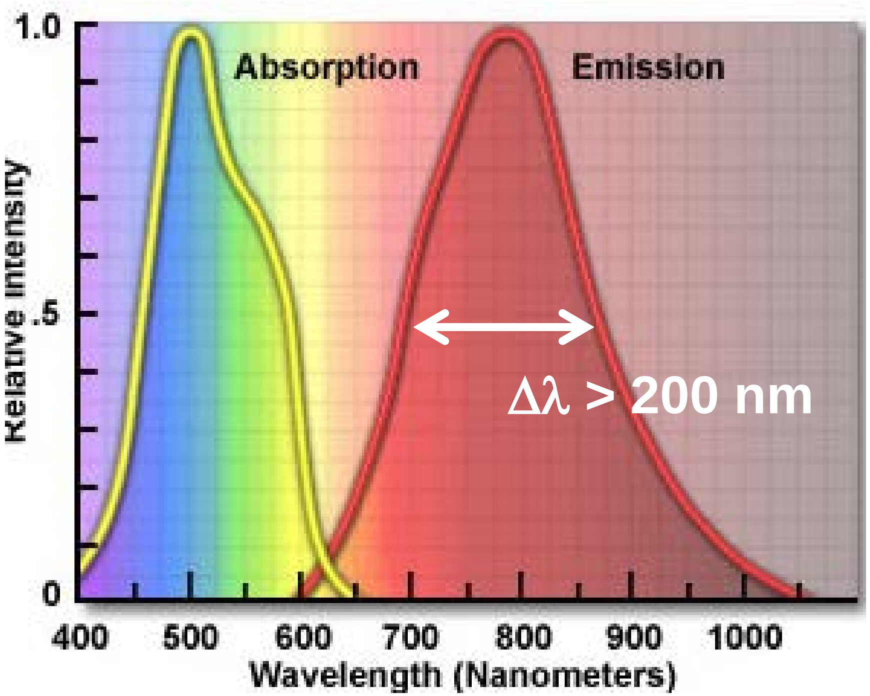
|2⟩

|3⟩ (long-lived)

Broad emission
(650...1080nm)

|4⟩ (short-lived)

|1⟩



Light amplification by stimulated emission of radiation (LASER)

Note: Ti:sapphire exhibits a strong optical Kerr effect

➡ Kerr lens mode locking

Passive (self-) mode locking

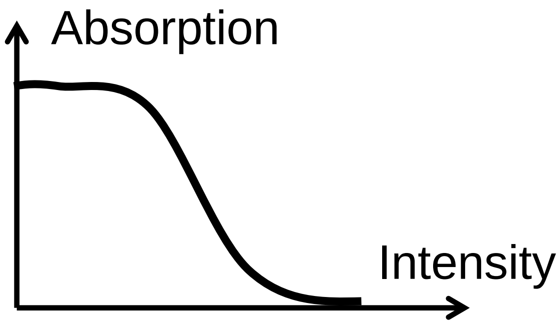
Assume we have a pulse: oscillates in resonator with frequency $\Delta\omega = \pi c/L$

$\Rightarrow$ Can be used for self-modulation of the resonator

Several realizations:

1. **Saturable absorber**

   becomes transparent
   at high intensities,
   once per round trip

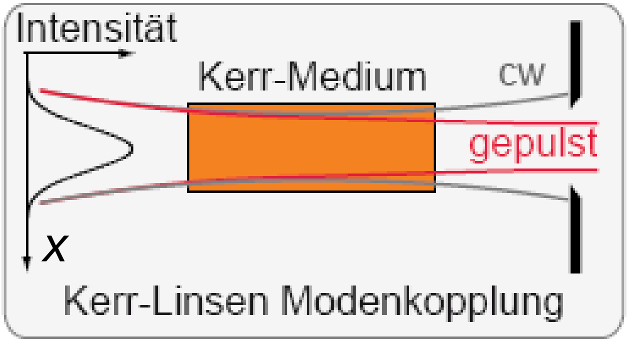


2. **Transient optical Kerr effect**

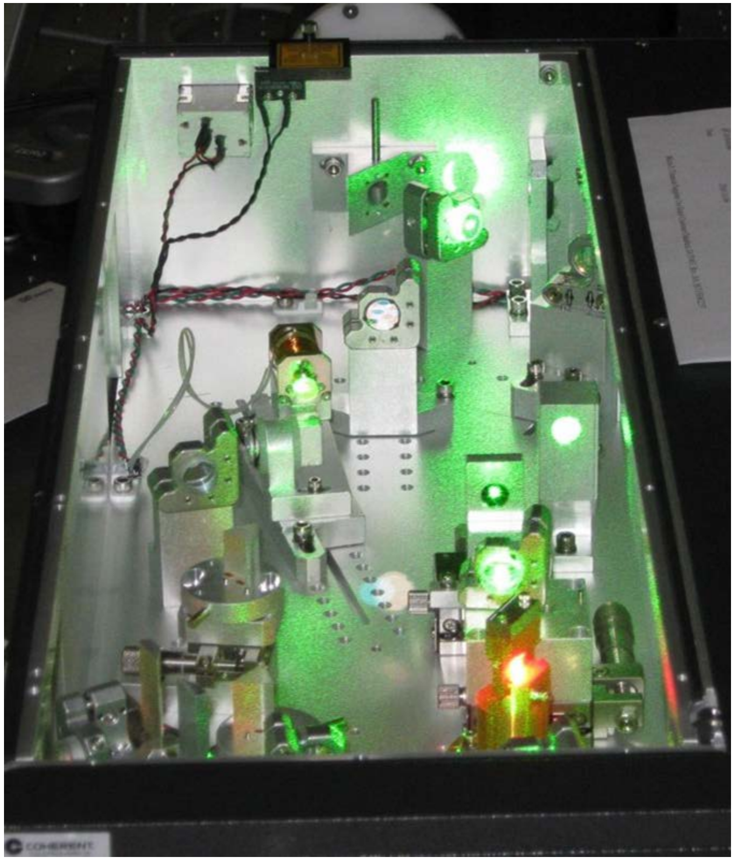
   leads to self-focusing
   at high intensities,
   once per round trip

   refractive index:

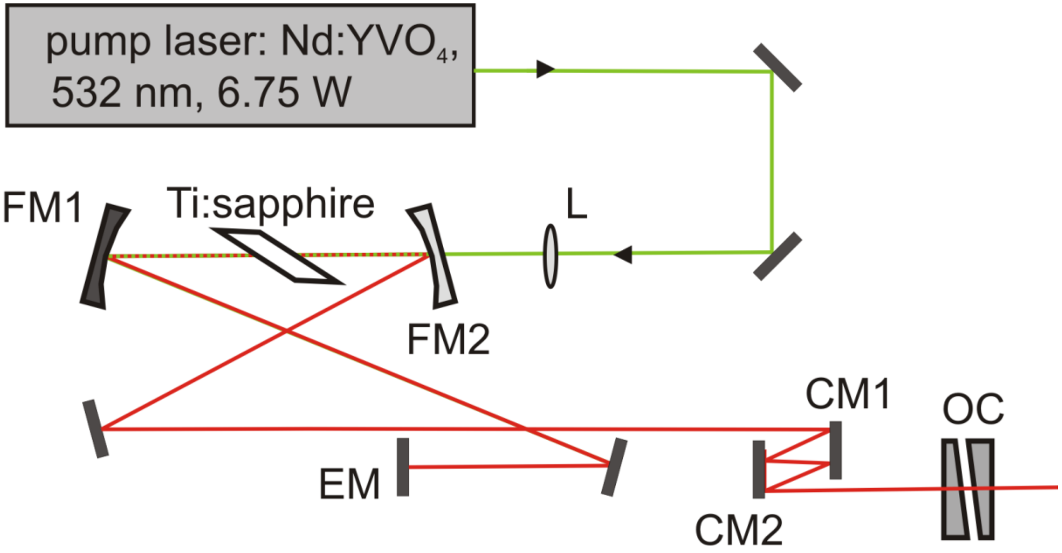
   $$n(x) = n_o + n_2 I(x)$$



Typical fs lasers: Ti:sapphire oscillator



- Most popular gain medium: Ti:sapphire
- Typically 1 to 10 W average laser power

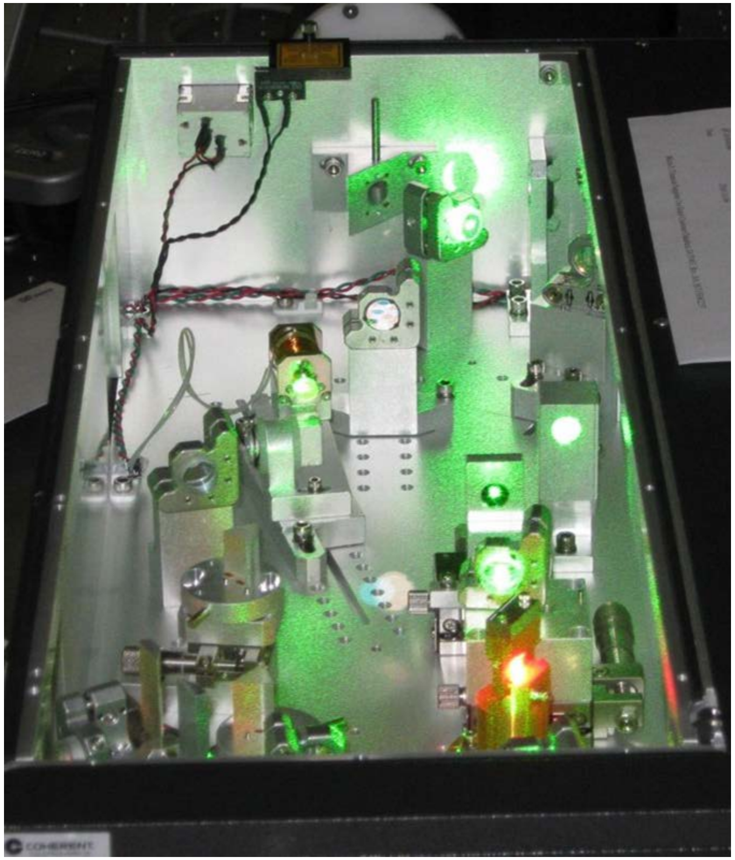


- 10 fs pulse duration
- 10 nJ pulse energy
- 80 MHz repetition rate

Passively mode locking

⇒ 10^6 coupled modes

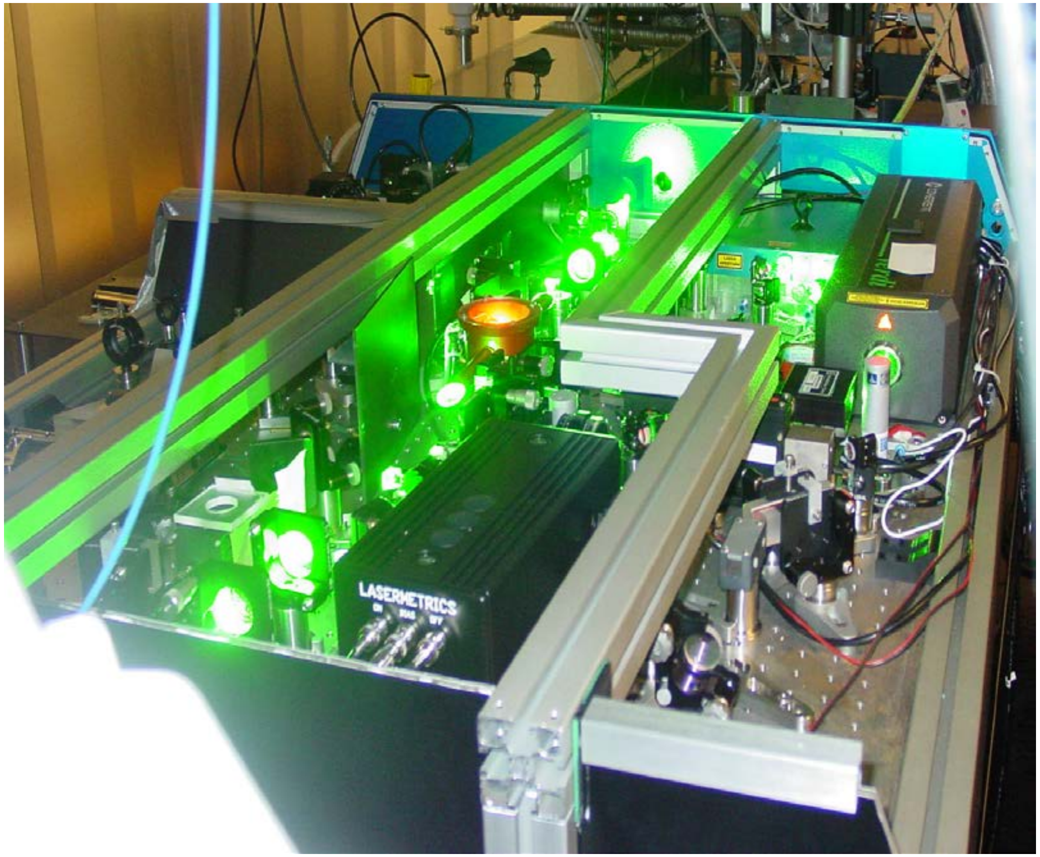
Typical femtosecond lasers



Laser oscillator: $f_{rep} \sim 80$ MHz

$\Rightarrow$ pulse energy ~ 10 nJ

$\Rightarrow$ laser is on for ~ 1s/day



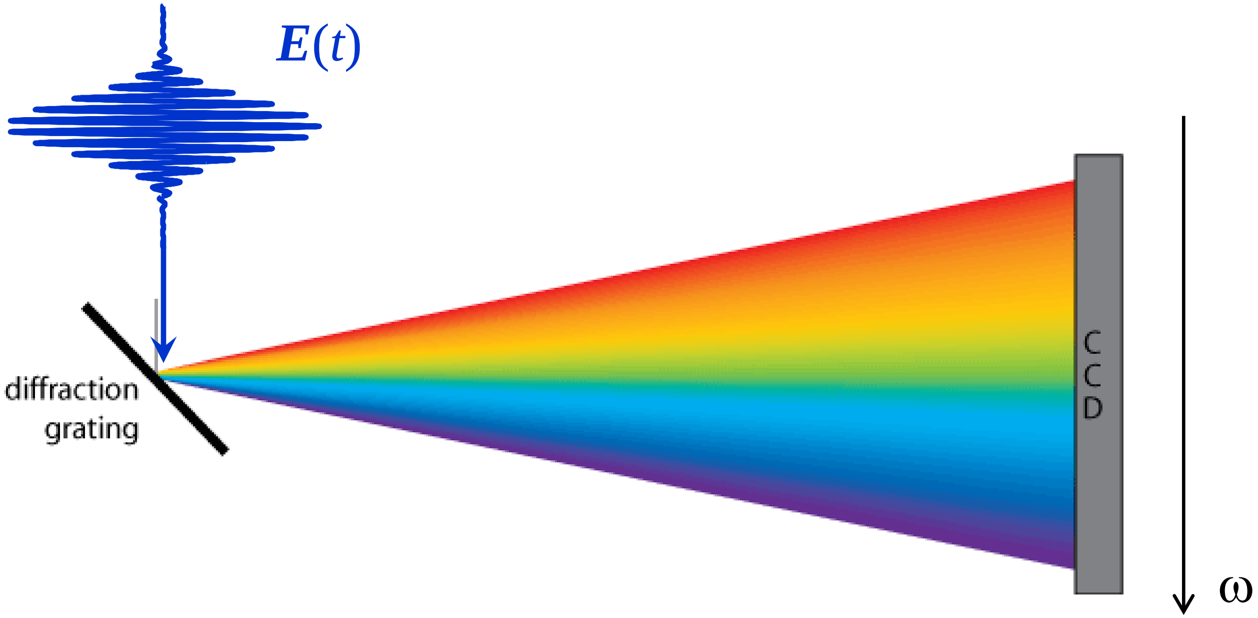
Amplified laser system: $f_{rep} \sim 1$ kHz

$\Rightarrow$ pulse energy ~ 1 to 10 mJ

$\Rightarrow$ laser is on for ~ 1s/300years

How to characterize femtosecond laser pulses ?

