Coherent control of quantum phenomena using shaped UV pulses

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- Coherent control using femtosecond pulses
- Application to biology
- Extending the shaping to UV
- Outlook

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Control strategies

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

Brumer-Shapiro
CPL 126, 54 (1986)

Potential Energy

A

B

time delay: $\Delta t$

phase difference: $\Delta \phi = \phi_\omega - \phi_{3\omega}$
Closed-loop coherent control

Define control goal

Derive 48 better control fields

Realise the desired pulse shapes

Algorithm

Pulse shaper

Initial guess

Experiment

Test each shape for effect on photoreaction

Obtain optimal shape within technical limits

Efficient also for intricate processes.

Inversion?? Tends to produce complex pulse shapes.

Femtosecond Pulse Shaper

4f arrangement

Liquid crystal spatial light modulator

schematic of liquid crystal

novel shaper with 640 stripes

Cooperation with: IOQ-Universität Jena
Jenoptik AG

Evolutionary Algorithms

"survival of the fittest"

Chromosome: vector of numbers

Recombination: multiple cross-over

Mutation: Change the value of a vector element

Coherent control of two photon transition

term scheme of Na

5s \[ \omega_2 \] \[ 1/2 \omega_0 \] \[ \Delta \omega \] \[ \omega_1 \] \[ 1/2 \omega_0 \] 4p 3s

Maximization

Minimization

Selection of successful applications of optimal control:

- Automated pulse compression \((Gerber, Silberberg)\)
- Fluorescence in a dye \((Wilson)\)
- Photodissociation of complex systems \((Gerber, Lewis)\)
- Shaping of Rydberg wavepackets \((Bucksbaum)\)
- Control of 2-photon transitions in atoms \((Silberberg)\)
- Optimization of high harmonic generation \((Murnane+Kapteyn)\)
- Control of dynamics in clusters \((Wöste)\)
- Control of ultrafast semiconductor nonlinearities \((Keller)\)
- Photoselective control in the liquid phase \((Gerber)\)
- etc...
LH2 of *Rps. Acidophila* - Standard model

Competing deactivation IC-EET

- Significant loss channel IC
- Negligible cross talk IC-EET
- Energy funnel precludes back transfer
64-parameter optimisation of IC/EET

Convergence curve

Optimal pulse FROG trace

Nature 417 (2002) 533
Resonant and nonresonant broadband femtosecond degenerate four wave mixing (DFWM) to detect vibrational ground state modes
Control of vibrational modes in $\beta$–Carotene

DFWM scheme

$\Omega$ $\Delta t$

FFT spectrum in FL case

DFWM signal
## 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>
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<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>
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<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>
Non – Resonant DFWM

Modes can be selectively excited
Non – Resonant DFWM

- Non – resonant pulse trains don’t enhance vibrations
- The unshaped (Fourier transformed) case is the upper limit

Resonant DFWM

Modes can be selectively excited

Fourier limited
Resonant pulse trains enhance vibrations

Reasons can be:
- Enhanced population transfer
- Stronger Coherence

J. Hauer et al.

Resonant DFWM

FFT

wavenumbers (cm$^{-1}$)
Histogram of successive IC/EET optimisations in LH2

$$2\pi/b = 160 \pm 25 \text{ cm}^{-1}$$
Control of conical intersection in the carotenoid

Optimized field drives bending modes which are the coupling modes for internal conversion
Some applications for coherent control using UV pulses

- **complex molecular systems:**
  - intramolecular dynamics in organic systems:
    - control of conical intersections, isomerization, fragmentation
  - DNA, proteins
  - Controlled photochemistry of atmosphere
    - synthesis of vinylene, ozone

- **Control of atomic processes:**
  - control of ionization, fragmentation
  - control of inner shell processes

- **Probing of structural changes as perfect feedback signal:**
  - ultrafast x-ray diffraction, electronic 2-D-spectroscopy
    - shaped excitation (Vis or UV) and x-ray probe
Spectral range of a liquid crystal mask

Transmission spectrum of liquid crystal mask CRI-256

No modulation of pulses in the UV and mid IR
Shaping of UV fs pulses

• **Indirect shaping by sum frequency mixing:**
  → appropriate crystals, complex setup, delicate overlap with reference pulses
  
  *M. Hacker et al., JOSA B 18 (2001) 866*
  *C. Schriever et al., Opt. Lett. 31 (2006) 543*

• **Direct shaping:**
  adaptive mirror → Aluminum coating
  - micromirrors: high dynamical range, 2-D capability
  - membrane based mirrors: low dynamical range, good for pulse compression
    AOM’s: phase + amplitude, low efficiency, fused silica (> 180 nm)
    *M. Roth et al, Appl. Phys. B 80 (2005) 441*
    AOPDF (“DAZZLER”) TeO$_2$, (200-500nm), low efficiency, p + a
Shaped pulse transfer by difference frequency mixing

800nm <100fs 1-2mJ

OPA

Shaped fs Signal Pulse, e.g. @1,25μm

Stretched fs Idler Pulse

AgGaS₂

Filter

Shaped fs MIR Pulse e.g. @ 3μm
mid infrared shaping

Mixing of two shaped IR pulses followed by DFM

I.)

Idler
~ 2.5 µm

II.)

Signal
~ 1.3 µm

Shaped pulses 3-10 µm

Optics Letters 27 (2002) 131
Direct UV shaping

Micromirror SLM

Cooperation: University of Jena, IPMS Dresden

Direct shaping by a micro mirror

- 240 x 200 Pixel
- 40µm x 40µm size
- Piston elements
- Mechanical move ca. 400 nm
- Reflectivity down to 250 nm

Fraunhofer Institut IPMS, Dresden
Implementation in a 4-f-setup

- Modulator in Fourier-plane of 4-f-setup
- Reflective-only
- UV at $\lambda = 285 \text{ nm}$ (SHG 570 nm NOPA)
- Pulse duration $\leq 30 \text{ fs}$
Pulse sequences in the UV

- Theorie
- Experiment

Cross-correlation UV-VIS

- \( a = 1.25 \)
- \( b = 100 \text{fs} \)
Most flexible control of molecular dynamics

Direct excitation of vibrational ground state modes:
\( \rightarrow \) Mid IR pulses

Control via electronic states:
\( \rightarrow \) UV pulses
What is the perfect light source for coherent control?

- **Electronic resonance:**
  - many important molecular systems absorb in the UV to VUV, controlled excitation exploiting single photon transitions
  - (soft control vs strong field control)

- **Tunability:**
  - perfect resonance or near resonance might be important for mode enhancement

- **Energy:**
  - 10-100 mikroJoule / pulse, depending on shaper efficiency

- **Bandwidth:**
  - the broader, the better \(\Rightarrow\) allows multipulse path control, electronic coupling and IVR processes have to be beaten, (100 fs probably too long)

- **Coherent coupling with other wavelength ranges:**
  - UV plus Vis or MIR range \(\Rightarrow\) full control over all molecular degrees of freedom
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