Part II – Course Content

- Optical Bloch equations
- Nonlinear polarizations in matter: the perturbative expansion approach.
- Ultrafast Fourier-transform spectroscopy: two and more dimensions.
  - From THz to the ultraviolet: investigating transient states of matter with light
- More ways to see: Raman, CARS, & fluorescence - also good for imaging
- High harmonics and attosecond experiments: applications beyond the UV
- Ultrafast science with atomic resolution: the making of femtosecond molecular movies

Outline Lecture 9

- Elements of the last session
- 2-dimensional Fourier transform spectroscopy
- Time and Energy Scales
- Applications I: THz spectroscopy
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Nonlinear Spectroscopic Methods

- Pump-Probe Spectroscopy
- Quantum Beat Spectroscopy
- Photon-Echo Spectroscopy
- Peak Shift Spectroscopy

Frequency Correlations & Lineshapes

Correlations of frequency fluctuations manifest in spectroscopic lineshapes

\[ g(t) = \frac{1}{2} \int dt' dt'' \langle \delta \omega(t') \delta \omega(t'') \rangle \]

\[ A(\omega) = 2 \text{Re} \int_0^\infty dt e^{i\omega t} \langle \mu_\text{in}(t) \mu_\text{in}(0) \rangle \]

\[ = 2 \mu_\text{in}^2 \text{Re} \int_0^\infty dt e^{i\omega t} e^{-g(t)} \]

within the second order approximation, one lineshape function describes all nonlinear signals of a given transition.
2D Fourier Transform Spectroscopy

- Third-order signals feature two periods of a coherent superposition in the probe oscillator which are separated by the population time interval.
- Just as the Fourier transform (FT) of the free ‘induction’ decay yields $A(t_0)$, the 2D-FT of a third-order polarization decay along $t_1$ and $t_2$ is a 2D absorption spectrum, correlating $A(t_1)$ with $A(t_2)$ as a function of the ‘waiting time’ $t_2$.

$$
R_1 = \sum_{\alpha,\beta,\gamma} P(\alpha) P(\beta) P(\gamma) e^{-i\alpha t_1 - i\beta t_2 - i\gamma t_3 - \frac{i}{2}(\alpha t_1 + \beta t_2 + \gamma t_3)}
$$

$$
R_2 = \sum_{\alpha,\beta,\gamma} P(\alpha) P(\beta) P(\gamma) e^{-i\alpha t_1 - i\beta t_2 - i\gamma t_3 - \frac{i}{2}(\alpha t_1 + \beta t_2 + \gamma t_3)}
$$

$$
R_3 = \sum_{\alpha,\beta,\gamma} P(\alpha) P(\beta) P(\gamma) e^{-i\alpha t_1 - i\beta t_2 - i\gamma t_3 - \frac{i}{2}(\alpha t_1 + \beta t_2 + \gamma t_3)}
$$

$$
R_4 = \sum_{\alpha,\beta,\gamma} P(\alpha) P(\beta) P(\gamma) e^{-i\alpha t_1 - i\beta t_2 - i\gamma t_3 - \frac{i}{2}(\alpha t_1 + \beta t_2 + \gamma t_3)}
$$

How to Measure 3rd-Order Fields

Use of a reference field (the local oscillator) for spectral interferometry

Detector Array

Spectrograph

Measured spectrograms for different time delays $t_2$

$S(t_2, t_3; T)$

Field extraction

$E(t_1, t_2; T)$

Fourier transform

$E(t_2, t_3; T)$

‘Phasing’ 2D Spectra

Extraction of electric field by Fourier-filtering of spectrumogram

Detection frequency $v_1$

Time delay $t$

Detection frequency $v_2$

‘Contraction’ along $v_3$ is equivalent to pump-probe spectrum

Absorbance difference

Solvant

HAc, $T=0^\circ$C

HAc, $T=40^\circ$C

Detection frequency $v_3$ / cm$^{-1}$
Double Resonance 2D-Spectra

Double resonance spectroscopy

linear abs. spectrum \( \rightarrow \) along diagonal excited state abs. \( \rightarrow \) shifted along \( \nu_3 \)
inhomogeneity \( \rightarrow \) elliptical lineshape couplings \( \rightarrow \) anti-diagonal signals

\( T=0 \)

Absorption \( \nu_1 \)

Detection \( \nu_3 \)

\( T>0 \)

Absorption \( \nu_1 \)

Detection \( \nu_3 \)

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Improving Shutter Speeds

Measurements of Brief Time Intervals

Energy & Time Scales

- Energy spacing
  - MeV
  - keV
  - eV
  - meV

- Time [seconds]
  - pico
  - femto
  - attoseconds

- Time [attoseconds]
  - Collective motion of free electrons in solids
  - Solid matter / biomolecules / plasmon charge transfer

- Density of free electrons [cm\(^{-3}\)]

\[ \hbar c = 1240 \text{ eV nm} \]
\[ c = 300 \text{ mm/fs} \]
\[ \hbar = 4 \text{ eV fs} \]