How can we characterize a laser pulse?

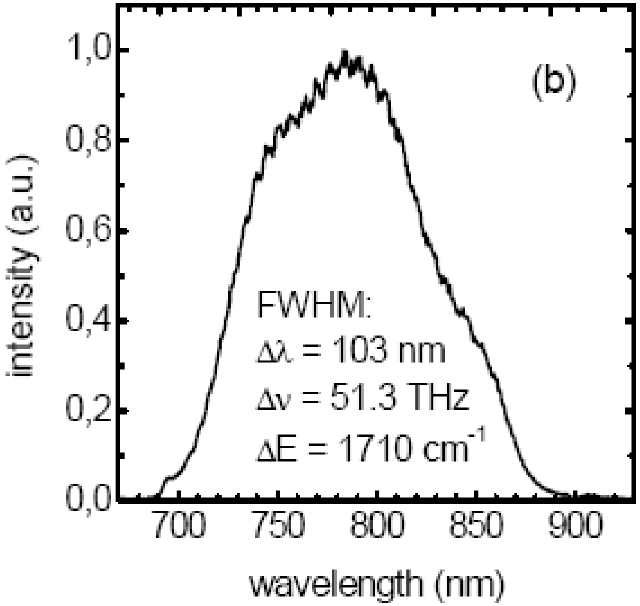


Ultimate goal:

Measure electric field $E(t)$

⇒ **Intensity spectrum**

$$|\tilde{E}(\omega)|^2$$



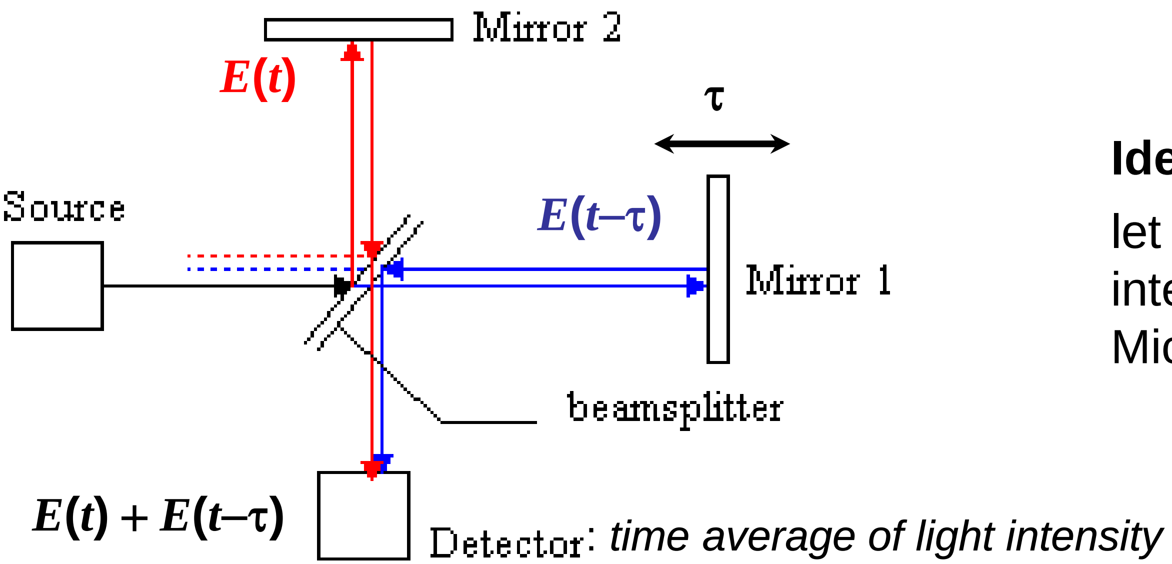
Example: spectrum of 10-fs Ti:sapphire pulse

Issue: no phase information $\arg \tilde{E}(\omega)$

⇒ One cannot decide whether light comes from a light bulb or a fs laser

What about an interferometer?

Autocorrelation measurement



Idea:

let the fs light pulse interfere with itself in a Michelson interferometer

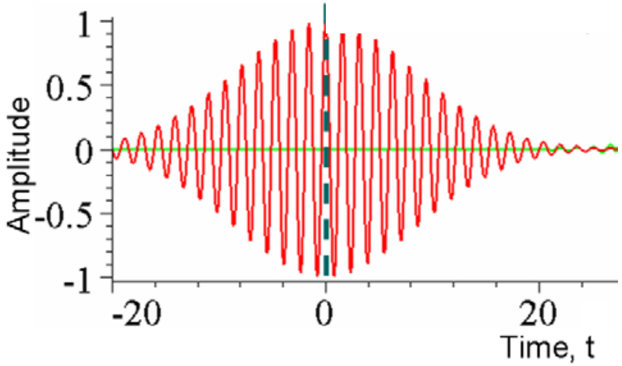
$$I(\tau) = \underbrace{\langle}_{\text{Time average}}[E(t) + E(t-\tau)]^2\rangle = \underbrace{2\langle E^2\rangle}_{\text{Single intensities}} + \underbrace{2\langle E(t)E(t-\tau)\rangle}_{\text{Interference term: linear autocorrelation}}$$

Time average

Single intensities

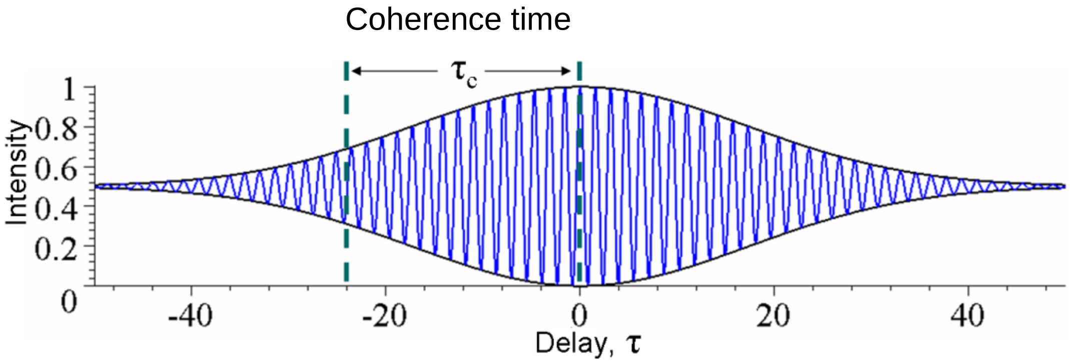
Interference term:
linear autocorrelation

Light pulse autocorrelation



Laser pulse:

- Fourier-limited
- Duration τ_p



Resulting autocorrelation:

- No interference for $\tau > \tau_p$
- Width $\tau_c \sim \tau_p$

$\Rightarrow$ Seems to work

Problem:

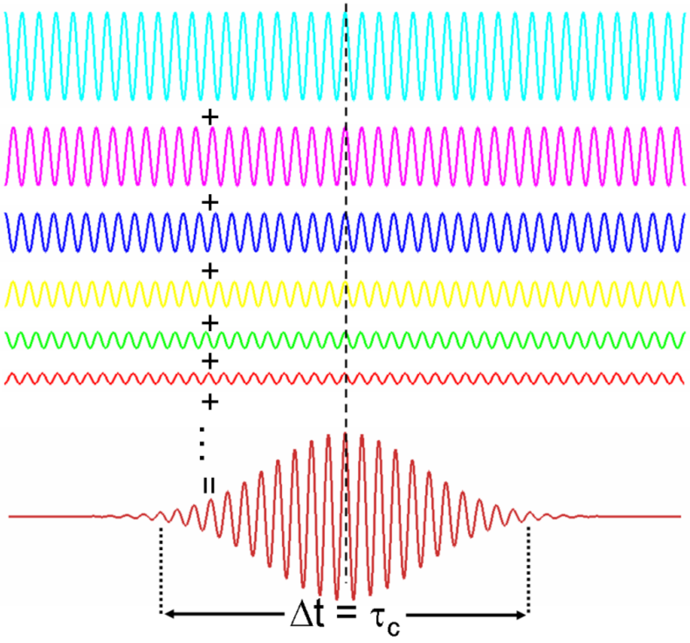
same information as in intensity spectrum $\left|\tilde{E}(\omega)\right|^2$

Why?

Wiener Chintchin theorem

Fourier synthesis:

$$E(t) = \int \mathrm{d}\omega\, \tilde{E}(\omega)\mathrm{e}^{-\mathrm{i}\omega t}$$



Linear Autocorrelation:

$$\langle E(t)E(t-\tau)\rangle$$

$$= \int \mathrm{d}\omega \int \mathrm{d}\omega'\, \tilde{E}(\omega)\tilde{E}(\omega')\mathrm{e}^{-\mathrm{i}\omega\tau}\left\langle \mathrm{e}^{-\mathrm{i}(\omega+\omega')t}\right\rangle$$

$= \delta(\omega+\omega')$

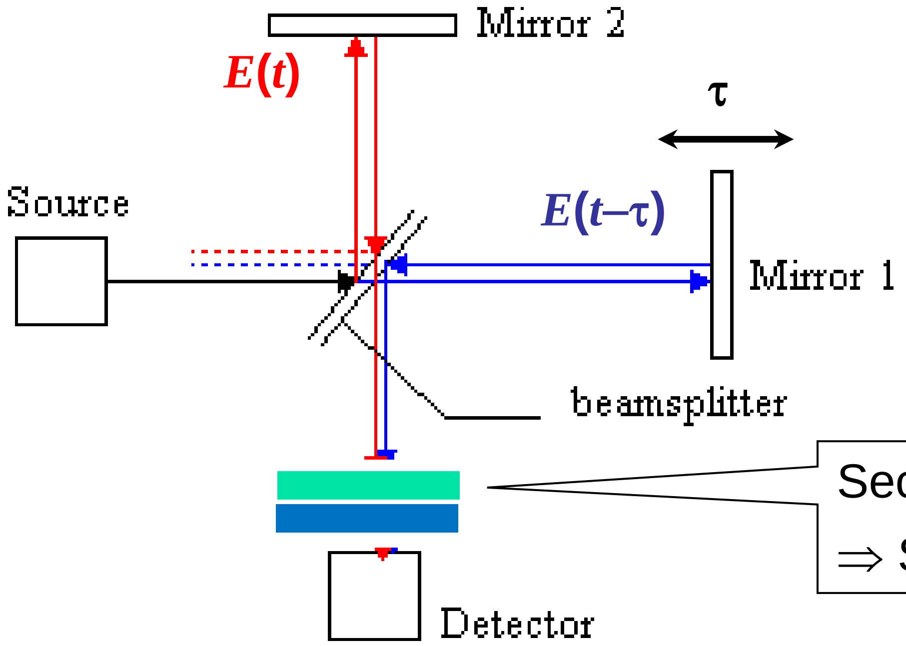
⇒ Different frequencies do not interfere

Result:

$$\langle E(t)E(t-\tau)\rangle = \mathcal{F}^{-1}\left(\left|\tilde{E}(\omega)\right|^2\right)$$

i.e. same information as intensity spectrum $\left|\tilde{E}(\omega)\right|^2$

Quadratic autocorrelation measurement



Idea: generate intermediate field

$$E_{\mathrm{SH}}(t) \propto E^2(t)$$

before detector

Second-harmonic (SH) crystal + filter

⇒ SH field is $\propto [E(t) + E(t-\tau)]^2$

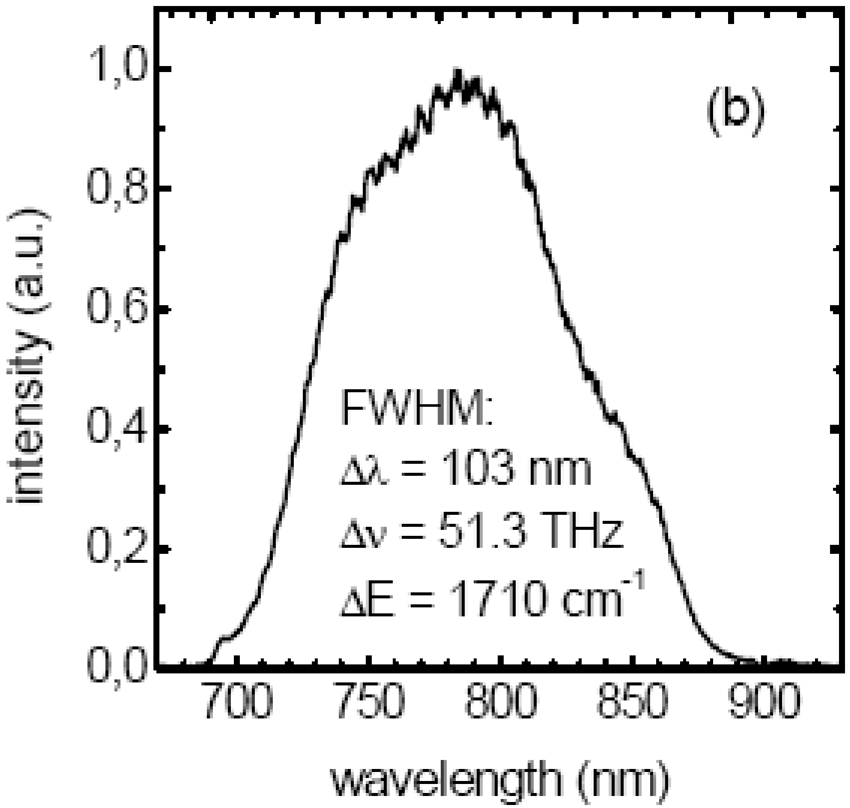
$$I(\tau) = \langle [E(t) + E(t-\tau)]^4 \rangle = \cdots + 2\langle E^2(t) E^2(t-\tau) \rangle$$

Time average

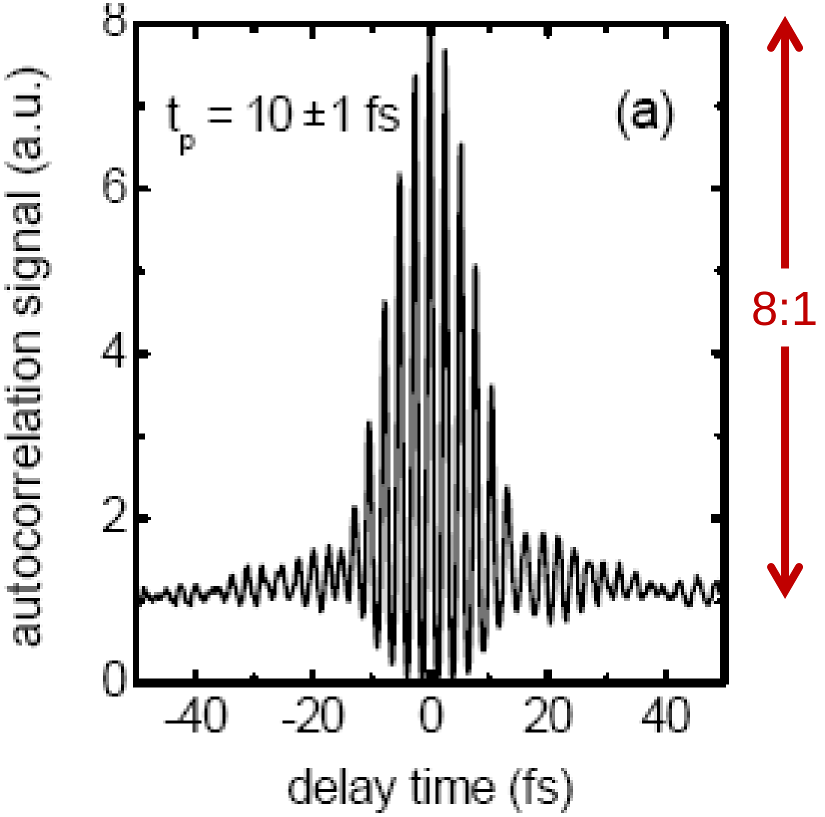
Quadratic autocorrelation

Quadratic autocorrelation

Intensity spectrum



Quadratic autocorrelation



Envelope width gives good approximation of pulse duration

Information (almost) sufficient to extract pulse field $E(t)$

Femtosecond pulses - what for?

