Ultrafast Coherent Nano-Control and Nano-Spectroscopy

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Ultrashort pulses

$$\psi(\vec{r}_j, t)$$

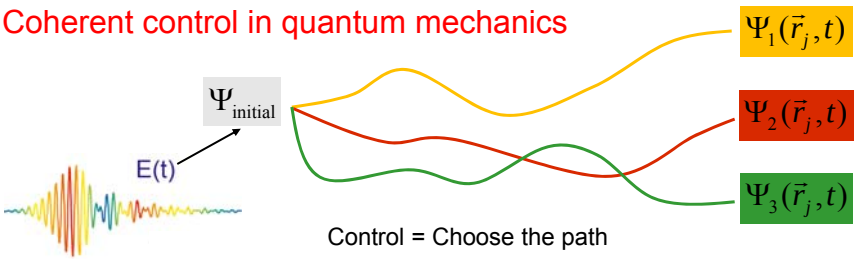
Photoelectron and optical detection

Space and time coordinates

Metals, semiconductors and molecular systems

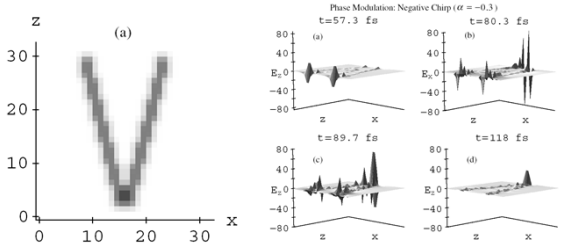
Coherent control and nano-control

Coherent control in quantum mechanics



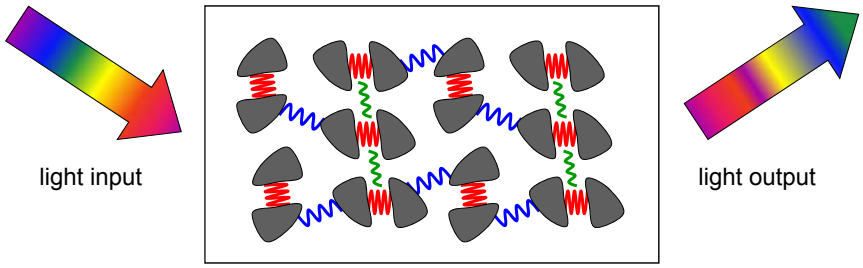
Control = Choose the path

Coherent control in nanoplasmonics



M. I. Stockman et al., *Phys. Rev. Lett.* **88**, 067402 (2002)

Nanomaterials



Complex material:
- heterogeneous / hybrid functional subunits
- type and structure of environment
- different kinds of coupling

Spatial and temporal resolution required

dynamics transport function

Artificially nanostructured systems

Metals

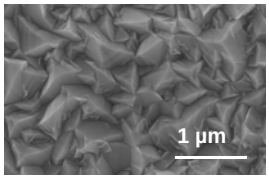
Plasmonics

SEM image of nanocircuits

J. Huang et al., *Nature Commun.* **1**, 150 (2010)
S. A. Maier, *Plasmonics: Fundamentals and Applic.*, Springer (2007)
M. I. Stockman, *Opt. Express* **19**, 22029 (2011)

Semiconductors

Si thin-film solar cells



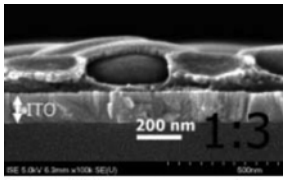
SEM image of nanotexture

A. Shah et al., *Science* **285**, 692 (1999)
S. Guha et al., *Prog. Photovoltaics* **8**, 141 (2000)

and many more...

Molecular systems

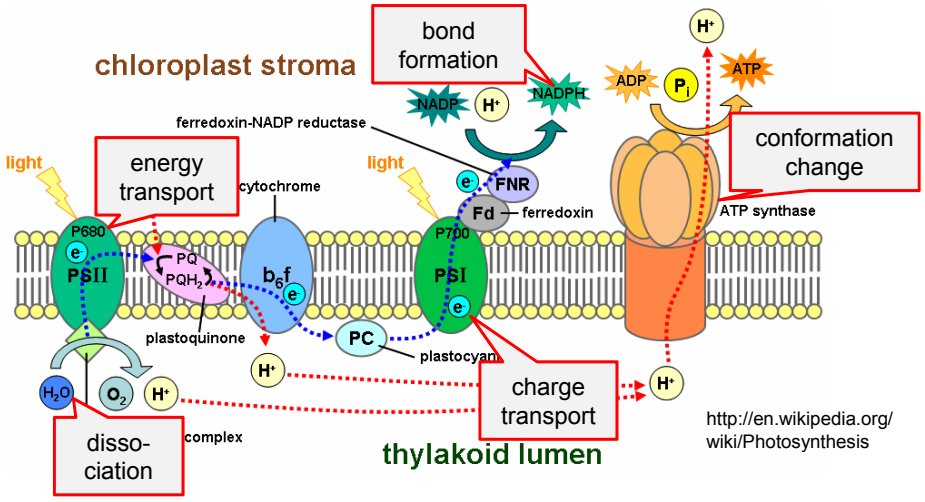
Organic photovoltaics



SEM cross section of MDMO−PPV/PCBM blend film cast from toluene

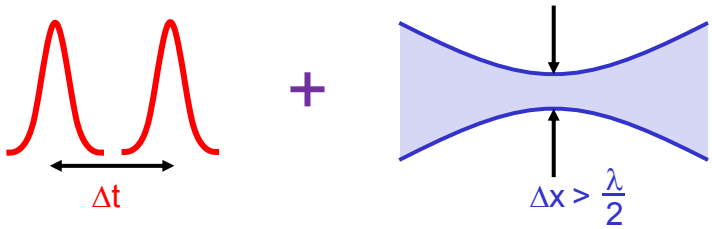
S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **107**, 1324 (2007)

Naturally nanostructured systems



Complex parallel spatial–temporal dynamics

Temporal and spatial resolution



We combine these approaches using pulse shaping and imaging.

