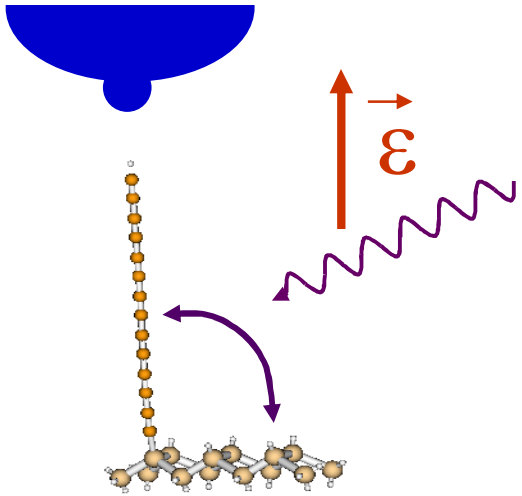
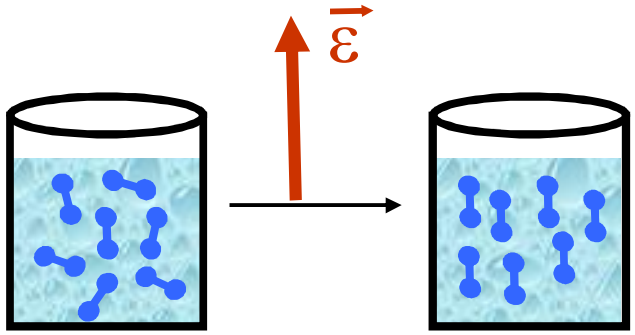
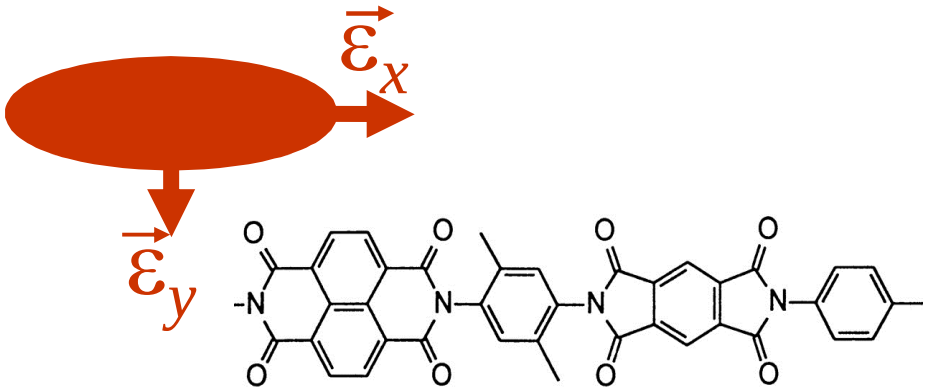
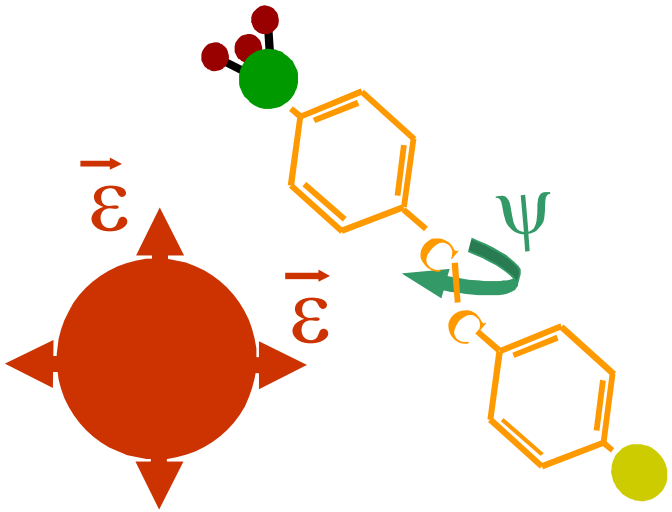




Coherent Alignment. New Directions and Potential Opportunities in Complex Systems





Thanks!

$ NSF CHE
$ NSF MRSEC
$ NSF NCN
$ NSF NCLT
$ NSF IGERT
$ AFOSR
$ BSF
$ DOE AMOS
$ DOE SISGR
$ Keck Foundation

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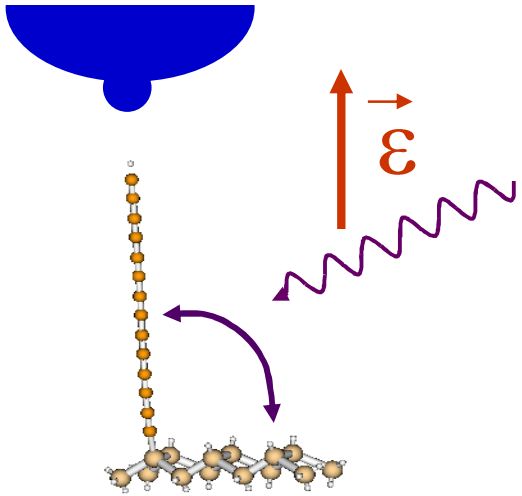
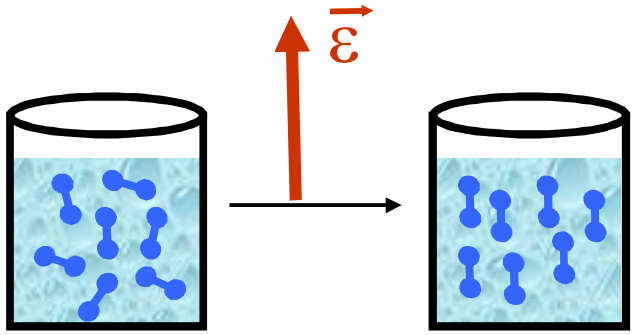
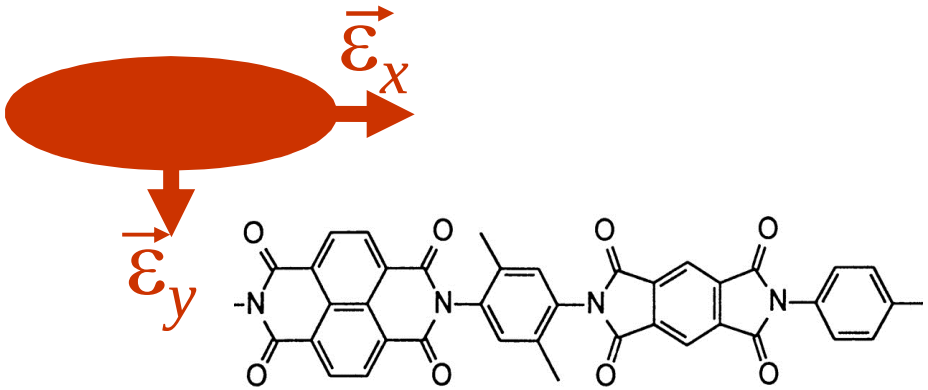
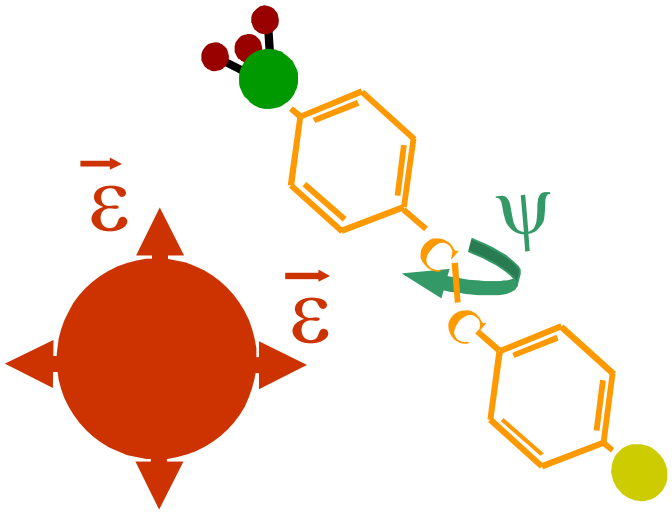




Coherent Alignment. New Directions and Potential Opportunities in Complex Systems

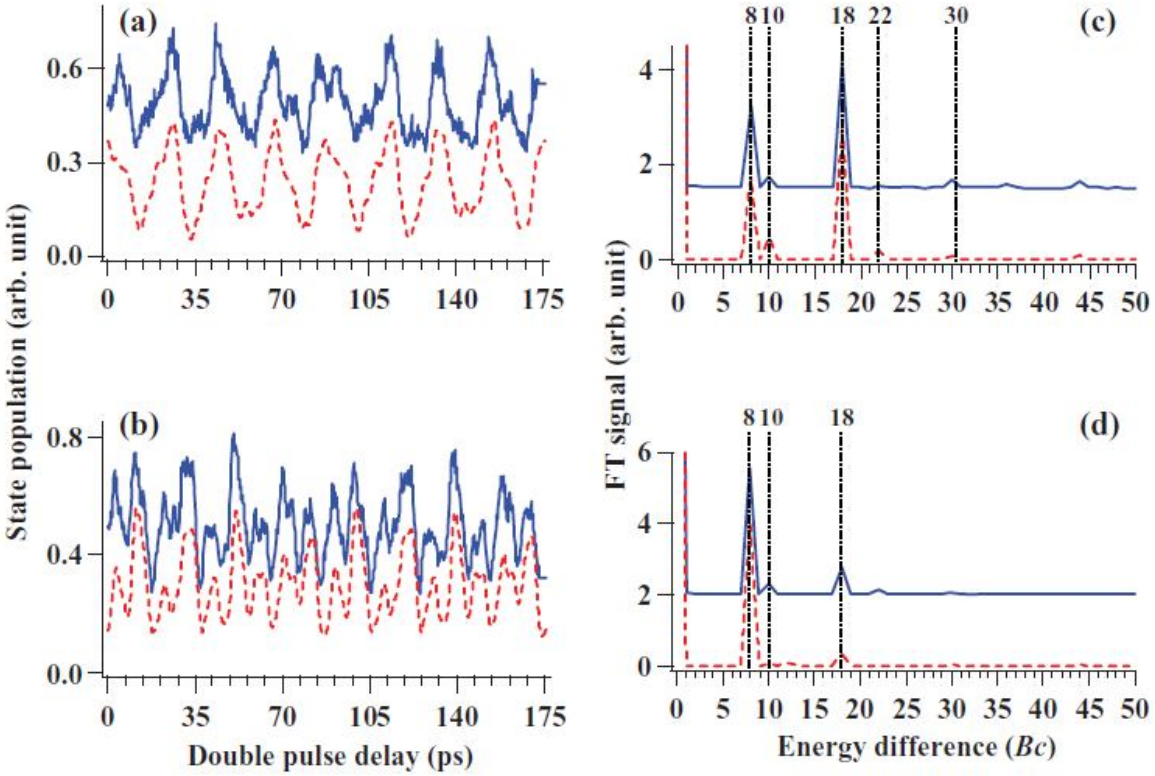




THE JOURNAL OF CHEMICAL PHYSICS **134**, 224302 (2011)

Unveiling the nonadiabatic rotational excitation process in a symmetric-top molecule induced by two intense laser pulses

Daeyul Baek,[a)] Hirokazu Hasegawa,[b)] and Yasuhiro Ohshima[c)]
Institute for Molecular Science, National Institutes of Natural Sciences, Myodaiji, Okazaki 444-8585, Japan and SOKENDAI, The Graduate University for Advanced Studies, Okazaki 444-8585, Japan



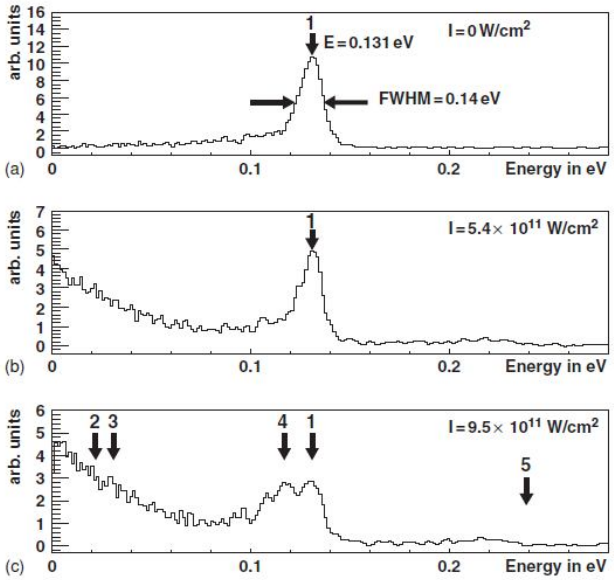
THE JOURNAL OF CHEMICAL PHYSICS **134**, 104306 (2011)

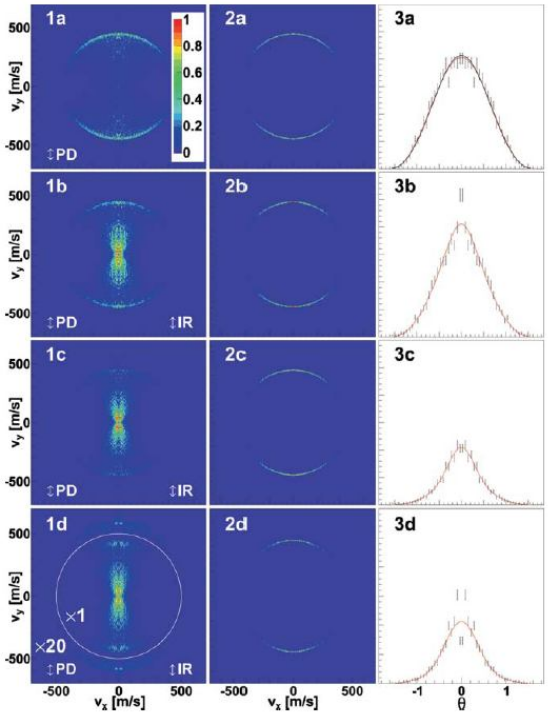
Nanosecond photofragment imaging of adiabatic molecular alignment

S. Trippel, M. Stei,[a)] C. Eichhorn, R. Otto, P. Hlavenka, M. Weidemüller,[b)] and R. Wester[a,c)]

Physikalisches Institut, Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany

(Received 12 November 2010; accepted 1 February 2011; published online 11 March 2011)



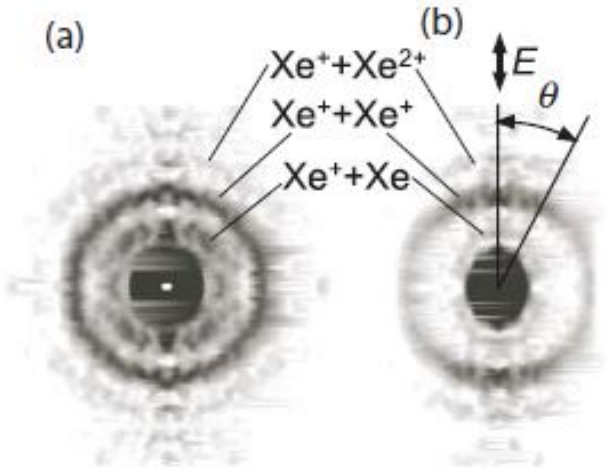


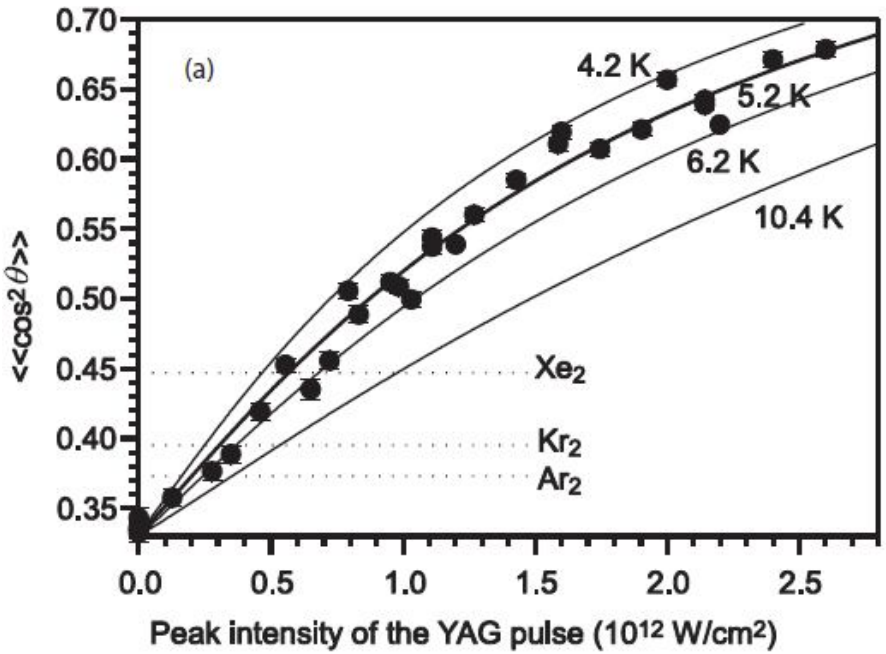
THE JOURNAL OF CHEMICAL PHYSICS **134**, 214305 (2011)

Measuring polarizability anisotropies of rare gas diatomic molecules by laser-induced molecular alignment technique

Shinichirou Minemoto[a)] and Hirofumi Sakai[b)]
Department of Physics, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

(Received 10 March 2011; accepted 6 May 2011; published online 6 June 2011)





International Reviews in Physical Chemistry
Vol. 29, No. 4, October–December 2010, 619–663

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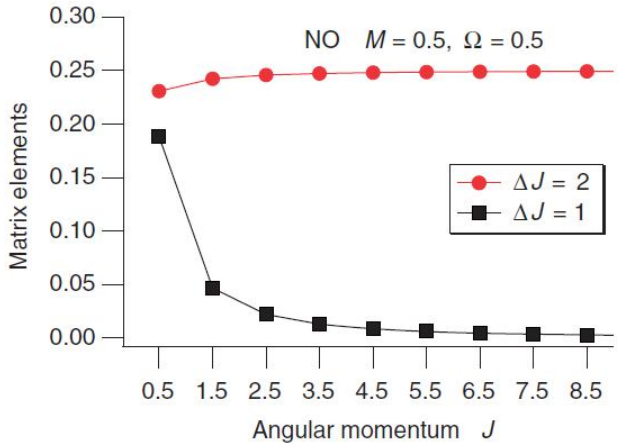
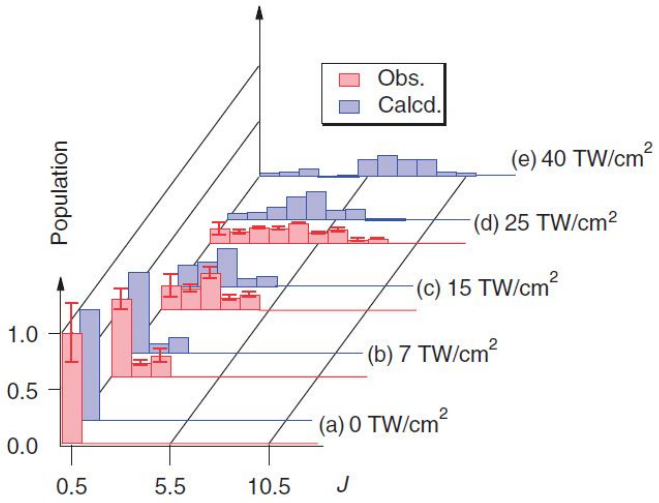
Coherent rotational excitation by intense nonresonant laser fields

Yasuhiro Ohshima* and Hirokazu Hasegawa

Institute for Molecular Science, National Institutes of Natural Sciences, Myodaiji, Okazaki 444-8585, Japan; The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan





PHYSICAL REVIEW A **83**, 063409 (2011)

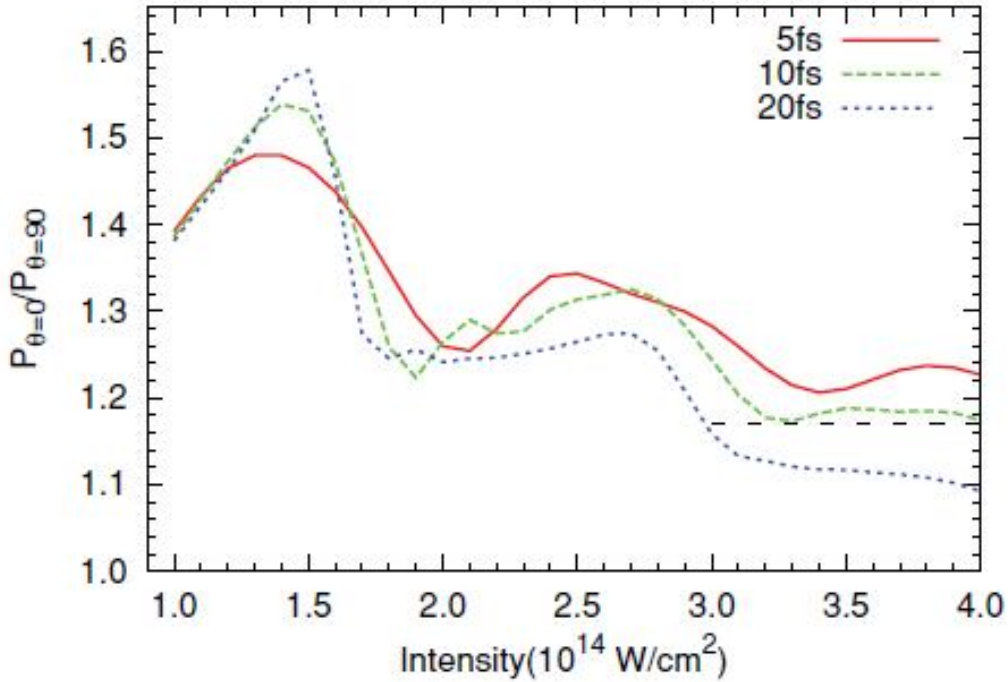
Alignment-dependent ionization of hydrogen molecules in intense laser fields

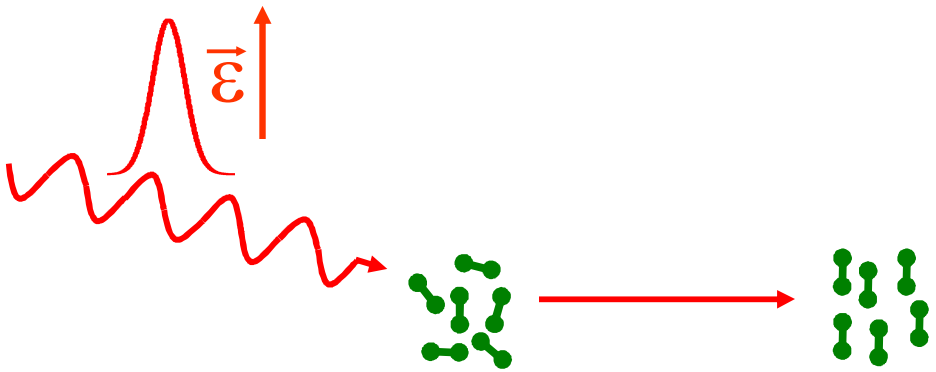
Ying-Jun Jin,[1,*] Xiao-Min Tong,[1,2,†] and Nobuyuki Toshima[1]

[1]*Institute of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba,1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*

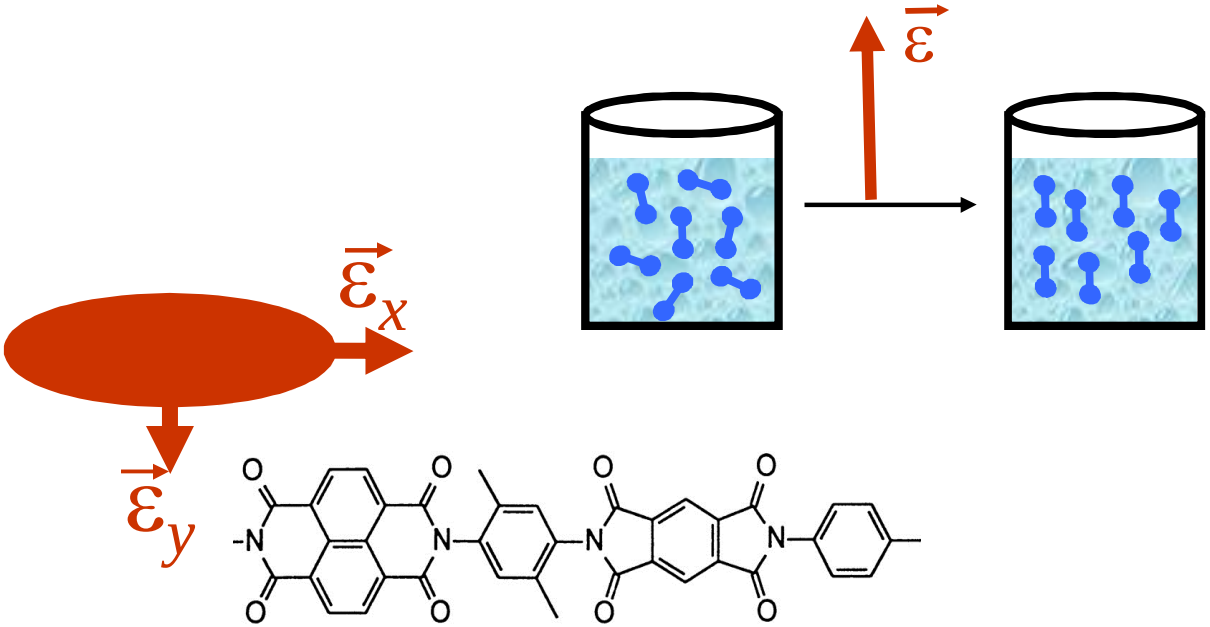
[2]*Center for Computational Sciences, University of Tsukuba,1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan*