F. Krausz, M. Ivanov
Review of Modern Physics 81, 163 (2009)
The Right Timing

The energy scale of an excitation limits the time scale of associated dynamics. The required time-resolution to follow dynamics depends on the dephasing time of the initial excitation. For homogeneous lineshapes with $\Delta \tau$ in energy units, the dephasing time is

$$\tau = \frac{\Delta \tau}{\hbar}$$

in the non-relativistic limit, standard deviations for Energy $E$ and an observable $O$ are linked as

$$\sigma_E \sigma_O \geq \frac{\hbar}{2}$$

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THz Generation via Antennas

- Based on dipole antennas
- Earliest implementation
- High-repetition rate
- Limited field strength with above-band gap excitation (damage threshold)

Antenna-THz Applications

- Protein-Water 'Dynamics' upon Folding
- Phase Transitions in Molecular Crystals
- Size-Dependent Photoconductivity in CdSe NPs
- Nonlinear THz Generation in Nanostructures

From Tarbet's Science Research Group, University of Fukui. See also M. van Exter et al., Appl. Phys. lett. 58, 227 (1991).
Optical Rectification

Difference-frequency generation between low- & high-frequency parts of the driving pulse

$\Delta \omega$ Spectral width of driving pulse determines THz spectrum

ZnTe GaAs GaP

Optical Rectification


THz from Tilted Pulse Fronts

$\eta_{THz} = \frac{2 \omega^3 d_{eff}^2 L^3 I}{c v_{g} n_{pl} n_{THz}^2 c^3}$

$\alpha$: THz frequency

$d_{eff}$: second order nonlinearity

$L$: phase-matched length

$I$: laser intensity

$n_{g}$: optical group refractive index

$n_{THz}$: THz phase refractive index

József András Fülöp and János Hebling, DOI 10.5772/6914

THz from Tilted Pulse Fronts

• Very high fields (>1MV/cm)

• Robust implementation

But:

• Need for amplified laser system

• Limited spectral width

THz-gated Charge Transport

• THz-induced superconductivity in High-Tc superconductors at room temperature

• d.c. resistivity vanishes for charge carriers between oxide places

• Modulation of $\text{Im}(\sigma_C)$ of conductivity $\sigma_C$.

Meissner effect appears: $\sigma_C \rightarrow 0$ as $\omega \rightarrow 0$

József András Fülöp and János Hebling, DOI 10.5772/6914

THz-gated Charge Transport

Cavalleri group, MPISD, Nature Photonics 5, 485 (2011)
**2D-THz spectroscopy**

THz fields can be measured easily in real time via the electro-optic effect. The THz field modulates the birefringence of a crystal which rotates the polarization of a short reference pulse, sampling the THz field.

**Extraction of Nonlinear Signals**

Differential measurements allow to extract the nonlinear THz field by synchronized light modulators (a - c).

The signal is the nonlinear electric field emitted from the sample (e).

A 2D-Fourier transformation provides all nonlinear signals at once. Depending on their nature, they will manifest in spectral regions.


**Collinear vs. Noncollinear Geometries**

In non-collinear geometries, nonlinear signals of different order are spatially separated by different superpositions of wavevectors of the generating pulses.

**2D-THz spectroscopy of Graphene**

Graphene which a vanishing energy gap between the highest valence and the lowest conduction bands with linear dispersion and 'massless' charge carriers with velocities independent of energy. 2D-THz spectroscopy studies carrier dynamics on ultrafast time scales close to the Dirac points $E(K) = E(K') = 0$. 
2D-THz spectroscopy of Graphene

Both the induced absorption and the absence of the photon-echo signals are explained by a model using a pseudopotential bandstructure for graphene including the electron–light coupling via the vector potential.


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Optical Parametric Generation

- Smooth spectra spanning hundreds of nanometers in the visible to infrared range
- Supercontinua are fully coherent and compressible
- The resulting wide-bandwidth pulses are used for seeding in OPAs, probing absorption changes, and high-harmonic generation (HHG)

Supercontinuum Generation

- few-cycle pulses
- noise suppressing
- scalable

Delocalization without Relaxation

Transient population grating ($t_1 = 0$) similar to pump-probe signal

Population relaxation with a lifetime of 200 fs
Anisotropy decay with time constants of 80 fs

Revealing Chemical Shifts

One more application using transient 2DIR spectroscopy concerns the understanding of how vibrations shift upon a photoinduced chemical reaction. In the specific system it was not clear how to assign excited-state spectra, which is crucial for verifying theoretical predictions.

By photoinducing the chemical reaction and then probing the resulting structure via 2DIR spectroscopy it is also not obvious how the two peaks in question shift. But when reversing the order of UV and IR pump pulses, ‘vibrational’ labeling allows to assign the excited-state absorption features to the right functional groups: the equatorial $\nu_{CO}$ shifts from 1910 cm$^{-1}$ to 1950 cm$^{-1}$. 

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Resonant Energy Transfer (cont’d)

Fenna–Matthews–Olson (FMO) photosynthetic light-harvesting protein

- ‘downhill’ energy transport among chromophores
- Identification of energy flow maps energetic and spatial correlations
- Current intense debate about nature of ps-long coherences (vibrational vs. electronic) in light-harvesting proteins