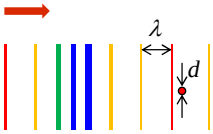
Examples

1) Space–time excitation control
2) Analytic propagation control
3) Random-structure control
4) Coherent 2D nanoscopy
5) Von Neumann control

Molecular vs. nano-optical control

control field | system | output / observable

$\vec{E}_{\text{external}}(t)$ → $\Psi(\vec{r},t)$ → $\vec{E}_{\text{signal}}(t)$, $\vec{J}_{\text{electrons}}(t)$ → !? → target



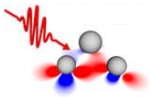
$d \ll \lambda$

molecule

control field | local field | system | output / observable

$\vec{E}_{\text{external}}(\vec{k},t)$ → $\vec{E}_{\text{local}}(\vec{r},t)$ ↔ $\Psi(\vec{r},t)$ → $\vec{E}_{\text{signal}}(\vec{r},t)$, $\vec{J}_{\text{electrons}}(\vec{r},t)$ → !? → target

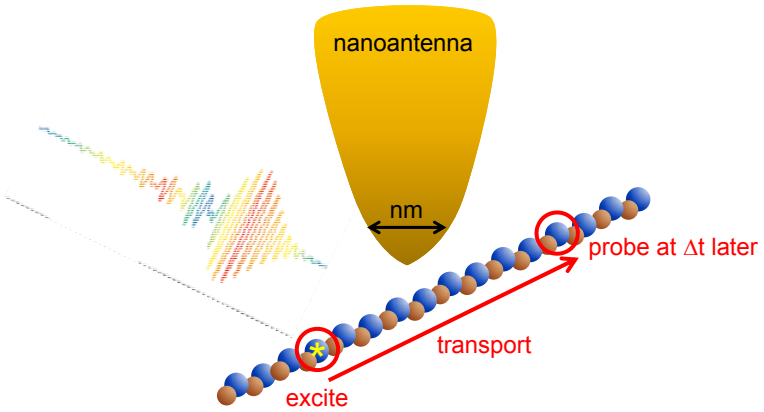
$d \approx \lambda$



nano-object

New effects and possibilities by additional degrees of freedom

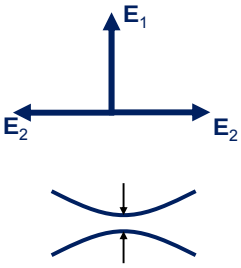
Subdiffraction nm–fs resolution



Phys. Rev. Lett. **95**, 093901 (2005)

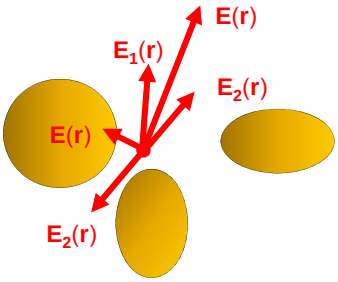
Near-field coherent control

Far field:
$\mathbf{E}_1 \perp \mathbf{E}_2$
no interference



diffraction limit ≈ λ/2

Local near field:
$\mathbf{E}_1(\mathbf{r}) \angle \mathbf{E}_2(\mathbf{r})$
interference

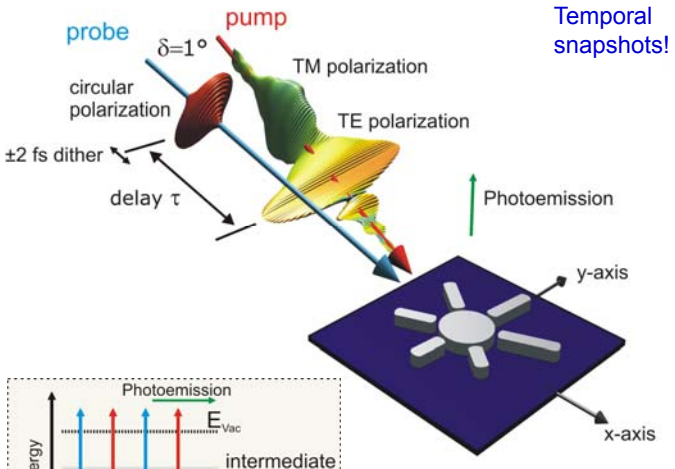


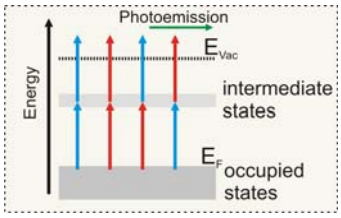
subdiffraction control
of **E(r)** via E_1 and E_2

Control parameter:
$\Phi(\omega) = \varphi_1(\omega) - \varphi_2(\omega)$

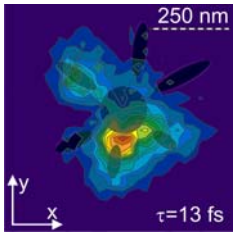
Phys. Rev. Lett. **95**, 093901 (2005)
Phys. Rev. B **73**, 125437 (2006)

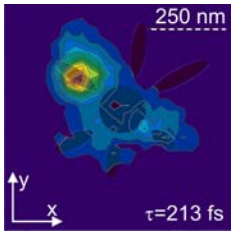
Space–time control (experiment)





Temporal
snapshots!



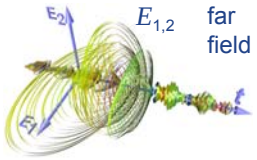


Subwavelength ultrafast
excitation control on the way
to nm–fs spectroscopy

PNAS **107**,
5329 (2010)

Analytic control for plasmon junction

response function R



$E_{1,2}$ far field

spectral near field

$$\mathbf{E}(\mathbf{r},\omega)=\sum_{k=1}^{2}\begin{pmatrix} R_x^k(\mathbf{r},\omega)\,e^{i\varphi_x^k(\mathbf{r},\omega)} \\ R_y^k(\mathbf{r},\omega)\,e^{i\varphi_y^k(\mathbf{r},\omega)} \\ R_z^k(\mathbf{r},\omega)\,e^{i\varphi_z^k(\mathbf{r},\omega)} \end{pmatrix}\sqrt{I_k(\omega)}\,\exp\{i\varphi_k(\omega)\}$$

flux contrast

$$I_{A-B}(\omega)=\mathbf{E}^*(\mathbf{r}_A,\omega)\,\mathbf{E}(\mathbf{r}_A,\omega)-\mathbf{E}^*(\mathbf{r}_B,\omega)\,\mathbf{E}(\mathbf{r}_B,\omega)=f[\underbrace{\varphi_1(\omega)-\varphi_2(\omega)}_{\Delta\Phi(\omega)}]$$

