Coherent control of chemical reactions. II

Jennifer L. Herek
FOM-Institute for Atomic and Molecular Physics [AMOLF]
Amsterdam, The Netherlands
http://www.amolf.nl
J.Herek@amolf.nl
Control of chemical reactions

General goal: Maximize yield of desired products and suppress formation of unwanted byproducts
Lasers “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

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

time delay: $\Delta t$

phase difference: $\Delta \phi = \phi_{1\omega} - \phi_{3\omega}$
Pulse timing control

AB + C
AC + B

Reactant Product

Reaction coordinate

Potential Energy

Control of dissociation pathways in NaI

- Femtosecond probing of reactions
- Femtosecond control from the transition state region
- Reaction channels
- Population control
- Channel switching
- Magnitude of depletion
- Control vs. probe

Multiple-path interference control

Excite the desired product channel via two different pathways:

Path 1

Path 2

Probability ($P$) of forming a product:

$$P = P_1 + P_2 + P_{12}$$

Interference term depends on phase of optical fields

Coherent Laser Control of the Product Distribution Obtained in the Photoexcitation of HI

Langchi Zhu, Valeria Kleiman, Xiaoong Li, Shao Ping Lu,\textsuperscript{*}
Karen Trentelman,\textsuperscript{†} Robert J. Gordon\textsuperscript{‡}

\textsuperscript{*}Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1504.
\textsuperscript{†}Department of Chemistry, California Institute of Technology, Pasadena, California 91125.
\textsuperscript{‡}School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332.

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\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\end{figure}
Tuning the phase difference

• “Counterintuitive” pulse sequence: Stokes, then Pump
• Stokes pulse creates coherent superposition of two initially unpopulated states
• No population transfer to intermediate state; direct transfer to product
STIRAP applied to SO$_2$ molecules

Counterintuitive pulse sequence: signature of STIRAP

Combining these concepts:

For a given target distribution of photoproducts and the quantum mechanical equations of motion, what electric field is required to guide the temporal evolution of the system appropriately?
OCT: Optimal Control Theory

Electric field design

\[ i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H(t) |\psi(t)\rangle \]

\[ H(t) = H_0 - \vec{\mu} \cdot \vec{E}(t) \]

find optimal \( \vec{E}(t) \) such that

\[ |\langle \psi_{\text{target}} | \psi(T) \rangle| \] maximized

OCT methodology

- Forward/backward propagations of wavepackets $\Psi(t)$ or density matrices $\rho(t)$ from initial to final states and vice versa

- Optimization algorithm selects best fields $\varepsilon(t_i)$

Inherent difficulties with OCT...

- Need potential energy surfaces!

  Rarely known over all range of nuclear separations necessary to describe a reaction

- Search space too large to be scanned completely

- Predicted fields difficult to reproduce accurately enough under laboratory conditions
Experimental approach

“Teaching lasers to control molecules”

The molecular view

- A molecule knows its own Hamiltonian
- Given $\varepsilon(t)$, a molecule solves $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$ rapidly!

Advantages

- No prior knowledge of PESs needed
- Broadly applicable (not limited to molecular systems)
  - Automated pulse compression
  - Control of 2-photon transitions in atoms
  - Shaping of Rydberg wavepackets
  - Optimization of high-harmonic generation
  - Control of ultrafast semiconductor nonlinearities
  - Laser cooling
- Laboratory conditions accounted for automatically
Advantage of fs lasers

Broadband!

- allows for manipulation of many pathways to provide control over complex dynamics
- allows different control mechanisms: phase, timing, etc.
Experimental realization

*Feedback-driven adaptive femtosecond pulse shaping*

Femtosecond pulse shaping

A pulse is defined by its intensity and phase in either the time or frequency domain.

\[ E(t) = \sqrt{I(t)} e^{-i\phi(t)} \quad \tilde{E}(\omega) = \sqrt{S(\omega)} e^{-i\varphi(\omega)} \]

Modulation in time domain: \[ E_{out}(t) = h(t) E_{in}(t) \]

fs pulses too fast

Modulation in frequency space: \[ \tilde{E}_{out}(\omega) = H(\omega) \tilde{E}_{in}(\omega) \]

frequency disperse the pulse in space and create a spatially varying transmission and phase delay
Shaped pulse = “optical melody”