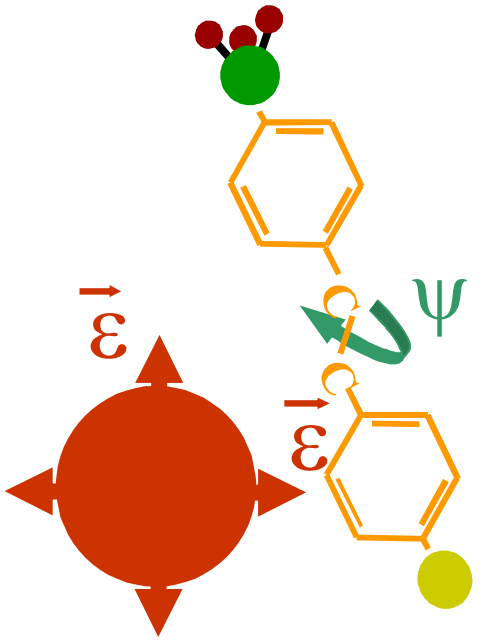
(Received 12 April 2011; published 14 June 2011)

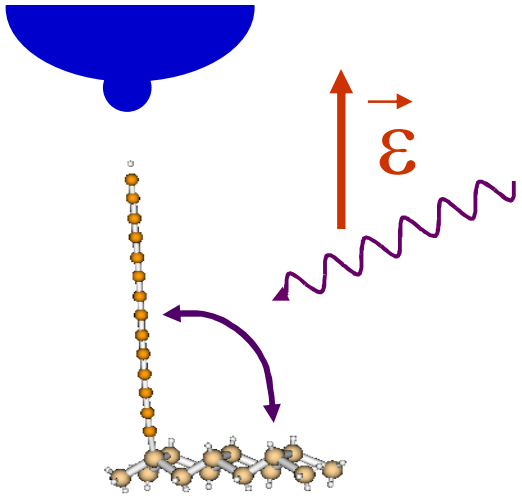


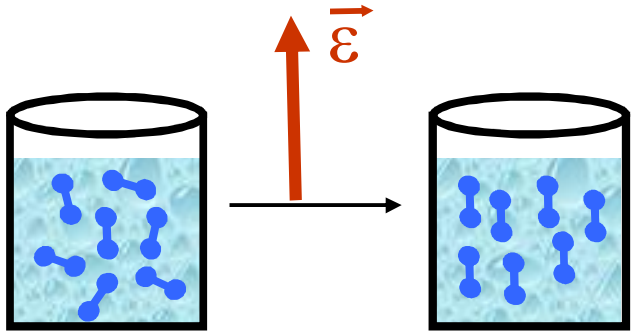


But molecules are more interesting than that:

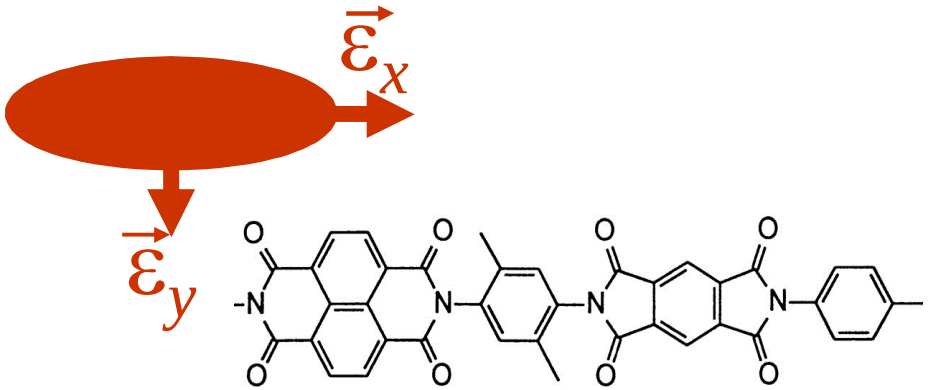


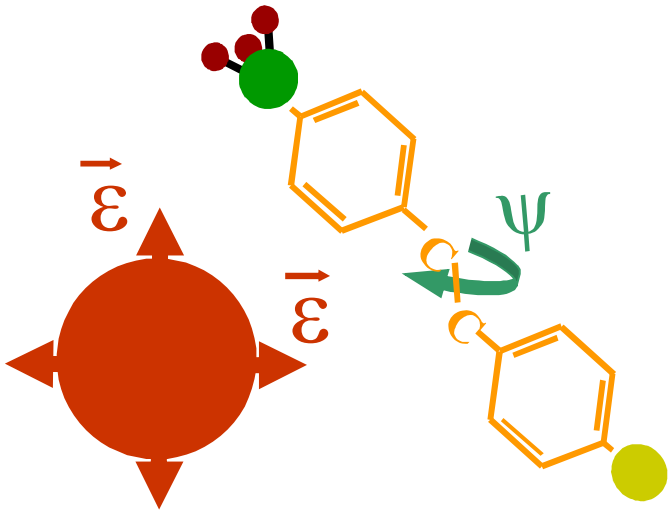






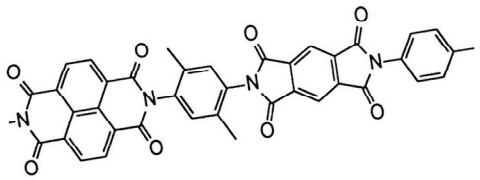
Coherent Alignment. New Directions and Potential Opportunities in Complex Systems



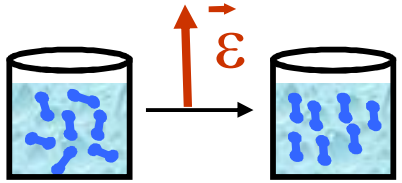


Outline

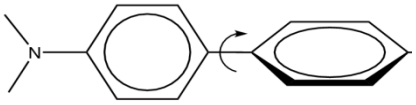
- Coherent nonadiabatic alignment. A brief review of the qualitative physics

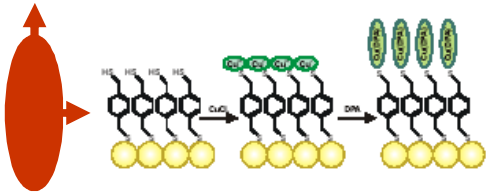


- Toward complex systems:
  - Beating the transition to unstable dynamics

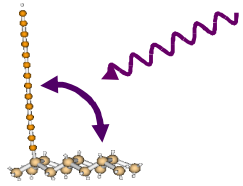


  - Alignment in solutions
  - Torsional control





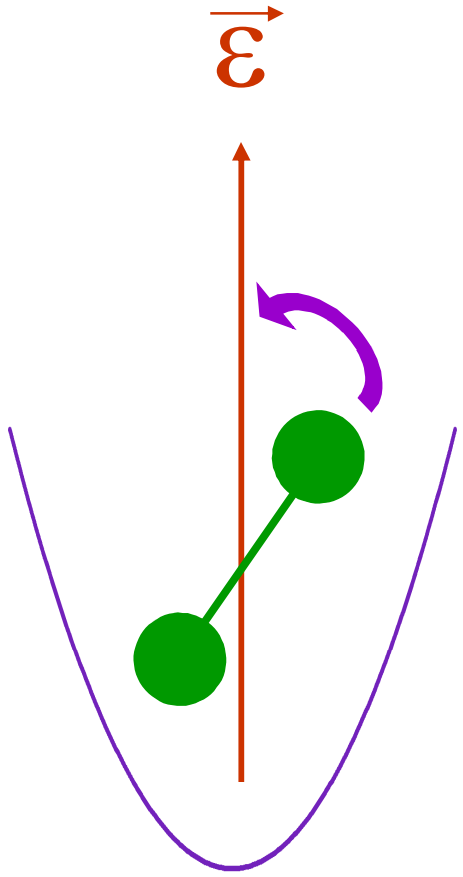
  - Guided molecular assembly
  - Coherent control of transport via junctions



  - Alignment and focusing in the nanoscale

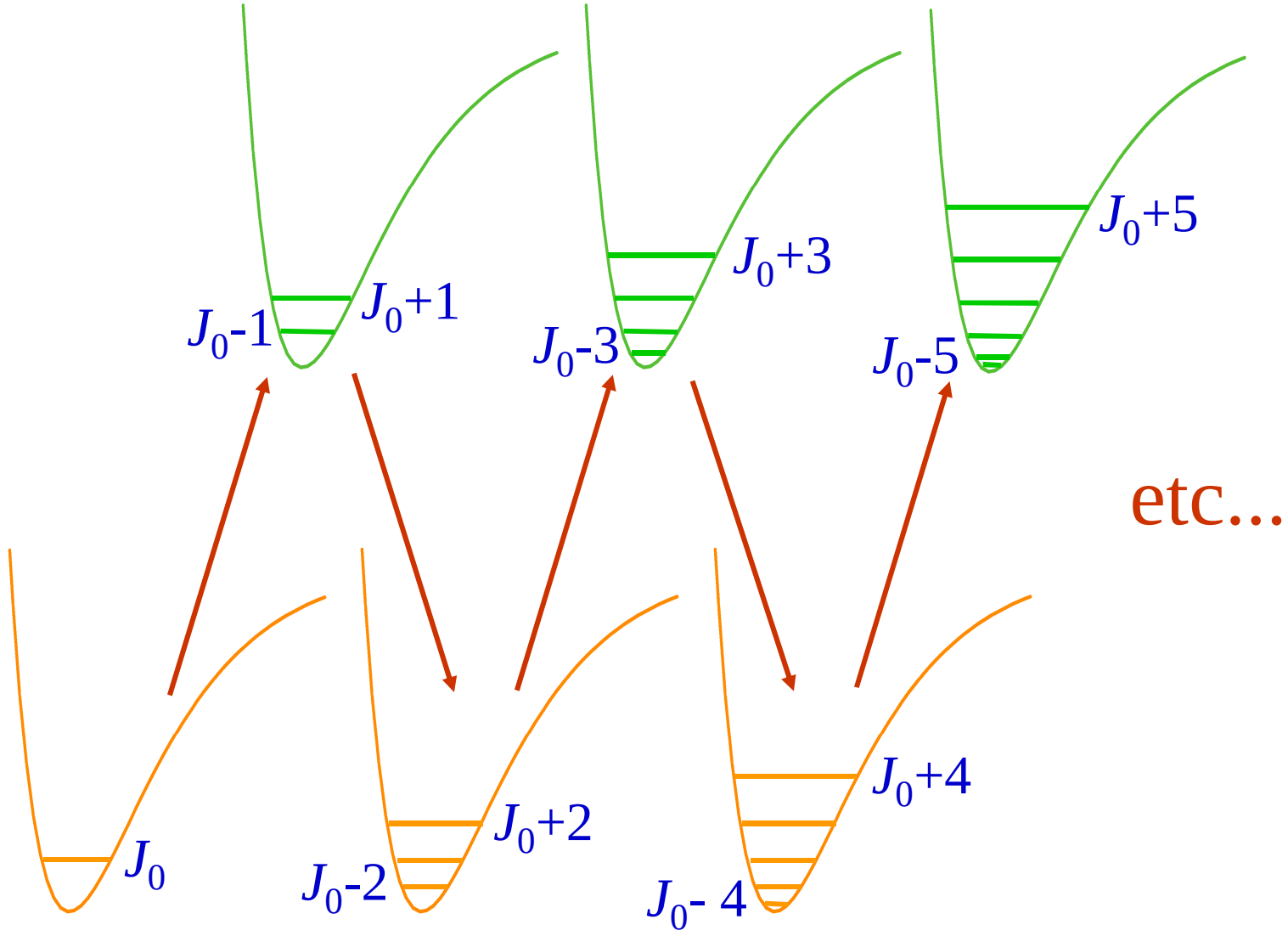
- Few of my favorite dreams

$$mR_e^2 \ddot{\theta} = -\frac{\partial}{\partial \theta} V[\, \theta \,;\, \vec{\varepsilon}\,]$$



Alignment by short, moderately intense, laser pulses

At near electronic resonance frequencies:

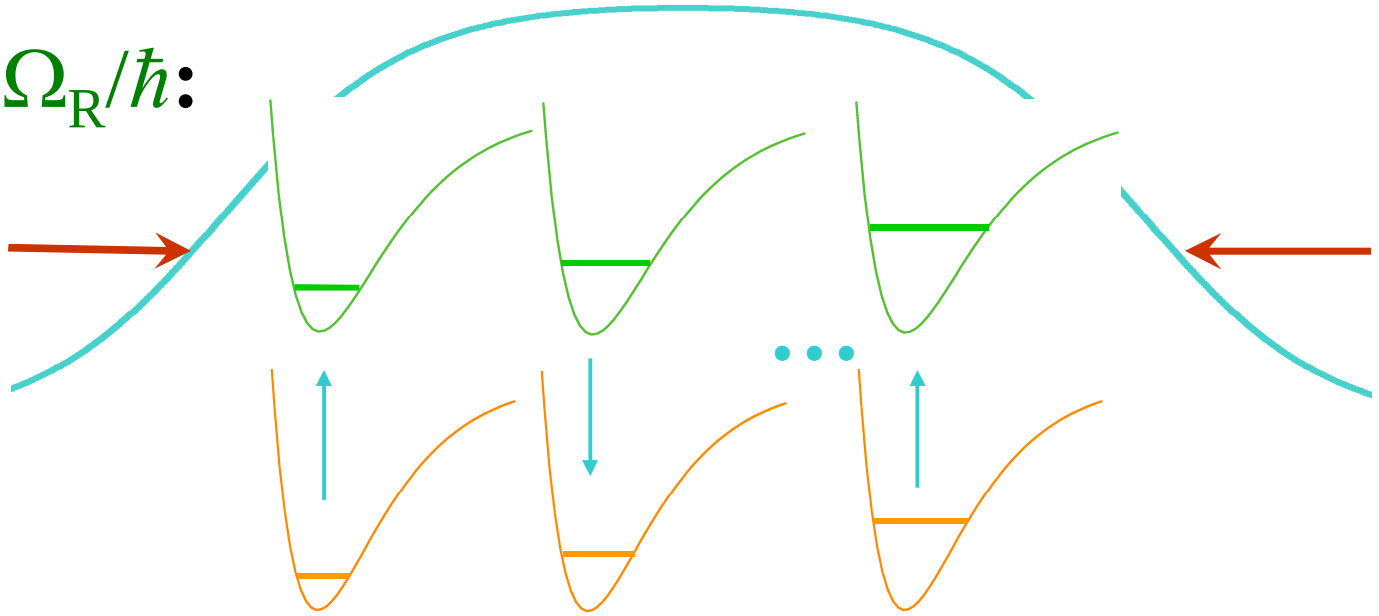


etc...

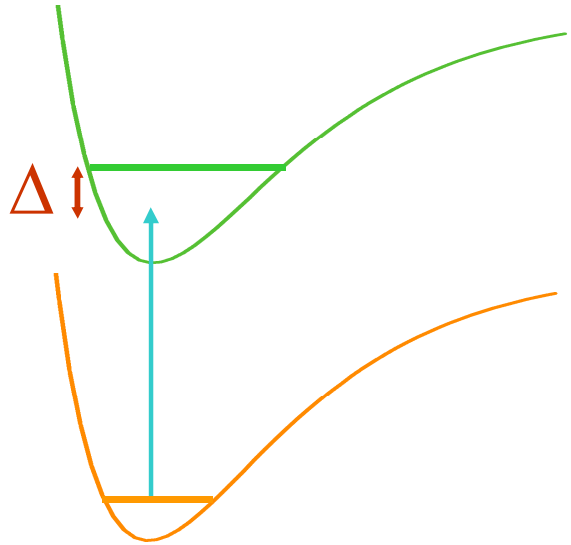
T.S., J.Chem.Phys. **103**, 7887 (1995)

What terminates the rotational excitation?

Either $J_{max} \sim \tau\ \Omega_R/\hbar$:

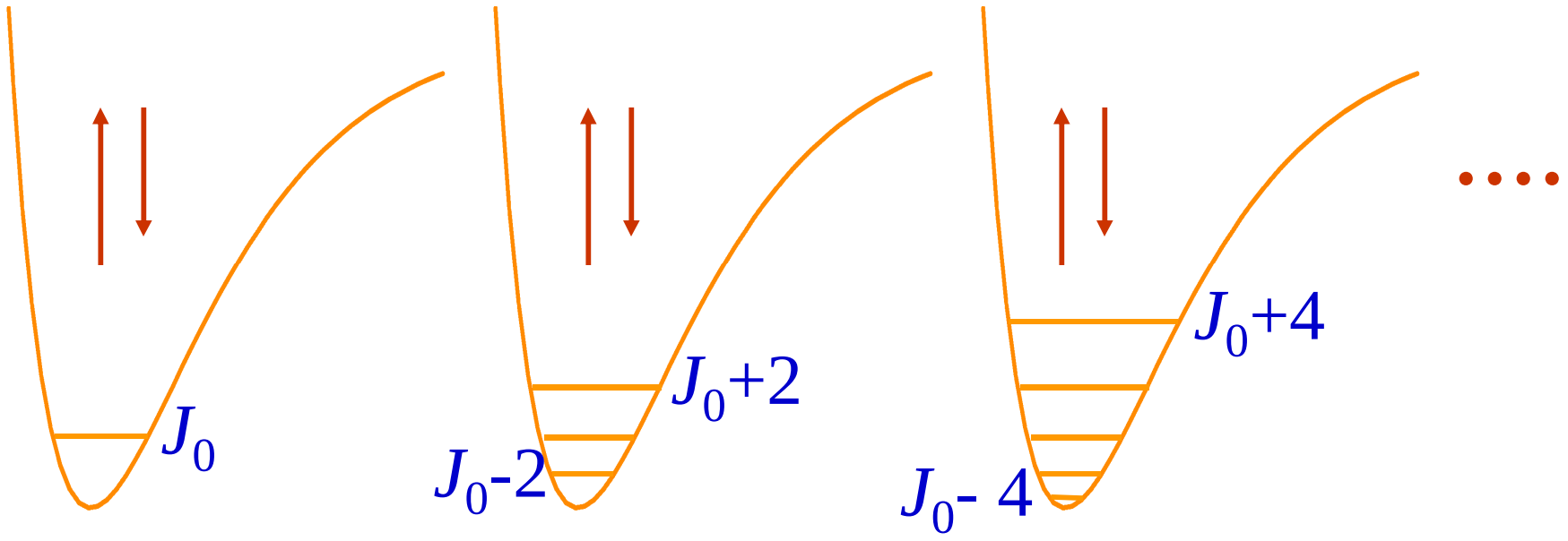


Or $\Omega_R \sim \Delta(J_{max})$:

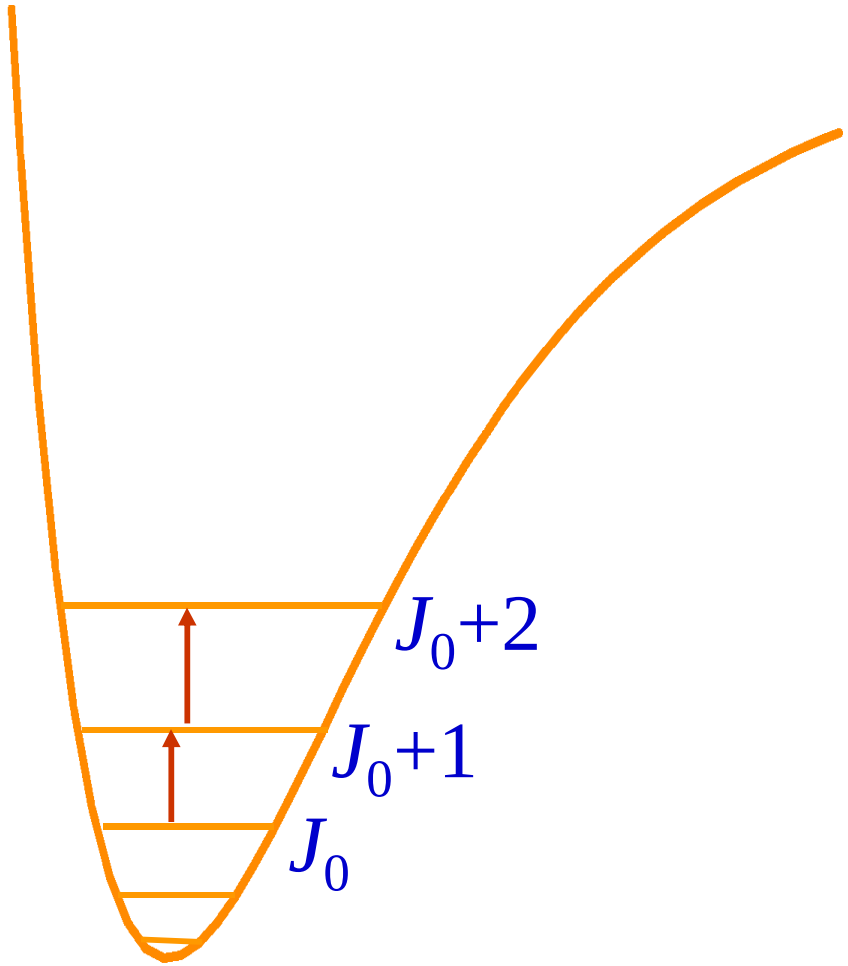


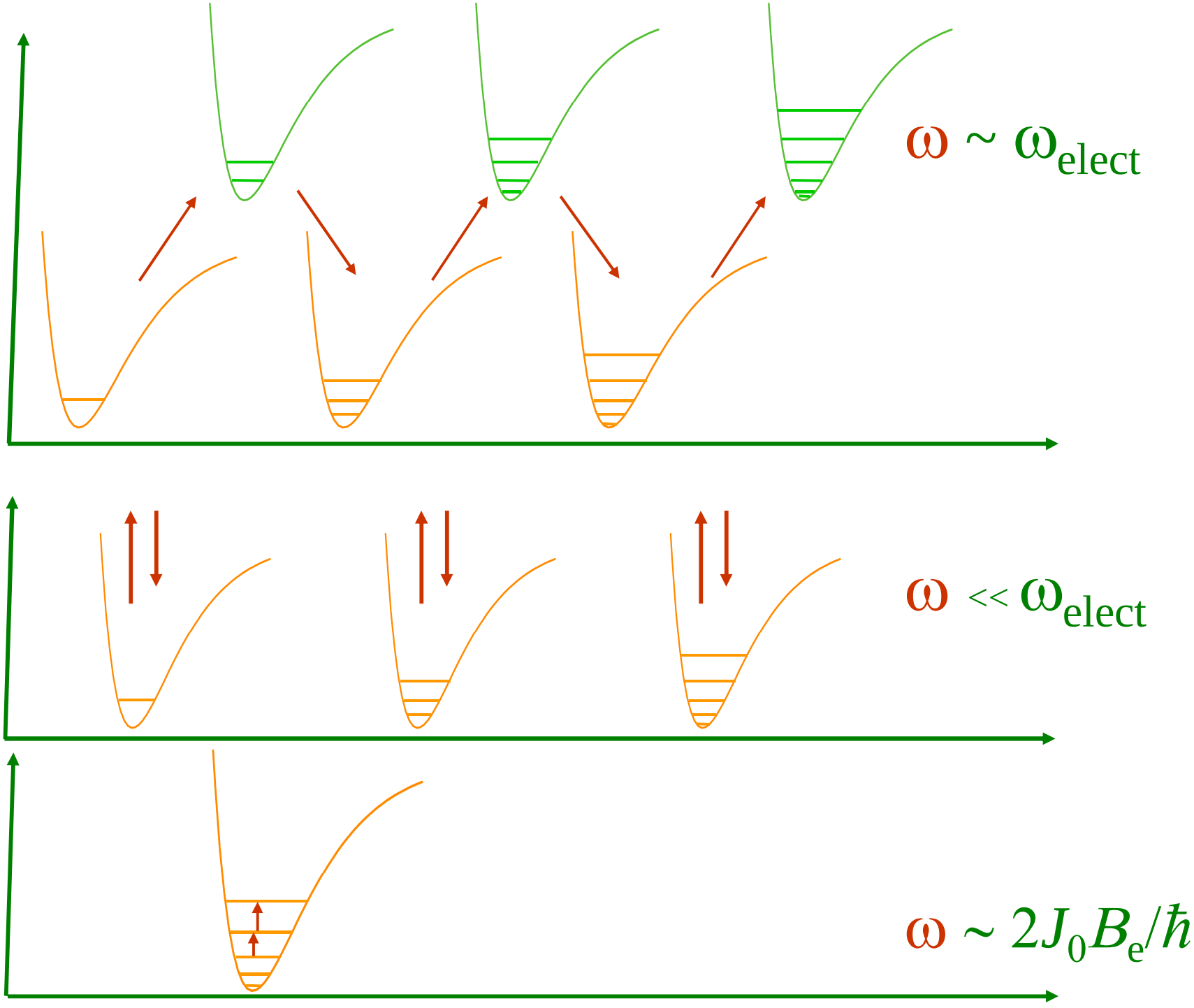
$$[\ \Delta(J) \sim B_e J(J+1)\ ]$$

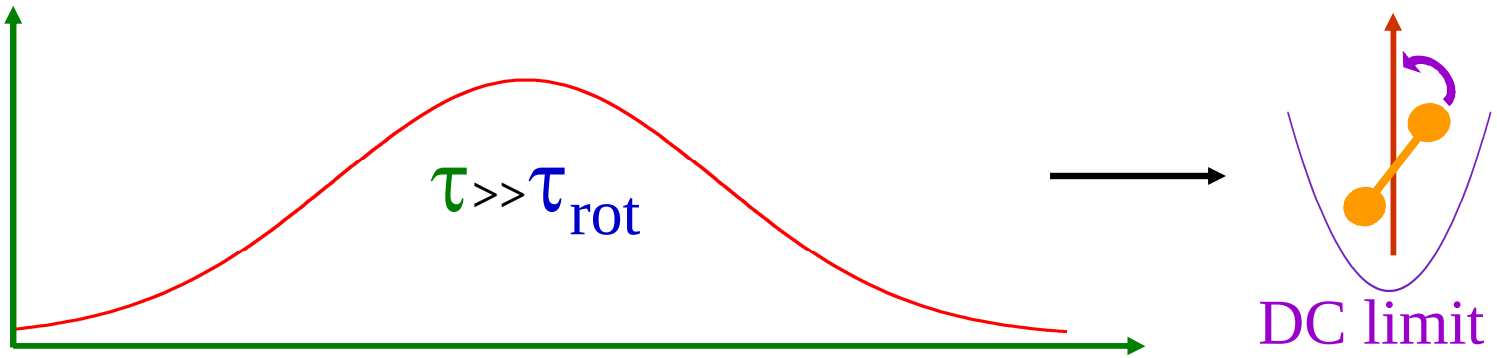
At IR frequencies ($\omega << \omega_{elect}$), rotational excitation takes place via two-photon ($|\Delta J| = 2$) cycles:



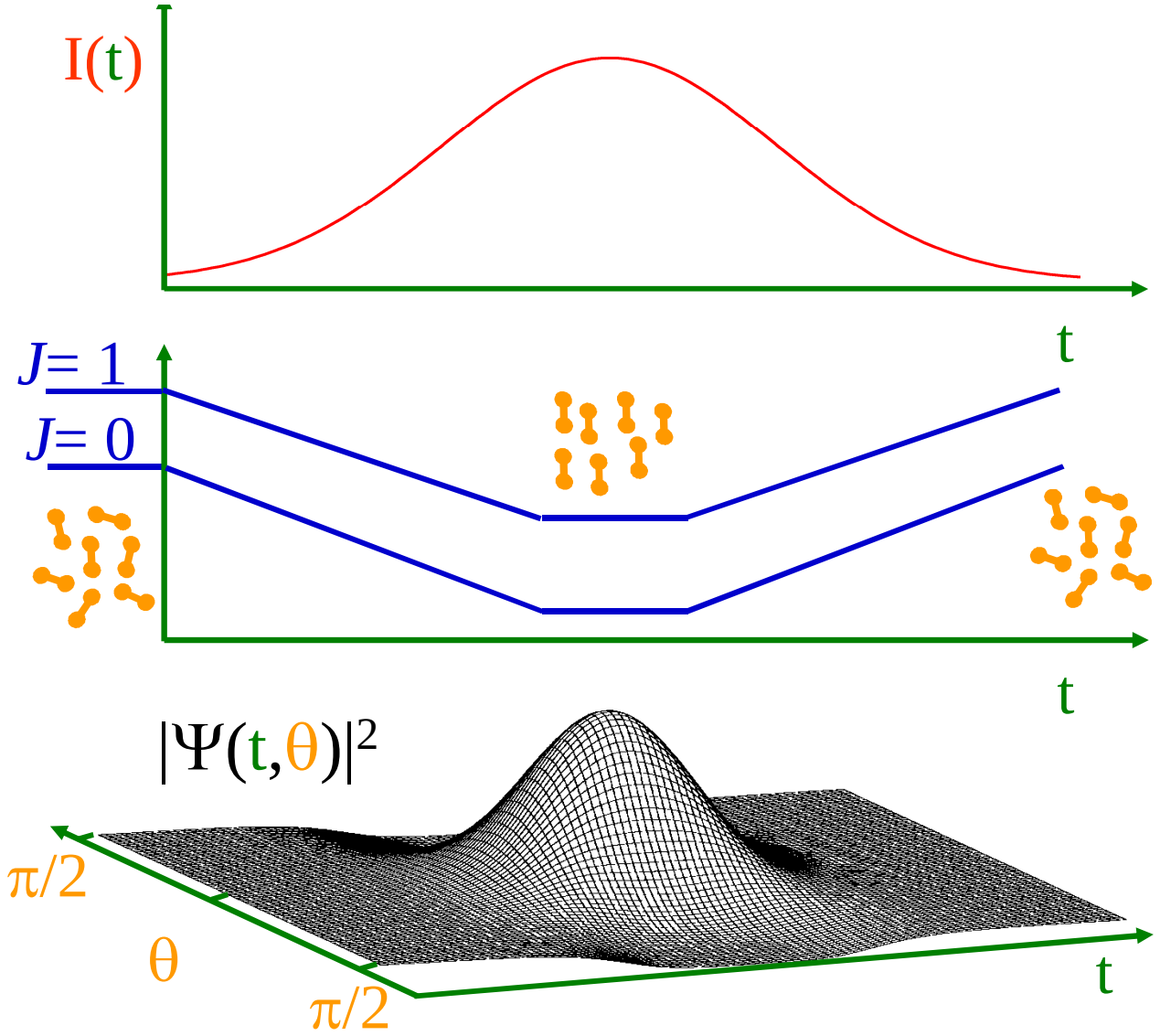
At very low frequencies ($\omega \sim 2J_0B_e/\hbar$), rotational excitation takes place via sequential pure rotational transitions:



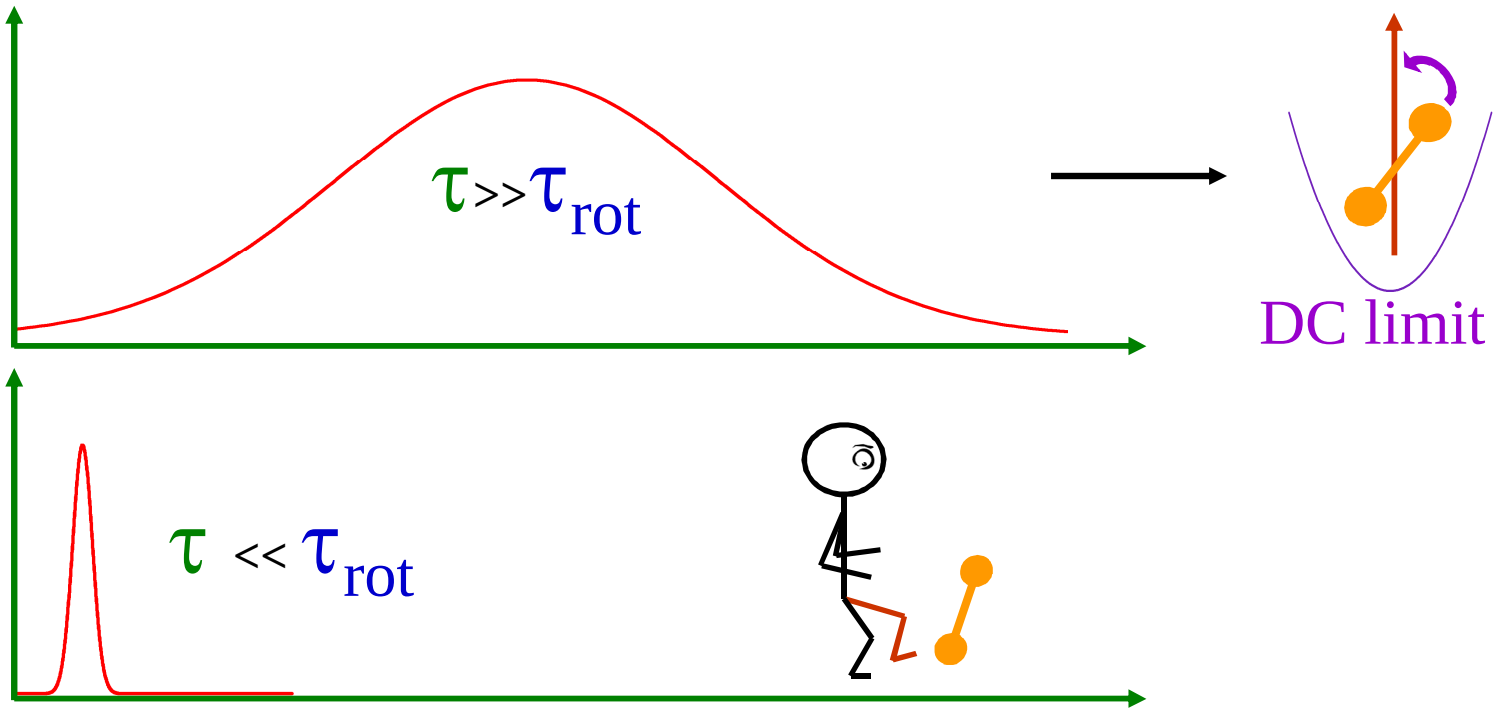

ω ~ ω_elect
ω << ω_elect
ω ~ 2J_0B_e/ħ


τ>>τrot
DC limit

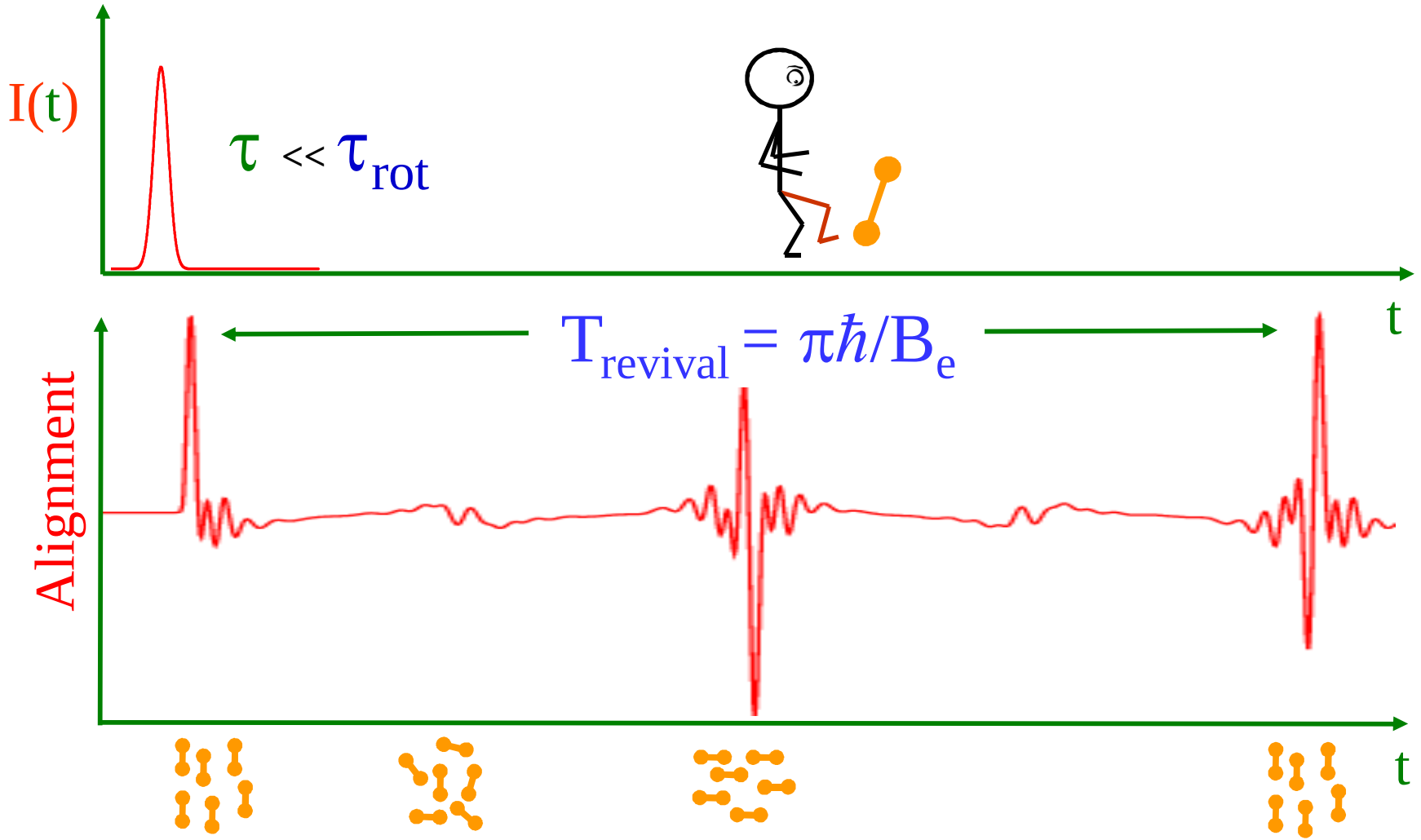
Static (adiabatic) alignment, $\tau \gg \tau_{rot}$



Friedrich & Herschbach, Phys.Rev.Lett. 74, 4623 (1995)
Kim & Felker, J.Chem.Phys. 104, 1147 (1996)
Larsen *et al*, J.Chem.Phys. 109, 8857 (1998)


τ>>τrot
DC limit
τ << τrot

Nonadiabatic alignment: Alignment takes place after the pulse peak, & subsequently exhibits a coherent revival pattern



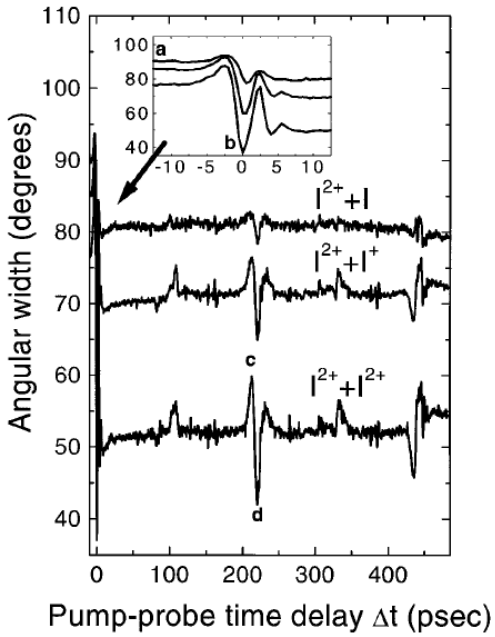
T.S., Phys.Rev.Lett. 83, 4971 (1999)

The first experimental realization

VOLUME 87, NUMBER 15 PHYSICAL REVIEW LETTERS 8 OCTOBER 2001

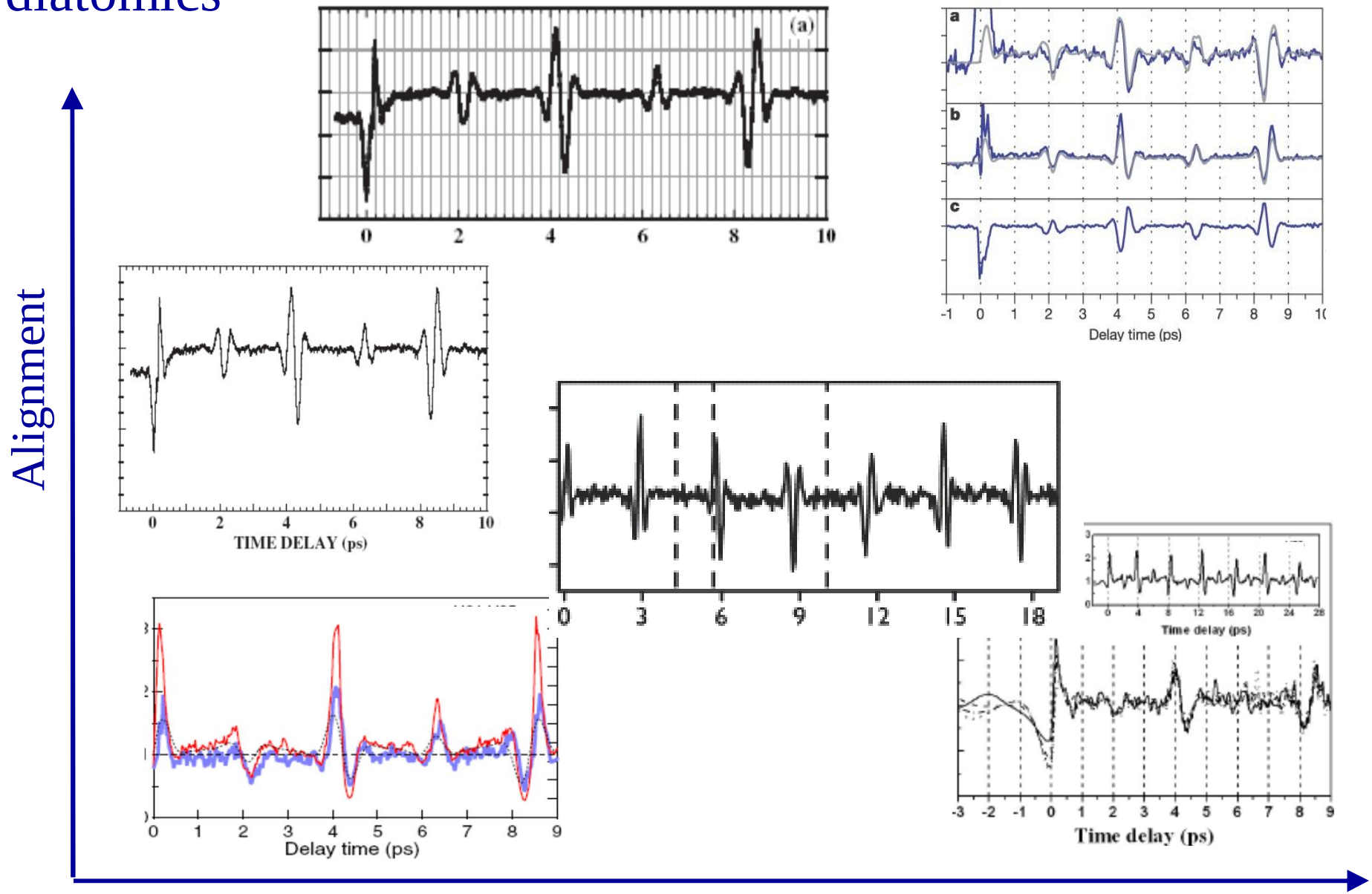
Experimental Observation of Revival Structures in Picosecond Laser-Induced Alignment of I_2

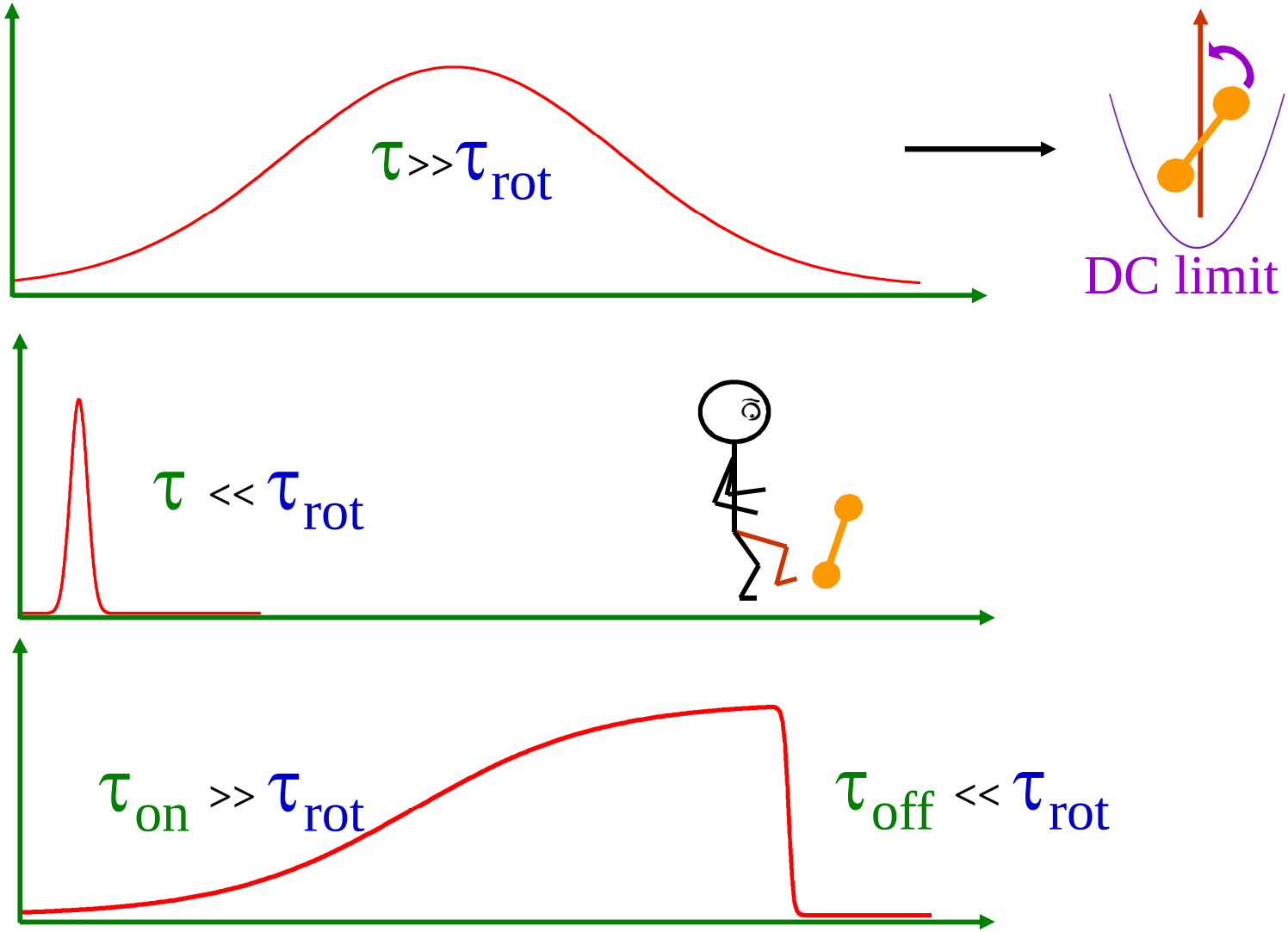
F. Rosca-Pruna and M. J. J. Vrakking*
FOM Institute for Atomic and Molecular Physics (AMOLF), Kruislaan 407, 1098 SJ Amsterdam, The Netherlands
(Received 1 May 2001; published 20 September 2001)



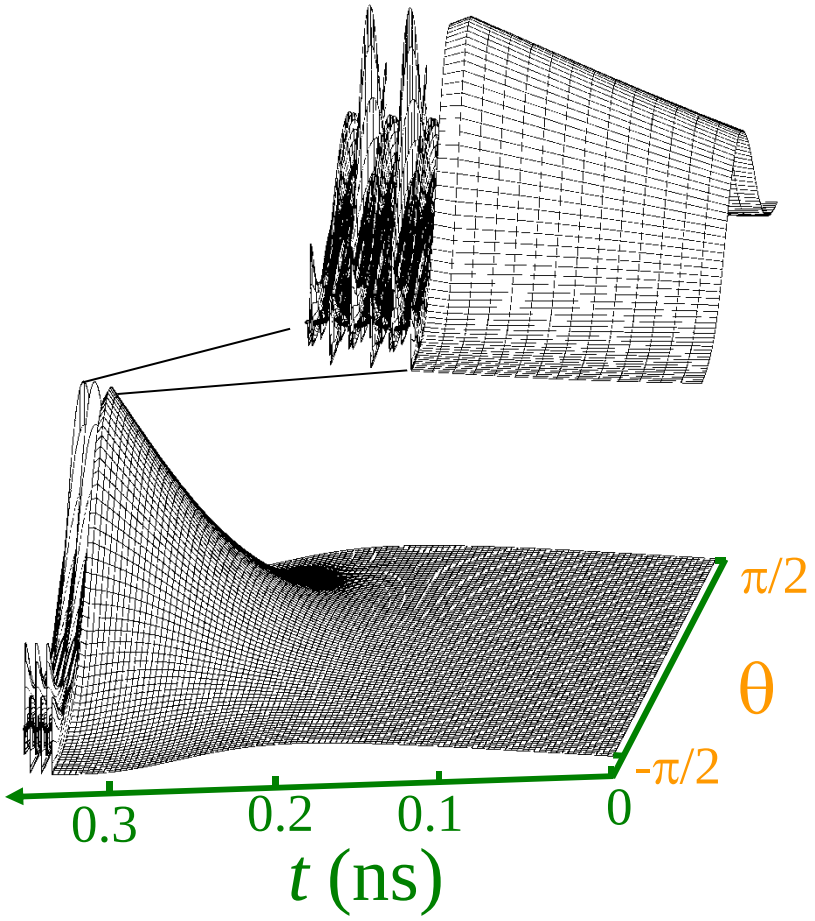
The molecules align during the pulse turn-off and subsequently exhibit a revival pattern - as predicted