Femtosecond laser pulses have unique properties:

- short duration
- high peak intensities
- stable repetition rate (“clockwork”)

Applications:

1. Metrology: measure frequency of light
2. Nonlinear optics: new frequencies, new probes
3. fs spectroscopy: resolve ultrafast dynamics
4. Novel states: extreme non-equilibrium, new processes
5. …

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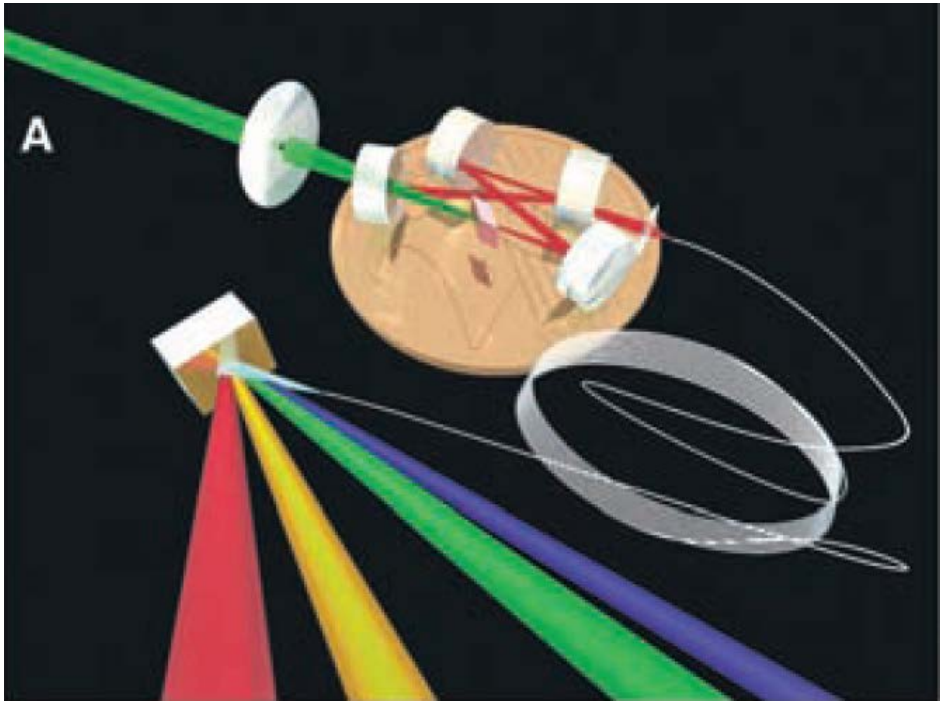
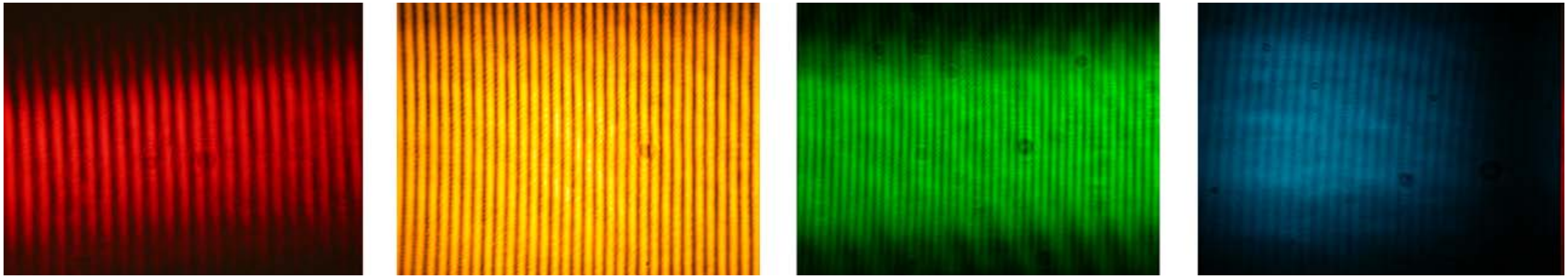
Frequency comb



Femtosecond pulse train (“comb”)
in time domain correspond to
⇒ A comb in frequency domain

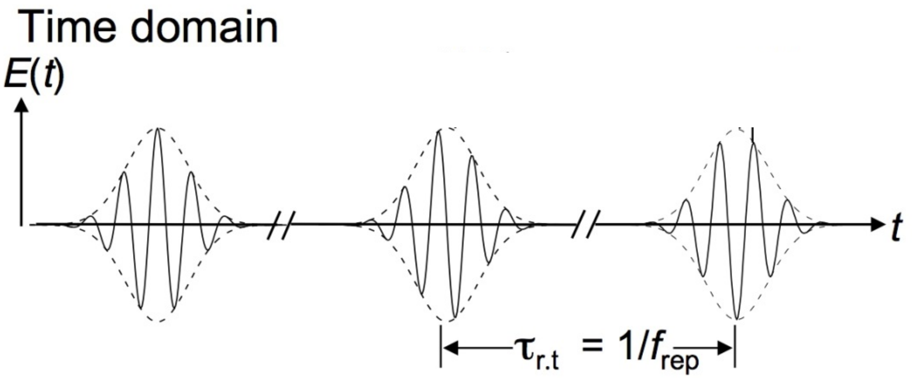
Laser cavity only ~1 cm long
⇒ frequency comb with GHz spacing
⇒ even visible with optical grating

A. Bartels *et al.*, Science 326, 681 (2009)



Application: measurement of optical frequencies with high accuracy

Frequency comb



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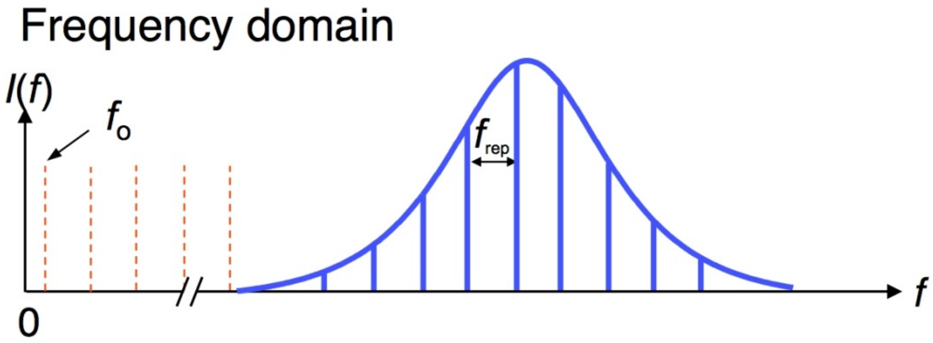
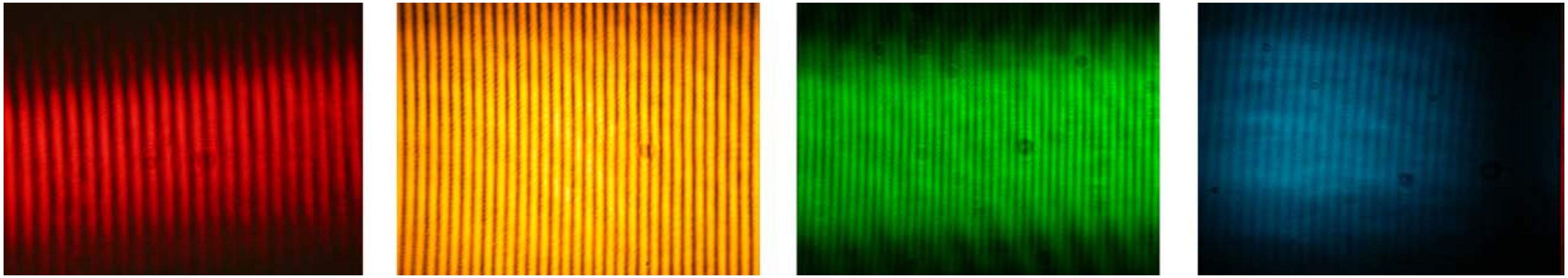


Typically there is a phase
offset $\Delta\phi$ between pulses
(if not phase locked)
⇒ frequency offset f_0

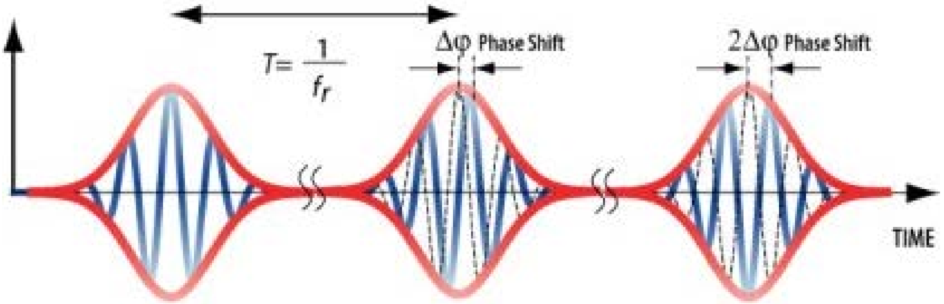


Frequency measurement with frequency comb

How to measure an optical frequencies with very high accuracy?

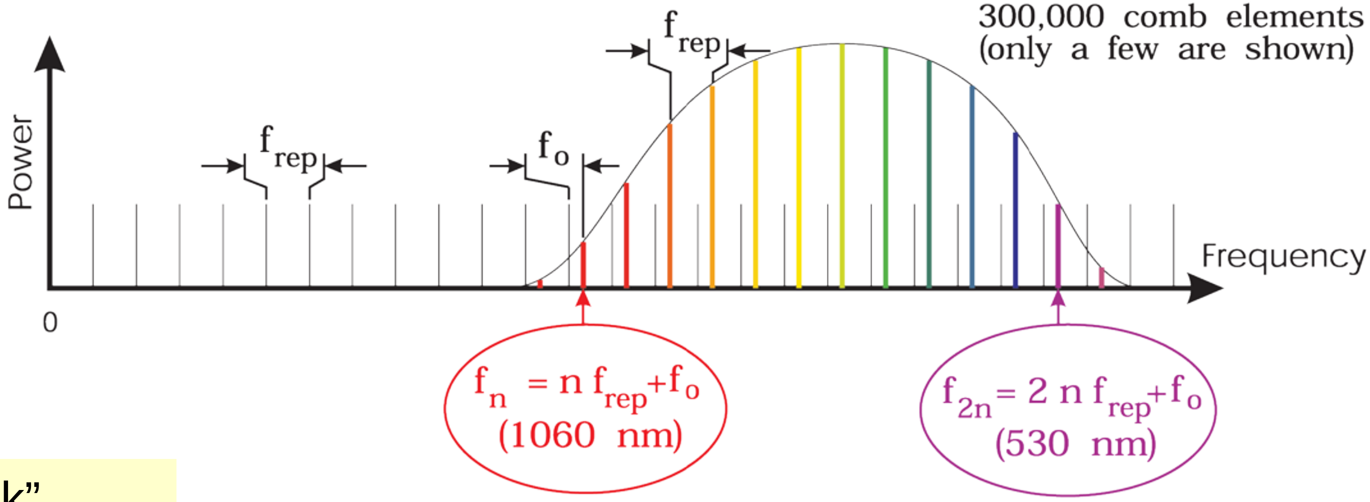
Trick: exploit extremly high precision of a frequency comb

Time domain:
pulse train



$\mathcal{F}$

Frequency domain:
frequency comb



$$2(f_n) - f_{2n} = 2(n f_{rep} + f_o) - (2 n f_{rep} + f_o) = f_o$$

$\Rightarrow$ Measurement of phase offset f_0

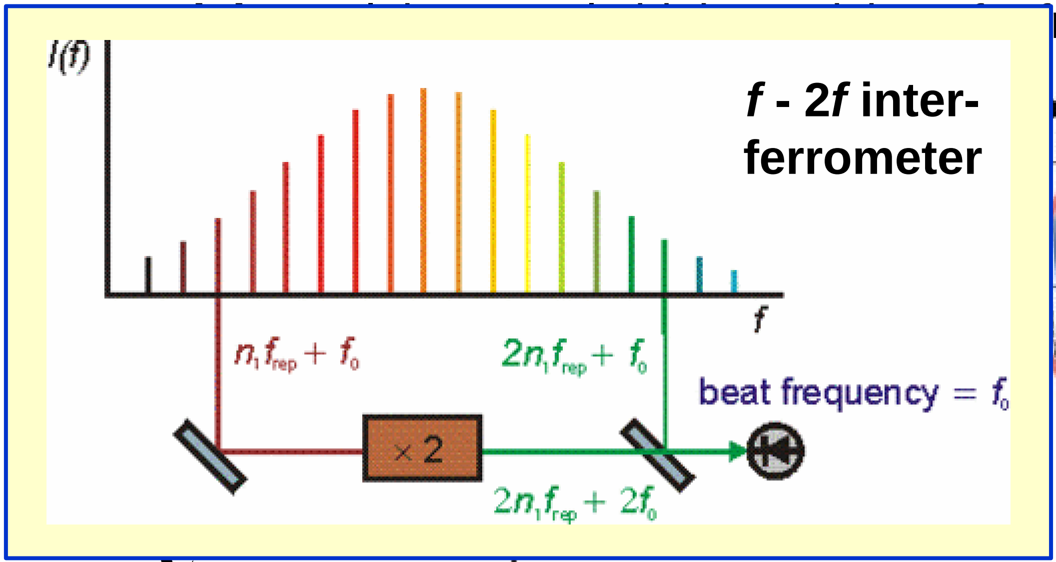
"Optical clockwork"

T. Hänsch, Nobel prize 2005

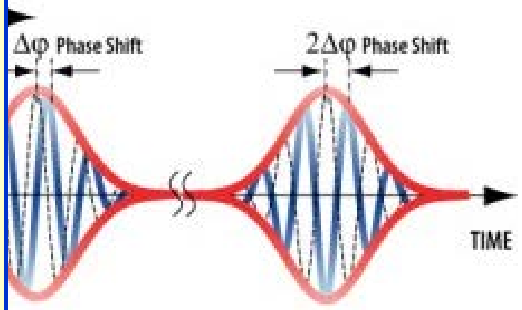
Frequency measurement with frequency comb

How to measure an optical frequencies with very high accuracy?

