Ultrafast Laser Spectroscopy and Applications to Dynamics at Interfaces and Solids

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Motivation: Elementary interactions in solids

Coupling between the various degrees of freedom

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 H₂ 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)

\textit{cis-trans} isomerization

\[ \text{Retinal} \xrightarrow{h\nu} \text{all-trans} \]
Ultrafast elementary processes

Spreading of a Gaussian wave packet

Example: alkali atom at metal surface

\[ \langle \Delta x \rangle^2 = d^2 \left( 1 + \Delta^2 \right) \]

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

characteristic time

spreading of Gaussian wave packet

\[ t [s] = 10^4 \cdot (d [m])^2 \]

\[ d = 5 \text{ Å} \Rightarrow t = 2.5 \text{ fs} \]

see F. Schwabl, *Quantum Mechanics*
Ultrafast elementary processes

Spreading of a Gaussian wave packet

Example: alkali atom at metal surface

Chulkov et al., Chem. Rev. 106, 4195 (2006)
Ultrafast elementary processes

Electrons in solids: scattering time between subsequent collisions

Simple picture (Drude 1900)

Electric conductivity of metals:

\[ \vec{j} = \sigma \vec{E}, \quad \sigma = \frac{n e^2 \tau}{m_{\text{eff}}} \]

with scattering time \( \tau \)

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 $E(x,t)$
- Peak field can be $> 10$ V/Å

shown here:

- 100-fs pulse, centered at 800 nm (frequency ~400 THz, 2.5 fs per cycle)
- Bandwidth-limited ($\omega_c = \text{const}$)

How to generate such fs pulses?

$E(t) = \text{Re} \left[ A(t) \exp(-i\omega_c t + \varphi) \right]$
Most popular gain medium: Ti:sapphire
Typically 1 to 10 W average laser power

Laser oscillator: $f_{\text{rep}} \sim 100$ MHz
$\Rightarrow$ pulse energy $\sim 10$ 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,
$\quad \omega_j = j\Delta\omega = j\pi c/L$

Mirror Mirror
Light wave

$\lambda_j = \frac{2L}{j}$

Mode comb

Idea:
superposition of modes should yield a wavepacket or pulse
Mode locking

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$\Rightarrow$ frequency comb of modes,

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

Idea:
superposition of modes should yield a wavepacket or pulse

$\Rightarrow$ mode locking
Mode locking

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

Mirror

Light wave

Gain medium

Active mode locking: Modulator

Gain curve

Mode comb

Modulate cavity:
sidebands appear at modulation frequency $\omega_{\text{mod}}$

Choose $\omega_{\text{mod}} = \Delta \omega = \pi c / L$:
Sidebands are amplified, new sidebands etc.

Mode locking $\Rightarrow$ fs pulse

What is a typical gain medium?
**Gain by laser-pumped Ti:sapphire**

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

- $|2\rangle$ (long-lived)
- $|3\rangle$ (long-lived)
- $|4\rangle$ (short-lived)

Pump (514...532nm)

Broad emission (650...1080nm)
Gain by laser-pumped Ti:sapphire

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

Pump (514...532nm)

|2⟩

|3⟩ (long-lived)

Broad emission (650...1080nm)

|4⟩ (short-lived)

|1⟩

Δλ > 200 nm

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 $\Delta \omega = \frac{\pi c}{L}$
⇒ 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

Pump laser: Nd:YVO$_4$, 532 nm, 6.75 W

- Passively mode locking
  \[ \Rightarrow 10^6 \text{ coupled modes} \]
Typical femtosecond lasers

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

- pulse energy $\sim 10$ nJ
- laser is on for $\sim 1$ s/day

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

- pulse energy $\sim 1$ to 10 mJ
- laser is on for $\sim 1$ s/300 years

How to characterize femtosecond laser pulses?
How can we characterize a laser pulse?

Example: spectrum of 10-fs Ti:sapphire pulse

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

$\Rightarrow$ One cannot decide whether light comes from a light bulb or a fs laser

Ultimate goal: Measure electric field $E(t)$

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

What about an interferometer?
Autocorrelation measurement

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

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

Time average  Single intensities  Interference term: linear autocorrelation
Light pulse autocorrelation

Laser pulse:
- Fourier-limited
- Duration $\tau_p$

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 $|\tilde{E}(\omega)|^2$  
  Why?
Wiener Chintchin theorem

Fourier synthesis:

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

Linear Autocorrelation:

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

⇒ Different frequencies do not interfere

Result:

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

i.e. same information as intensity spectrum \( |\tilde{E}(\omega)|^2 \)
Quadratic autocorrelation measurement

\[ E(t) \]

\[ E(t-\tau) \]

\[ \tau \]

\[ \text{Mirror 1} \]

\[ \text{Mirror 2} \]

\[ \text{Source} \]

\[ \text{Detector} \]

\[ \text{Beam splitter} \]

\[ E(t) \]

\[ E(t-\tau) \]

\[ \text{Idea: generate intermediate field} \]

\[ E_{SH}(t) \propto E^2(t) \]

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

Ensemble width gives good approximation of pulse duration

Information (almost) sufficient to extract pulse field $E(t)$
Femtosecond 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. …
Femtosecond pulses - what for?