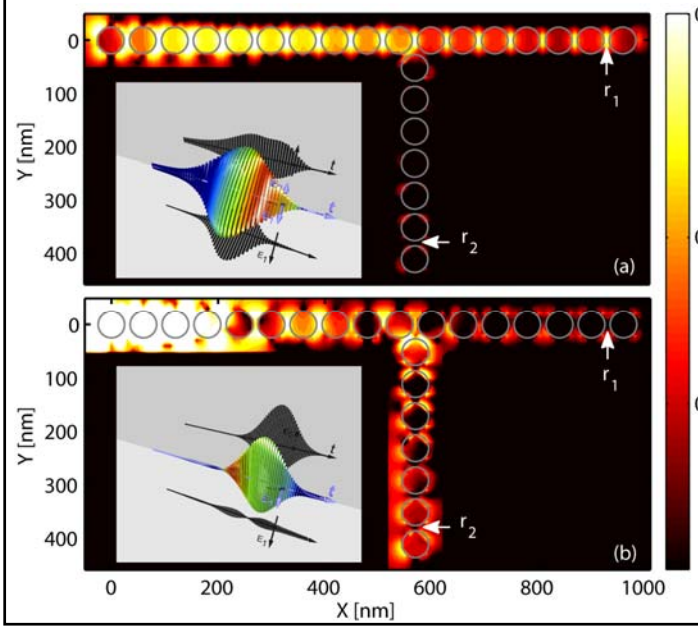
maximum contrast $\dfrac{dI_{A-B}}{d(\Delta\Phi)}=0$ ⇒ step 1: optimal phase difference for each ω

3 degrees of freedom left ⇒ step 2: use $I_1(\omega), I_2(\omega)$ for perfect contrast

⇒ step 3: use $\varphi_1(\omega)$ to compress pulse

Opt. Express **17**, 14235 (2009)

Analytic space-time control



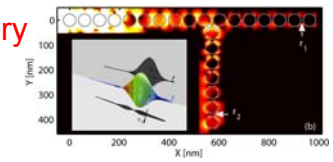
$\Delta\Phi$:= $\Phi(\mathrm{LCD}_1)$ – $\Phi(\mathrm{LCD}_2)$

$\Delta\Phi \rightarrow \Delta\Phi + \pi$

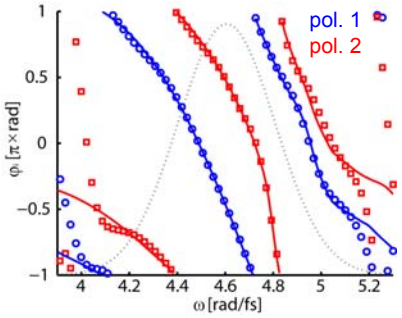
Opt. Express **17**, 14235 (2009)

Closed-loop vs. open-loop control

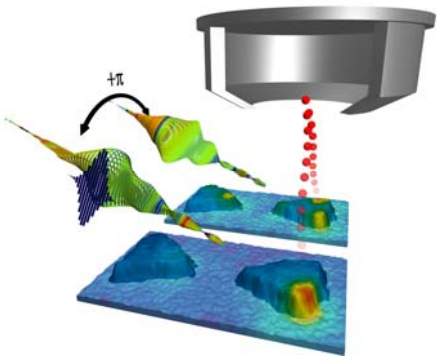
Theory



Analytically derived control rule



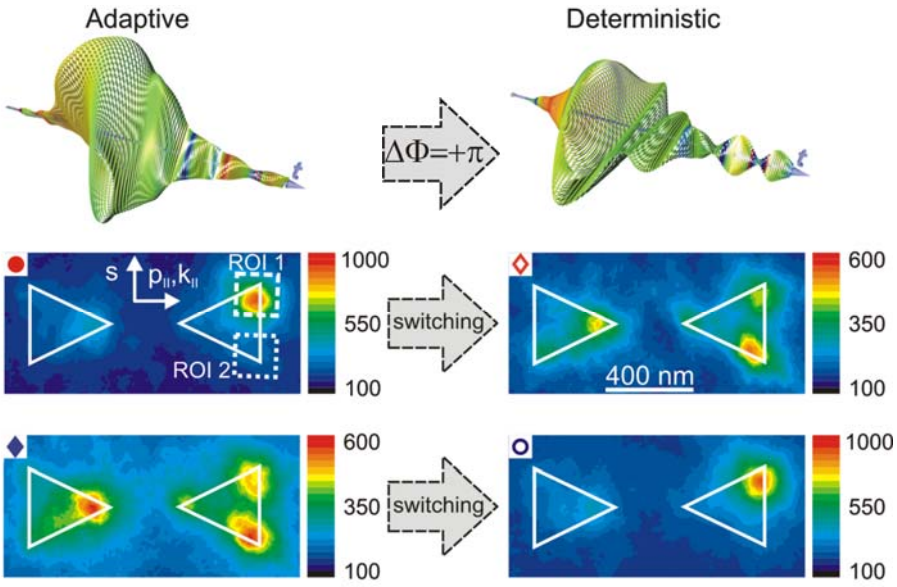
Experiment



Opt. Express **17**, 14235 (2009)

New J. Phys. **14**, 033030 (2012)

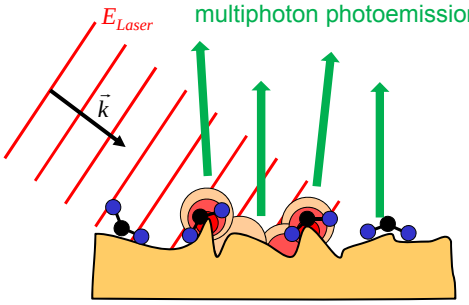
Deterministic control – results



New J. Phys. **14**, 033030 (2012)