Recent experiments on nonadiabatic alignment in isolated diatomics



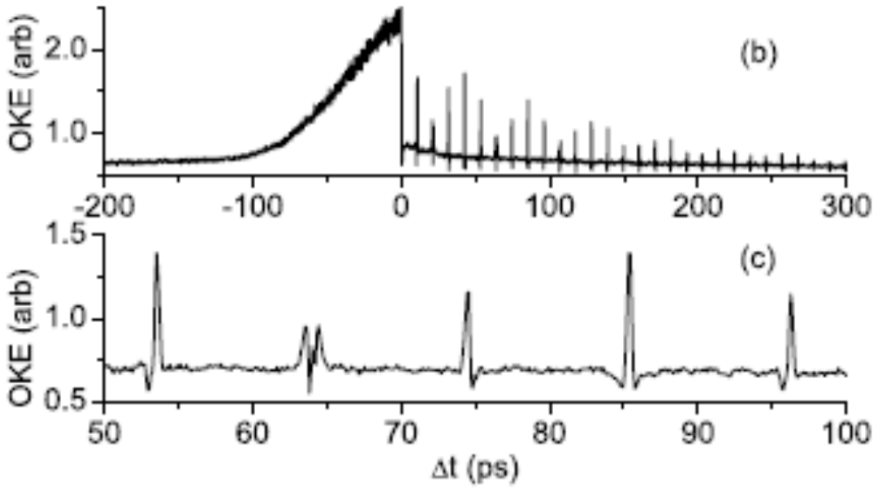

τ >> τrot
DC limit
τ << τrot
τon >> τrot
τoff << τrot

e.g., Cl_2, 3K, $6x10^{12}$ Wcm^{-2},
τ_{on}=700ps, τ_{off}=100fs

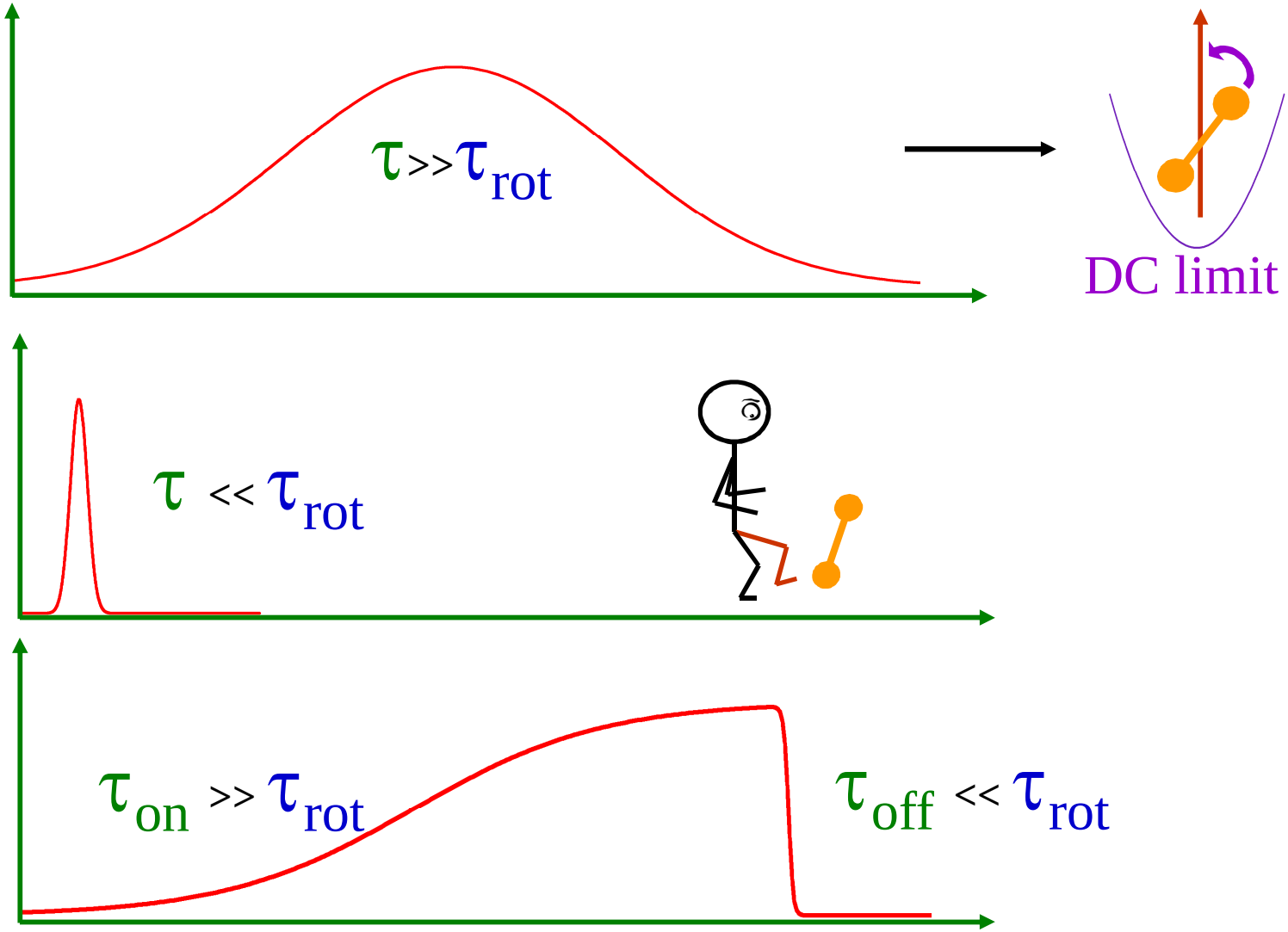


Z.C. Yan & T.S. J.Chem.Phys. 111, 4113 (1999)

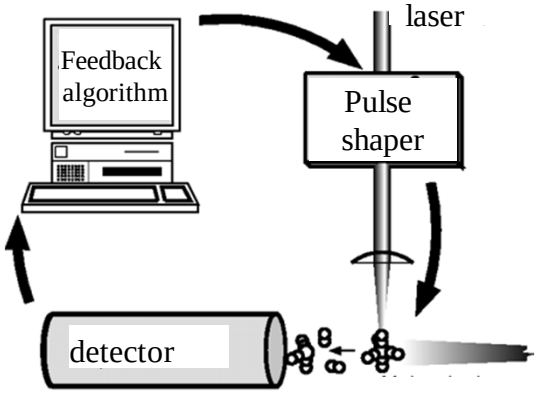
A first experimental demonstration:



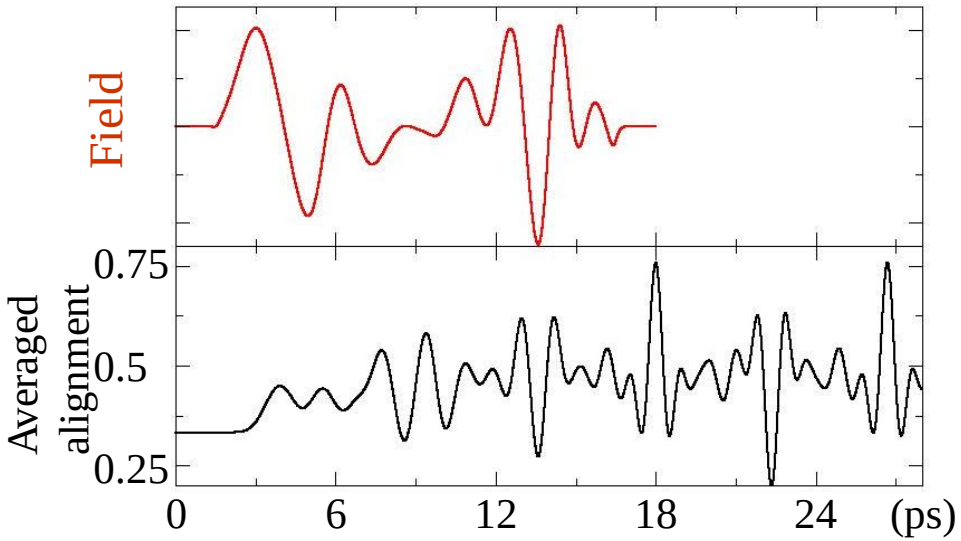
J.G. Underwood *et al*, Phys.Rev.Lett. 90, 223001 (2003)


τ >> τrot
DC limit
τ << τrot
τon >> τrot
τoff << τrot

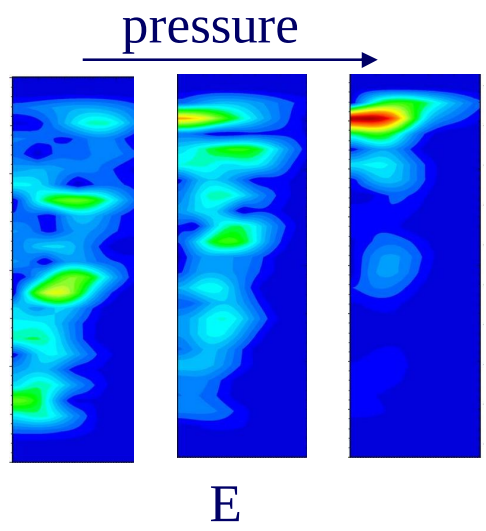
More generally, optimal control theories build in that phase relation among the light waves that will translate into a desired phase relation among the matter waves:



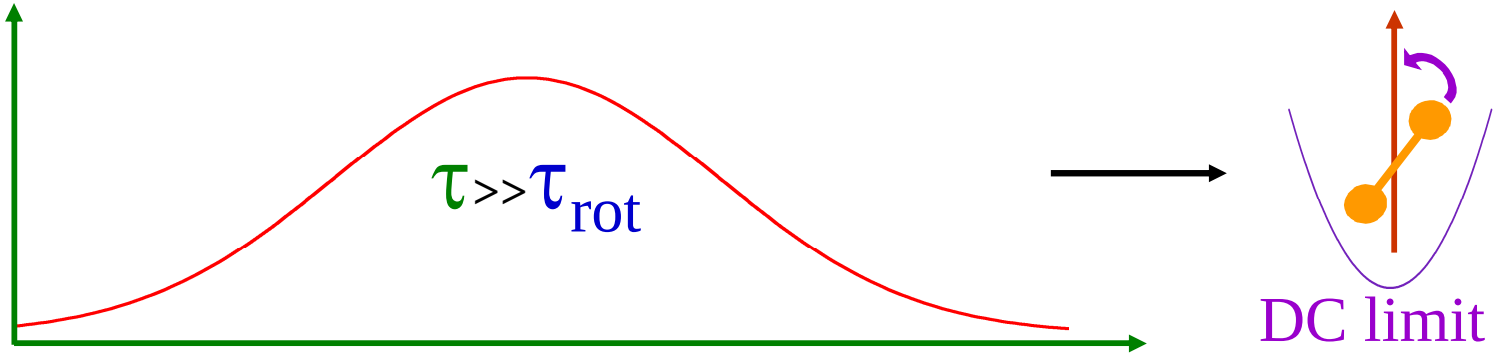
See talk by Hersch Rabitz

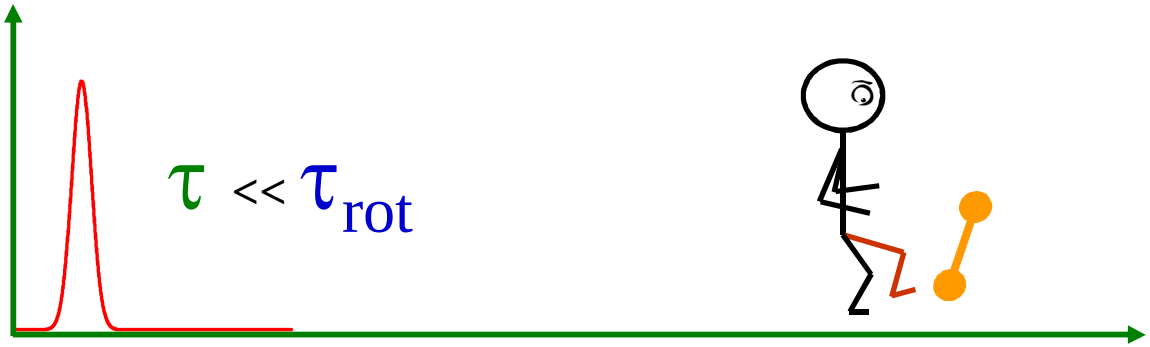


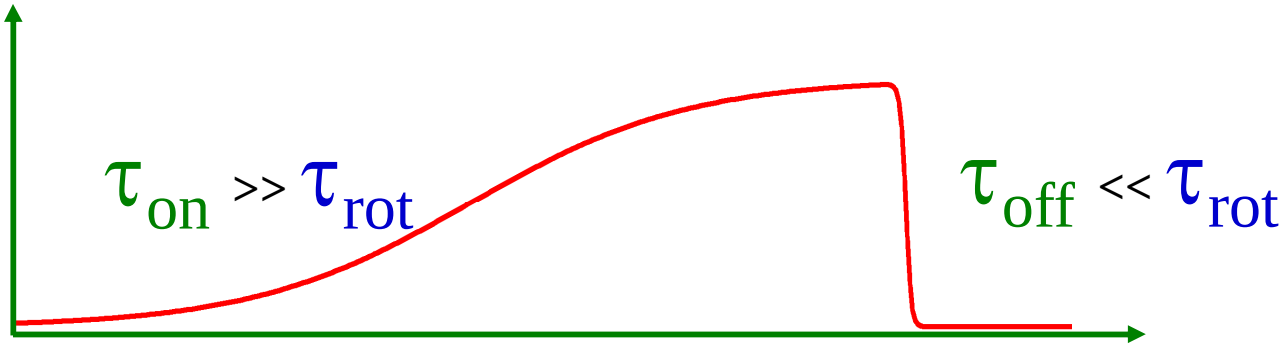
Short-time Fourier transforms are particularly telling:

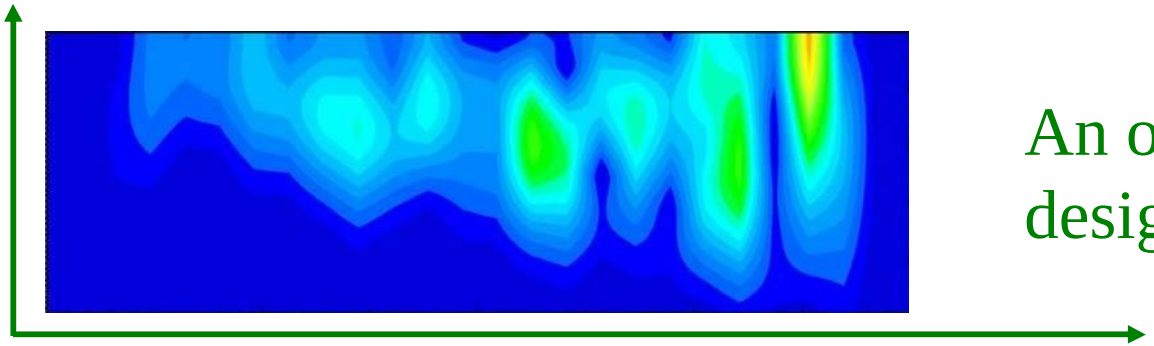


A. Pelzer, S. Ramakrishna & T.S., J.Chem.Phys., 126, 034503 (2007).









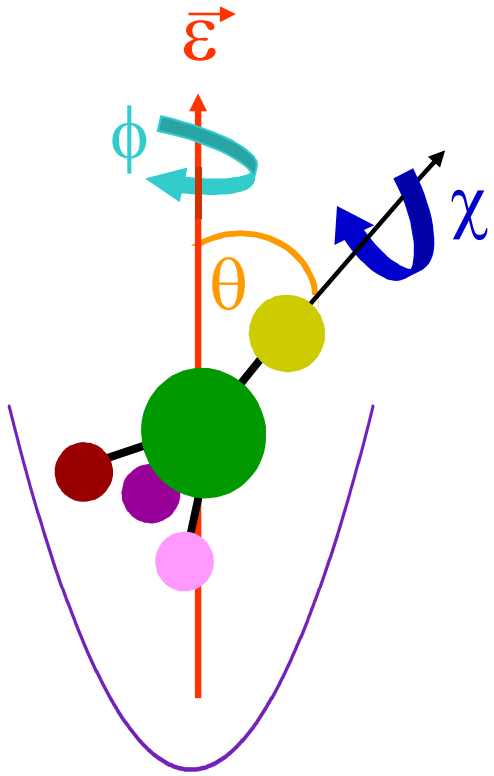
An optimally designed pulse

Alignment (as discussed so far) is a one-dimensional concept:

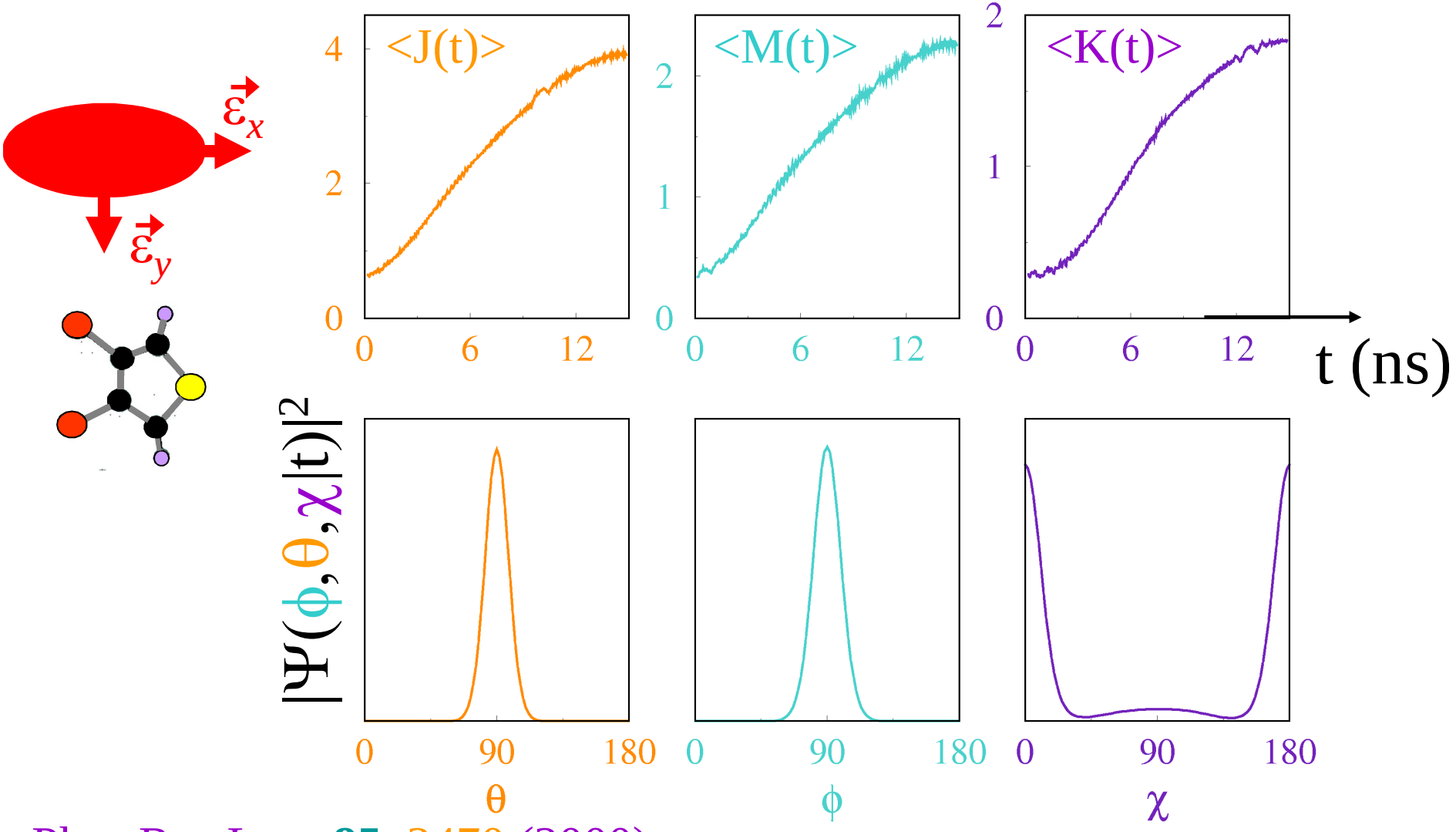
θ confined

χ free

ϕ free

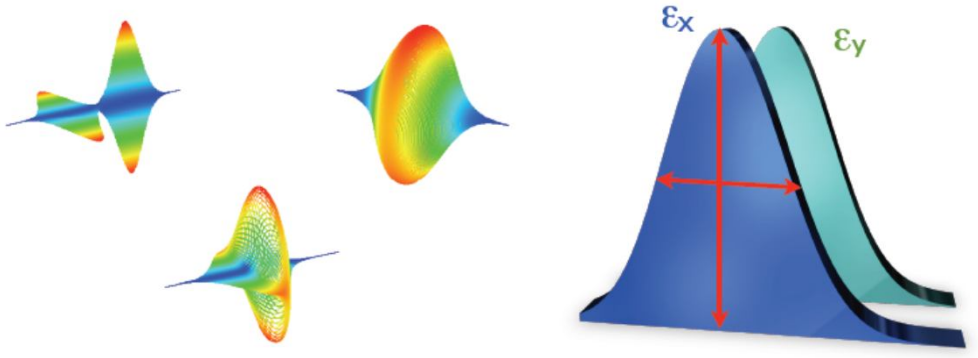


The elliptically polarized field populates a coherent wavepacket of *J*, *M* and *K* states, and establishes a probability density that is correspondingly well defined in the 3 Euler angles



Phys.Rev.Lett. **85**, 2470 (2000)

On the optimal approach to (field-free) 3D alignment



Phys.Rev.Lett. 94, 143002 (2005): Two pulses with the second fired at the revival of the first

Phys.Rev.Lett. 97, 173001 (2006): Two pulses with the second immediately following the first

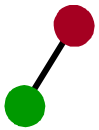
Phys.Rev.Lett. 99, 143602 (2007): A long and a short overlapping pulses

Phys.Rev.A 77, 043412 (2008): One elliptically polarized pulse

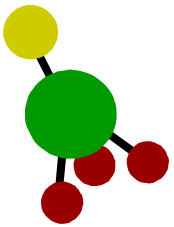
Optimal control theory shows that the long+short route very generally wins (but a single elliptically polarized pulse is nearly equivalent):
M. Artamonov & T.S., Phys.Rev.A 82, 023413 (2010)

Spectrum

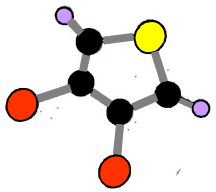
$E_J = B_e J(J+1)$



$E_{JK} = C_e J(J+1) + (A_e - C_e)K^2$



$2E_{J\tau} = (A_e + C_e)J(J+1) + (A_e - C_e)E_{J\tau}(\kappa)$

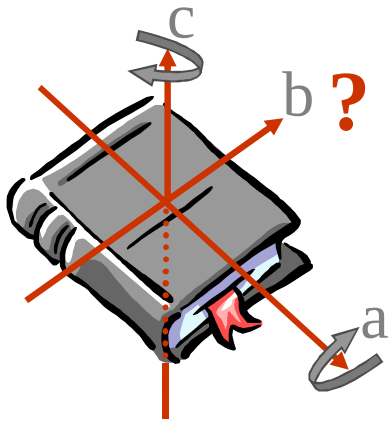


Classical motion

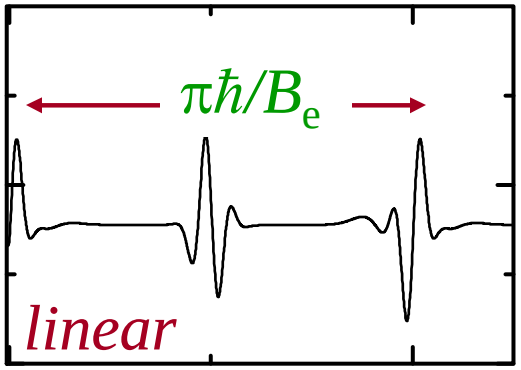
$\dot{\theta} = 0, \quad \dot{\phi} = J/I$