A musical score is a plot of frequency vs. time:

Transform-limited pulse: chord

Shaped pulse: melody
“Ordinary” femtosecond laser pulses
“Shaped” femtosecond laser pulses

The temporal shape of the laser pulse can be changed by varying the phases between its frequency components.
Acoustic analogy

2 frequencies

4 frequencies

16 frequencies

Many frequencies

K.A. Nelson and J.C. Vaughan, MIT
Linear phase modulation

\[ I(\omega) \quad \phi(\omega) \]
“V” & quadratic phase modulation

Waveform  
Amplitude [A.U.]  
Time [s]

Spectrum  
Intensity [A.U.]  
Frequency [Hz]

Sonogram  
Frequency [Hz]  
Time [s]

Waveform  
Amplitude [A.U.]  
Time [s]

Spectrum  
Intensity [A.U.]  
Frequency [Hz]

Sonogram  
Frequency [Hz]  
Time [s]
Cubic or periodic phase modulation

Waveform

Spectrum

Sonogram
Methods of pulse shaping

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

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

**Deformable mirror**
- Movable elements allow smooth phase variation

Liquid crystal spatial light modulator

Dual stack—phase & amplitude control

State-of-the-art:
2 x 640 elements = 1280 adjustable parameters!!
Dual stack LC-SLM

Modulation of phase and amplitude

Side view

- \( T \sim \cos^2 \left[ \frac{1}{2}(\phi_1 - \phi_2) \right] \)
- \( \phi = \frac{1}{2}(\phi_1 + \phi_2) \)
Shaped pulses with LC-SLMs

Square pulse

Pulse sequence

Pulse sequence with different chirp rates
The learning loop
Evolutionary algorithms

Survival of the fittest

descendants differ from parents

surviving organisms produce offspring

selection
Metaphors of biological evolution

- A **breeding population**, in which those individuals (pulses) that are more “fit” have a higher probability of spawning offspring and passing their genetic information to succeeding generations.

- **Genetic makeup of the offspring is a mixture** (characterized by a crossover rate) of the genetic makeup of the parents.

- Genetic material is **occasionally altered by mutation**, thereby generating offspring that can be more or less “fit” than they would have been otherwise.

- **Cloning** is possible.
Evolutionary operators

Recombination

(a) Multiple-point crossover

(b) Single-point crossover

(c) Double-point crossover

(d) Intermediary recombination

Mutation

Cloning
Evolutionary algorithm example

1. The first generation evenly samples the parameter space. From this we select the parents for the next generation.

2. The second generation is concentrated around the first set of parents, and from this we select the next set of parents.

The learning curve

![Learning curve diagram](image-url)
The learning loop
Examples of closed-loop experiments

- Fluorescence spectrum manipulation (Wilson 1997)
- Atomic excitation tailoring (Bucksbaum 1999)
- High-harmonic X-ray tailoring (Murnane & Kapteyn 2000)
- Ultrafast optical switching (Keller 2000)
- Molecular rearrangement selectivity (Levis & Rabitz 2001)
- Chemical discrimination in mixtures (Gerber 2001)
- Distortion-free transmission through optical fibers (Omenetto 2001)
- Vibrational excitation tailoring in polymers (Motzkus 2002)
- Decoherence management (Walmsley 2002)
- Energy transfer in photosynthesis (Herek & Motzkus 2002)

So far, more than 40 systems successfully controlled
Control of Chemical Reactions by Feedback-Optimized Phase-Shaped Femtosecond Laser Pulses

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

Ausgangsstoff

Cyclopentadienyl-Eisen-dicarbonyl-chlorid

Endprodukte

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

Produktausbeuten

4,9 : 1

1,2 : 1

Zeit

optimierter Laserpuls
(Produktverhältnis maximal)

optimierter Laserpuls
(Produktverhältnis minimal)
Simultaneous but selective absorption of two different molecules using shaped femtosecond pulses:
Quantum Control of Population Transfer in Green Fluorescent Protein by Using Chirped Femtosecond Pulses

Christopher J. Bardeen,† Vladislav V. Yakovlev,‡ Jeff A. Squier,§ and Kent R. Wilson*
Control of energy flow in light harvesting