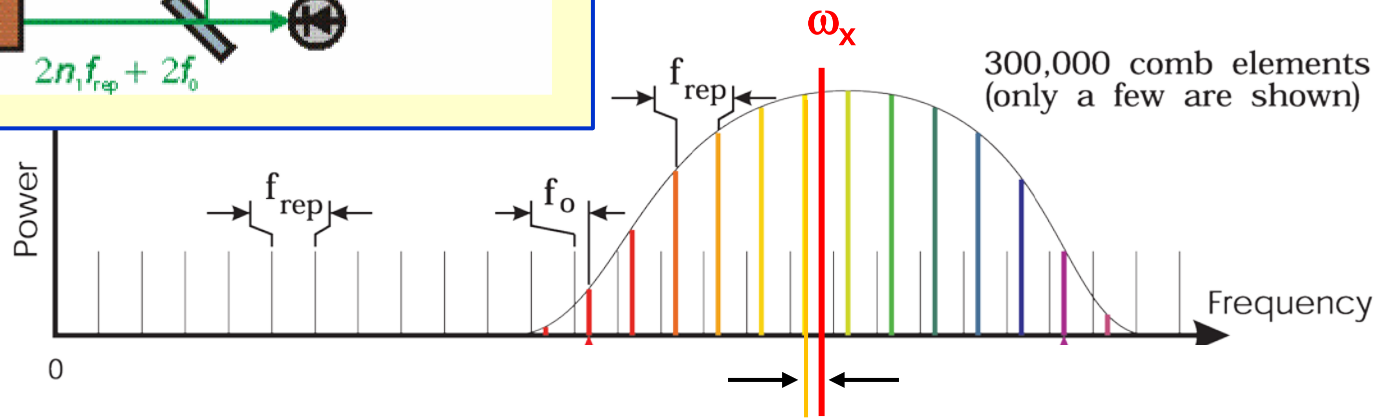
requency comb



***f* - 2*f* inter-ferrometer**



Frequency domain:
frequency comb



⇒ Measurement of frequency ω_x via beating signal at $\Delta\omega$

“Optical clockwork”

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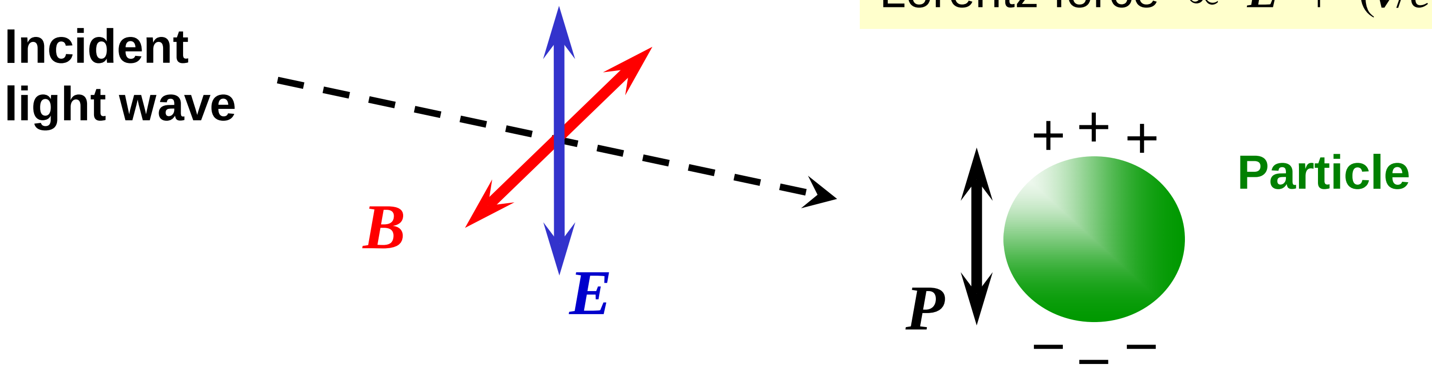
3. fs spectroscopy: resolve ultrafast dynamics
4. Novel states: extreme non-equilibrium, new processes
5. …

Nonlinear light-matter interaction

Lorentz force $\propto \boldsymbol{E} + (\boldsymbol{v}/c) \times \boldsymbol{B}$



⇒ Charge displacement $\boldsymbol{P}$ ⇒ Re-radiation of light (“scattering”)

If light fields $\boldsymbol{E}$ comparable to intraatomic fields ($\boldsymbol{E}_{\text{at}} \sim$ 10 ... 100 V/Å)

⇒ Nonlinear response

Phenomenological approach: Taylor expansion

$$\boldsymbol{P}[\boldsymbol{E}] = \chi^{(1)}\boldsymbol{E} + \chi^{(2)}\boldsymbol{E}^2 + \chi^{(3)}\boldsymbol{E}^3 + \ldots$$

1st 2nd 3rd ... order in $\boldsymbol{E}/|\boldsymbol{E}_{\text{at}}|$

see also Boyd, *Nonlinear Optics*

Quadratic nonlinearity: SFG

Lowest nonlinear response: $$P_i^{(2)}(t) = \chi^{(2)} \boldsymbol{E}^2(t)$$

Phenomenological constant
(from experiment or model)

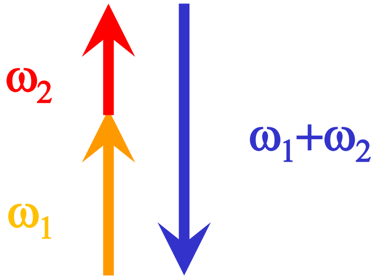
$\Rightarrow$ **Nonlinear optics**

- Superposition principle not valid,
  waves influence each other (light controls light)
- Generation of new frequencies

Consider two-field input: $$E(t) = \mathrm{Re}\left[A_1(t)\mathrm{e}^{-\mathrm{i}\omega_1 t} + A_2(t)\mathrm{e}^{-\mathrm{i}\omega_2 t}\right]$$

e.g. sum-frequency term (SFG):

$$P_i^{(2)}(t) = \chi^{(2)} \mathrm{Re}\left[A_1(t)A_2(t)\mathrm{e}^{-\mathrm{i}(\omega_1+\omega_2)t}\right]$$



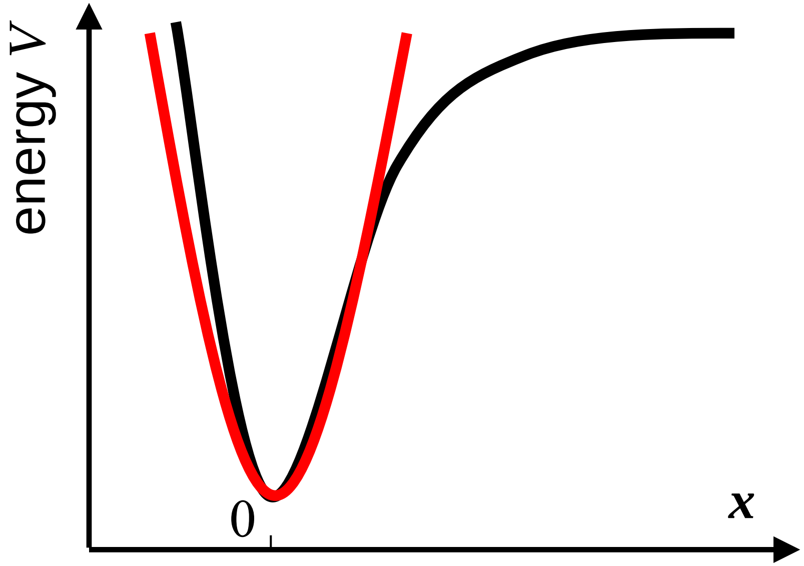
- Sum-frequency generation (SFG): $\omega_{\text{SFG}} = \omega_1 + \omega_2$
- Second-harmonic generation (SHG): $\omega_{\text{SHG}} = 2\omega$ (*i.e.* $\omega_1 = \omega_2$)

Model: nonlinear Lorentz oscillator

Large elongation $\boldsymbol{x}$

- harmonic approximation invalid
- additional force nonlinear in $\boldsymbol{x}$

$$\nabla V = -\omega_0^2 \boldsymbol{x} + \underbrace{a\boldsymbol{x}^2 + b\boldsymbol{x}^3 + \ldots}_{\boldsymbol{F}_{\mathrm{nl}}(\boldsymbol{x})}$$



$\Rightarrow$ Equation of motion

$$\hat{L}\boldsymbol{x} = q\boldsymbol{E}(t) + \boldsymbol{F}_{\mathrm{nl}}(\boldsymbol{x}) \quad \text{with} \quad \hat{L} = \partial_t^2 + 2\gamma\partial_t + \omega_0^2$$

solution: $\boldsymbol{x} \approx \boldsymbol{x}_0 + \Delta\boldsymbol{x}$

from perturbation $\boldsymbol{F}_{\mathrm{nl}}(\mathrm{x})$

$$\boldsymbol{x}_0(\omega) = L^{-1}(\omega) q\boldsymbol{E}(\omega)$$

Linear response ($\boldsymbol{F}_{\mathrm{nl}} = 0$)

$$\Delta\boldsymbol{x}(\omega) = L^{-1}(\omega) \mathsf{F}\left[\boldsymbol{F}_{\mathrm{nl}}(\boldsymbol{x}_0(t))\right]$$

1st-order nonlinear correction

$\Rightarrow$ Model for nonlinear polarization $P[E]$

see also Boyd, *Nonlinear Optics*

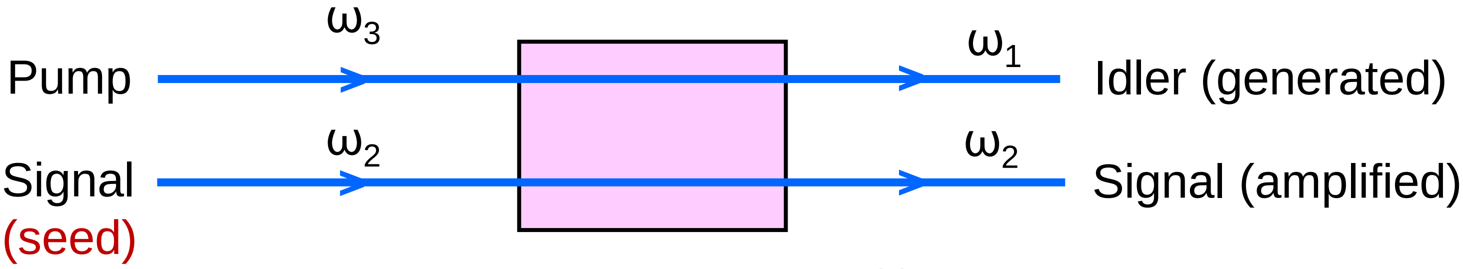
$\chi^{(2)}$-application: frequency doubling

800nm (red) from Ti:sapphire → **400nm (blue)** in β-BaBO$_3$ crystal

- SFG, SHG nowadays: phase-matched generation, conversion efficiency up to 80%
- Phase matching for fs pulses over large ω bandwidth: use thin nonlinear crystals to still get $\Delta kd < \pi$ for all ω (reduced thickness is compensated by high intensity)

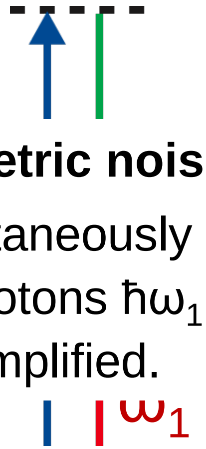
Optical parametric amplification (OPA)

Goal: Generate 2 tunable photons $\hbar\omega_1$ and $\hbar\omega_2$ from $\hbar\omega_3$ pump photon (annihilated)



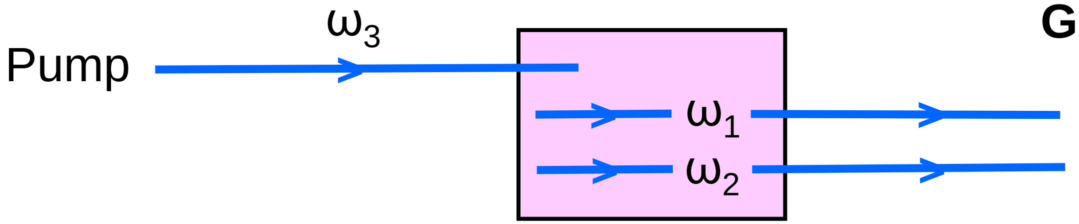
Transparent nonlinear $\chi^{(2)}$ crystal

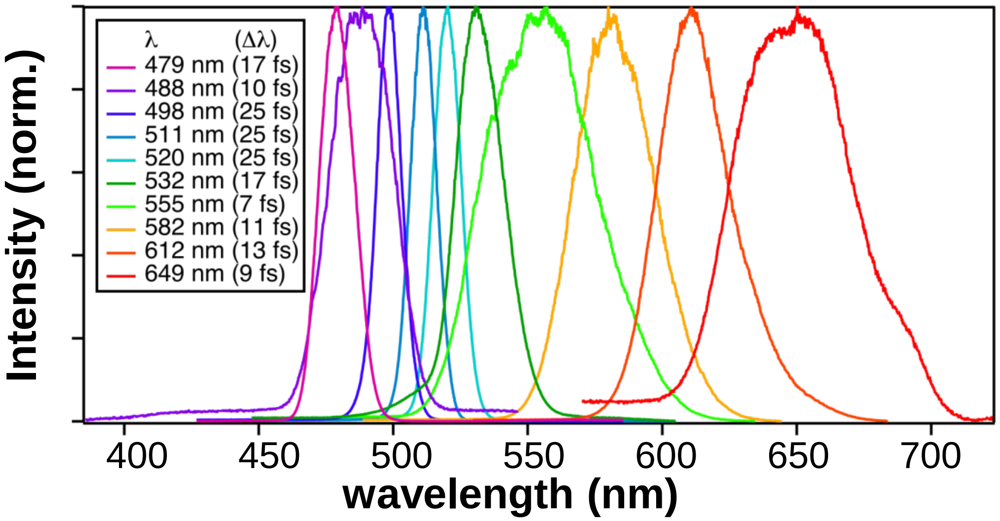
$$\omega_3 - \omega_2 = \omega_1$$



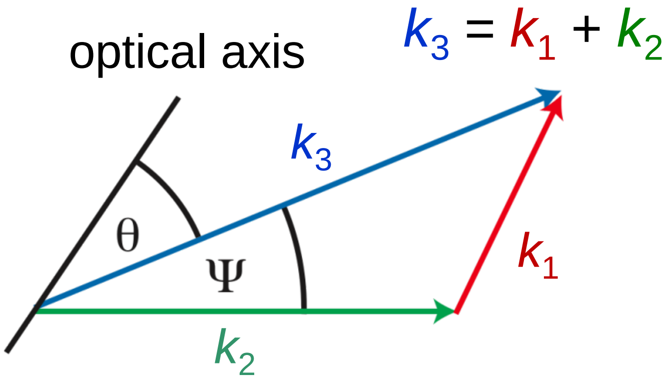
Generation from parametric noise:

Input pump $\hbar\omega_3$ spontaneously generates pairs of photons $\hbar\omega_1$, $\hbar\omega_2$ which are then amplified.





Non-collinear OPA (β-$BaBO_3$)



Femtosecond pulses - what for?