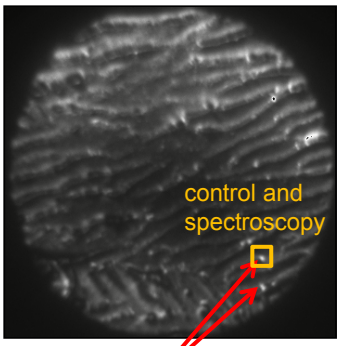
Coherent control: coherence measure

Corrugated metal (Ag)



Important applications, e.g.
Surface-Enhanced Raman
Spectroscopy (SERS)

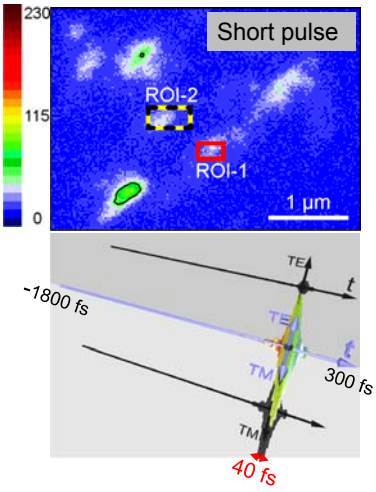
Photoemission
electron microscopy (PEEM)

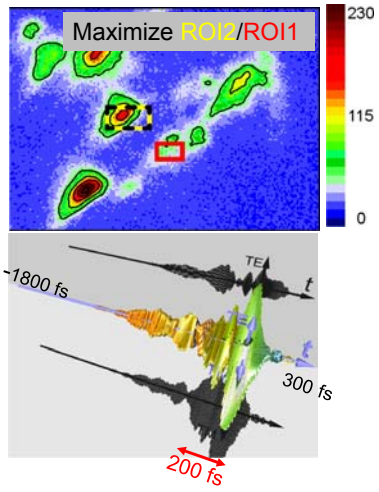


"Hot Spots"

IEEE J. Sel. Top. QE **18**, 275 (2012)

Hot-spot control – long coherences





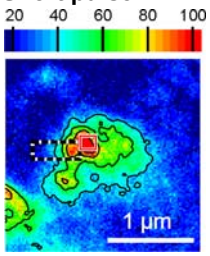
Higher yield for longer pulse!

Long local coherence lifetime!?

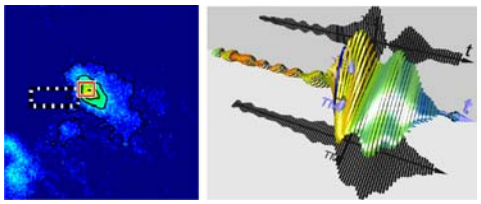
IEEE J. Sel. Top. QE **18**, 275 (2012)

Reproducibility

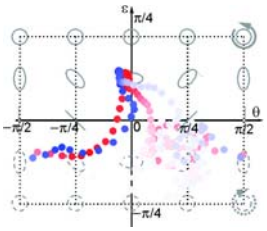
Short pulse



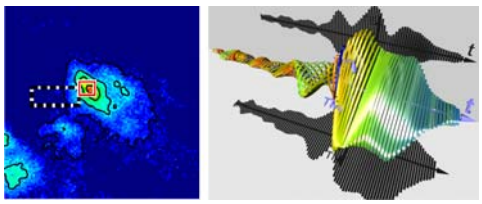
Optimization 1



Poincaré Plot



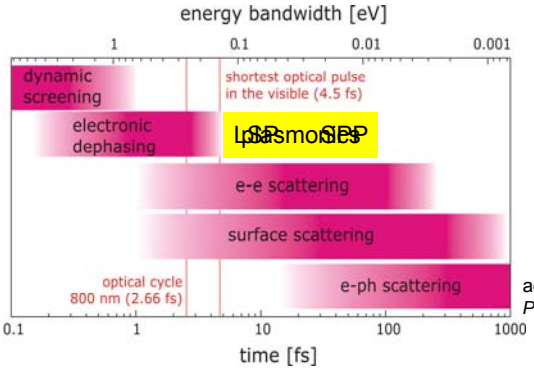
Optimization 2



Subsequent optimizations find very similar pulses

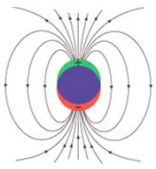
IEEE J. Sel. Top. QE **18**, 275 (2012)

Time scales of plasmonics



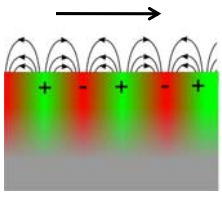
Plasmonic dephasing times experimentally accessible

adopted from Petek et al., *Prog. Surf. Sci.* **56**, 239 (1997)



LSP
Localized
surface plasmon
(Mie resonance)

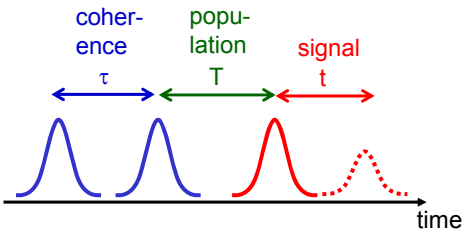
Lifetime:
< 10 fs



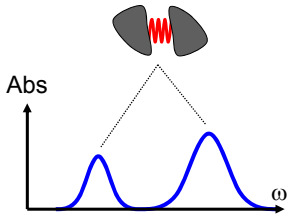
SPP
Propagating
surface plasmon
polariton

