Coherent control of chemical reactions. I

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Objective: To monitor and manipulate molecular dynamics in real time

Outline:
- Ultrafast processes
- Femtosecond spectroscopy
  - femtosecond lasers
  - pump-probe methodology
- Examples
- Concepts of control
  - time and frequency domain
- Advantages of fs lasers
- “Teaching lasers to control molecules”
- Pulse shaping techniques
- Examples
Fast tools are needed to study fast dynamics

Time resolution too slow to identify the motions of interest

With sufficient time resolution, a detailed understanding of the fast dynamics can be extracted
Time scales

- Stopclock: 1 s
- Fast camera shutter: $10^{-3}$ s
- Explosion: $10^{-6}$ s
- Fast digital electronics: $10^{-9}$ s
- Molecular rotation/vibration: $10^{-12}$ s
- Primary processes in photosynthesis: $10^{-15}$ s

Time scales include:
- Milli: $10^{-3}$ s
- Micro: $10^{-6}$ s
- Nano: $10^{-9}$ s
- Pico: $10^{-12}$ s
- Femto: $10^{-15}$ s
\[ c = 3 \times 10^8 \text{ m/s} \]

- **in 1 s**: a light pulse travels 300000 km, i.e. the distance from Earth to the Moon.
- **in 1 ps**: a light pulse travels 0.3 mm, i.e. the thickness of cardboard.
- **in 1 fs**: a light pulse travels 300 nm, i.e. less than the wavelength of visible light and a typical dimension of present day electronic circuit elements.
“Snapshots” of molecular motion

The pump pulse excites the molecule

and the delayed probe pulse monitors the dynamics.

\[ v \sim 1000 \text{ m/s} = 1 \text{ Å / 100 fs} \]
Nobel Prize for Chemistry 1999

Ahmed Zewail
Caltech

...for showing that it is possible with rapid laser techniques to see how atoms in a molecule move during a chemical reaction.
Elementary reactions in chemistry and biology

- Ballistic motion on excited state potential (fs-ps)
- Diffusive motion on ground state potential well (ms)
20 fs

1000 cm⁻¹

3 x 10⁴ GHz

0.13 eV

100 nm
Concept of wavepackets

Quantum mechanics $\equiv$ Superposition of wavefunctions produces spatially localized and moving coherent wave packet.

Classical mechanics $\equiv$ Moving point objects

Erwin Schrödinger, “Der kontinuierliche Übergang von der Mikro zur Makromechanik,” Die Naturwissenschaften, Heft 28, 1926, 664-660: (Translation)

...I show, that a group of eigenmodes with high quantum number $n$ and relatively small differences in their quantum numbers describe a point mass which moves according to usual mechanics...

$$
\Psi(x,t) = \sum a_n \phi_n e^{-i\frac{E_n}{\hbar} t}
$$
Wavepacket dynamics

\[ \Psi(r,t) = \sum_n a_n \phi_n(r) e^{-iE_n t / \eta} \]
Seeing is believing

Ultrafast camera

- The fs pump pulse initiates the reaction.
- The fs probe pulse provides the shutter speed for freezing molecular motion with the necessary spatial resolution.
- A slow detector records the signal.

\[ \Delta t = \frac{2\Delta L}{c} \]

(1 \( \mu \text{m} = 3 \text{ fs} \))
Ultrafast lasers

- a 4.5-fs pulse...
- Also attosecond pulses are now available 2002....

Ultrafast dye laser: Femtoland 1, Caltech 1988
Record-breaking short

NEWLY REVISED WITH ALL-NEW PHOTOS AND FEATURES

THE GUINNESS BOOK OF RECORDS 1999™

WORLD RECORD

THE SHORTEST FLASH OF LIGHT PRODUCED AND MEASURED, LASTED FOR 4.5 FEMTOSECONDS, MEASURED BY ANDRIUS BALTUSKA, MAXIM PSHENCHNIKOV AND DOUWE WIERSSMA AT THE UNIVERSITY OF GRONINGEN, THE NETHERLANDS IN EARLY 1996

Keeper of the Records

GUINNESS PUBLISHING
How are fs pulses made?

Typically, many longitudinal modes (standing waves) can oscillate in the laser resonator (integer number of half wavelengths).

Number of modes present depends on emission profile of active medium.
• Modes have statistical, independently fluctuating phases.