Femtosecond laser pulses have unique properties:

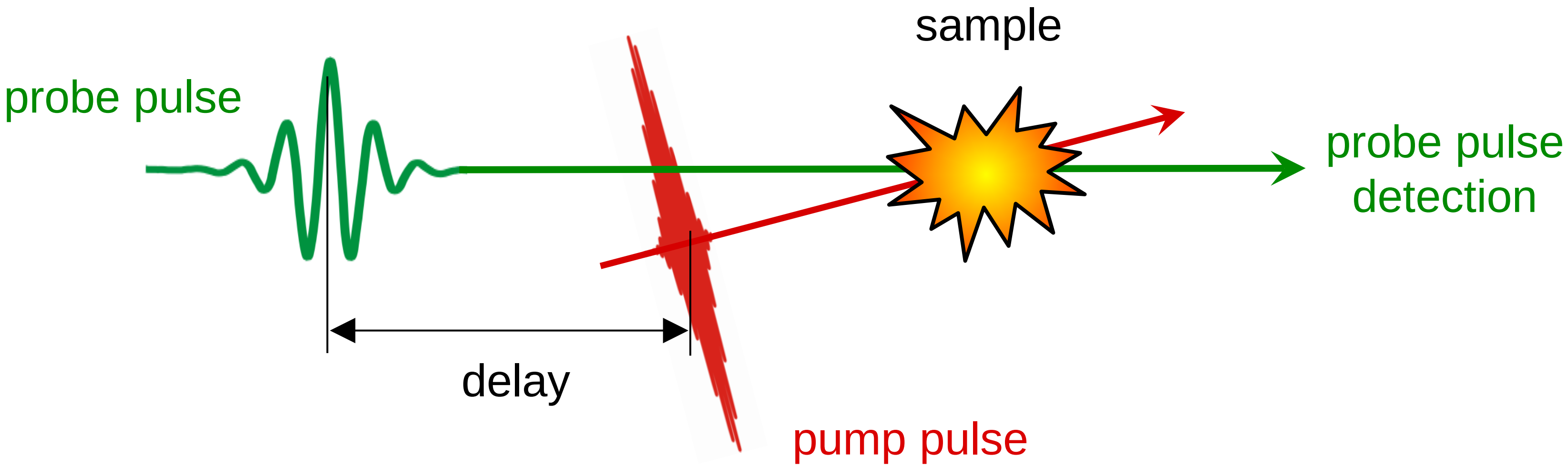
- short duration
- high peak intensities
- stable repetition rate (“clockwork”)

Applications:

1. Metrology: measure frequency of light
2. Nonlinear optics: new frequencies, new probes
3. fs spectroscopy: resolve ultrafast dynamics
4. Novel states: extreme non-equilibrium, new processes
5. …

Pump-probe spectroscopy

Resolve ultrafast processes in matter:



Pump pulse triggers

- Nuclear motion
- Electron dynamics
- Spin dynamics

…optical excitation
IR or THz pumping

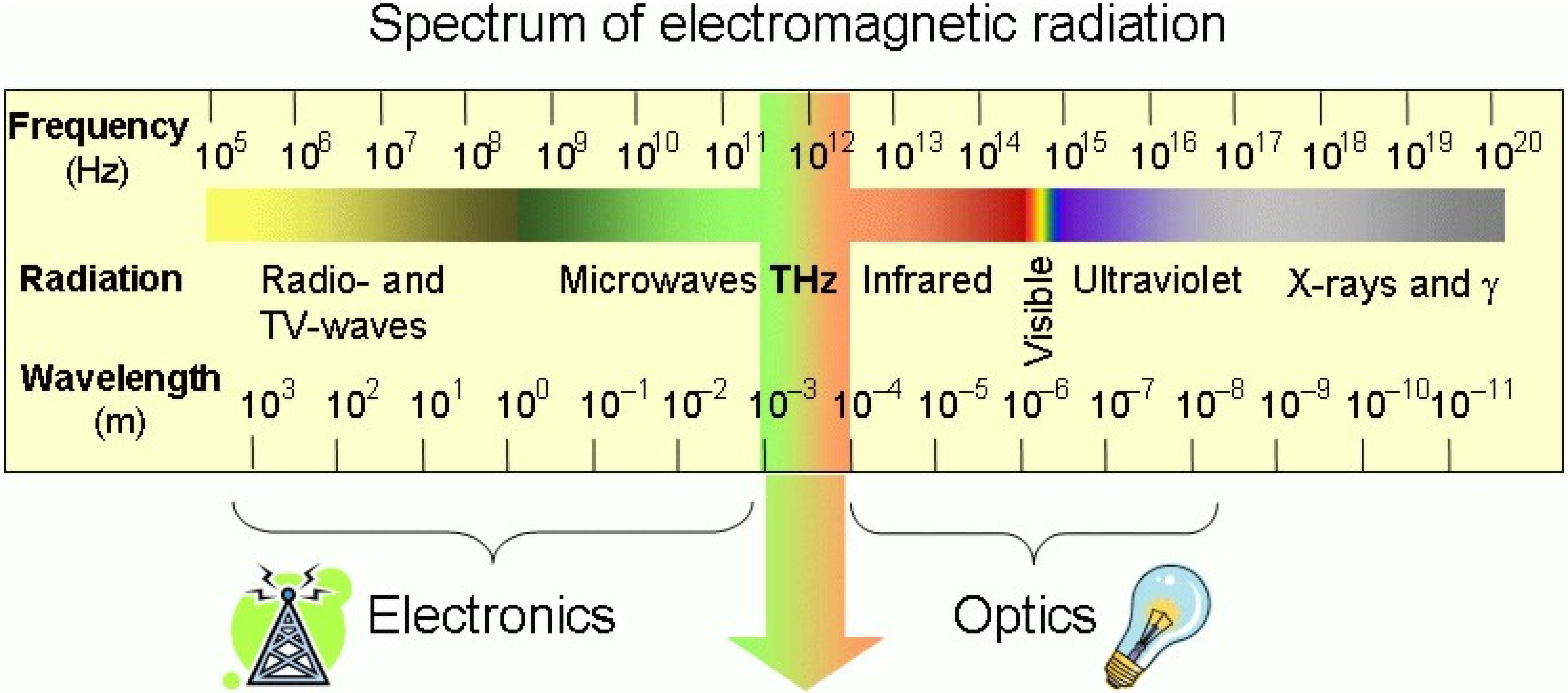
Probe pulse monitors

- Phonon occupation & lattice structure
- Electronic structure & population,
- Spin polarization & magnetization

…linear & nonlinear optical probes
photoemission & x-ray spectroscopy

Example: time-resolved THz Spectrocopy

1THz = 10^{12} Hz

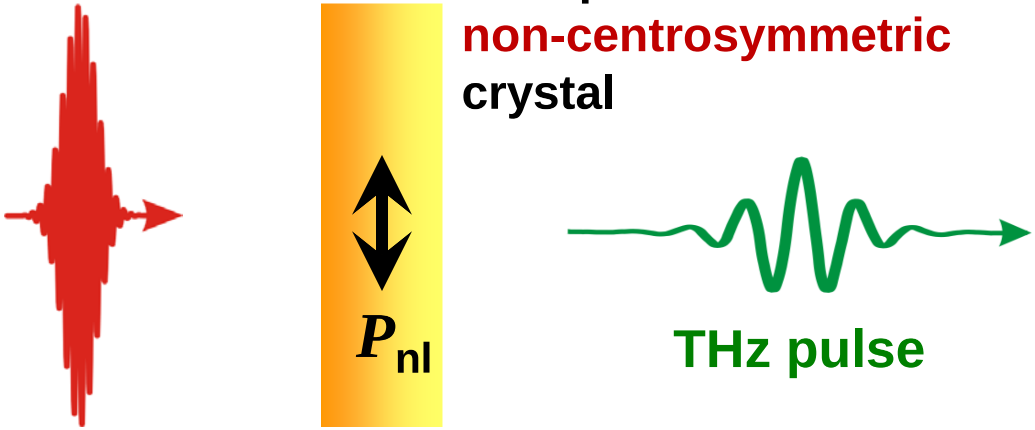


Terahertz (THz) window: 0.3 to 30THz

THz spectroscopy: photon energy of only **4.1 meV per THz**

⇒ **probe of elementary excitations with low energy ΔE**

THz generation with ultrashort laser pulses



transparent
non-centrosymmetric
crystal

intense
fs pulse

P_{nl}

THz pulse

- **fs pulse induces nonlinear charge displacement**

$$\boldsymbol{P}_{\mathrm{nl}} \propto \boldsymbol{E}_{\mathrm{fs}}^2 = \left\{\mathrm{Re}\left[A(t)\,\mathrm{e}^{\mathrm{i}\omega_0 t}\right]\right\}^2 = \mathrm{Re}\left[A^2(t)\,\mathrm{e}^{\mathrm{i}2\omega_0 t}\right] + |A(t)|^2$$

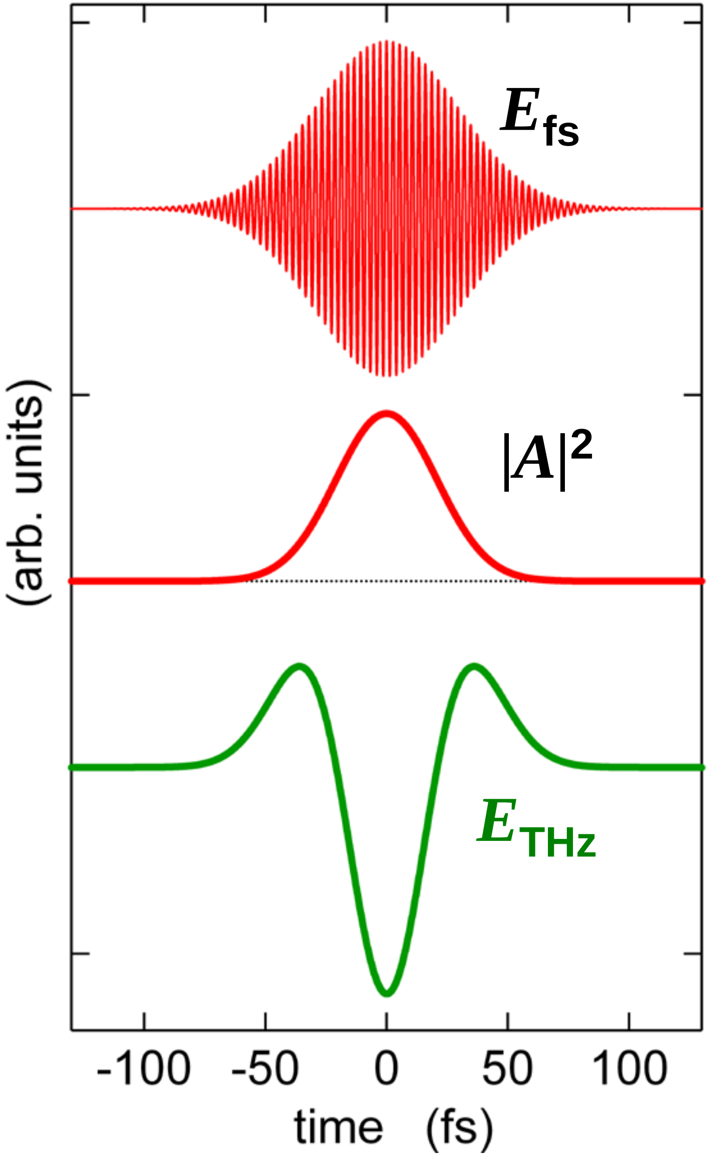
2nd harmonic generation

0th harmonic: optical rectification (THz)

- **radiated THz field**

$$\boldsymbol{E}_{\mathrm{THz}} \propto \partial_t^2 \boldsymbol{P}_{\mathrm{THz}} = \partial_t^2 |A(t)|^2$$

THz generation with ultrashort laser pulses



$$\boldsymbol{E}_{\mathrm{THz}} \propto \partial_t^2 \boldsymbol{P}_{\mathrm{THz}} = \partial_t^2 |A(t)|^2$$

Example:

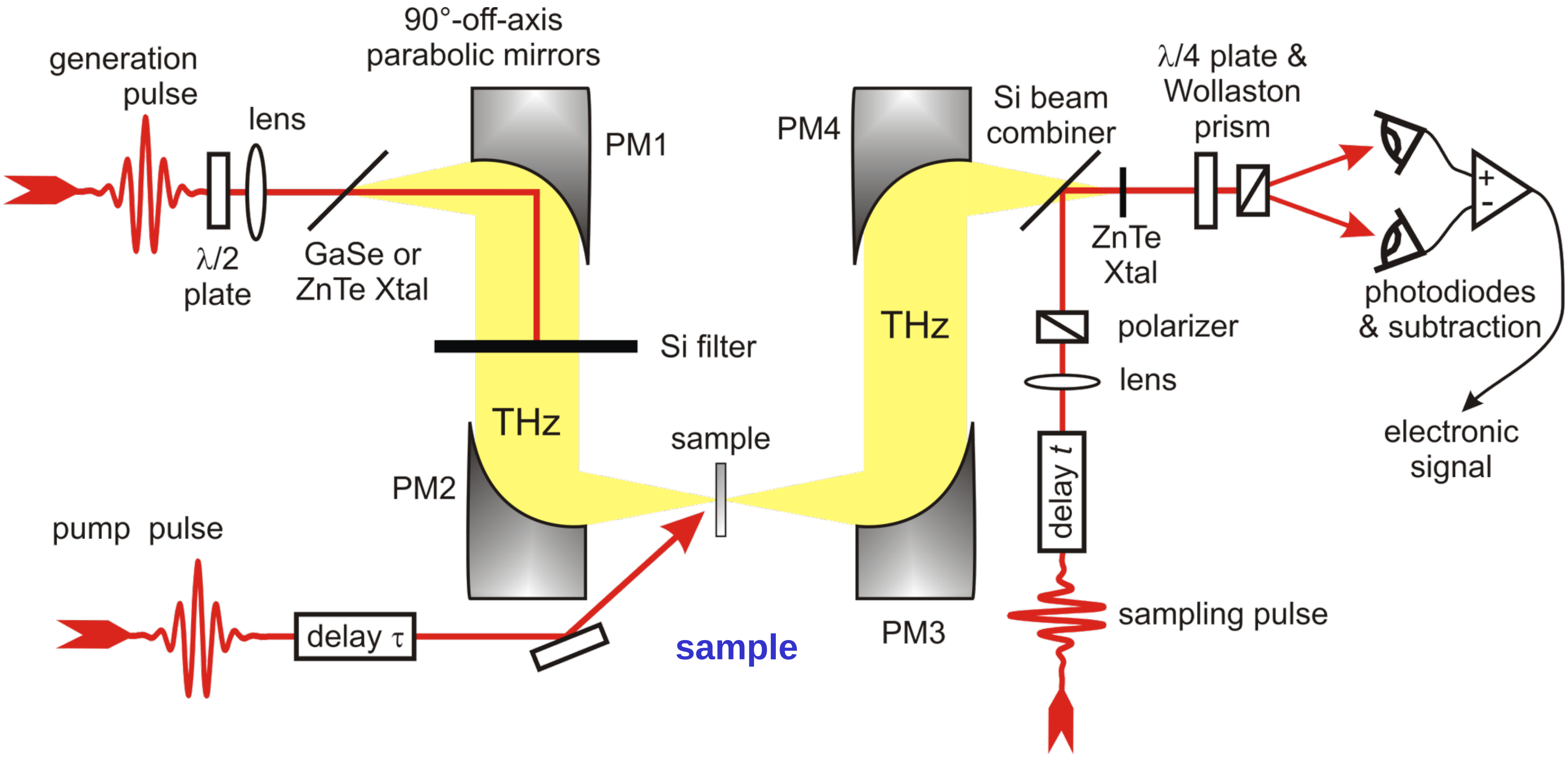
- 50fs optical input pulse yields 50fs single-cycle output