Lifetime (Ag@1.55 eV):
200 fs

Coherent 2D spectroscopy

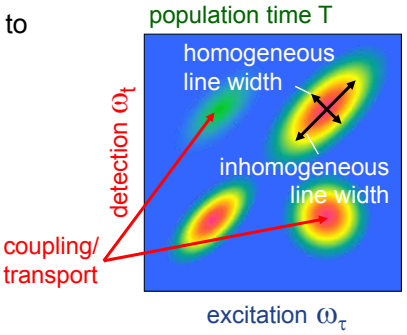


coupled chromophores

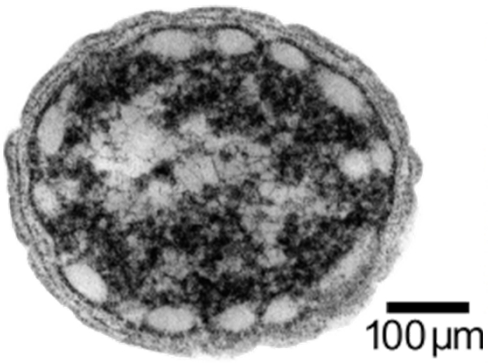


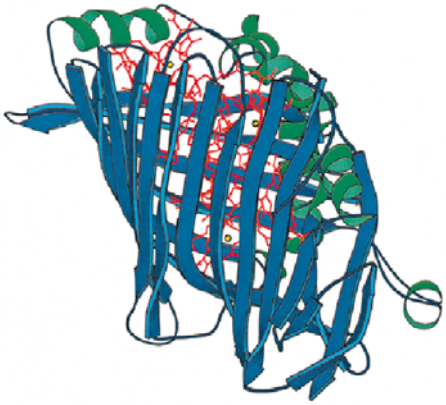
2D spectrum = probability to
- start with ω_τ,
- wait for time T,
- end with ω_t

"Like transient absorption with frequency resolution for pump **and** probe pulse"



Natural light harvesting





Photosynthetic
green sulfur bacterium
Chlorobium tepidum

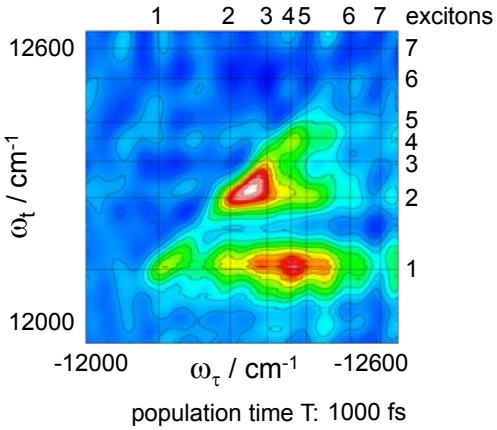
Image: N.-U. Frigaard, D. A. Bryant (Penn State University)
http://www.bmb.psu.edu/faculty/bryant/lab/chlorobiumtepidum/

Fenna–Matthews–Olson (FMO)
complex contains 7(8) molecules
bacteriochlorophyll *a*

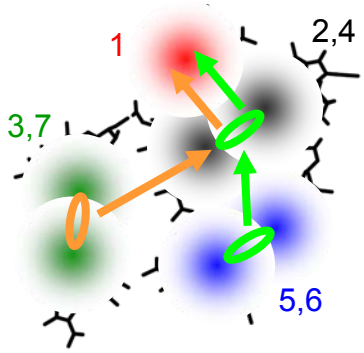
Structure: R. E. Blankenship et al. (Arizona State University)
J. Mol. Biol. **271**, 456 (1997), *Photosynth. Res.* **75**, 49 (2003)

Energy transport in light harvesting

2D spectrum



Fenna-Matthews-Olson

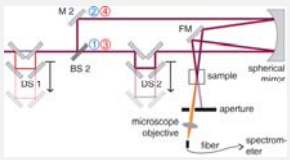


Nature **434**, 625 (2005)
JPCB **109**, 10542 (2005)

Couplings / exciton delocalization
Spatial-temporal energy transport

2D Methods at Würzburg

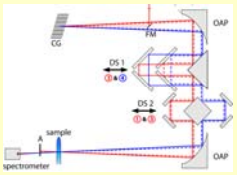
2D-VIS



- noncollinear
- convent. optics
- simple design
- IR/VIS/UV
- efficient
- λ/100 stability

Opt. Lett. **33**, 2851 (2008)

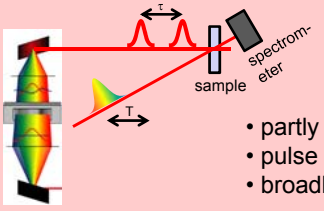
2D-UV



- noncollinear
- all-reflective
- 20×30 cm^2
- 250…400 nm
- λ/80 stability

Opt. Lett. **35**, 4178 (2010)

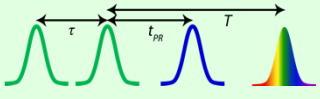
2D-VIS-whitelight



- partly collinear
- pulse shaping
- broadband

JACS **133**, 13074 (2011)

Triggered-exchange 2D-VIS

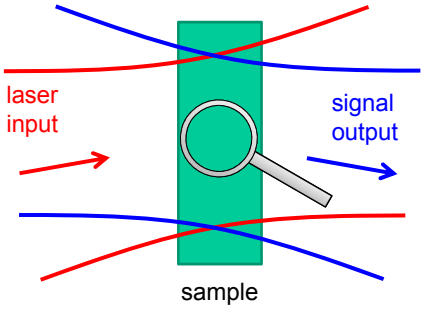


- three colors
- chemical dynamics

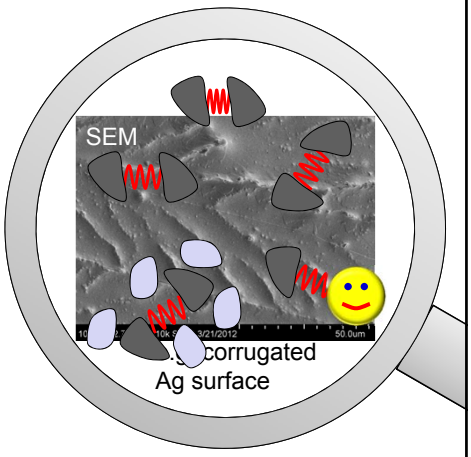
Ultrafast Phenomena XVIII (2012)

Coherent 2D nano-spectroscopy

Spatially averaged measurement



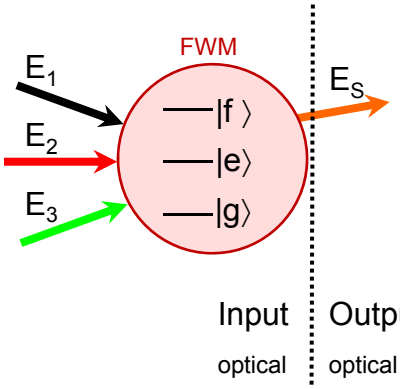
Heterogeneous distribution



Can we avoid
unwanted averaging?