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

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 extremely high precision of a frequency comb

“Optical clockwork”
T. Hänsch, Nobel prize 2005

Time domain:
pulse train

\[ F \]

Frequency domain:
frequency comb

\[ f_n = n f_{rep} + f_o \]
(1060 nm)

\[ f_{2n} = 2 n f_{rep} + f_o \]
(530 nm)

\[ 2 (f_n) - f_{2n} = 2 (n f_{rep} + f_o) - (2 n f_{rep} + f_o) = f_o \]

⇒ Measurement of phase offset \( f_0 \)
How to measure an optical frequencies with very high accuracy?

Trick:

exploit extremely high precision of a frequency comb

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

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Nonlinear light-matter interaction

If light fields $E$ comparable to intraatomic fields ($E_{\text{at}} \sim 10 \ldots 100 \text{ V/Å}$)
⇒ Nonlinear response

⇒ Charge displacement $P$ ⇒ Re-radiation of light ("scattering")

Phenomenological approach: Taylor expansion

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

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

see also Boyd, *Nonlinear Optics*
Quadratic nonlinearity: SFG

Lowest nonlinear response:

\[ P_i^{(2)}(t) = \chi^{(2)} E^2(t) \]

⇒ Nonlinear optics

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

Consider two-field input:

\[ E(t) = \text{Re}\left[ A_1(t)e^{-i\omega_1 t} + A_2(t)e^{-i\omega_2 t} \right] \]

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

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

- 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 $x$
- harmonic approximation invalid
- additional force nonlinear in $x$

\[ \nabla V = -\omega_0^2 x + ax^2 + bx^3 + ... \]

$F_{\text{nl}}(x)$

$\Rightarrow$ Equation of motion

\[ \hat{L}x = qE(t) + F_{\text{nl}}(x) \quad \text{with} \quad \hat{L} = \partial_t^2 + 2\gamma \partial_t + \omega_0^2 \]

solution: $x \approx x_0 + \Delta x$

from perturbation $F_{\text{nl}}(x)$

$x_0(\omega) = L^{-1}(\omega) qE(\omega)$

$\Delta x(\omega) = L^{-1}(\omega) F \left[ F_{\text{nl}}(x_0(t)) \right]$ 

Linear response ($F_{\text{nl}} = 0$) 1st-order nonlinear correction

$\Rightarrow$ Model for nonlinear polarization $P[E]$ see also Boyd, Nonlinear Optics
SFG, SHG nowadays: phase-matched generation, conversion efficiency up to 80%

Phase matching for fs pulses over large $\omega$ bandwidth: use thin nonlinear crystals to still get $\Delta kd < \pi$ for all $\omega$ (reduced thickness is compensated by high intensity)

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

800nm (red) from Ti:sapphire $\rightarrow$ 400nm (blue) in $\beta$-BaBO$_3$ crystal
Goal: Generate 2 tunable photons $\hbar \omega_1$ and $\hbar \omega_2$ from $\hbar \omega_3$ pump photon (annihilated)

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

Optical parametric amplification (OPA)

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

Non-collinear OPA ($\beta$-BaBO$_3$)

Intensity (norm.)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td></td>
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<tr>
<td>450</td>
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<tr>
<td>500</td>
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<td>600</td>
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<tr>
<td>650</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>

Generation from parametric noise:

$\omega_3 - \omega_2 = \omega_1$
Femtosecond laser pulses have unique properties:

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Pump-probe spectroscopy

Resolve ultrafast processes in matter:

**Pump pulse** triggers
- Nuclear motion
- Electron dynamics
- Spin dynamics

**Probe pulse** monitors
- Phonon occupation & lattice structure
- Electronic structure & population,
- Spin polarization & magnetization

…optical excitation
IR or THz pumping

…linear & nonlinear optical probes
photoemission & x-ray spectroscopy
**Example: time-resolved THz Spectroscopy**