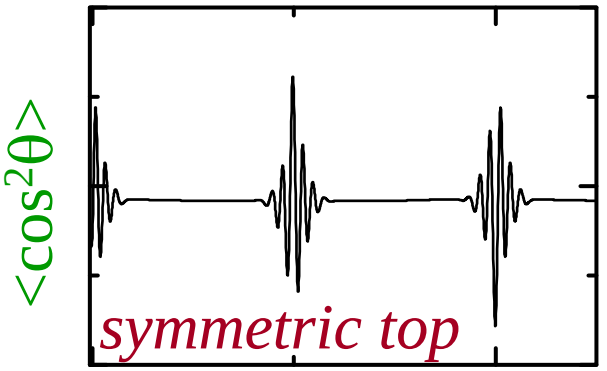
$\dot{\theta} = 0, \quad \dot{\phi} = J/I_a$

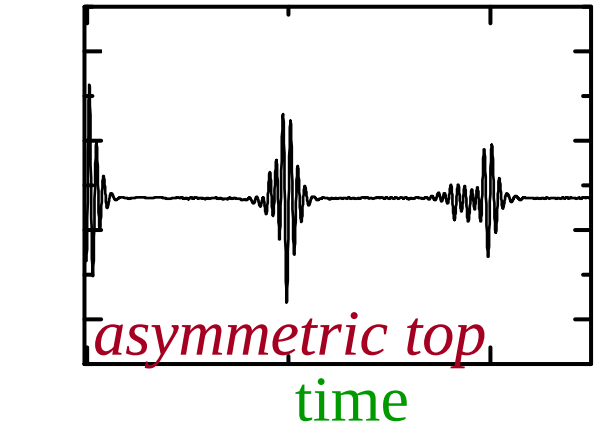
$\dot{\chi} = J\cos\theta\left(\frac{1}{I_c} - \frac{1}{I_a}\right)$



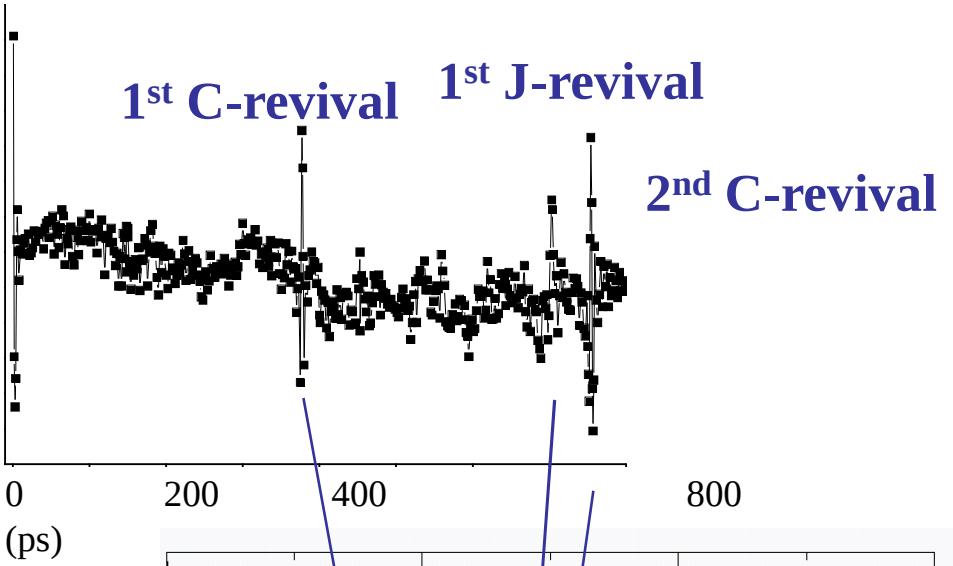
Quantum revivals



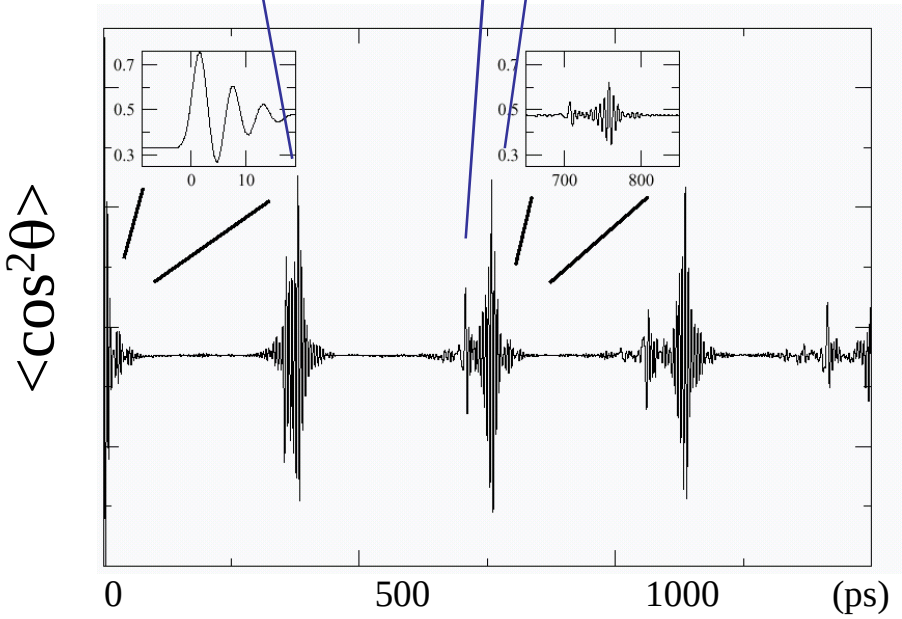




Experiment:
(H. Stapelfeldt
& coworkers)

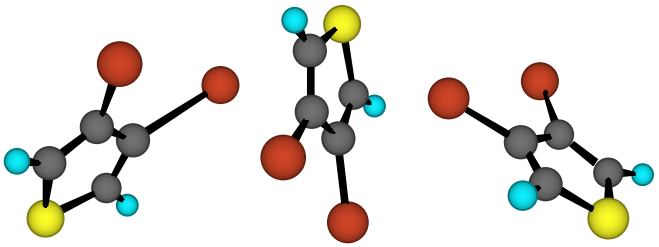


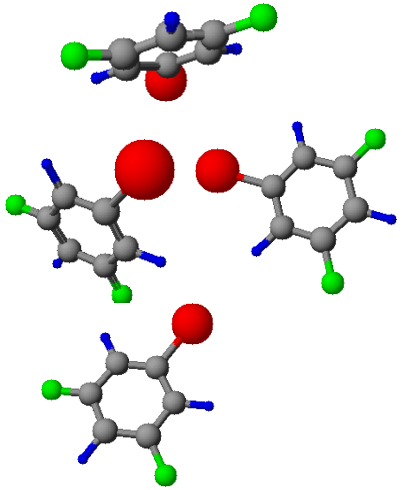
Calculation:

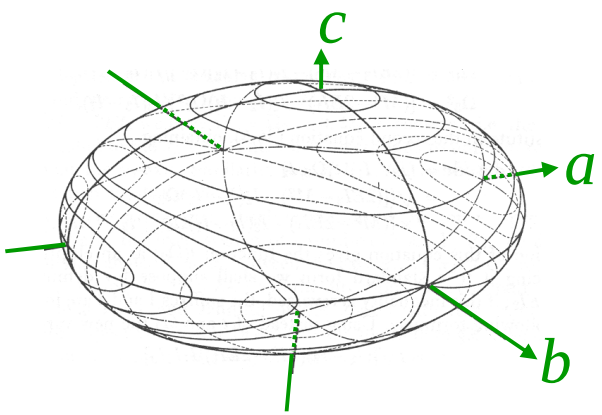


E. Peronne, M.D. Poulsen,
H. Stapelfeldt & T.S., Phys. Rev. Lett. **91**, 043003 (2003).

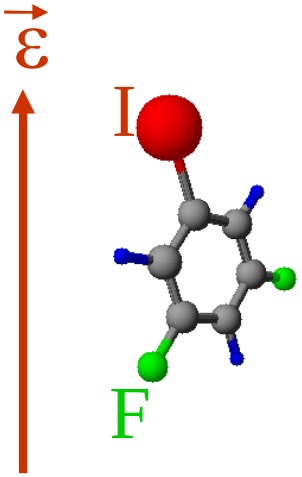
Toward taming the rotations of asymmetric tops with strong fields

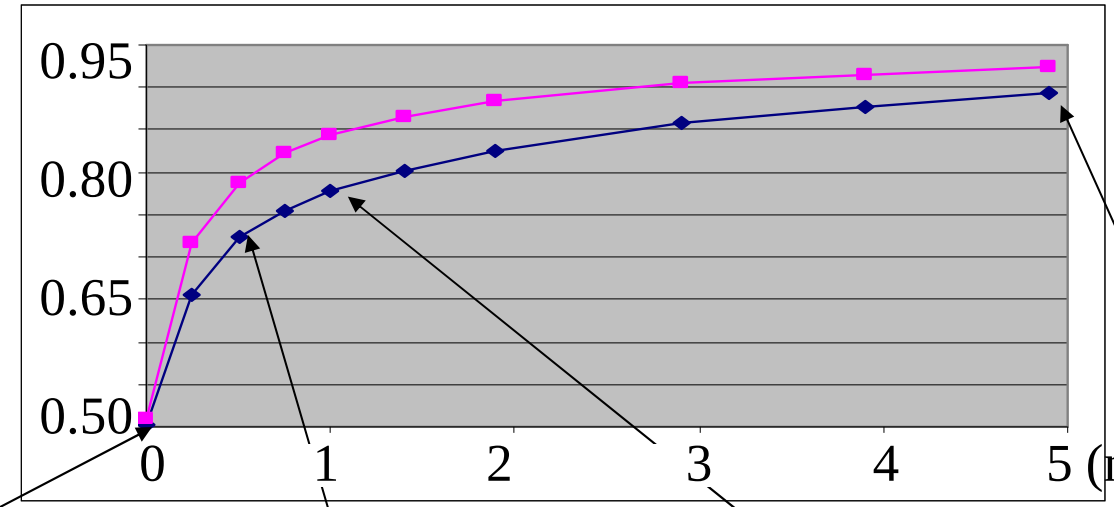


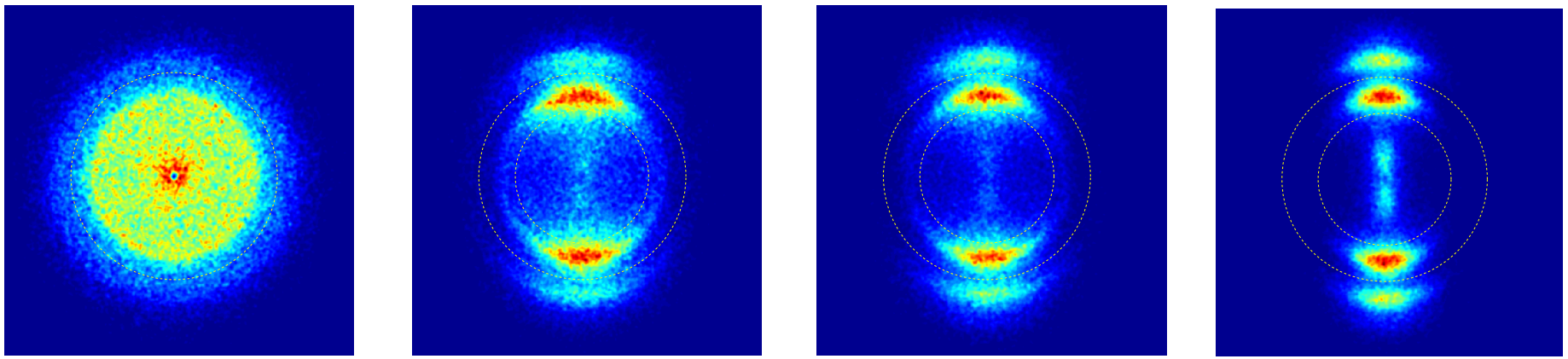




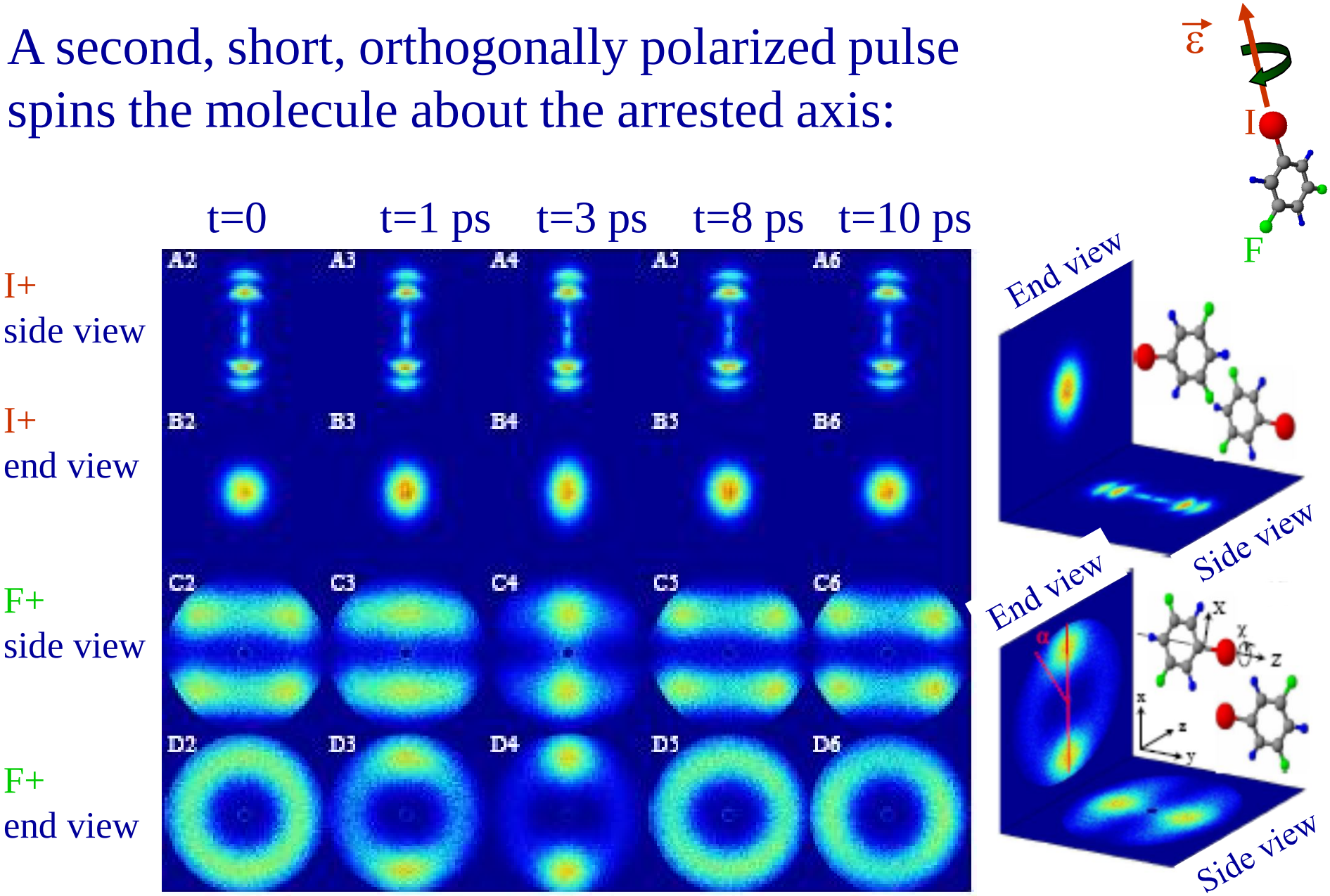
A first, long pulse tightly aligns the most polarizable axis to the polarization vector:



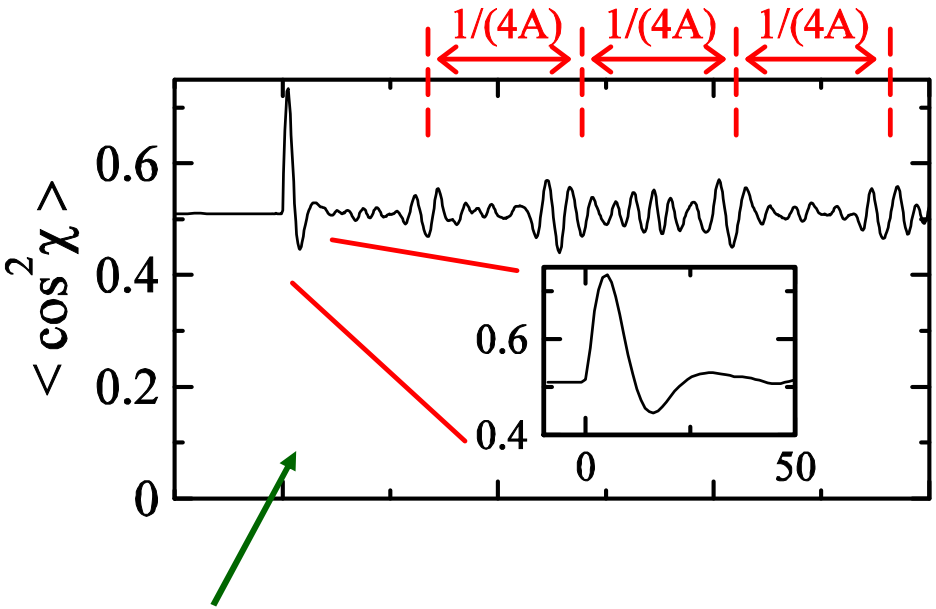


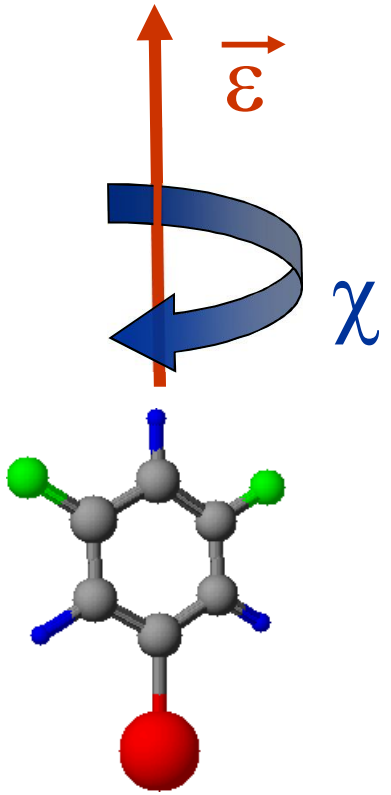


A second, short, orthogonally polarized pulse spins the molecule about the arrested axis:



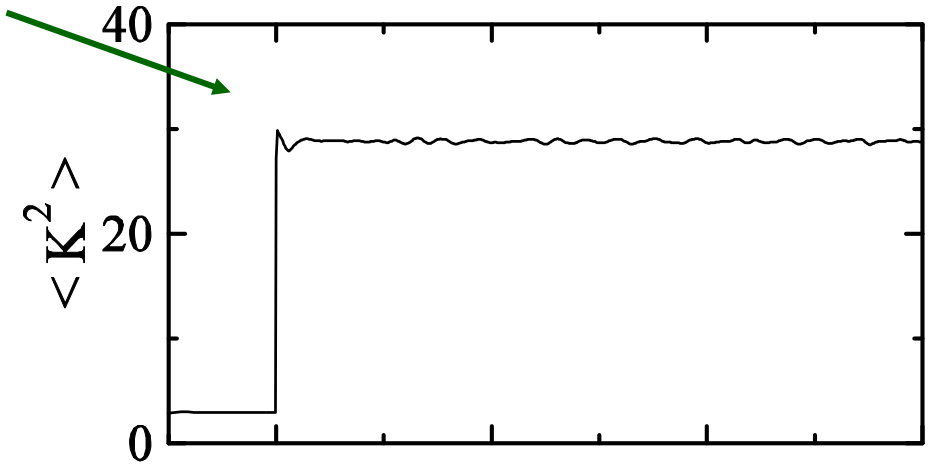
S. S. Viftrup, V. Kumarappan,
H. Stapelfeldt, E. Hamilton & T.S. Phys. Rev. Lett., 99, 143602 (2007)





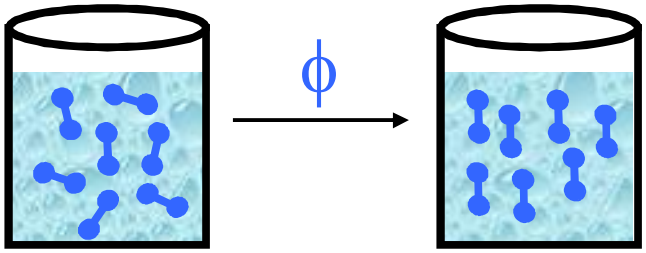
Computed revivals of the
azimuthal angle alignment &
corresponding helicity excitation

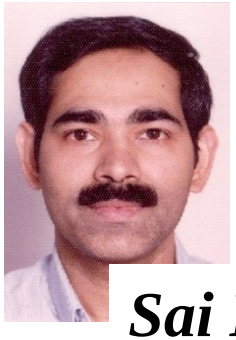
Max Artamonov



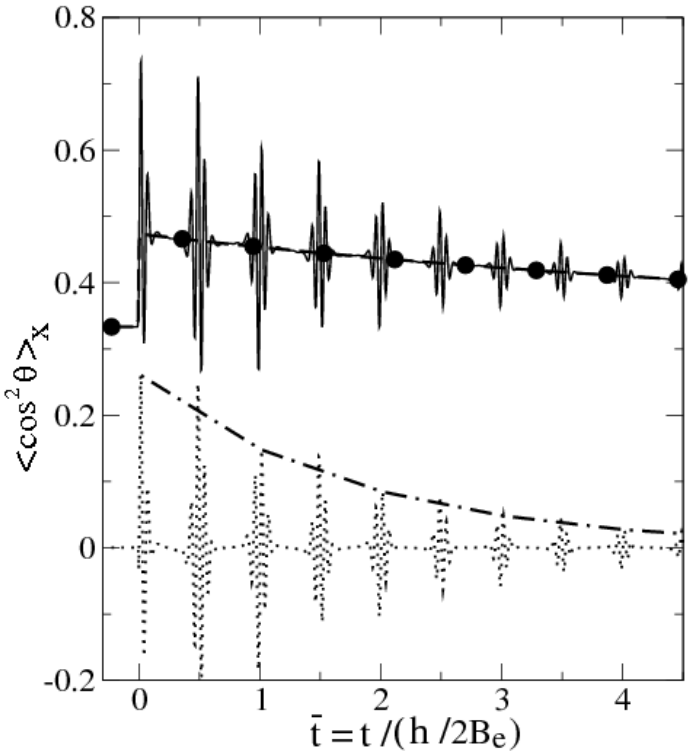
S. S. Viftrup, V. Kumarappan,
H. Stapelfeldt, E. Hamilton & T.S. Phys. Rev. Lett., 99, 143602 (2007)

Rotational coherences as a probe of the dissipative properties of media:



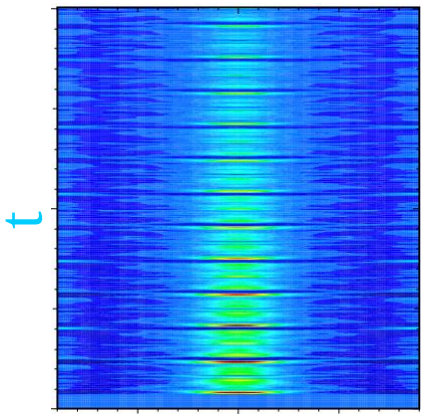


Sai Ramakrishna

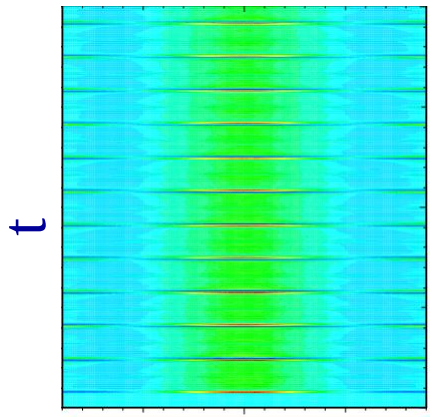


⇒ Elastic and inelastic collision rates

CO/Ar, 10 K



CO/Ar, 100 K



S. Ramakrishna & T.S.
Phys.Rev.Lett. 95, 113001 (2005)

A first experimental realization

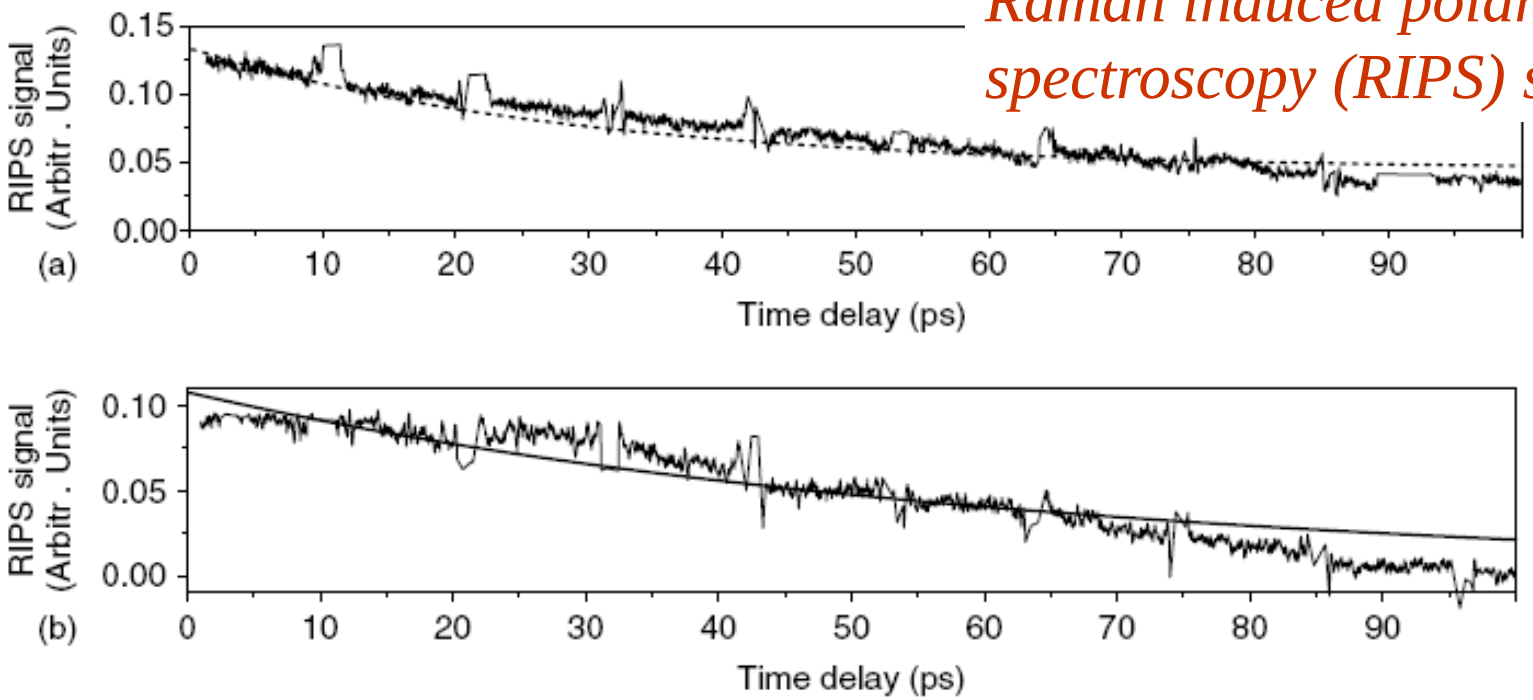
JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2008; **39**: 694–699
Published online 4 April 2008 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/jrs.1976

JRS

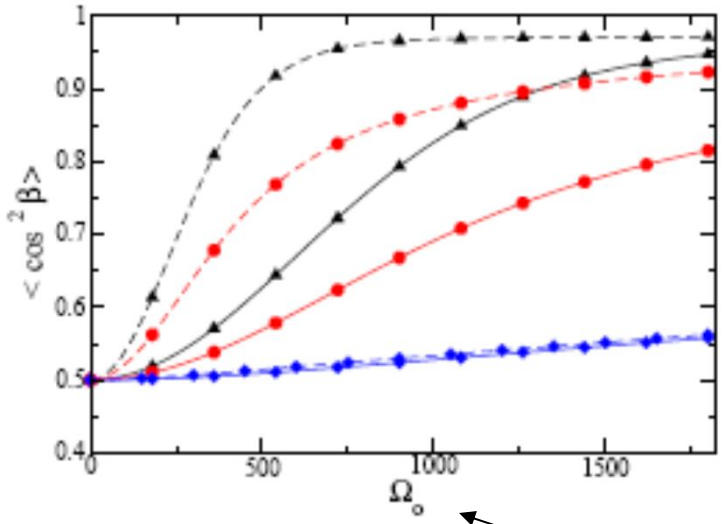
Field-free molecular alignment of CO_2 mixtures in presence of collisional relaxation

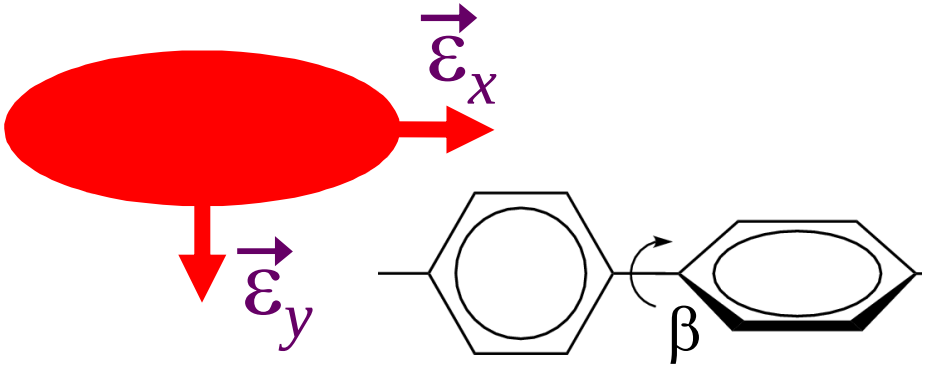
T. Vieillard, F. Chaussard,* D. Sugny, B. Lavorel and O. Faucher

Raman induced polarization spectroscopy (RIPS) signal



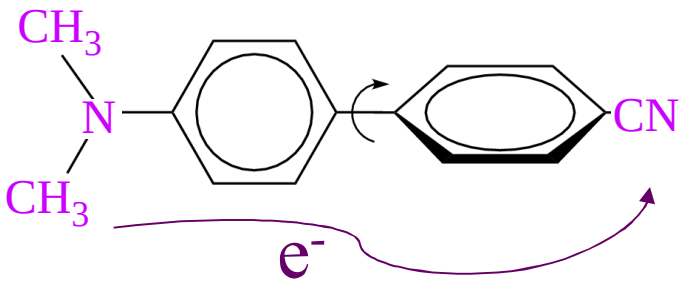
Torsional alignment

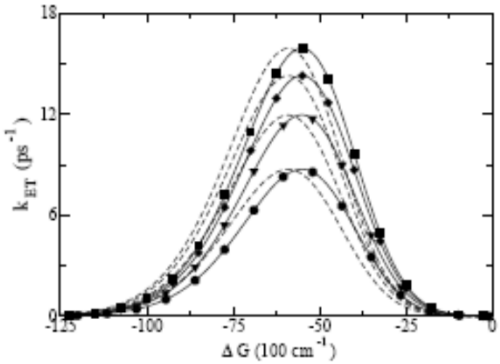




$\Omega_0 = 0.16(|\Delta\alpha|/B_e)I_0$

E.g., control of charge transfer events :





S. Ramakrishna & T.S., Phys. Rev. Lett. 99, 103001 (2007)

THE JOURNAL OF CHEMICAL PHYSICS **130**, 234310 (2009)

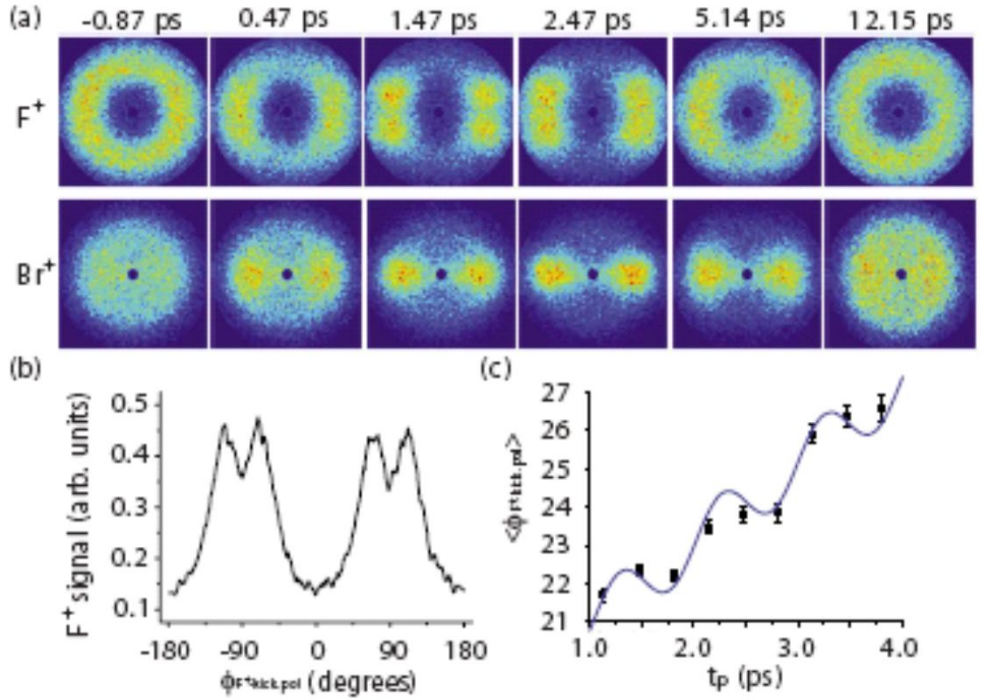
A combined experimental and theoretical study on realizing and using laser controlled torsion of molecules

C. B. Madsen,[1] L. B. Madsen,[1,a)] S. S. Viftrup,[2] M. P. Johansson,[2] T. B. Poulsen,[2] L. Holmegaard,[2] V. Kumarappan,[2] K. A. Jørgensen,[2] and H. Stapelfeldt[3,a)]

[1]*Department of Physics and Astronomy, Lundbeck Foundation Theoretical Center for Quantum System Research, Aarhus University, 8000 Aarhus C, Denmark*

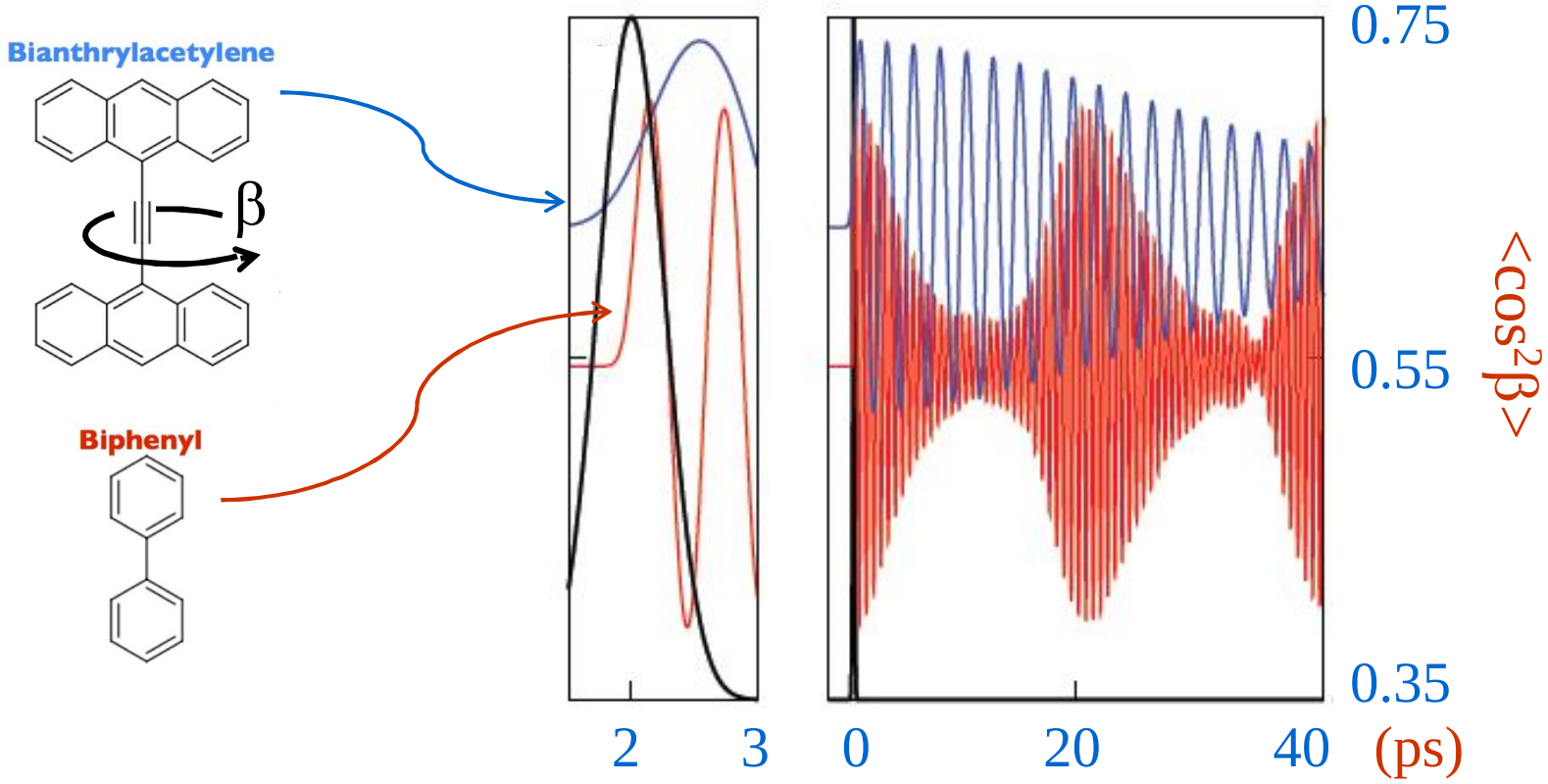
[2]*Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark*

[3]*Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark*

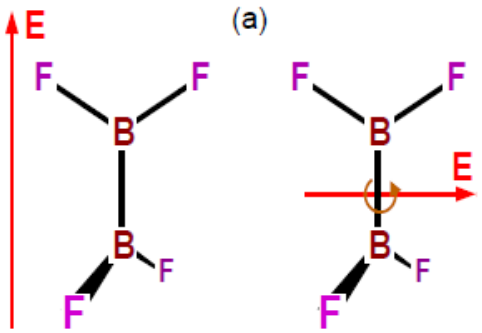


About the controllability of torsional coherences subject to dissipative media

Benjamin Ashwell

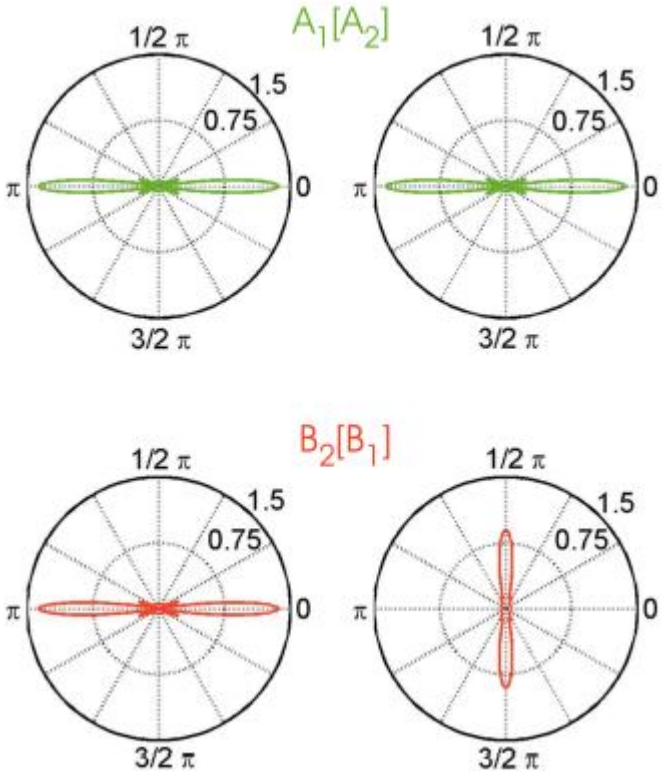


Nuclear Spin Selective Torsional Control



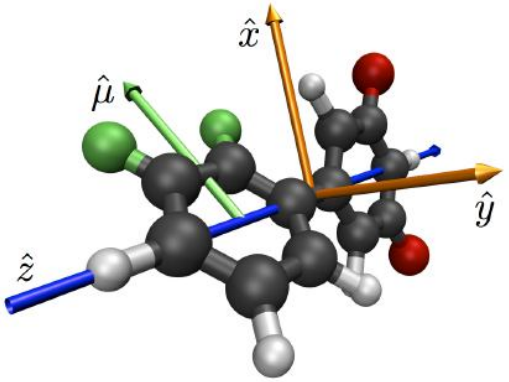
Monika Leibscher

Probability densities of the two BF_2 groups after the pulse: The two isomers are torsionally-aligned along perpendicular directions

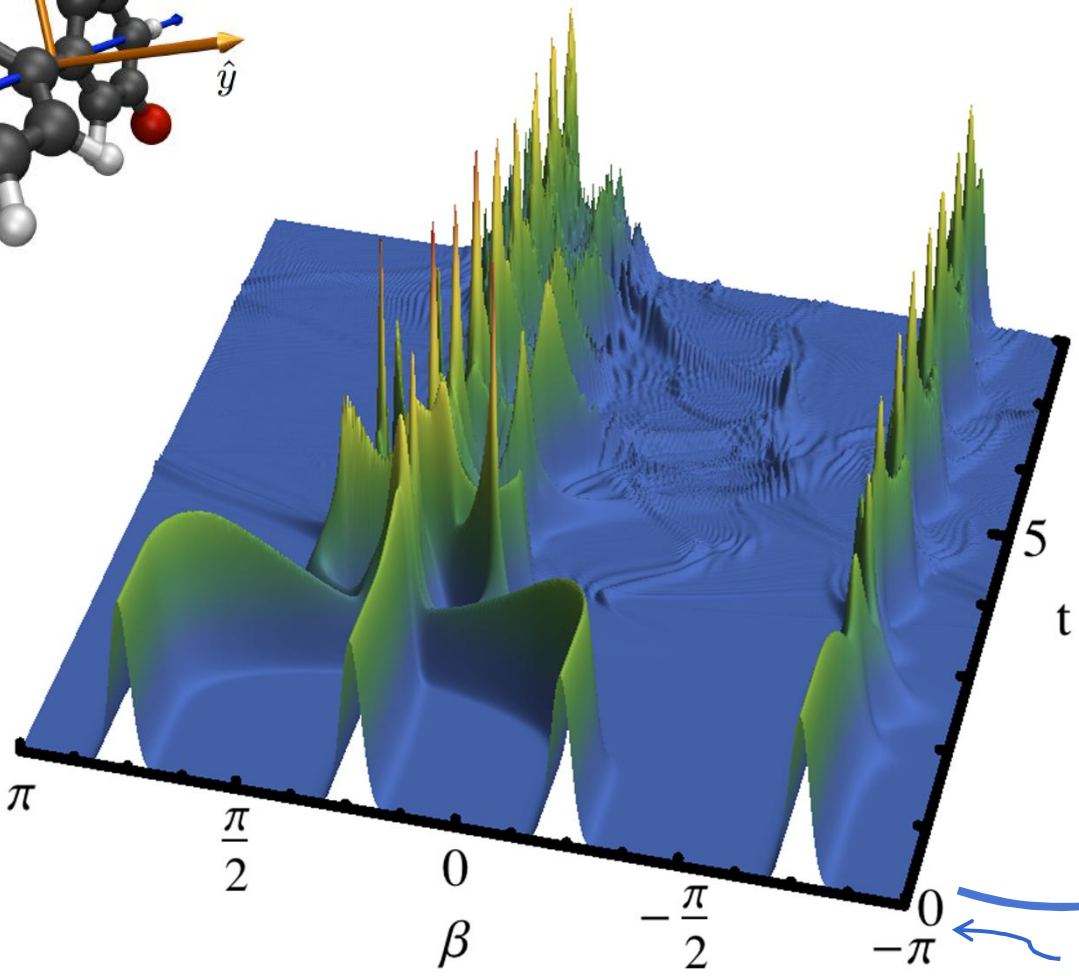


J. Chem. Phys. 136, 084309 (2012)

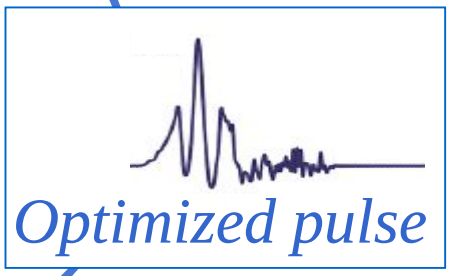
Torsional control of chirality



Shane Parker



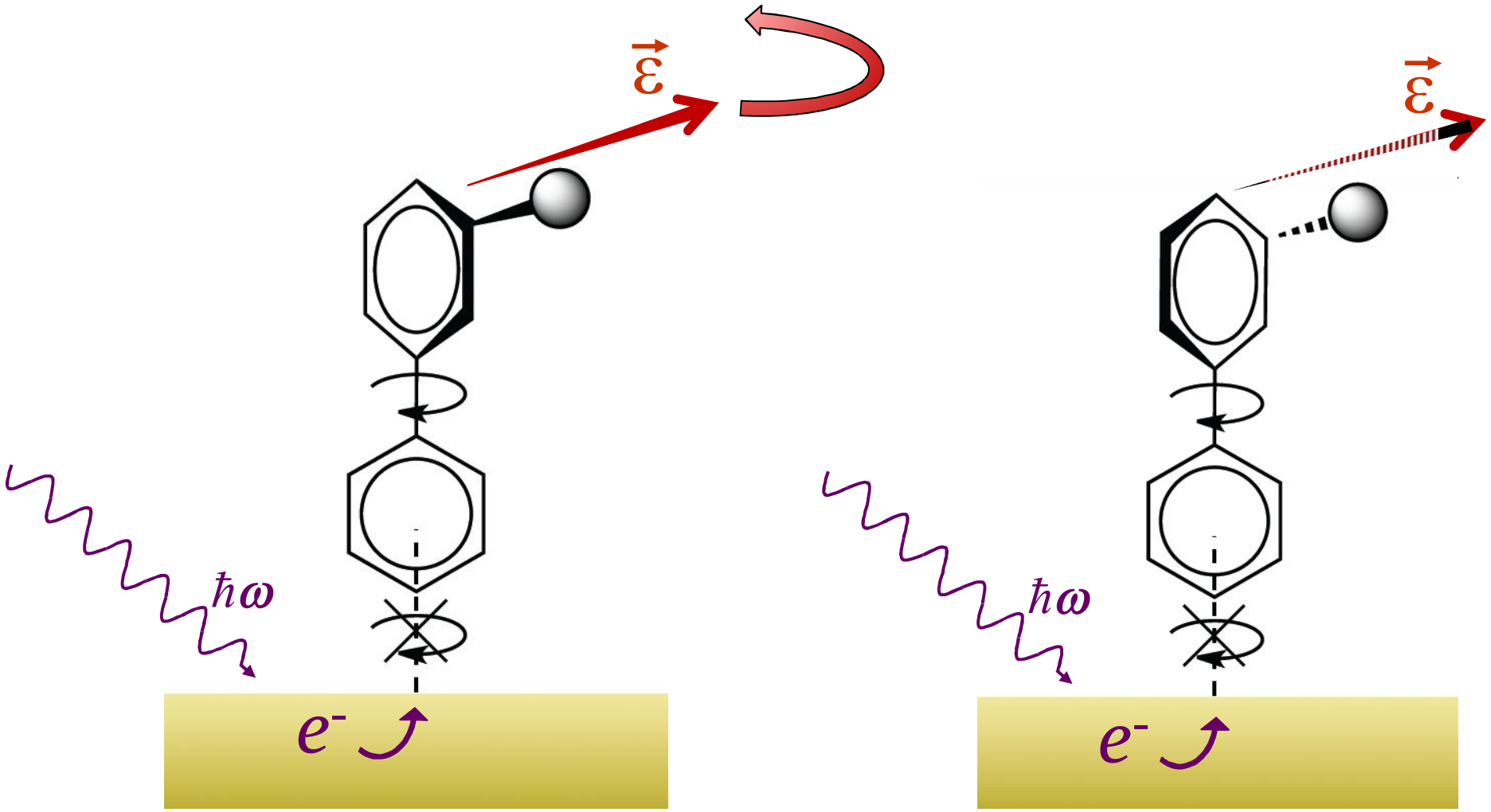
Pure enantiomer



Thermal racemic mixture

Special Issue of Mol. Phys., in press

Toward a Spin Switch

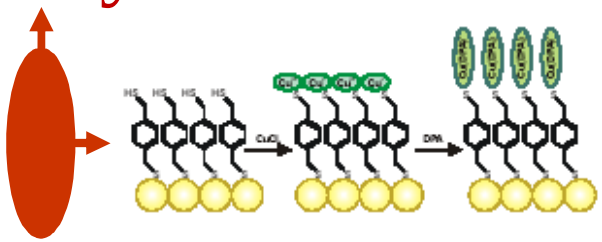


Other potential opportunities that could be envisioned (but are yet to be explored)

- Perhaps control of energy transfer
- Probably control of charge transport
- Hopefully control of chemical reactions

