Multimodal Quantum Control Micro-Spectroscopy I
Coherent control of ultrafast molecular dynamics
Outline

I. Coherent Control
   - Concepts of Coherent Control
   - Learning Loop: Pulse shaping, algorithms
   - Applications:
     Control of 2-Photon-Absorption
     Control of energy transfer

II. Single beam CARS
   - Nonlinear Raman spectroscopy
   - Shaped CARS
   - Multimodal microscopy

Multimodal Quantum Control
Micro-Spectroscopy
Femtochemistry

Ultimate timescale for chemical dynamics

\[ v = 1 \text{ km/s} = 0.01 \text{ Å/fs} \]
Introduction

Chemistry (microscopic) ≡ Breaking and making bonds

\[ \text{ABC} \rightarrow \text{AB} + \text{C} \]
\[ \rightarrow \text{A} + \text{BC} \]
\[ \text{.........} \]

General goal: Maximize yield of desired products and suppress yield of unwanted byproducts
Cut through a multidimensional PES:

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>1. Reactant molecules and any surrounding solvent molecules are <strong>not subjected to manipulation by external influences</strong> during the evolution from reactants to products.</td>
<td></td>
<td></td>
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<tr>
<td>2. Evolution of energized reactant molecules is largely or completely <strong>incoherent</strong></td>
<td></td>
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<tr>
<td>3. 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></td>
<td></td>
</tr>
<tr>
<td>• Temperature</td>
<td></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>
<tr>
<td><strong>External manipulation</strong> of molecular dynamics so as to <strong>influence the evolution</strong> of the reactant molecule to generate more or all of a particular product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Electric fields</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Optical fields</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• ......</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Intensity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Polarization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Spectral content</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Time dependence</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Coherent control of chemical reactions

- calculation for real molecules complicated (if not impossible)
- experimental realization of predicted E-fields difficult

Laser field $E(t)$
Control strategies

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

Brumer-Shapiro
CPL 126, 54 (1986)

Potential Energy

A

Δt

B

time delay: Δt

phase difference: Δφ=φ_ω-φ_{3ω}
Brumer-Shapiro scheme: *Multiple-path interference control*

Excite the desired product channel via two different pathways:

\[
P = P_1 + P_3 + 2P_{13}\cos(\phi + \delta_{13})
\]

Probability \((P)\) of forming a product:

\[P. \text{Brumer and M. Shapiro, Chem. Phys. Lett. 126 (1986) 541}\]
"teaching lasers to control molecules"

R.S. Judson and H. Rabitz, PRL 68 (1992) 1500
positive chirp

From R. Trebino, GaTech
Simple shaping of fs pulses

Different frequencies travel at different group velocities in materials, causing pulses to expand to highly "chirped" (frequency-swept) pulses.

Longer wavelengths almost always travel faster than shorter ones.

From R. Trebino, GaTech
Shaping of fs-Laser Pulses

Liquid crystal spatial light modulator

schematic of liquid crystal

novel shaper with 640 stripes

Cooperation with: IOQ-Universität Jena
Jenoptik AG

Liquid crystal spatial light modulator

Front view

2 mm

3 µm

100 µm

3 µm

100 µm

Side view

AR-coated cover
polarizer
substrate buffed at +/-45°
liquid crystal
indium tin oxide patterned substrate
index-matching epoxy

Modulation of phase and amplitude

Polarizer

$E_{\text{out}}$

$\phi_1 - \phi_2$

$\phi = \frac{1}{2}(\phi_1 + \phi_2)$

$T \sim \cos^2 \left[ \frac{1}{2}(\phi_1 - \phi_2) \right]$
**Principles of pulse shaping (cont´d)**

- Singlebeam-CARS uses most often femtosecond laser pulses due to their large bandwidth.
- Pulse shaping cannot be accomplished in the time domain, because no modulator is fast enough.

\[ H(\omega) \]

\[ H(\omega) \] is a complex mask function, this means amplitude an phase can be controlled.
Principles of pulse shaping

Parameterization of excitation mechanism

chirped  impulsive  phase-locked

phase on mask

pixel

pulse

time

Spectral range of a liquid crystal mask

NIR / VIS: 4-f-setup

Transmission spectrum of liquid crystal mask CRI-256

No modulation of pulses in the UV and mid IR
Direct UV shaping

Micromirror SLM

Methods of pulse shaping

Liquid-crystal modulator
Individually-addressed pixels can vary phase or amplitude

Acousto-optic modulator
Modulated rf field creates an amplitude- and phase-dependent grating

Deformable mirror
Array of movable elements allows phase variations of spectral components

Review: “Femtosecond pulse shaping using spatial light modulators “

Tutorial: “A newcomer's guide to ultrashort pulse shaping and characterization”
# Complex fs-pulse shaping techniques