• Total intensity is just the square of the sum of the individual mode amplitudes.
Mode locked

- The individual modes have a fixed phase relationship.
- At the positions of constructive interference there are maxima in the intensity.
Laser resonator

Δν = c/2L

One mode
→ single-mode operation
ΔE minimal

Mode locking:

NΔν

T_{repetition} = 1/Δν
Time-bandwidth product

Harmonic potential

Δν = \frac{1}{2\pi} \left( \frac{D}{\mu} \right)^{\frac{1}{2}}

One eigenstate
→ time-independent
ΔE minimal

Coherent superposition:

NΔν

T_{oscillation} = 1/Δν
Uncertainty relation
Dependence on number of modes

Pulse separation
\[ T = \frac{2L}{c} \]
(round-trip time for light in the laser resonator)

Pulse duration
\[ \Delta T = \frac{1}{\Delta \nu} = \frac{2L}{Nc} \]
where \( \Delta \nu \) is the frequency spread of laser output

The broader the laser gain profile, the shorter the pulse duration
Laser media

$\Delta T = 200$ ps

- Ar$^+$ vapor
- Nd:YAG crystal, 5 ps
- Dye, 10 fs
- Titanium-doped sapphire crystal, 3 fs

*Also, short pulses implies high power*
Power of energy sources and consumers

Watt = Joule/sec

Short pulse power:
- flashlight
- bomb
- typical fs laser
- lightening
- (planned) high power laser

Continuous power:
- electric bulb
- electric stove
- car
- small city
- nuclear power station
- Germany
- world
- sun

1 watt
1 kilowatt = $10^3 W$
1 megawatt = $10^6 W$
1 gigawatt = $10^9 W$
1 terawatt = $10^{12} W$
1 petawatt = $10^{15} W$

Watt = Joule/sec
High-power lasers worldwide

- Rutherford (Nd Glass)
- Osaka (planned)
- GSI (planned)
- Rutherford (planned)
- LOA Paliseau
- UCSD
- MBI (TiSa + Glass)
- Michigan (TiSa + Glass)
- Kyoto/Tokyo
- Lund/MQ/Jena
- Rutherford (Nd Glass)
- CPA table top
- CPA fusion
- commercial systems

- MBI TiSa
- 1-kHz TiSa
- commercial "tabletop"

- Livermore (discontinued)

- 10 J

- 1 J

- 100 mJ

- 100 ps

- 10 ps

- 1 ps

- 100 fs

- 10 fs

- 100 J

- 10 J

- 1 J

- 100 mJ

- 1 mJ

- 100 ps 10 ps 1 ps 100 fs 10 fs pulse length
Almost black box

CPA 2001 amplified femtosecond laser
**NO TWEAK™**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Wavelength</td>
<td>775 nm</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>&gt;1 mJ</td>
</tr>
<tr>
<td>Pulsewidth</td>
<td>&lt;150 fs</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>1 kHz</td>
</tr>
<tr>
<td>Energy stability</td>
<td>~0.5% rms</td>
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</table>

NOPA
non-collinear optical parametric amplifier

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength range</td>
<td>470-1600 nm</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>5-25 µJ</td>
</tr>
<tr>
<td>Pulsewidth</td>
<td>&lt;20 fs</td>
</tr>
<tr>
<td>Energy stability</td>
<td>&lt;1% rms</td>
</tr>
</tbody>
</table>
Short ($\Delta t$) pulses are broad ($\Delta E$) pulses

For Gaussian pulses: $\Delta \tau \Delta \nu = 0.442$

<table>
<thead>
<tr>
<th>$\Delta \tau$</th>
<th>$\Delta \nu$</th>
<th>$\Delta \lambda$ (nm) at 600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 ns</td>
<td>88 MHz</td>
<td>0.000106</td>
</tr>
<tr>
<td>1 ps</td>
<td>44 GHz</td>
<td>0.53</td>
</tr>
<tr>
<td>20 fs</td>
<td>22 THz</td>
<td>27</td>
</tr>
</tbody>
</table>
Measuring ultrashort pulses

The cross- or autocorrelation is given by

\[ C(\tau) \equiv \int_{-\infty}^{\infty} I(t) I_g(t - \tau) \, dt \]
Measuring with ultrashort pulses:

Pump parameters:
- Wavelength tuning
- Polarization
- Intensity
- Multiple pulses
- “Shaped” pulses

Detection schemes:
- Laser-induced fluorescence
- Multiphoton ionization
- Mass spectrometry
- Photoelectron spectrum
- Velocity/Angular resolution
- Imaging
- Transient absorption
- Fluorescence upconversion
- Non-linear spectroscopy
- Diffraction

Probe possibilities:
- Dispersed white light
- Polarization-resolved
- Multi-pulse (nonlinear)
- Infrared (vibrations)
- X-rays, Electrons (structure)
Example: ICN

Dissociation of Sodium Iodide

Potential Energy (V) / 10^3 cm^{-1}

wavepacket motion

Ionic: Na^+ + I^-

Covalent: Na + I

Zewail group: 1988-1992

Time delay (t) / ps

Intensity
Transient absorption pump-probe setup

Amplified Ti:Sapphire femtosecond laser

NOPA

Sapphire

Optical Delay Line

Moving sample cell

Pump

Chopper

Probe

Grating

Diode array detector

20 μJ
<25 fs
1 kHz
450-1600 nm

1 mJ
150 fs
1 kHz
775 nm

1 μm = 3 fs

Dispersed probe
Transient absorption pump-probe setup

Amplified Ti:Sapphire femtosecond laser

NOPA

20 μJ
<25 fs
1 kHz
450-1600 nm

NOPA

1 mJ
150 fs
1 kHz
775 nm

Optical Delay Line

Moving sample cell

Pump

Probe

Chopper

Photodiode

Selected λ probe

1 μm = 3 fs
What do we actually measure?