The LH2 light harvesting antenna from *Rps. acidophila*

Energy transfer

Donor
Car

Energy loss

Acceptor
BChl

Carotenoid

$S_2$

BChl

$Q_y$ B850

B800

B800/B850

Wavelength, nm
Two competing channels: internal conversion vs. energy transfer

Can we control the IC/ET branching ratio?
Experimental setup

Excitation
- nc-OPA
- $\lambda_0=510\text{nm}$
- $\Delta\tau=30\text{fs}$

Probe
- white light gen.
- $\Phi(\lambda), A(\lambda)$
- $\eta$
- $\phi$

Rotating sample
- ET
- IC

Feed-back

Evolutionary algorithm

Excitation and Probe:
- Excitation Probe Rotating sample
- Improved shape

Levels:
- $S_n$ with $\lambda_{pr} = 580\text{nm}$
- $S_2$ with $\lambda_{exc} = 510\text{nm}$
- $S_1$ with $\lambda_{pr} = 880\text{nm}$
- $S_0$ with $\lambda_{pr} = 580\text{nm}$
“Blind” optimization (64 parameters)

Target: maximize ratio of IC/ET signals

![Graph showing the optimization process with a line and scattered points representing the IC/ET ratio over generations. The graph indicates a trend towards maximizing the ratio, with a notable "best" individual result.]
What is the pulse shape?

Unshaped pulse

Shaped pulse

IC ET

IC ET

Wavelength, nm

Time

40 fs

1500 fs
Reducing the complexity: restricted optimization

Sinusoidal phase mask in FREQUENCY DOMAIN:

$$\phi(\text{pix}) = a \cdot \sin(b \cdot \text{pix} + c)$$

Only 3 parameters:
- $a$: modulation depth
- $b$: frequency
- $c$: phase offset

Result in TIME DOMAIN: pulse train
- $a$: length of pulse train
- $b$: inter-pulse separation
- $c$: carrier phase pattern
Restricted optimization (3 parameters)

Target: maximize ratio of IC/ET signals

![Graph showing IC/ET ratio and ΔOD over generations.](image-url)
Effect of the phase

Shift the offset parameter (c) changes the phase pattern of the excitation pulse.
Optimized vs. $\pi$-shifted-optimized pulses

Phase offset of optimal mask pattern shifted by half a period

Result: No change in pulse envelope, energy or spectrum. Different phase pattern between subpulses.
Energy flow depends on the carrier phase.

![Graph showing energy flow depending on the carrier phase](image)

**IC**

**ET**

*Flow (relative to $\pi$ phase shifted)*

*Shift of optimized phase parameter*

Evidence of coherent control

*Nature 417, 533 (2002)*
Histogram of successive optimizations

Spectroscopy by coherent control

Number of results

Active mode, cm\(^{-1}\)

155 \text{ cm}^{-1}
The carotenoid loss channel

Promoting modes for carotenoid internal conversion:

CC stretch
\(~1100, 1500\ \text{cm}^{-1}\)
symmetric (\(a_g\))

CCC bend
\(~120-180\ \text{cm}^{-1}\)
asymmetric (\(b_u\))

Resonant coupling to bending mode promotes internal conversion via conical intersection.

G. Cerullo, Politecnico di Milano
What is the control mechanism?

**Vibrational mode matching**
- Couple to specific molecular motion (155 cm$^{-1}$ bending mode)
- Manipulate quantum interferences (coherent control)
Reducing the complexity: *Model systems*

- Biological complexes (wild-type, mutants) *function*
- Biomimetic molecular assemblies *reactivity*
- Isolated molecules *motion*
A new spectroscopic tool for reducing biological complexity

Blind optimizations:
Identify *functionally important motion*

Restricted parameter space:
Test simple pulse shapes correlated to
• shapes of potential energy surfaces
• specific vibrational modes

Control knobs:
• Wavelength
• Spectral amplitude
• Temporal envelope
• Phase
• Polarization
Challenges and opportunities

Inversion: Can we extract microscopic information of the molecular system by analysis of the optimized laser field?

• Parametrization. Test/catalogue the effects of simple pulse shapes

  *Finessed quantum mechanical manipulations may provide a unique source of data on intramolecular forces*

  *Develop coherent control “rules of thumb”*

• Analyze relevant electric field shapes to obtain information about the temporal evolution of the system
Recent review articles:


A fun website:

http://www.physik.uni-wuerzburg.de/femto-welt/