Toward laser-guided molecular assembly

A route to molecular constructs with long-range orientational order

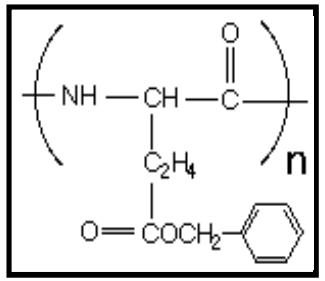


Alignment has a major role in applications of molecular assembly:

- Molecular electronics: alignment determines the electric & magnetic properties
- Crystalography: alignment circumvents “2D powder formation”
- Material research: preferred mechanical & optical properties
- Biology: structural determination of molecules that cannot be crystalized

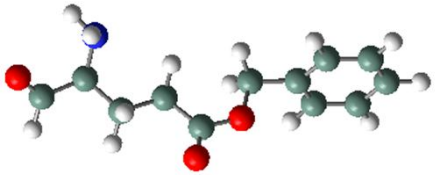
but in self-assembly alignment is very difficult to control

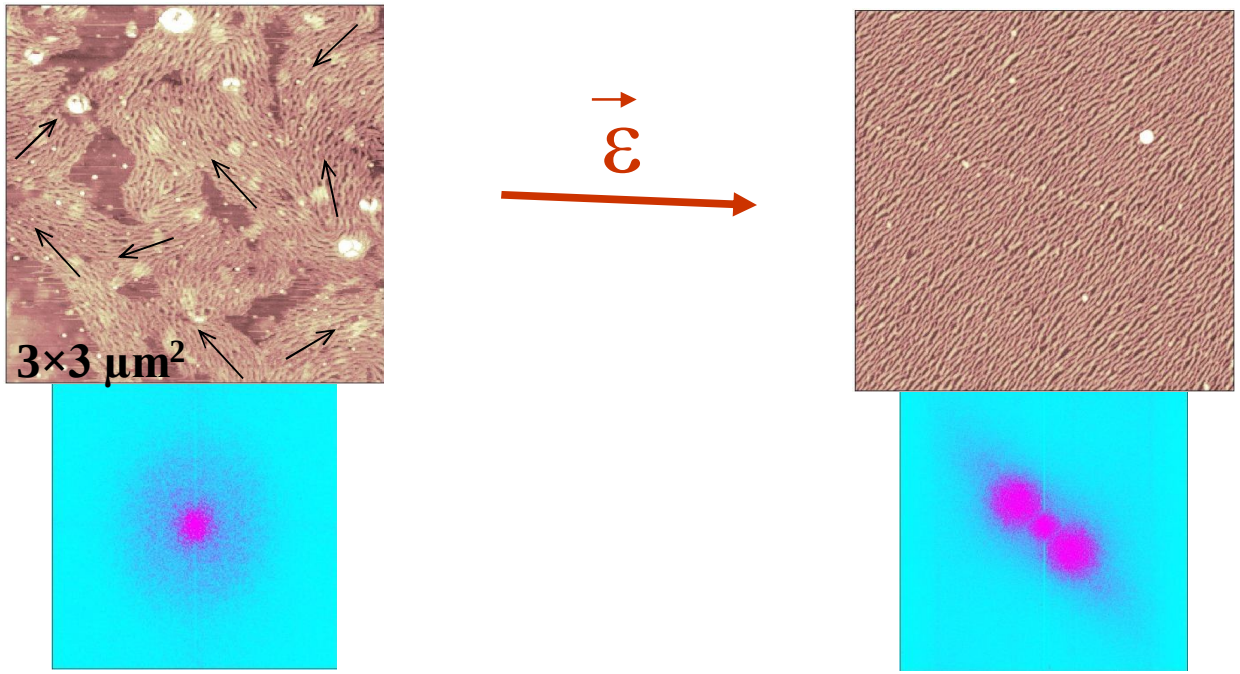
E.g., laser-guided molecular assembly of poly-γ-benzyl-L-glutamate on a water surface



Under field-free conditions the molecules are randomly oriented

The laser establishes mm-range order that lasts indefinitely





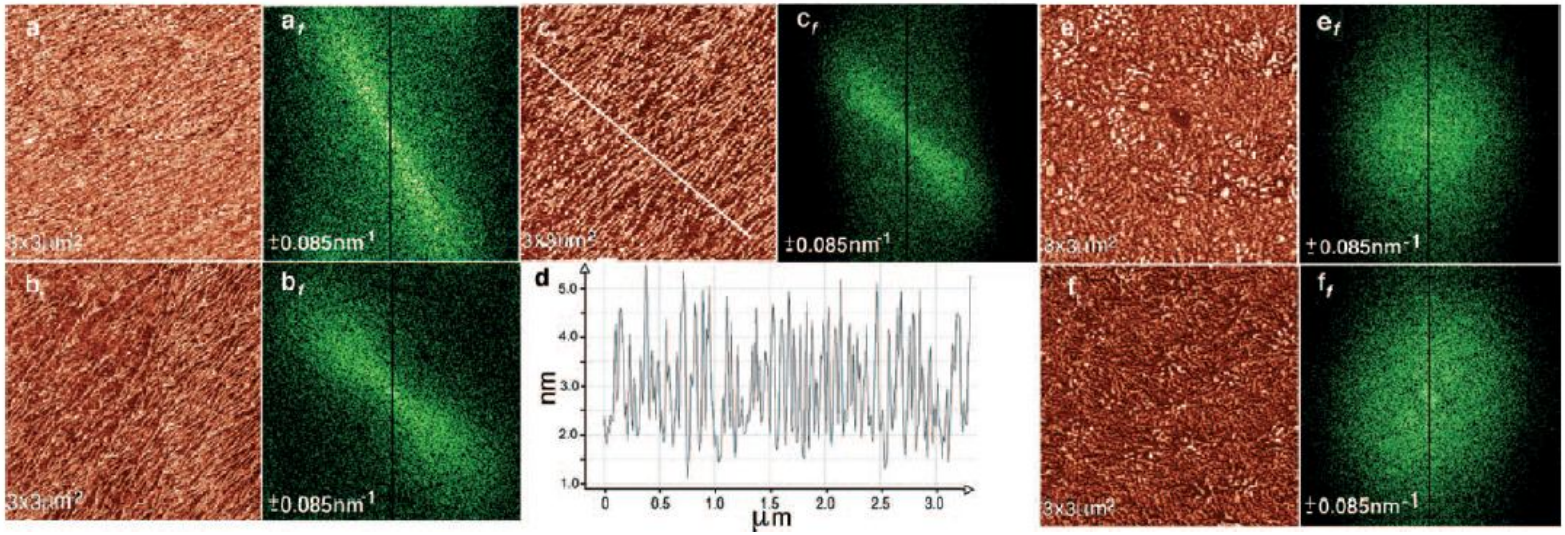
I. Nevo, S. Kapishnikov, A. Birman, M. Dong, F. Besenbacher, H. S., T.S., & L. Leiserowitz, J.Chem.Phys. 140, 144704 ; Science highlight "Molecular Choreography in Next Generation Nanofilms", D. Powel.

Peptide Films

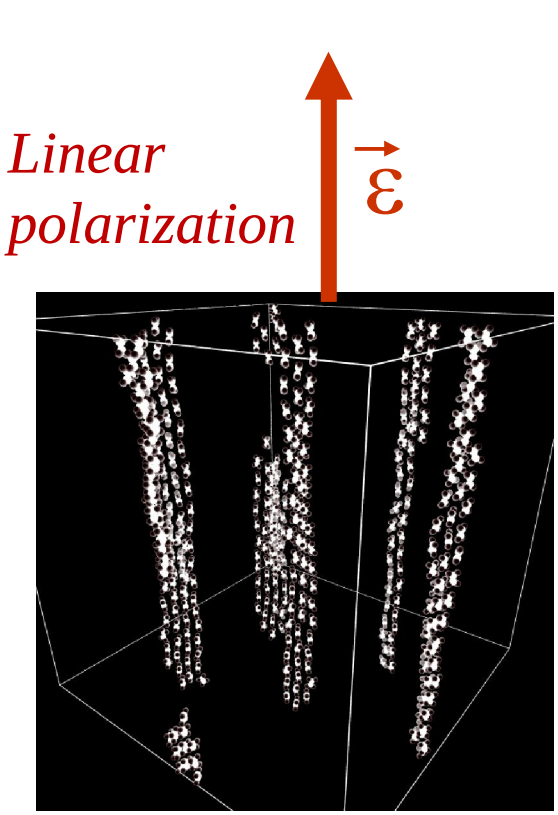
DOI: 10.1002/anie.200905927

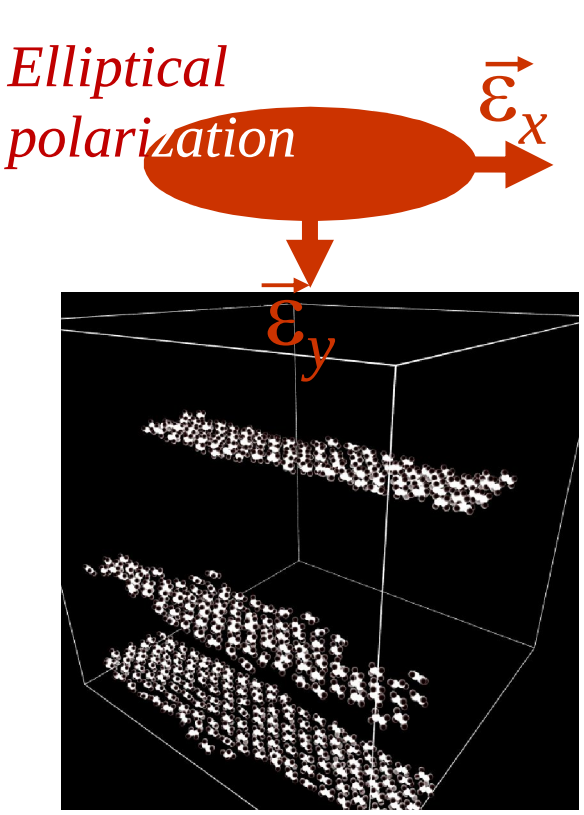
Laser-Induced Alignment of Self-Assembled Films of an Oligopeptide β Sheet on the Water Surface**

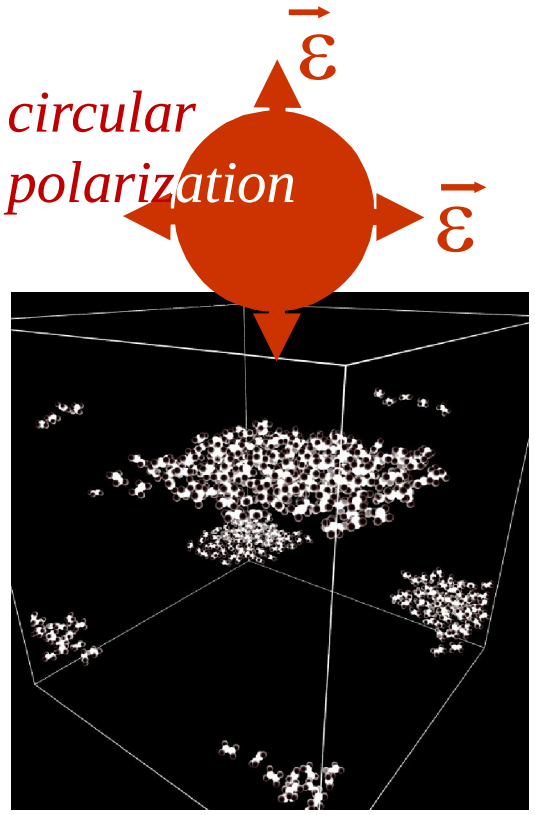
Atalia Birman, Kristian Kjaer, Yehiam Prior, Iftach Nevo, and Leslie Leiserowitz**



Purely laser-induced assembly (due to induced dipole-induced dipole interactions) is very general, and potentially offers control over the structure of the assembly*

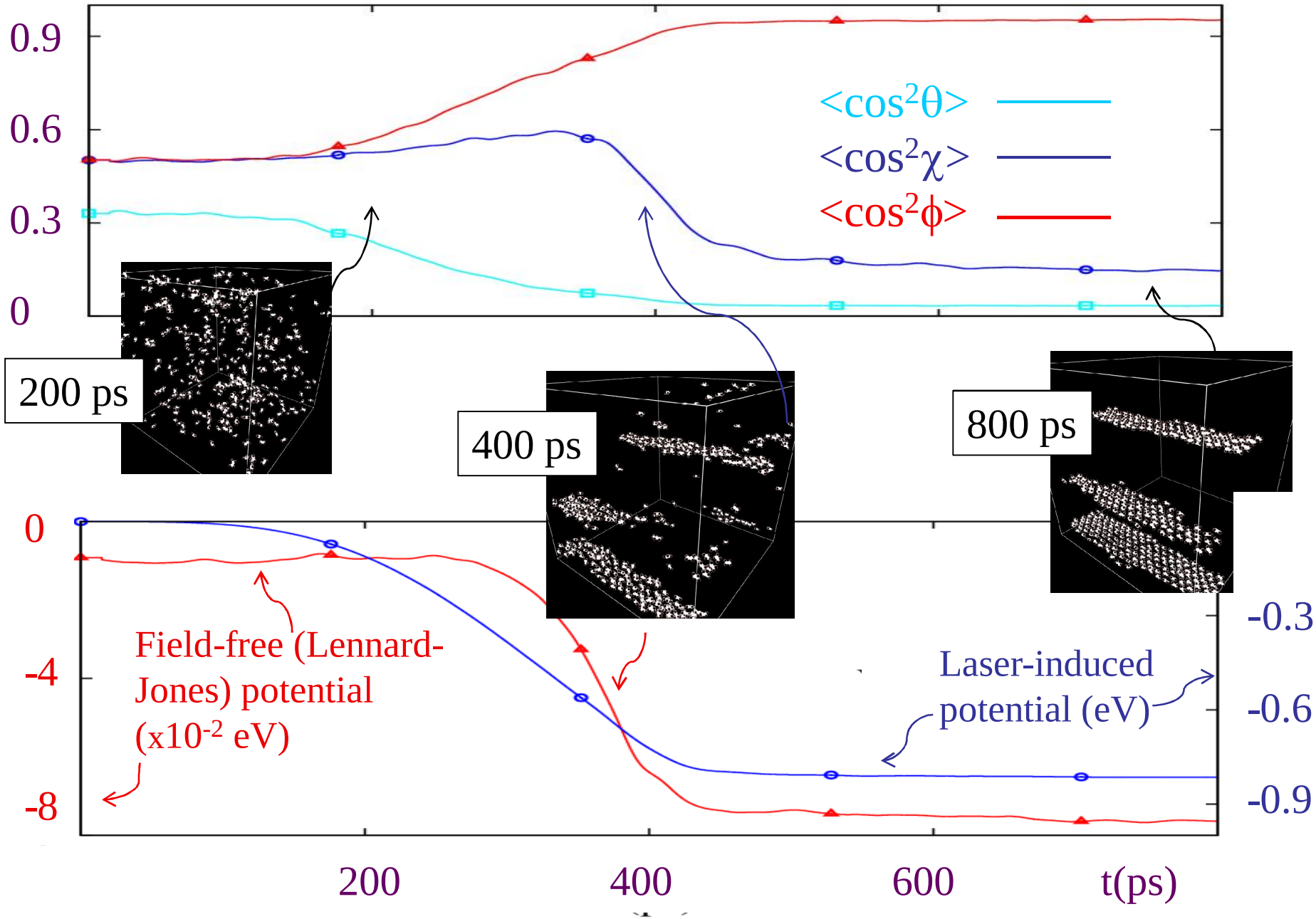






*Disclaimer: these are very preliminary results

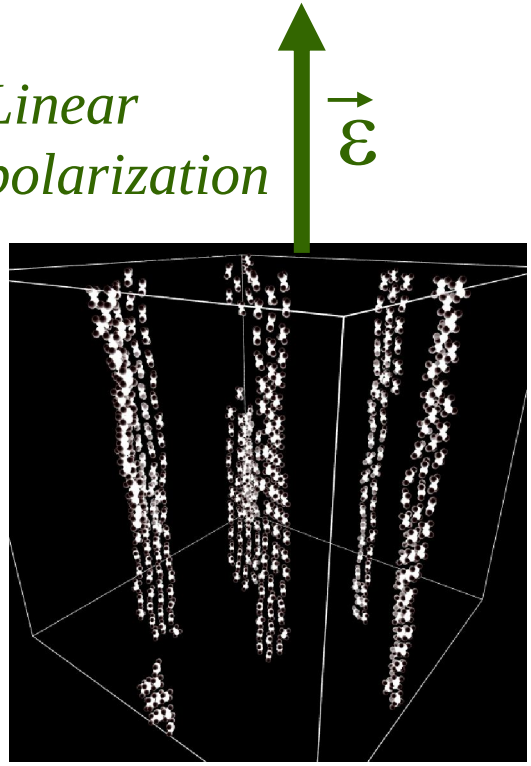
Classical simulations of collective alignment in a molecular ensemble



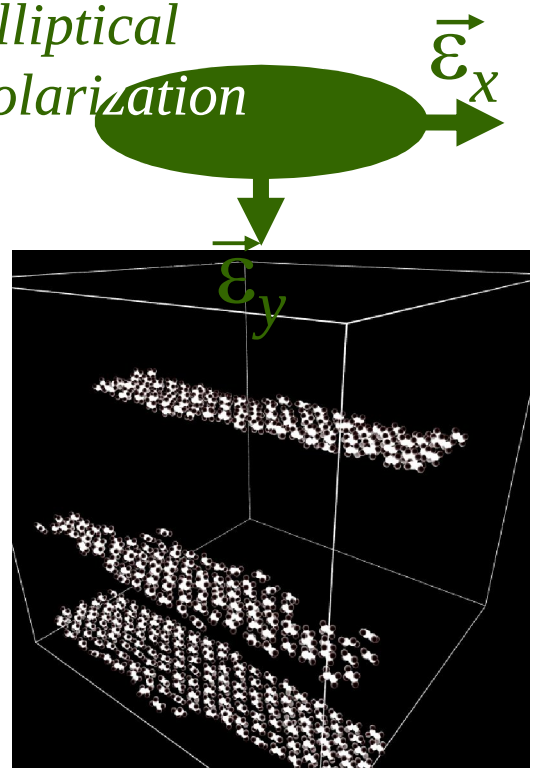
The polarization determines both the short range order of the molecules within an assembly and the long range order of the assembly with respect to one another

Max Artamonov

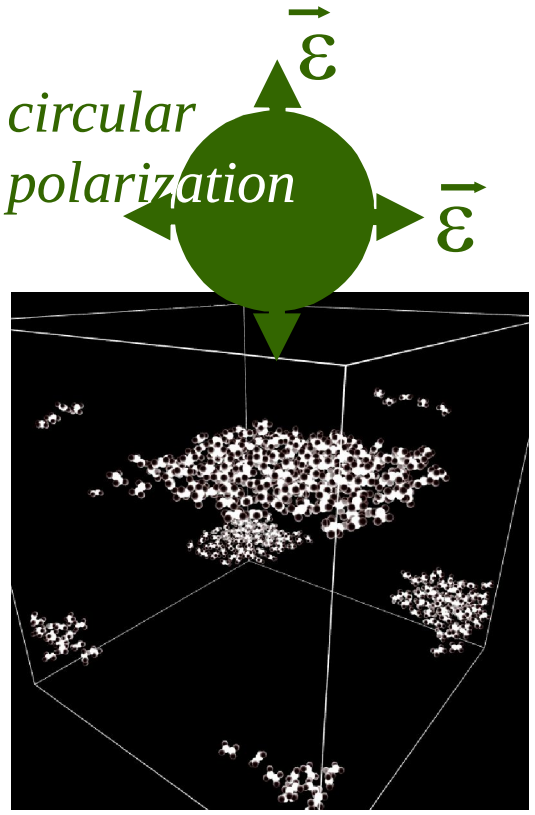
Linear polarization



Elliptical polarization

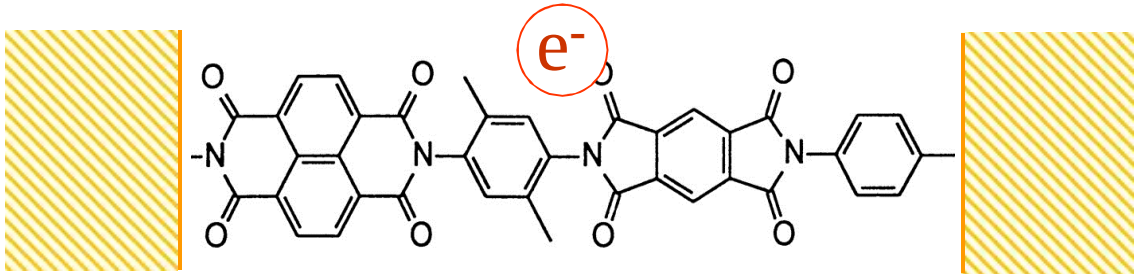


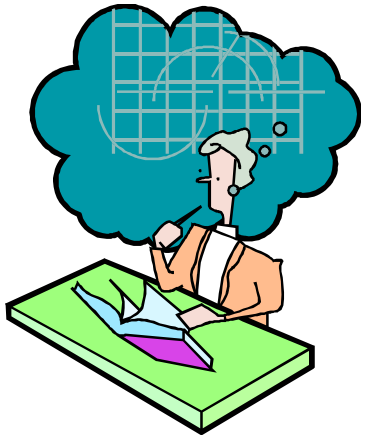
circular polarization



*Disclaimer: these are very preliminary results

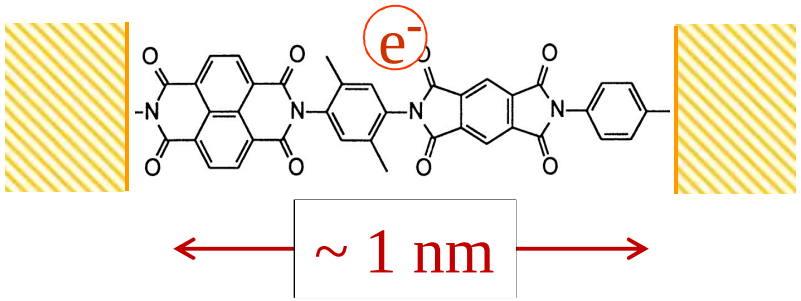
Transport through molecular-scale junctions:



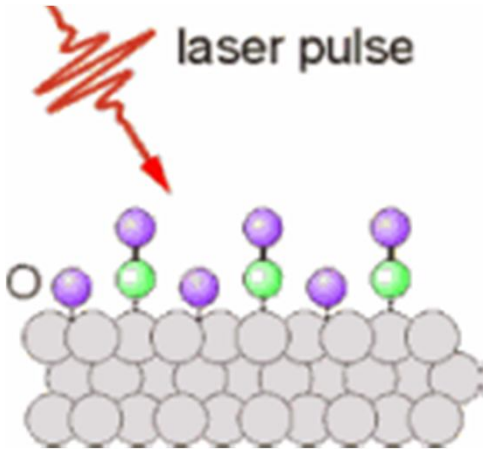


Coherently controlling the electron dynamics (in the lab) has long been a challenge….

First, laser beams are macroscopic (diffraction limited to approximately the wavelength)



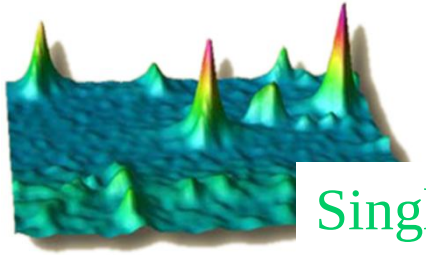
Second, photon-driven processes on metallic surfaces are dominated by substrate-mediated excitation in the vast majority of cases



Cartoon courtesy of Martin Wolf

Plasmonics as a route to combining spatial with temporal resolution: Sharp metal tips (like nanoparticles and corrugated metal surfaces) enhance and spatially localize an incident electromagnetic field via plasmon resonance effects

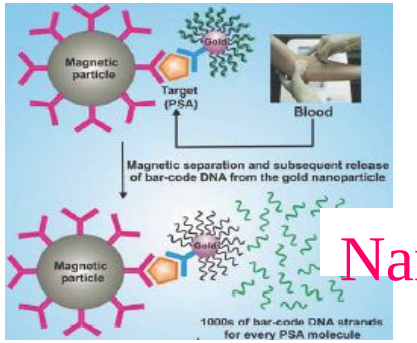
The Lycurgus cup: 4th century A. D.