2D Nanoscopy: The idea

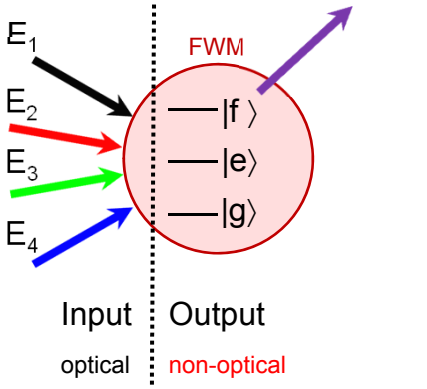
2D spectroscopy



Optical diffraction limit applies

2D nanoscopy

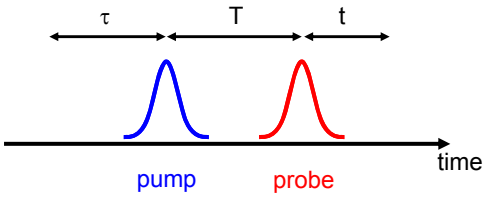
photo-
electrons

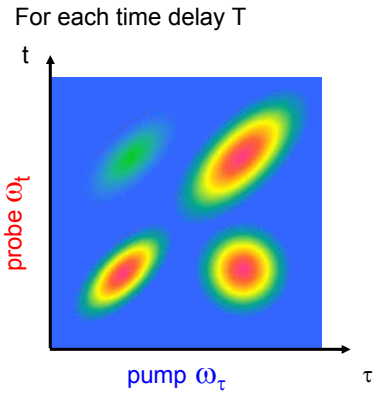


Optical diffraction limit does not apply

Fluorescence detection: W. S. Warren et al., *Science* **300**, 1553 (2003)
A. Marcus et al., *J. Chem. Phys.* **127**, 214307 (2007)
Attosecond X-ray: S. Ruhav and S. Mukamel, *Phys. Rev. A* **81**, 063810 (2010)

2D Nanoscopy

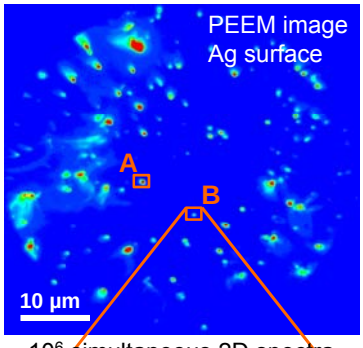




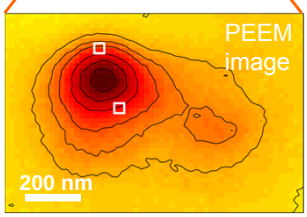
- Scanning τ and t
- 2D Fourier transformation

Science **333**, 1723 (2011)

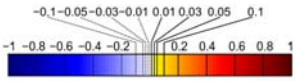
The first 2D nano-spectra

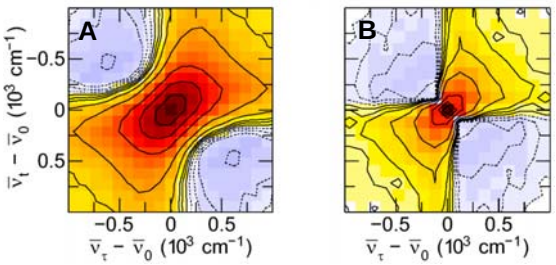


10⁶ simultaneous 2D spectra



„Absorptive" real part
(4-step phase cycling)





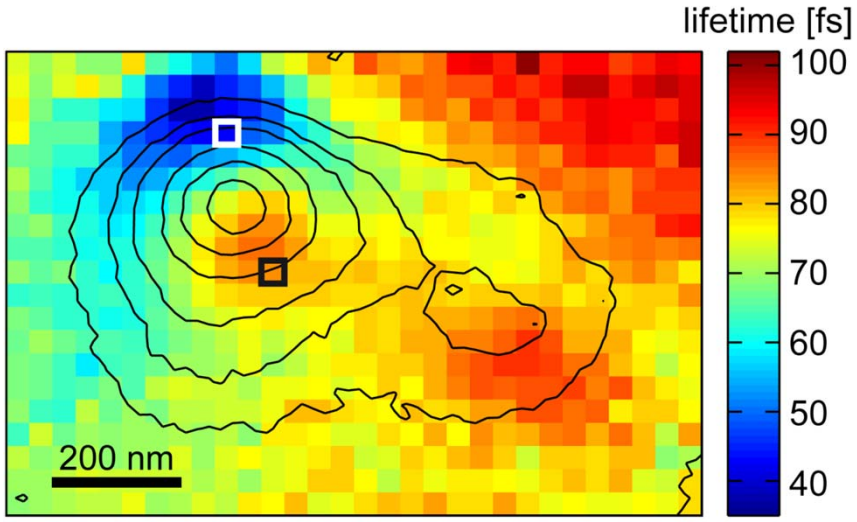
Significantly different local 2D spectra!

Modeling with damped Lorentzian oscillator → lifetime $T_2 = 1/\gamma$

Zoom in below diffraction limit

Science **333**, 1723 (2011)

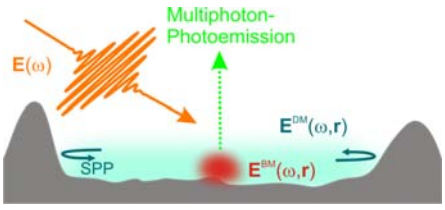
Spatial coherence lifetime map

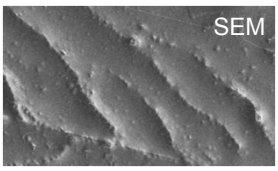


Long coherence lifetimes

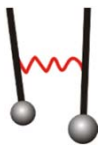
Science **333**, 1723 (2011)