1 THz = $10^{12}$ Hz

**Spectrum of electromagnetic radiation**

| Frequency (Hz) | 10^5 | 10^6 | 10^7 | 10^8 | 10^9 | 10^10 | 10^11 | 10^12 | 10^13 | 10^14 | 10^15 | 10^16 | 10^17 | 10^18 | 10^19 | 10^20 |
|----------------|------|------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Radiation      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|                | Radio- and TV-waves | Microwaves | THz | Infrared | Visible | Ultraviolet | X-rays and γ |
| Wavelength (m) | 10^3 | 10^2 | 10^1 | 10^0 | 10^-1 | 10^-2 | 10^-3 | 10^-4 | 10^-5 | 10^-6 | 10^-7 | 10^-8 | 10^-9 | 10^-10 | 10^-11 |

**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 $\Delta E$
THz generation with ultrashort laser pulses

- Intense fs pulse induces nonlinear charge displacement

\[ P_{nl} \propto E_{fs}^2 = \left\{ \text{Re} \left[ A(t) e^{i\omega_0 t} \right] \right\}^2 = \text{Re} \left[ A^2(t) e^{i2\omega_0 t} \right] + |A(t)|^2 \]

- Radiated THz field

\[ E_{\text{THz}} \propto \partial_t^2 P_{\text{THz}} = \partial_t^2 |A(t)|^2 \]
**THz generation with ultrashort laser pulses**

\[ E_{\text{THz}} \propto \partial_t^2 P_{\text{THz}} = \partial_t^2 |A(t)|^2 \]

**Example:**
- 50fs optical input pulse yields 50fs single-cycle output

**Practical issues:**
- material resonances induce non-instantaneous \( P_{\text{nl}} \)
- 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

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Detection of THz electric field by electro-optic sampling

Ellipticity of sampling pulse as function of THz delay $t \Rightarrow$ direct detection of $E(t)$

Wu et al., APL (1996)
THz detection: electro-optic sampling

Electro-optic (or Pockels) effect:
Change in refractive index $\propto E_{\text{THz}}(t)$ $\Rightarrow$ crystal becomes birefringent

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

Wu, Zhang, APL (1995)
Example: Ultrashort and broadband THz pulse

- complete information about electric field
- peak SNR $\approx 10^4 \text{ Hz}^{-1/2}$
- 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, ...)

$E(t)$
Experimental principle (example)

THz-Spectroscopy of plasma in ionized air

- **pump pulse** ionizes gas, creates free electrons and ions
- **THz probe pulse** measures plasma conductivity
... in the lab
Raw data and analysis

Fourier transformation

THz pulse
100 fs
10 to 30 THz

detection of electric field
(amplitude & phase)
Raw data and analysis

Fourier transformation

THz pulse
100 fs
10 to 30THz

pump pulse visible, 20fs

detection of electric field
(amplitude & phase)
Raw data and analysis

Maxwell equations

Fourier transformation

Instantaneous dielectric function $\varepsilon_\tau$

time after sample excitation
Dielectric function $\varepsilon$

$|\varepsilon|$ = ease to polarize a material with an external electric field.

$\text{Im}\ \varepsilon$ = strength to absorb light with frequency $\omega$.

**Drude model of $\varepsilon$ for free electrons:**

- electrons undergo collisions with rate $\Gamma$
- velocity is randomized after each collision

Drude model of $\varepsilon$ for free electrons:

- $n_e$ = free-electron density
- $\Gamma$ = electron collision rate
- @ time $\tau$ after sample excitation

Drude-Fit

Re: dispersion

Im: absorption

Drude-Fit

Re: dispersion

Im: absorption
SF6 acts as an ultrafast electron quencher.

- long-lived Ar plasma
- add 10% SF6: exponential electron decay with 80-ps time constant

\[ \Rightarrow \text{SF}_6 \text{ acts as an ultrafast electron quencher} \]

exponential decay via \( \text{SF}_6 + e^- \rightarrow \text{SF}_6^- \) reaction

Free carriers and excitons: graphite vs CNTs

Graphite

photoexcitation of free charge carriers

low frequency THz probe

optical excitation

$\Delta \varepsilon_\tau @ \tau = 0.1 \text{ps}$

frequency (THz)

E

$E_F$

$k_\perp$

Graphite
Free carriers and excitons: graphite vs CNTs

Graphite

Carbon Nanotubes (CNTs)

photoexcitation of free charge carriers

very different $\Delta \varepsilon$
Free carriers and excitons: graphite vs CNTs

- Graphite
  - Generation of free charge carriers
  - \( \Delta \varepsilon \tau \) at \( \tau = 0.1 \text{ps} \)

- Nanotubes
  - Very different \( \Delta \varepsilon \) in generation
  - Binding energy > 0.3eV
  - \( \Rightarrow \) invisible for THz!

Wang et al., Science (2005)
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