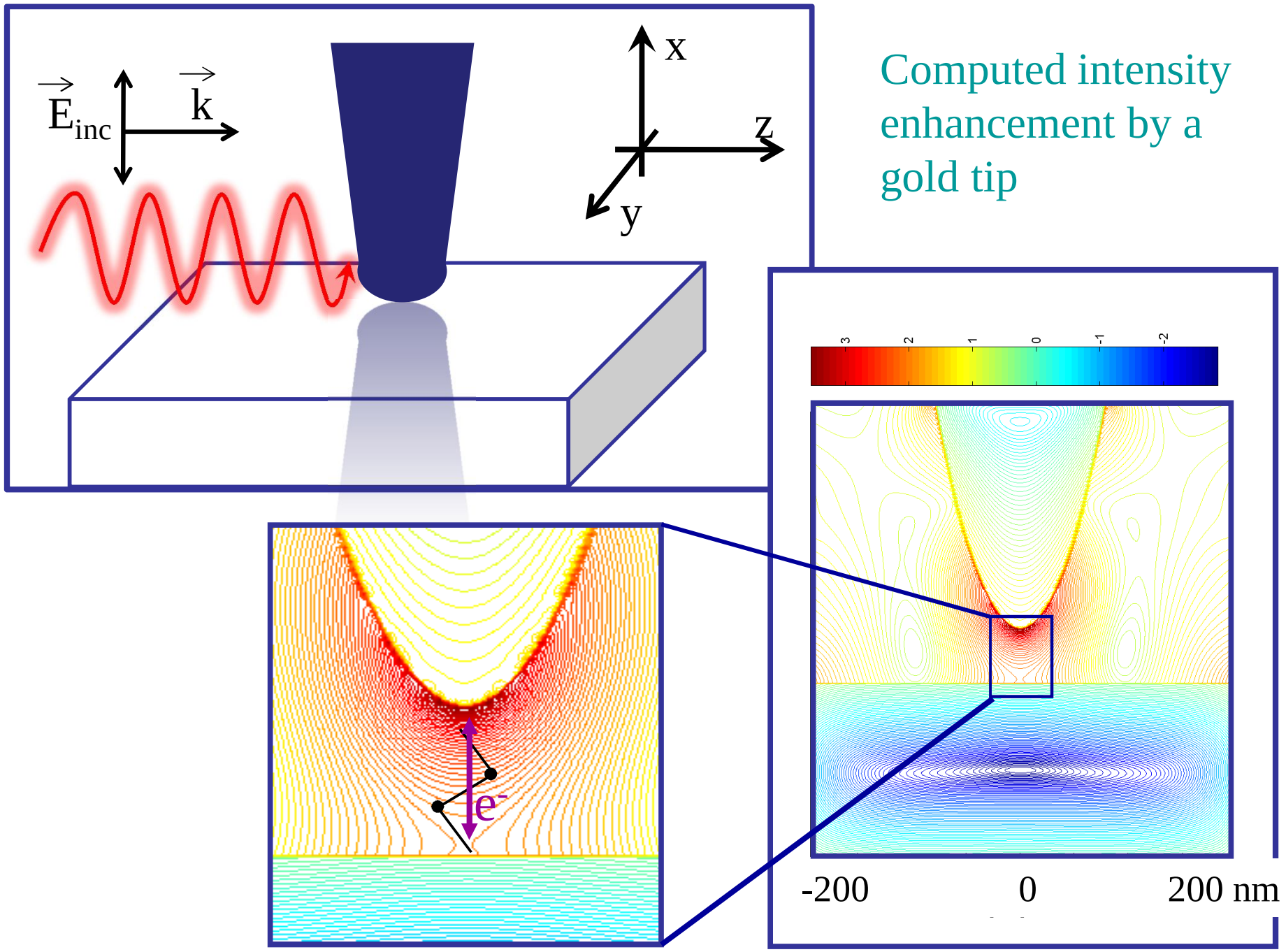
Single molecule spectroscopies

The Cathedral of Cologne: 1300 A.D.

Energy transport in the nanoscale

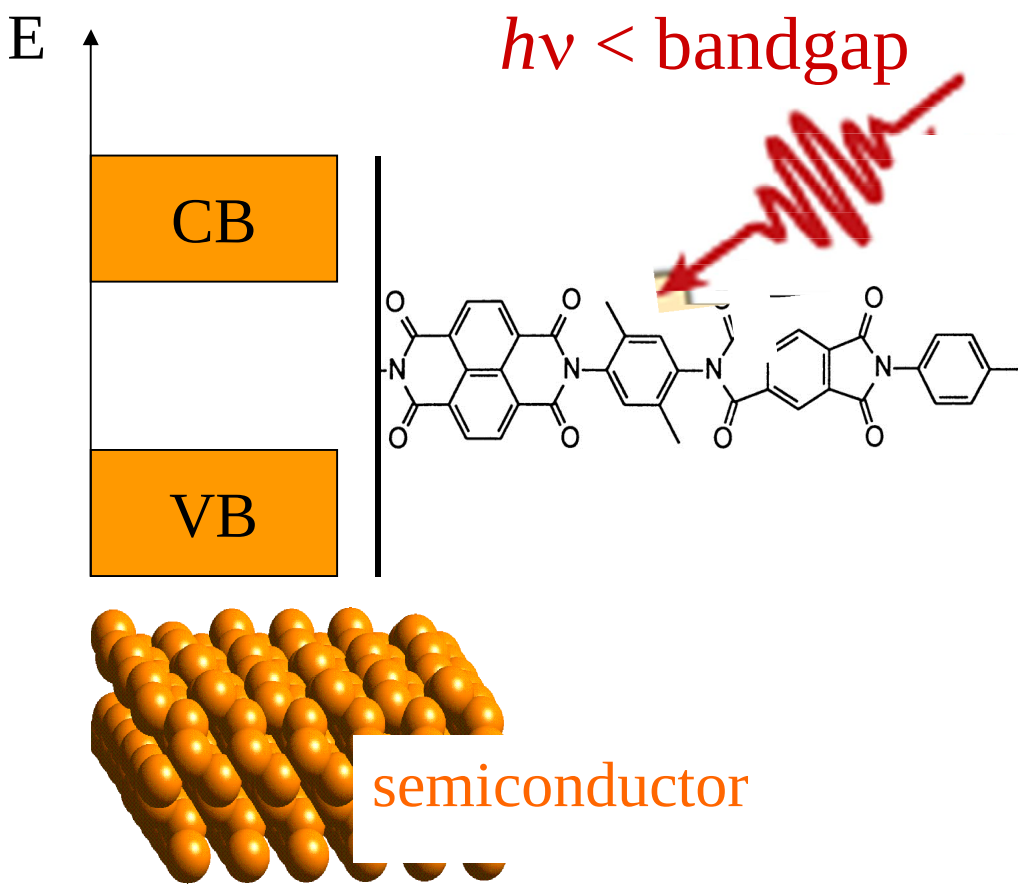


Nanosensing



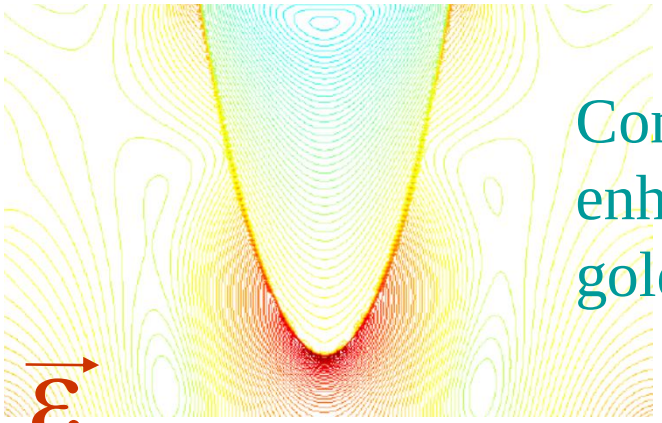
Computed intensity enhancement by a gold tip

Semiconductors offer an advantage if one can make use of sub-bandgap photons

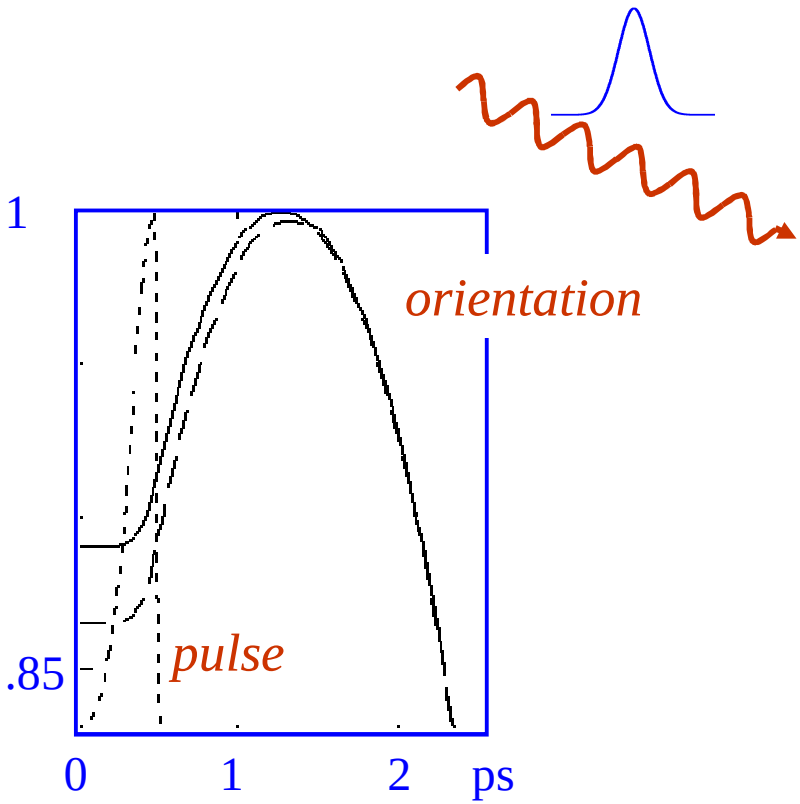


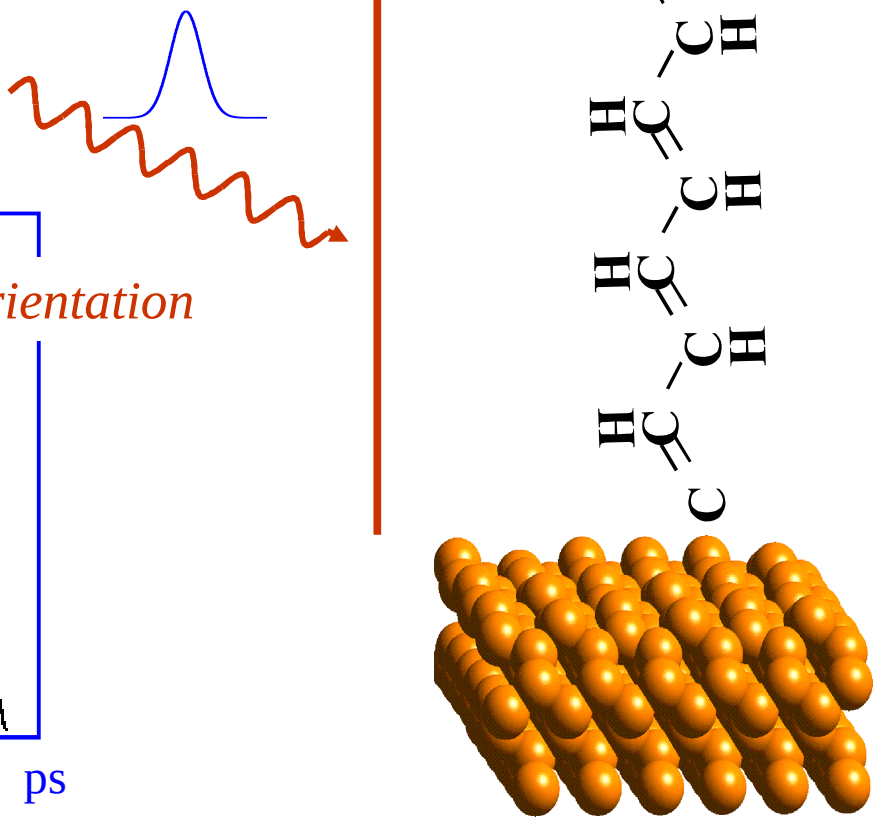
Toward control of junctions with light

M. Reuter, M. Sukharev & T.S., Phys.Rev.Lett, 101, 208303; highlight in Nature Photonics 3, 4-5.



Computed intensity enhancement by a gold tip

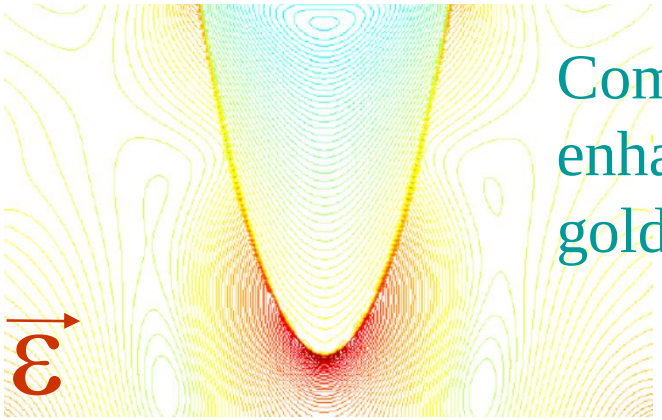




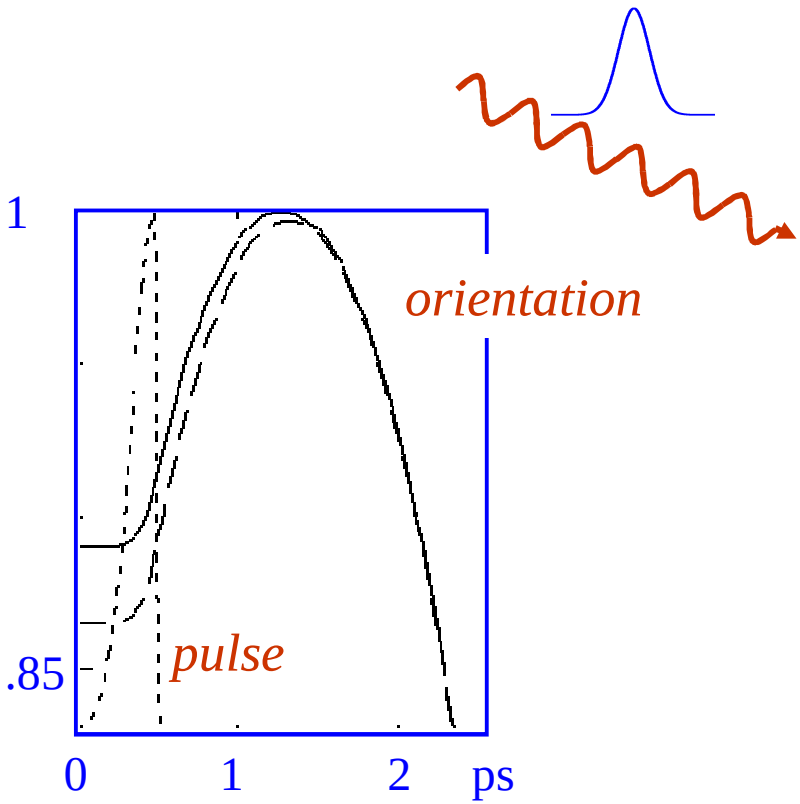
Matt Reuter

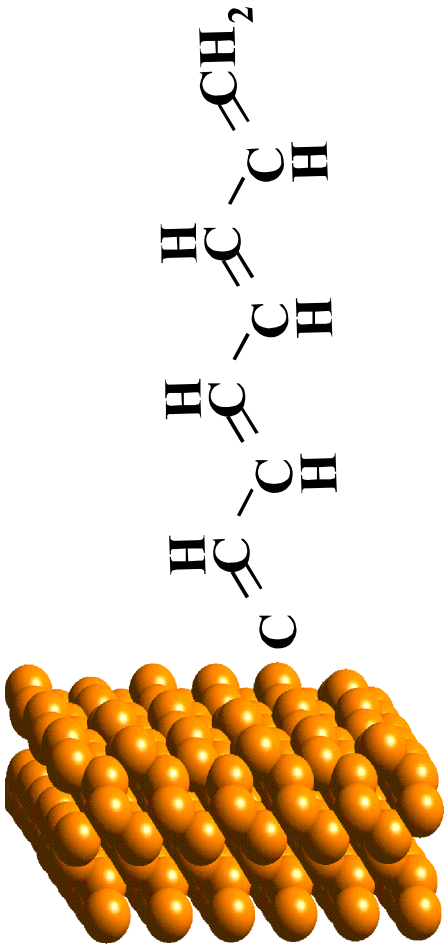
Toward control of junctions with light

M. Reuter, M. Sukharev & T.S., Phys.Rev.Lett, 101, 208303; highlight in Nature Photonics 3, 4-5.

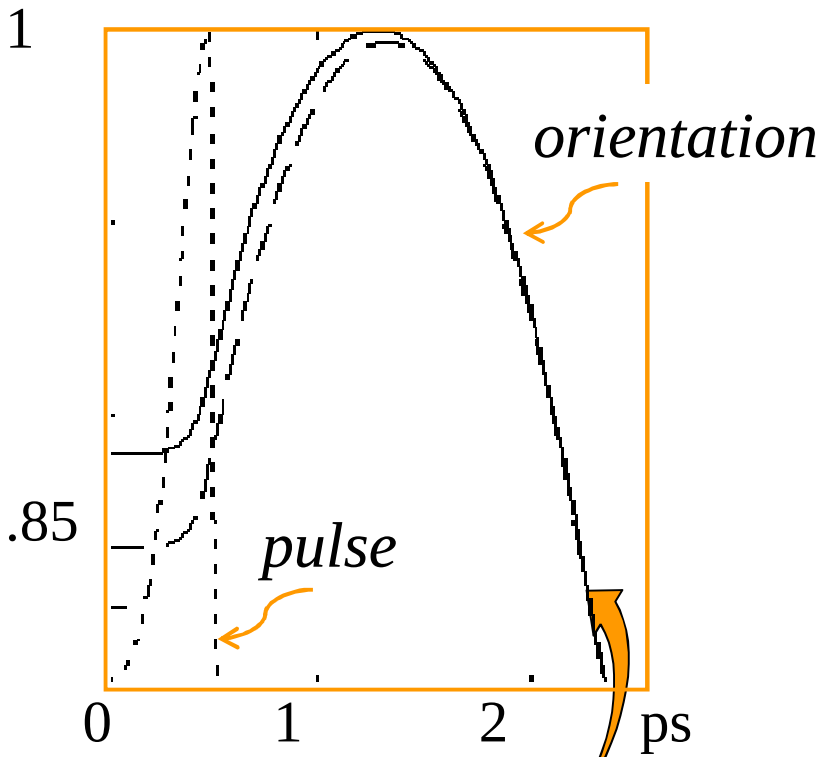


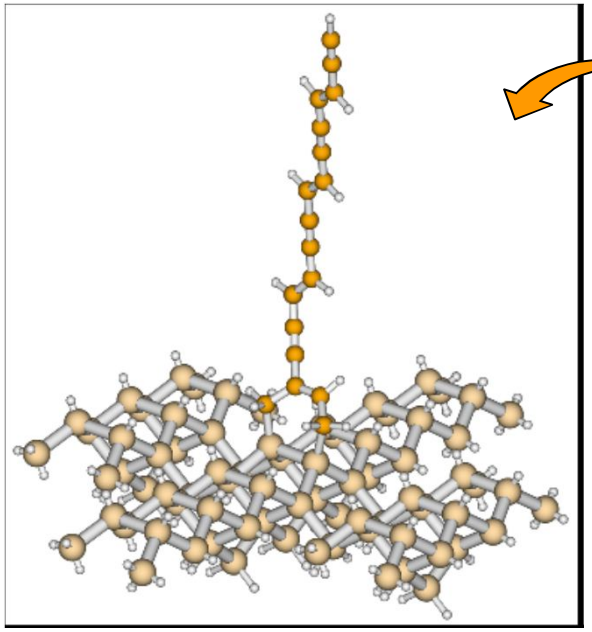
Computed intensity enhancement by a gold tip





An Ultrafast, Nanoscale Switch

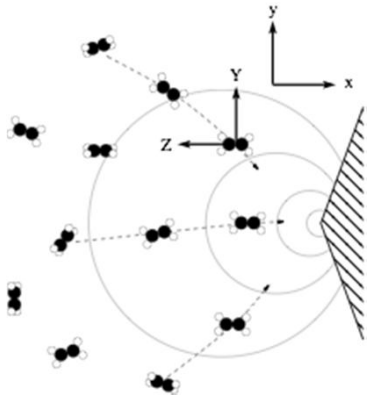


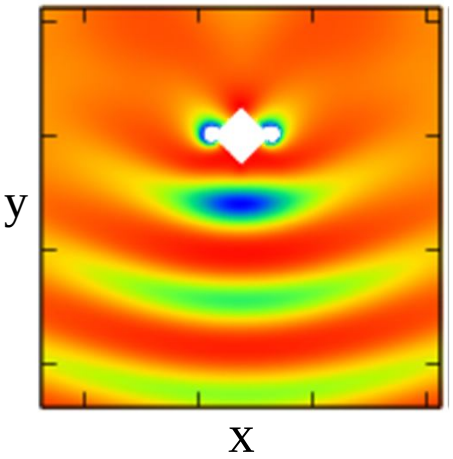


Numerical results for an oligo-diacetylene, attached to a Si(100) surface, translate into a conductance on-off ratio of just above 2 orders of magnitude and on-off time-scale of 0.6 ps

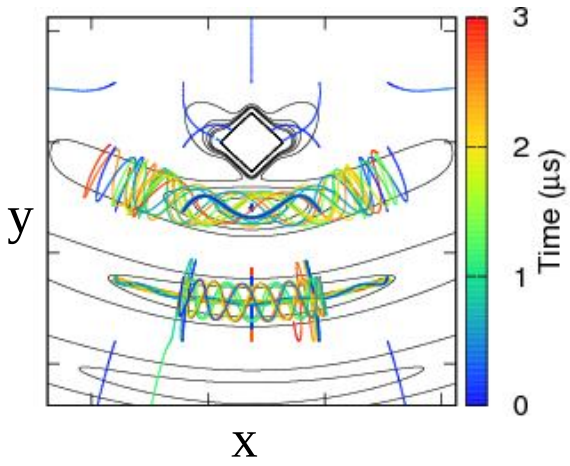
Focusing and Alignment in Plasmon-Enhanced Fields

The interaction of light with molecules in the vicinity of metal nanoparticles is common to a wide range of experiments in nanoplasmonics. Focusing and alignment will play an important role in many of these experiments.

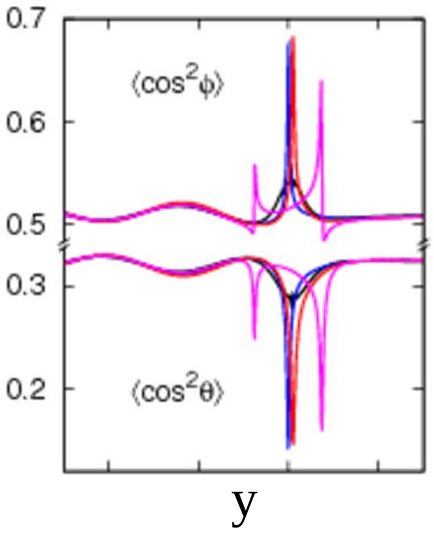




Rotationally averaged potential energy surfaces subject to which the center-of-mass evolves



Evolution of the center-of-mass trajectories toward the high intensity regions

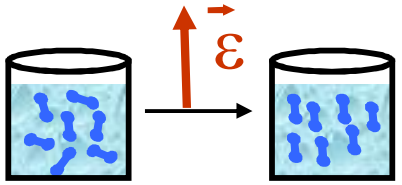


Molecular alignment for different particle shapes

M. Artamonov and T. S., NanoLett., 10 4908 (2011)

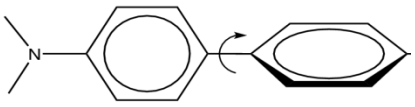
Epilogue

Our goal has been to extend alignment from a tool in physics and optics to make a tool in chemistry and material science.



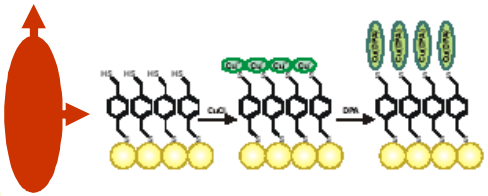
Specifically, we talked about:

- Asymmetric top molecules



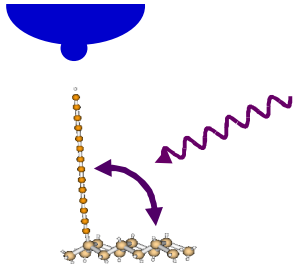
- Alignment in solutions

- Torsional control



- Guided molecular assembly

- Coherent control of transport via junctions



- Alignment and focusing in the nanoscale

Thanks!

$ NSF CHE
$ NSF MRSEC
$ NSF NCN
$ NSF NCLT
$ NSF IGERT
$ AFOSR
$ BSF
$ DOE AMOS
$ DOE SISGR
$ Keck Foundation

Experiments:

- Henrik Stapelfeldt & coworkers
- Emily Weiss & coworkers

NORTHWESTERN UNIVERSITY