Coupled-oscillator model





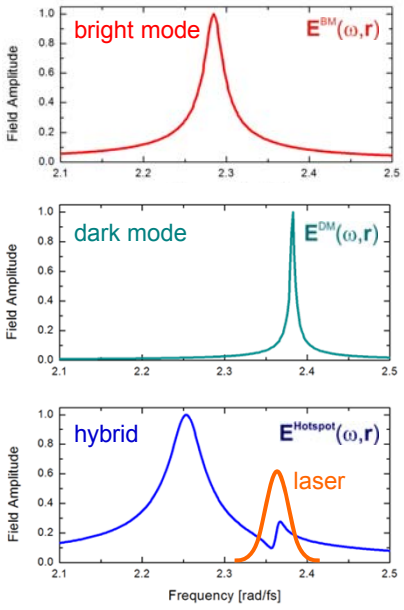
„Ag ridges“



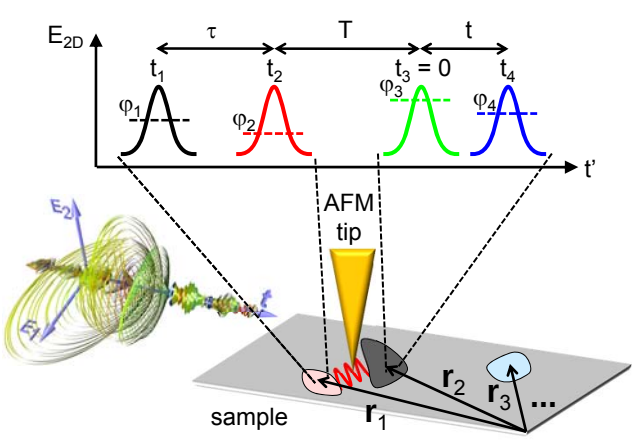
Mode hybridization

⇒ Fano-like line shape

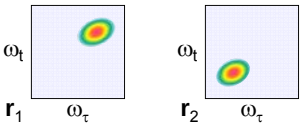
⇒ Long coherence lifetime



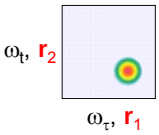
2D-Nano: Future possibilities



2D Nano-Spectroscopy
with far-field illumination



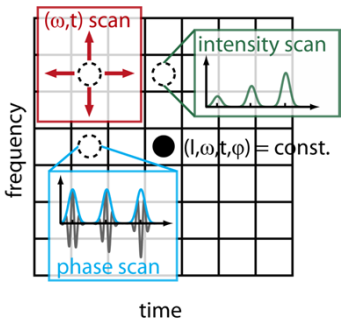
Outlook: 2D Nanoscopy with
near-field coherent control



Investigate:
- (Coupled) Nanostructures
- Nanooptical circuits / transport
- Single molecules / aggregates
- "Artificial" molecules / quantum dots
- Any inhomogeneous systems
- Whatever has been studied with conventional photoemission

Von Neumann coherent control

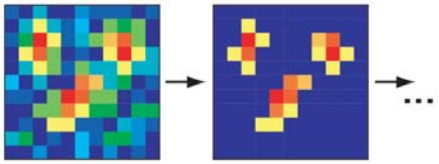
1) Control landscapes



JCP **133**, 164510 (2010)

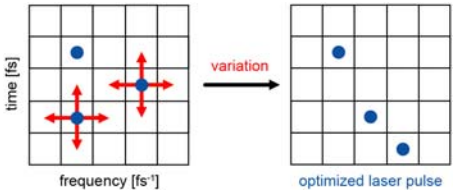
Von Neumann basis
(Coop.: David J. Tannor)
Opt. Express **15**, 15387 (2007)
Appl. Phys. B **93**, 763 (2008)
New J. Phys. **11**, 105052 (2009)

2) Information distillation



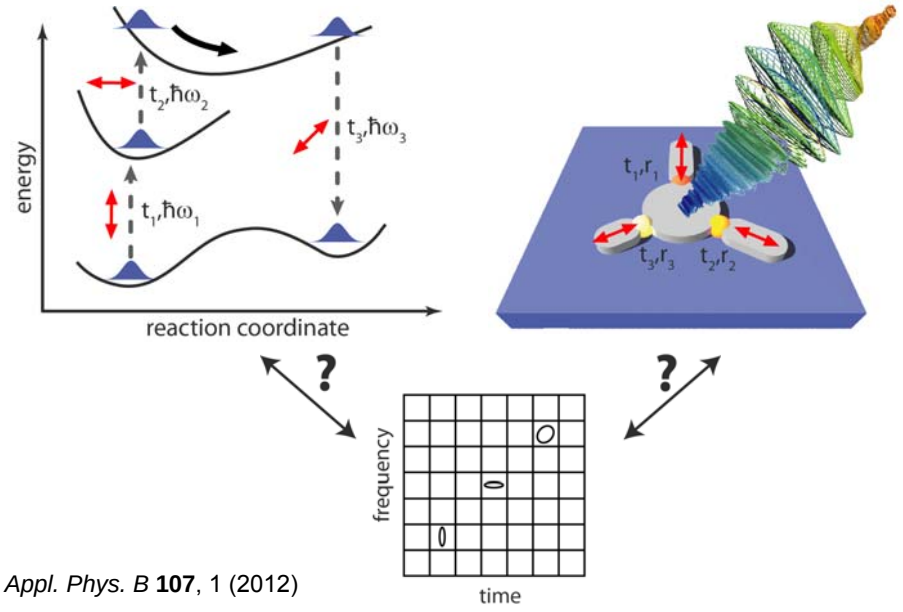
PCCP **13**, 8627 (2011)

3) Mechanistic learning control



PCCP **13**, 8627 (2011)

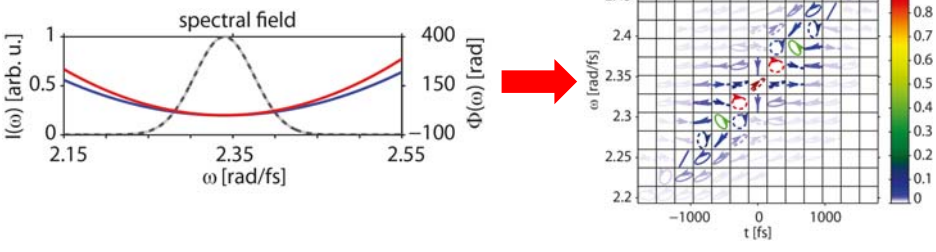
Von Neumann polarization analysis



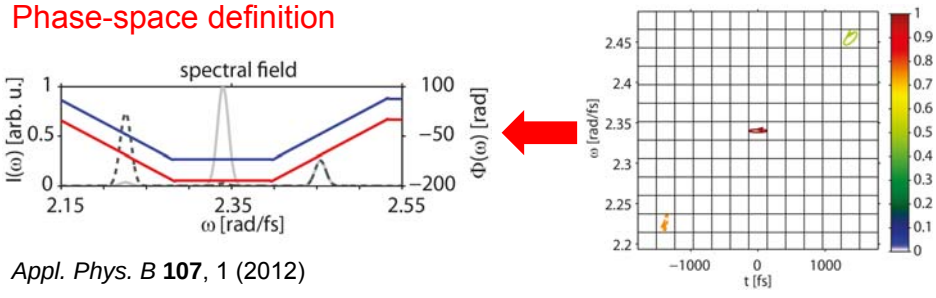
Appl. Phys. B **107**, 1 (2012)