<table>
<thead>
<tr>
<th>Pulse shaper</th>
<th>LCD</th>
<th>AOM</th>
<th>AOPDF</th>
<th>Def. Mirror</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Modulation</strong></td>
<td>Phase, amplitude and polarization</td>
<td>Phase and amplitude</td>
<td>Phase, amplitude and (polarization?)</td>
<td>Phase only</td>
</tr>
<tr>
<td><strong>Pixels</strong></td>
<td>128 (650)</td>
<td>1800</td>
<td>450</td>
<td>continuous (16 stamps)</td>
</tr>
<tr>
<td><strong>Transmission</strong></td>
<td>70 %</td>
<td>30 %</td>
<td>30 %</td>
<td>95 %</td>
</tr>
<tr>
<td><strong>Waveform update Rate</strong></td>
<td>10 Hz</td>
<td>100 kHz</td>
<td>100 kHz</td>
<td>few 10 Hz</td>
</tr>
<tr>
<td><strong>Group-delay range</strong></td>
<td>4 ps</td>
<td>3 ps</td>
<td>3 ps</td>
<td>few 5 fs</td>
</tr>
<tr>
<td><strong>Additional imposed chirp</strong></td>
<td>Negligible (reflective optics)</td>
<td>270000 fs²</td>
<td>12500 fs²</td>
<td>No chirp</td>
</tr>
</tbody>
</table>
Optimization Algorithms

- Deterministic Algorithms using deterministic generators for new search directions
- Indeterministic Algorithms using chance as a generator for new search directions

- Gradient methods
- Evolutionary Algorithms
- Simulated Annealing Methods
Evolutionary Algorithms

"survival of the fittest"

Chromosome : vector of numbers

Recombination : multiple cross-over

Mutation : Change the value of a vector element

also possible : intermediary recombination

Coherent control of two photon transition

term scheme of Na

Maximization

Minimization


See also Silberberg group, e.g. Nature 396 (1998)
Control of Chemical Reactions by Feedback-Optimized Phase-Shaped Femtosecond Laser Pulses

A. Assion, T. Baumert,* M. Berg, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, G. Gerber
Changing the pulse shape changes the product ratio

Control of photofragmentation, cont.

Ausgangsstoff

Cyclopentadienyl-Eisen-dicarbonyl-chlorid

Endprodukte

\[
\text{[Fe-Cl]}^+
\]

Produktausbeuten

\[
4,9 : 1 \quad 1,2 : 1
\]

optimierter Laserpuls (Produktverhältnis maximal)

optimierter Laserpuls (Produktverhältnis minimal)
Photosynthetic purple bacteria

Light harvesting + reaction center unit

[Diagram showing LH-I, LH-II, and RC with a scale of 20 Å]
LH2 from Rps. acidophila

B850 Bacteriochlorophyll (BChl)

B800 BChl

Rhodopin glucoside
Carotenoid (Car)

Collaboration with
J.L. Herek, AMOLF
R.J. Cogdell,
University of Glasgow
LH2 of *Rps. Acidophila* - Standard model

Competing deactivation IC-EET

- Significant loss channel IC
- Negligible cross talk IC-EET
- Energy funnel precludes back transfer
Closed-loop approach on LH2

nc OPA
\(\lambda_0=525\text{nm}\)
\(\Delta\tau=30\text{fs}\)

excitation

shaper

probe
white light gen.

IF

rotating sample

PD
ET

PD
IC

feedback

evolutionary algorithm

improved shape

excitation

probe IC

ET

Q_y

BChl
g

Car
64-parameter optimisation of IC/EET

Convergence curve

Optimal pulse FROG trace

Nature 417 (2002) 533
Coherent Control of Retinal Isomerization in Bacteriorhodopsin

Valentyn I. Prokhorenko, Andrea M. Nagy, Stephen A. Waschuk, Leonid S. Brown, Robert R. Birge, R. J. Dwayne Miller

www.sciencemag.org  SCIENCE  VOL 313  1 SEPTEMBER 2006
Reducing the complexity

Caroteno-porphyrin dyad

Donor

Acceptor

Biological complexes  
*Function*

Biomimetic molecular assemblies  
*Reactivity*

Isolated molecules  
*Motion*
Control of Dyad complex
IC/ET

Collaboration with AMOLF/Twente

ET/IC

PNAS 105 (2008) 7641
Multipulses: Impulsive stimulated Raman scattering

- Simple Femtosecond Pulse
- Femtosecond Pulse-Train

ISRS
Further reduction of complexity
Wavepackets in $\beta$–Carotene

![Wavepackets in $\beta$–Carotene](image)

Transient

![Transient signal](image)

FFT spectrum

![FFT spectrum](image)

### Pulse Spacings

<table>
<thead>
<tr>
<th>Energy (cm(^{-1}))</th>
<th>T(fs)</th>
<th>2 T(fs)</th>
<th>3 T(fs)</th>
<th>4 T(fs)</th>
<th>5 T(fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1524</td>
<td>21.9</td>
<td>43.8</td>
<td>65.7</td>
<td>87.6</td>
<td>109.5</td>
</tr>
<tr>
<td>1157</td>
<td>28.8</td>
<td>57.6</td>
<td>86.4</td>
<td>115.2</td>
<td>144</td>
</tr>
<tr>
<td>1004</td>
<td>33.2</td>
<td>66.4</td>
<td>99.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Diagram showing pulse spacings](image)
Control of ground state vibrations

Modes can be selectively excited

Nonlinear Raman spectra

Control of excited state dynamics in carotenoids

- Additive phase term $c$ affecting the wavepacket evolution?
- Need for further theoretical investigation
Coherent Control + Spectroscopy = Quantum Control Spectroscopy (QCS)$^{1-4}$

- Modify the excitation to learn more about the dynamics
- Several possible "new" molecular responses:

Example of QCS-approach:
→ Disentanglement of complex dynamics in carotenoids!

(1) Faraday Discuss. 153 (2011) 213
(2) IEEE J. Quantum Electronics 18 (2012) 449
(4) PNAS 105 (2008) 7641