Absorption:

\[ A = \text{OD} = -\log \frac{I}{I_0} \]

Transient (difference) absorption:

\[ \Delta A = \Delta \text{OD} = -\log \frac{I}{I_0} - (-\log \frac{I}{I_0}) \]
Transient absorption spectrum

\[ \Delta A(t, \lambda) = A(t, \lambda) - A(0, \lambda) \]

- **Ground state absorption**
- **Product absorption**
- **Excited state absorption**
- **Stimulated Emission**
- **Ground state bleach**
Light harvesting: the first step in photosynthesis

LH2 antenna complex

membrane of photosynthetic bacteria

Absorbance (a.u.)

Wavelength, nm
Transient spectral evolution

$T = 6 \text{ K}$

$\lambda_{\text{exc}} = 843 \text{ nm}$
Watching an energy transfer reaction

Decay of B800 signal

Rise of B850 signal
3-d transient absorption data

Dynamics following excitation of carotenoid molecules
Target analysis

Refinement of rates and amplitudes

\[ \Delta \lambda \left(\frac{\text{OD}()}{t}\right) = A() \times P(t) \]

\[ \sum_{i} A_{i}(\lambda) \]

Initial guess

Fit error

\[ \chi^{2} \]

Kinetetic model

\[ \Delta \text{OD}(\lambda, t) = \sum_{\text{species}} A_{i}(\lambda) \times P_{i}(t) \]

\[ k_{ji} = \{3.2, 2.1, 6.3, \ldots\} \times 10^{11}/s \]

\[ k_{j(i+1)} = \{12, 25, 7, \ldots\} \times 10^{11}/s \]
Energy flow network: best fit model
State spectra and population kinetics
Summary: pump-probe ultrafast spectroscopy

- **Femtoseconds**: The ultimate time scale for resolving atomic and molecular motion

- **Pump-probe**: The general method for initiating, clocking, and monitoring ultrafast dynamical processes

- **Future prospects:**
  - Even shorter time scales: attosecond pulses will reveal electronic motion
  - Novel probe/detection scheme
    - Electron, X-ray: ultrafast diffraction
    - High-order nonlinear spectroscopies
  - Control of ultrafast dynamics
“With sufficiently brief and intense radiation, properly tuned to specific resonances, we may be able to fulfill a chemist's dream: to break particular selected bonds in large molecules”

A. H. Zewail, 1980
Control of chemical reactions

General goal: Maximize yield of desired products and suppress formation of unwanted byproducts
How can we supply energy to get over barrier and achieve a specific product?

Typical macroscopic approach: Temperature

→ wanted and unwanted products formed statistically
<table>
<thead>
<tr>
<th>Passive control</th>
<th>vs.</th>
<th>Active control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evolution of energized reactant molecules is largely or completely incoherent</td>
<td></td>
<td>External manipulation of molecular dynamics so as to influence the evolution of the reactant molecule to generate more or all of a particular product</td>
</tr>
<tr>
<td>Role of experimenter is to initiate the reaction, without having control of subsequent evolution of the system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Concentration</td>
<td>• Electric fields</td>
<td></td>
</tr>
<tr>
<td>• Temperature</td>
<td>• Optical fields</td>
<td></td>
</tr>
<tr>
<td>• Pressure</td>
<td>• ......</td>
<td></td>
</tr>
<tr>
<td>• pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Synthetic criteria</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Intensity
Phase
Polarization
Spectral content
Time dependence
Lasers \rightarrow \text{“Bond-selective” chemistry?}

Can coherent light be used for selective bond activation and cleavage?

The concept:

• Choose the light frequency to be in resonance with the vibrational frequency of the bond to be broken

• Resonant activation of the proper vibrational mode leads to selective dissociation
Bond-selective chemistry in \( H + HOD \)

\[
H + HOD(\nu) \rightarrow H_2 + OD \\
H + HOD(4\nu_{OH}) \rightarrow H_2 + OD \\
H + HOD(5\nu_{OD}) \rightarrow HD + OH
\]

The problem: IVR

- Vibrational motion is coupled to many atoms within the molecule
- Intramolecular vibrational redistribution (IVR) leads to a loss of selective excitation and “heating” of the molecule
- Works only for small, prototype molecules
Coherent control

*Interfering for the good of a chemical reaction*

*The difference:*

- Exploits a broad range of quantum interference effects
- Many different feasible schemes
  - Frequency domain
  - Time domain
How is it possible that light can control a reaction?

Tannor-Kosloff-Rice
JCP 85, 5805 (1986)

Brumer-Shapiro
CPL 126, 54 (1986)

STIRAP
CPL 149, 463 (1988)

Potential Energy

Δt

time delay: Δt

phase difference: Δϕ=ϕ_1-ϕ_3ω

A

B

A

B