Practical issues:

material resonances induce

- non-instantaneous $\boldsymbol{P}_{\mathrm{nl}}$
- velocity mismatch of pulses
- THz absorption

…a typical THz spectrometer



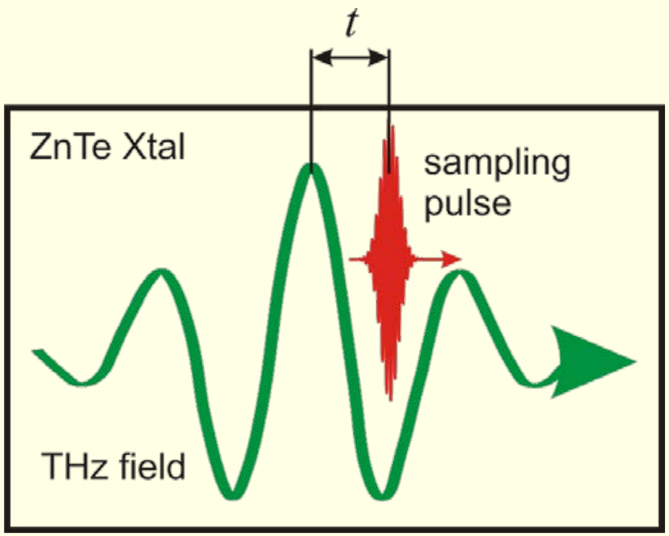
THz setups: 10 fs Ti:Sa Oscillator 80 MHz (1 - 40 THz with ZnTe, GaP, GaSe)
20 fs amplifier system (pulse shaper + 10 fs sampling pulse)

…a typical THz spectrometer

Detection

of THz electric field

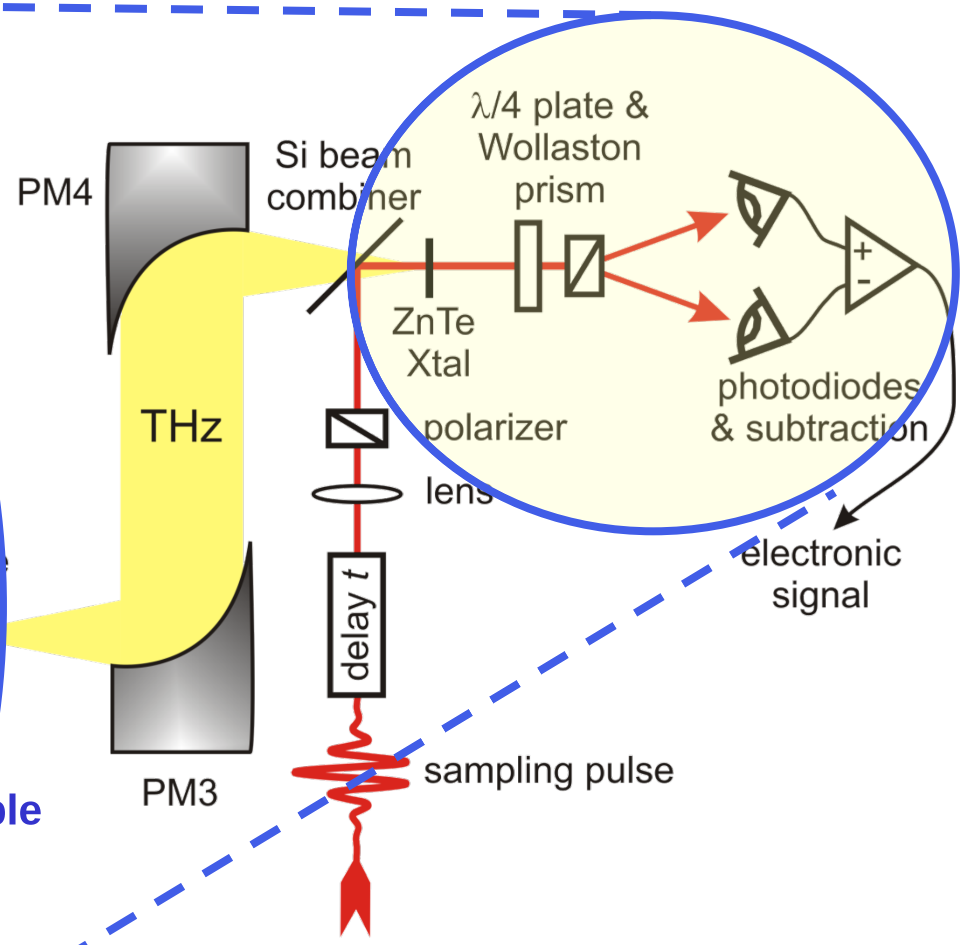
by electro-optic sampling)



Wu *et al.*, APL (1996)

Ellipticity of sampling pulse as function of THz delay t ⇒

direct detection of $E(t)$



generatio

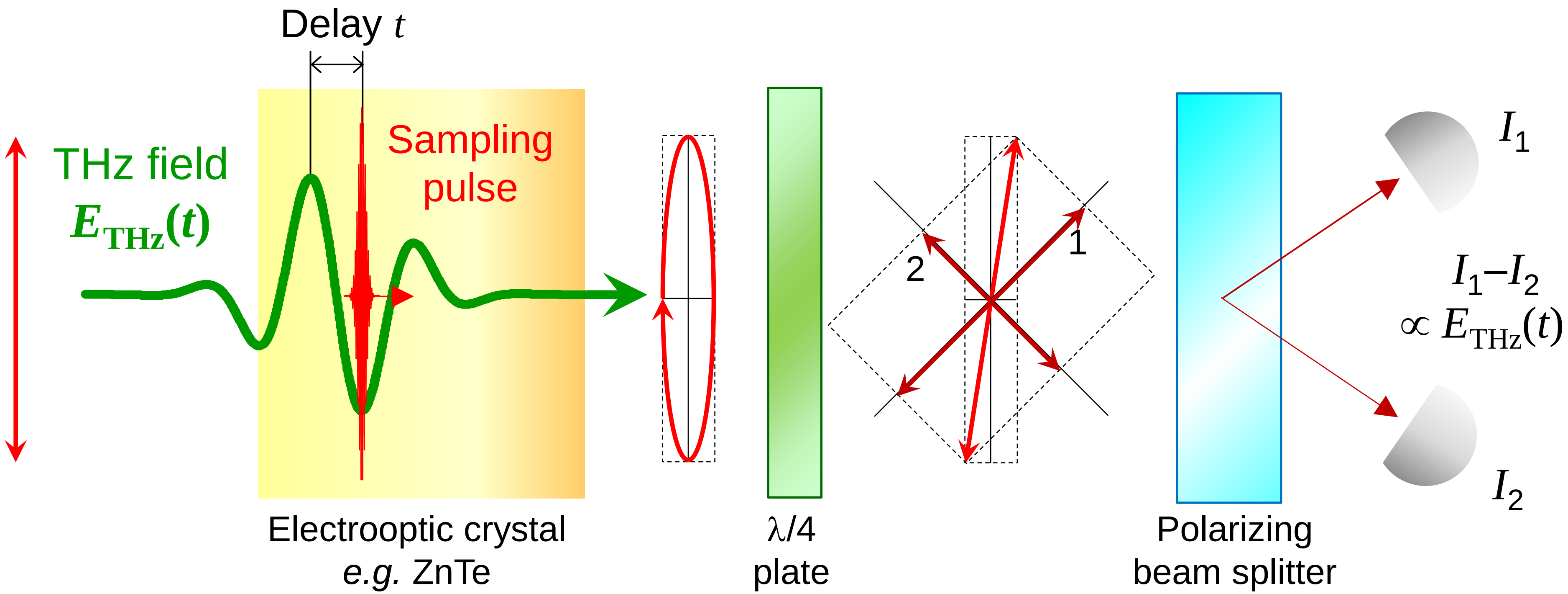
p

ple

THz s … ator 80 MHz (1 - 40 THz with ZnTe, GaP, GaSe)

… system (pulse shaper + 10 fs sampling pulse)

THz detection: electro-optic sampling



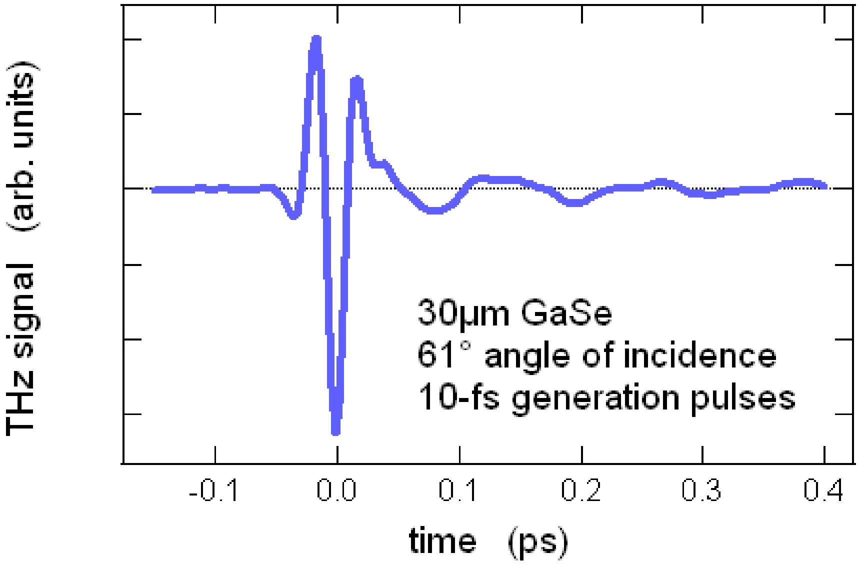
Electro-optic (or Pockels) effect:

Change in refractive index $\propto E_{\mathrm{THz}}(t) \Rightarrow$ crystal becomes birefringent

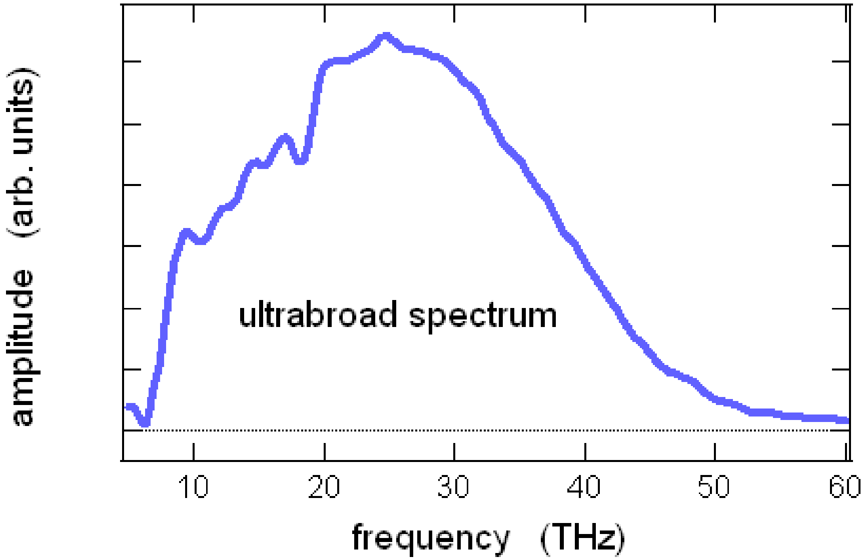
Scan $I_1 - I_2$ vs t $\Rightarrow$ get directly THz electric waveform $E_{\mathrm{THz}}(t)$

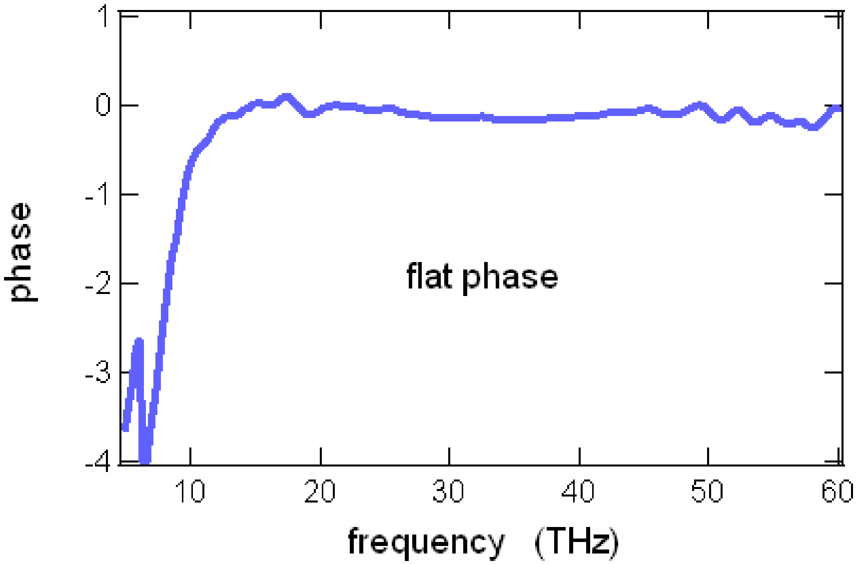
Wu, Zhang, APL (1995)

Example: Ultrashort and broadband THz pulse



- complete information about electric field
- peak SNR ≈ 10^4 Hz$^{-1/2}$
- spectrum ranges from 8 to 50THz





How to use THz pulses in spectroscopy

ultrafast Ohm-meter

transmit THz pulses through sample & detect *E*(t)
⇒ get instantaneous conductivity at THz frequencies

ultrafast Ampere-meter

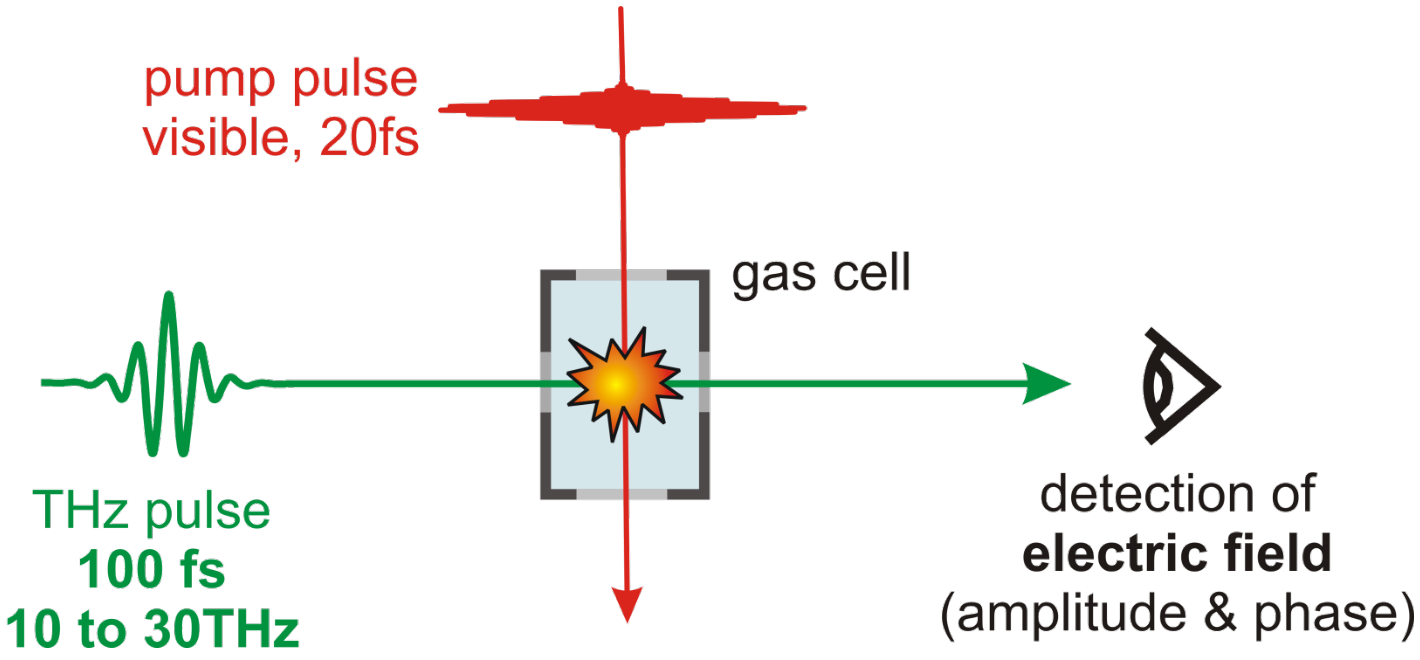
photo-excite sample and detect emitted THz pulse
⇒ get current as function of time

ultrafast voltage source

excite sample with intense THz pulses
⇒ drive low-energy excitations (excitons, magnons, ...)