Von Neumann polarization shaping

Phase-space analysis



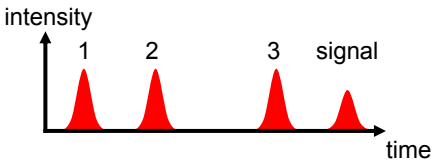
Phase-space definition



Appl. Phys. B **107**, 1 (2012)

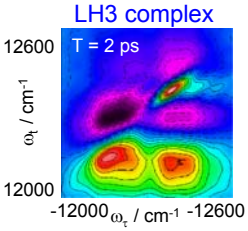
Multicolor multi-dim. spectroscopy?

Coherent 2D spectroscopy



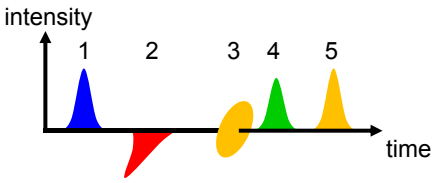
scanning parameters:
time delays

LH3 complex



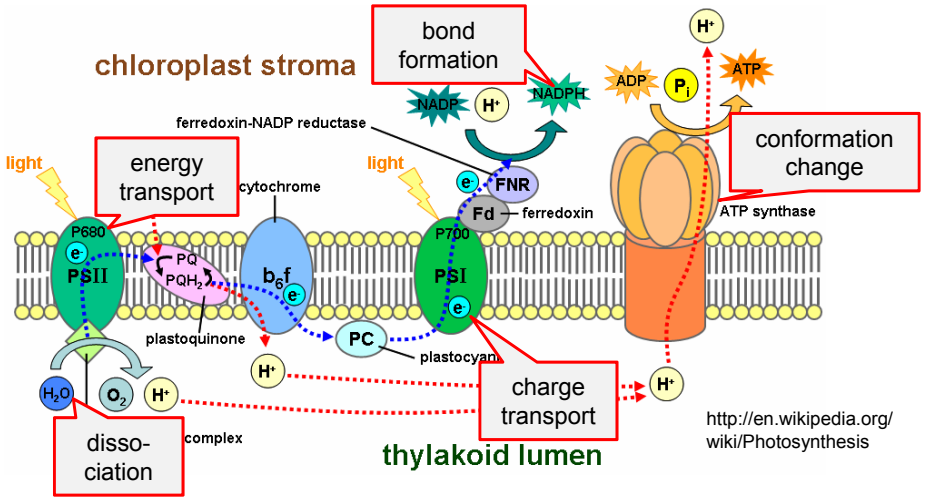
PNAS **103**, 12672 (2006)

Generalization (e.g. von Neumann)



scanning parameters:
time delays
center frequencies
intensities
polarization
relative phases
...

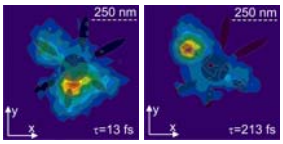
Outlook: 2D nanoscopy in biosystems



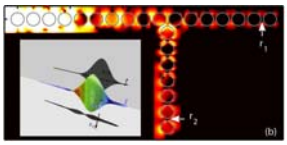
The dream: Observe processes simultaneously yet separately

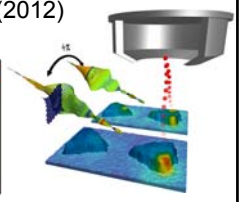
Ultrafast coherent nano-control

1) Space–time excitation control
PRL **95**, 093901 (2005)
Nature **446**, 301 (2007)
PNAS **107**, 5329 (2010)



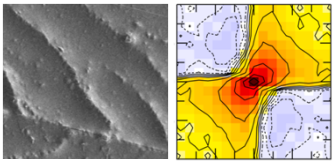
2) Analytic propagation control
Opt. Express **17**, 14235 (2009)
New J. Phys. **14**, 033030 (2012)



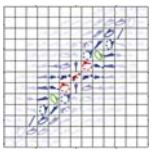


3) Random-structure control
IEEE JST-QE **18**, 275 (2012)

4) Coherent 2D nanoscopy
Science **333**, 1723 (2011)

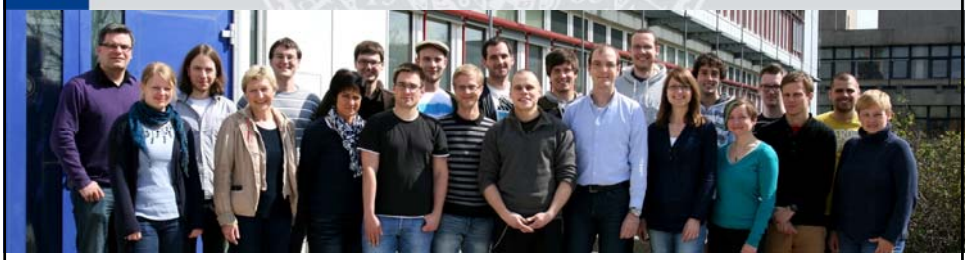


5) Von Neumann control
Opt. Express **15**, 15387 (2007)
JCP **133**, 164510 (2010)
PCCP **13**, 8627 (2011)
Appl. Phys. B **107**, 1 (2012)



Nanocontrol tutorial to appear in
M. Agio, A. Alù (Eds.), *Optical Antennas,*
Cambridge University Press (2012)

Many thanks



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