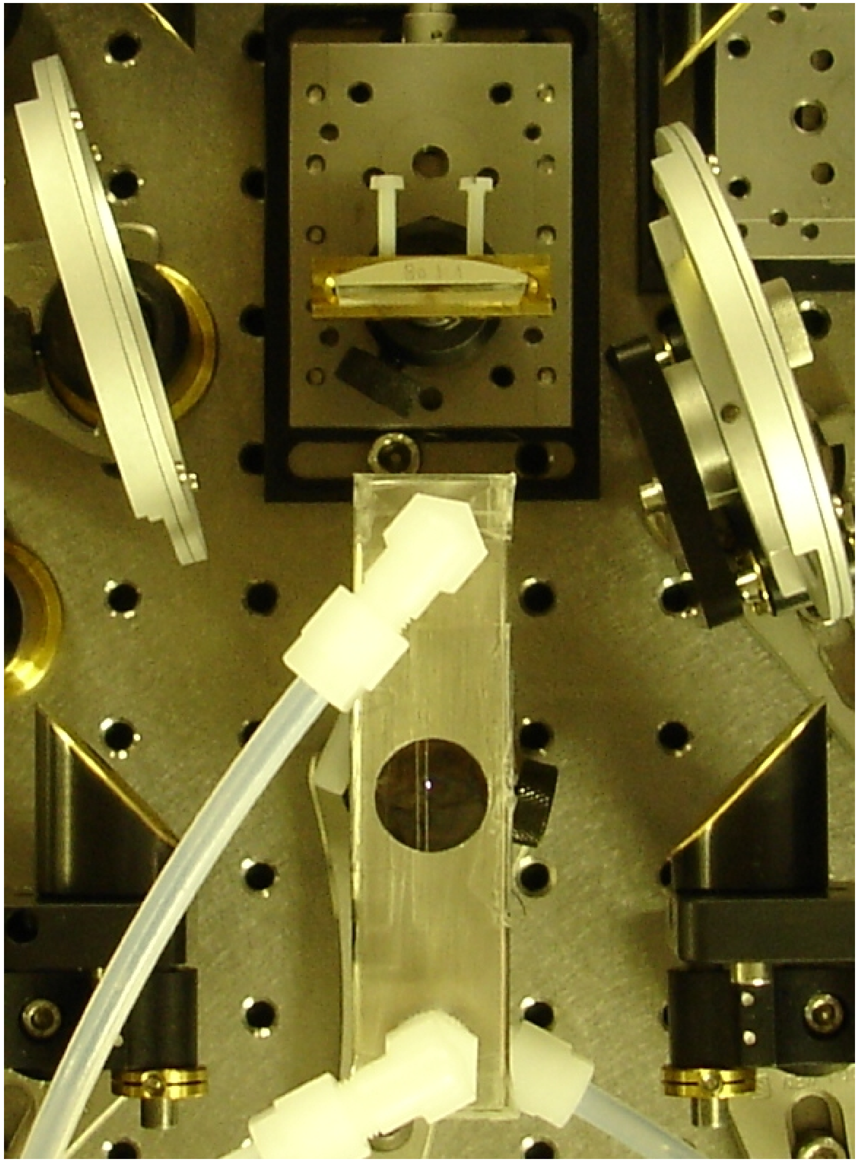
Experimental principle (example)

THz-Spectroscopy of plasma in ionized air

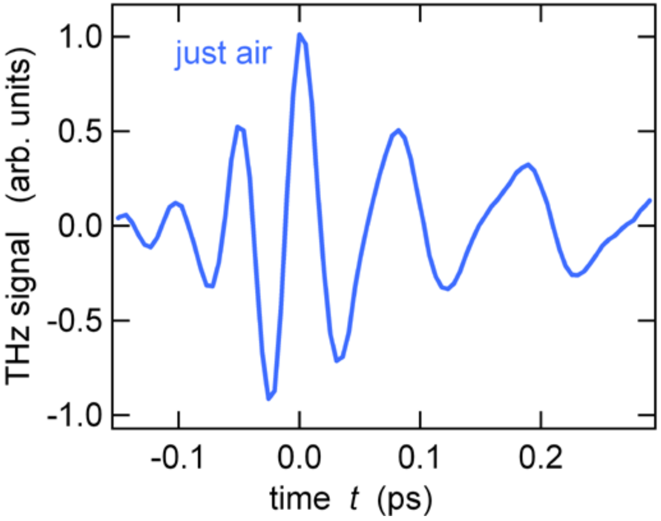


- **pump pulse ionizes gas, creates free electrons and ions**
- **wait ...**
- **THz probe pulse measures plasma conductivity**

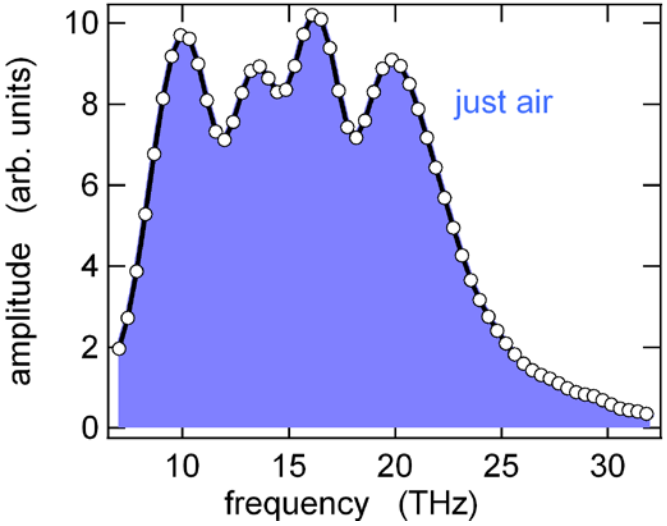
... in the lab



Raw data and analysis



Fourier transformation

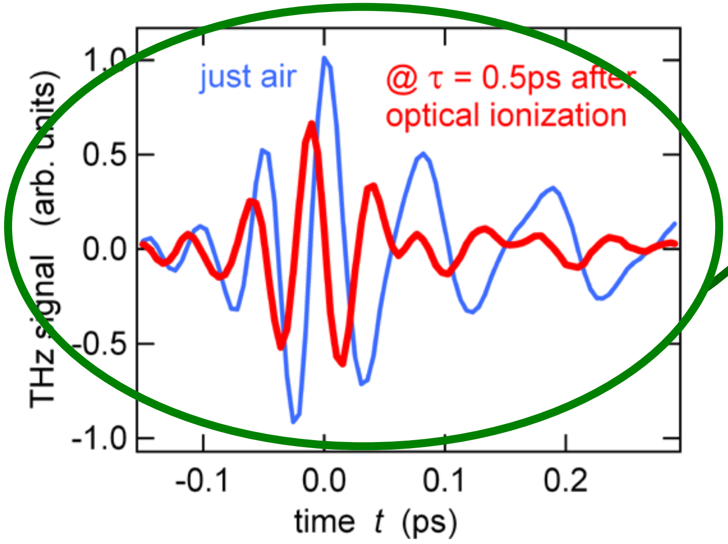


just air

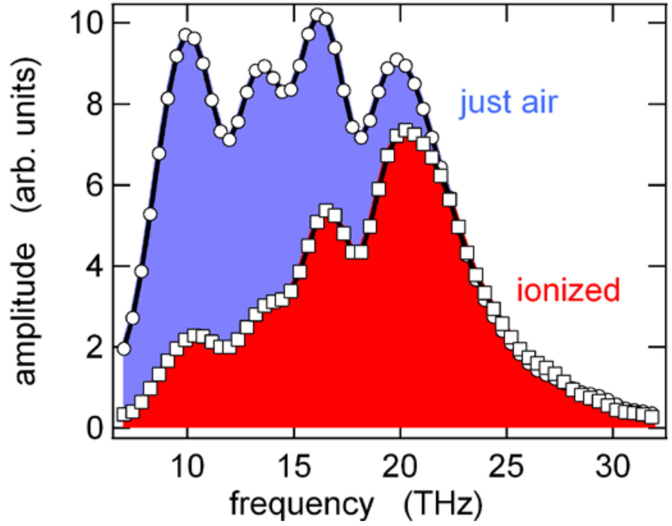
THz pulse
100 fs
10 to 30THz

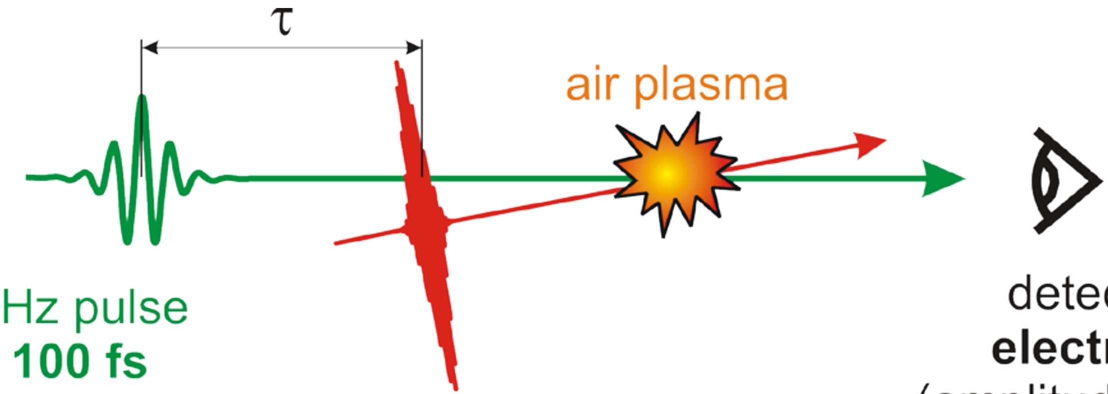
detection of
electric field
(amplitude & phase)

Raw data and analysis



Fourier transformation





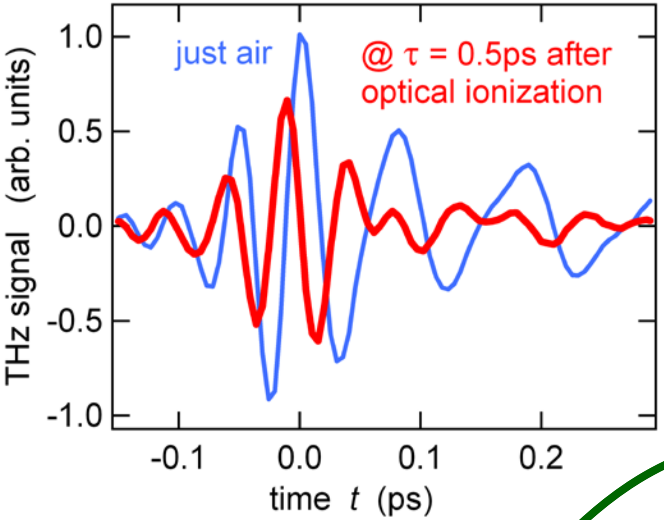
air plasma

THz pulse
100 fs
10 to 30THz

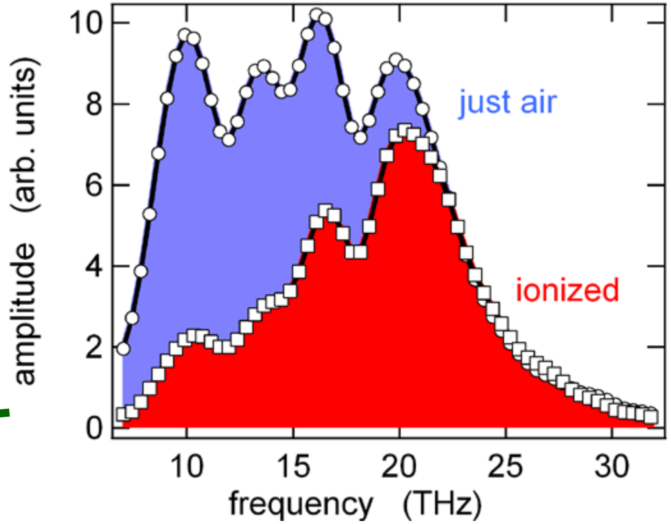
pump pulse
visible, 20fs

detection of
electric field
(amplitude & phase)

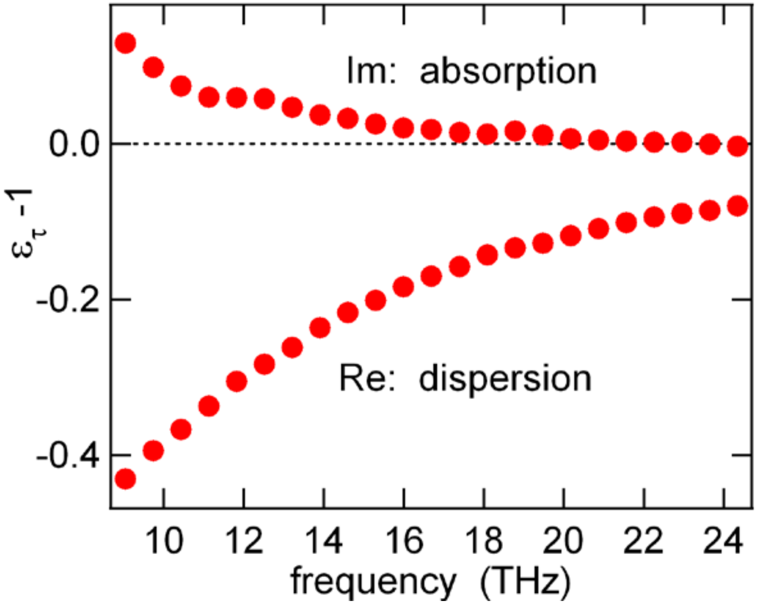
Raw data and analysis



Fourier transformation



Maxwell equations



instantaneous dielectric function ε_τ

time after sample excitation

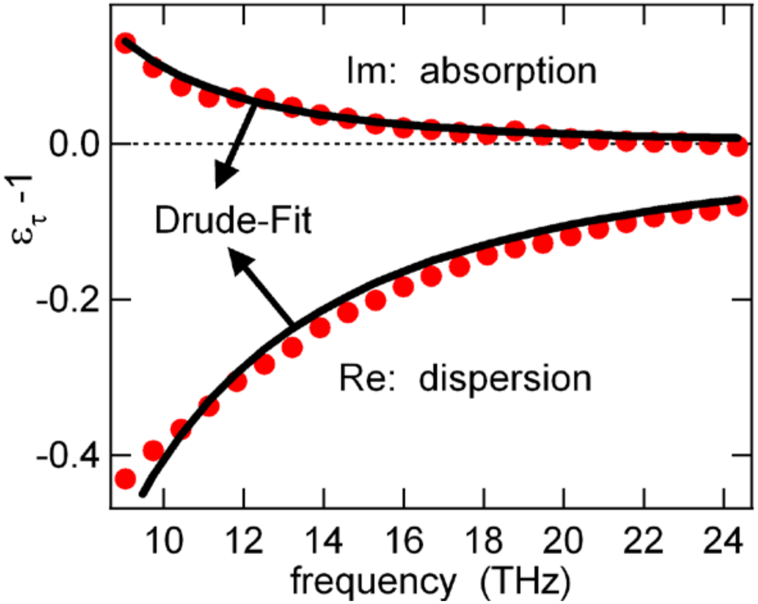
Dielectric function ε

|ε| = ease to polarize a material with an external electric field

Im ε = strength to absorb light with frequency ω

Drude model of ε for free electrons:

- electrons undergo collisions with rate Γ
- velocity is randomized after each collision

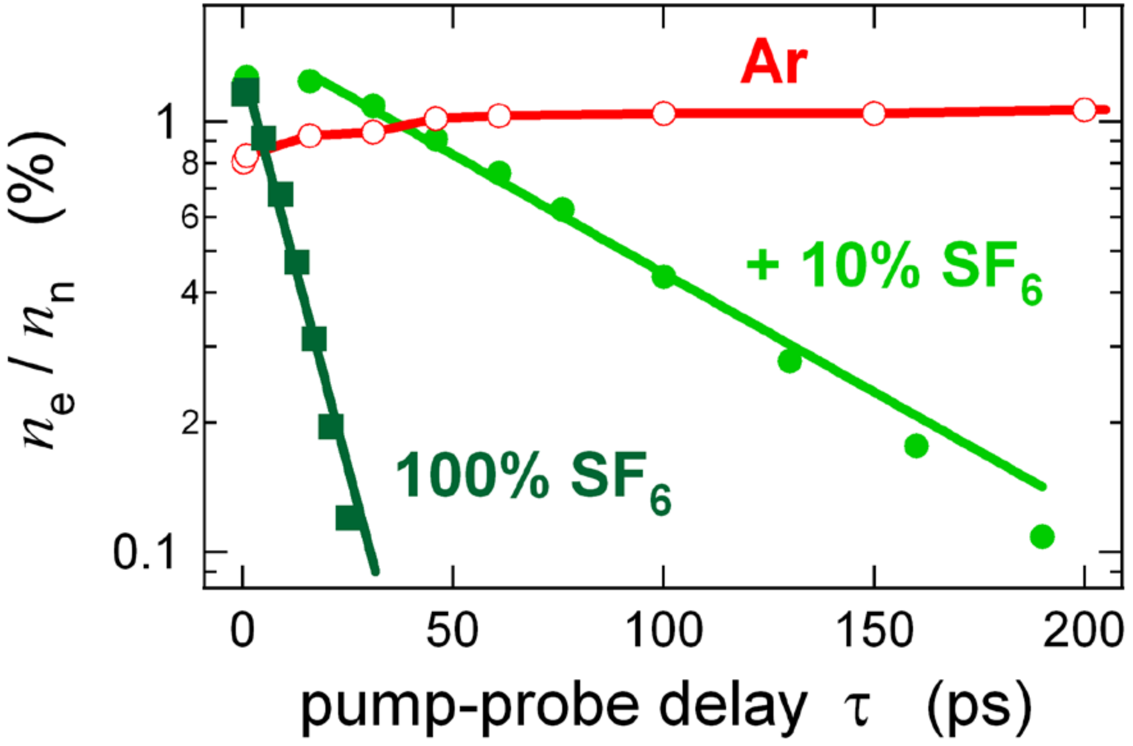


Drude model

n_e	**free-electron density**
Γ	**electron collision rate**

@ time τ after sample excitation

Ultrafast plasma quenching by SF_6



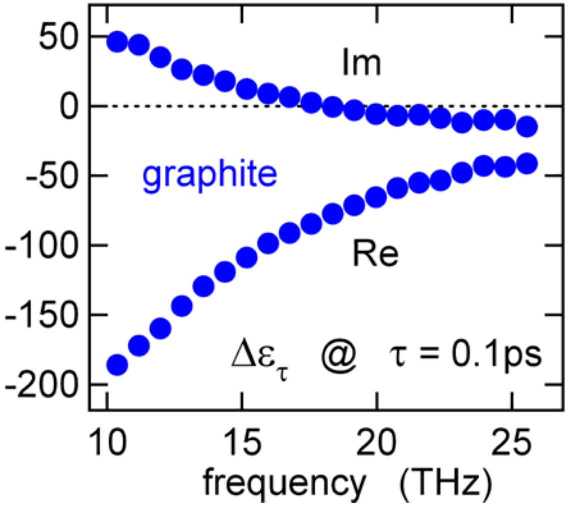
- **long-lived Ar plasma**
- **add 10% SF_6: exponential electron decay with 80-ps time constant**

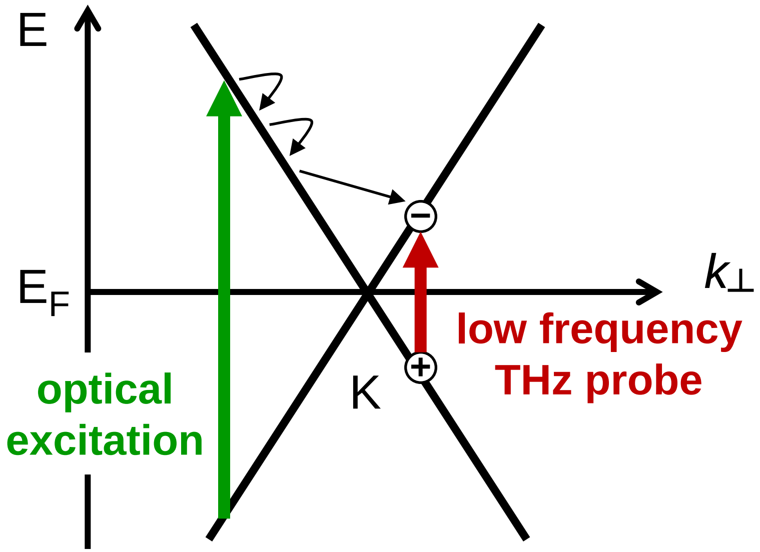
⇒ SF_6 acts as an ultrafast electron quencher

exponential decay via $SF_6 + e^- \rightarrow SF_6^-$ reaction

see CPL **96**, 350 (2006) & PRE **76**, 066401 (2007)

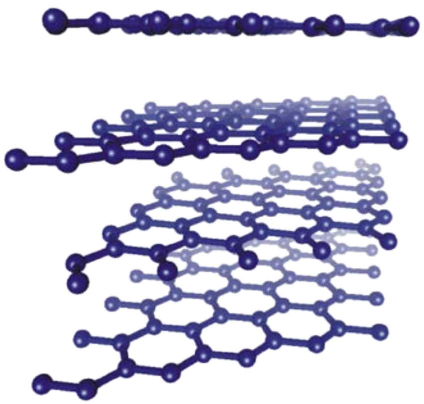
Free carriers and excitons: graphite *vs* CNTs



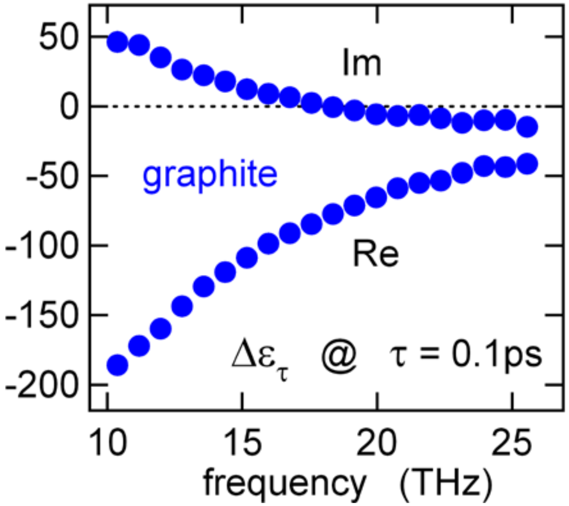


photoexcitation of free charge carriers

Graphite

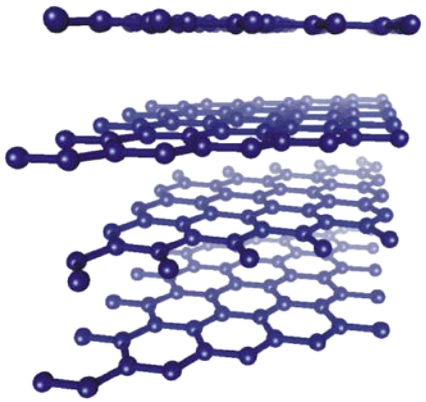


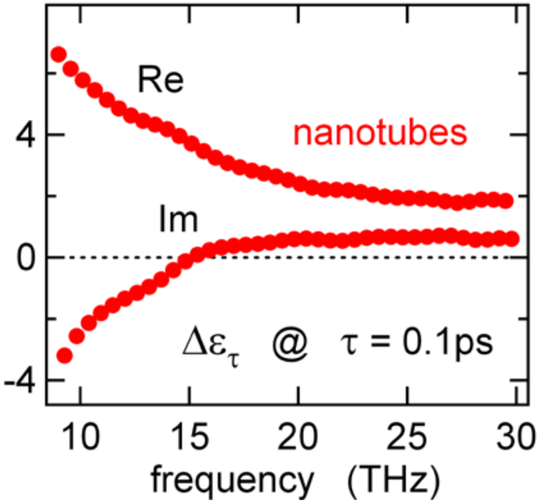
Free carriers and excitons: graphite *vs* CNTs



photoexcitation of free charge carriers

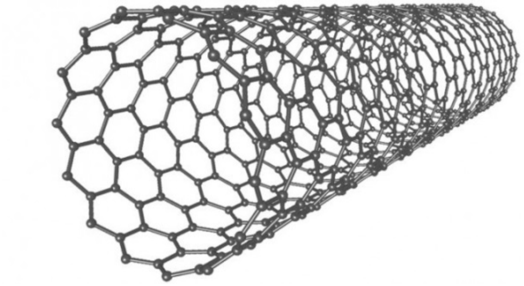
Graphite



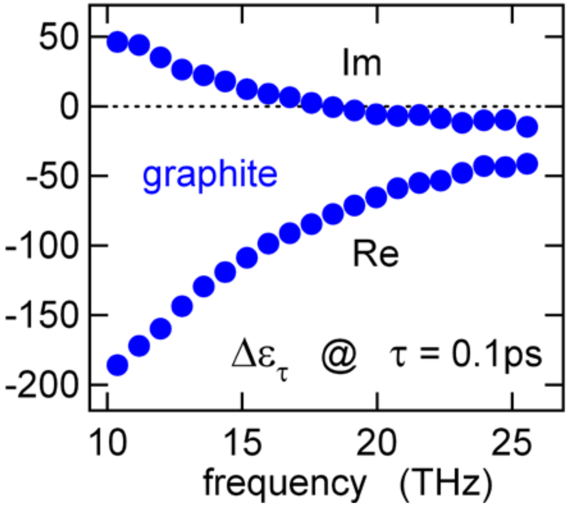


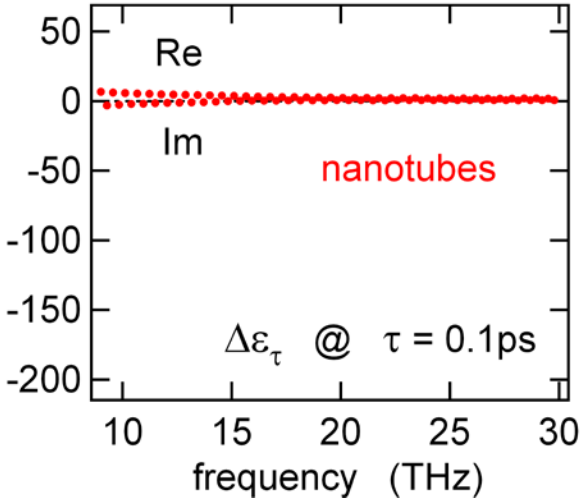
very different $\Delta\varepsilon$

Carbon Nanotubes (CNTs)



Free carriers and excitons: graphite *vs* CNTs



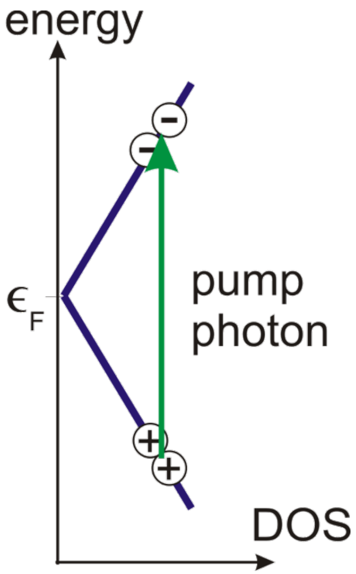


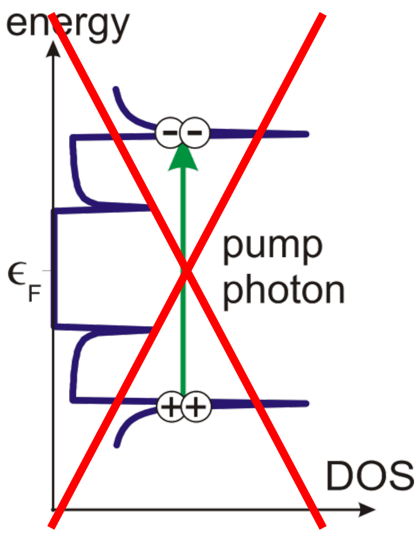
generation of free charge carriers

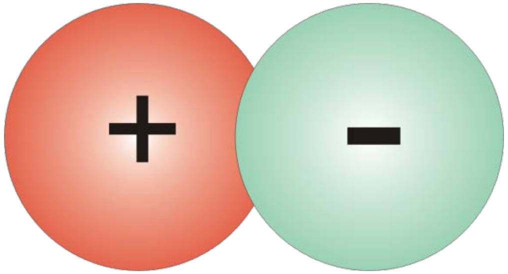
semicondu

very different Δε

n generation







binding energy > 0.3eV

Wang *et al.*, Science (2005)

⇒ invisible for THz!

Summary

- Various elementary processes in physics, chemistry, biology occur on femtosecond time scales.
- Femtosecond laser pulses exhibit unique properties for metrology of light, non-linear optics, ultrafast spectroscopy & more.
- Example: Time-domain THz spectroscopy of photoexcited carriers.

What‘s next?

- THz pumping of low frequency modes in solids (magnons, phonons)
- Photoinduced phase transitions probed by time-resolved ARPES
- Ultrafast surface chemistry probed by femtosecond x-rays