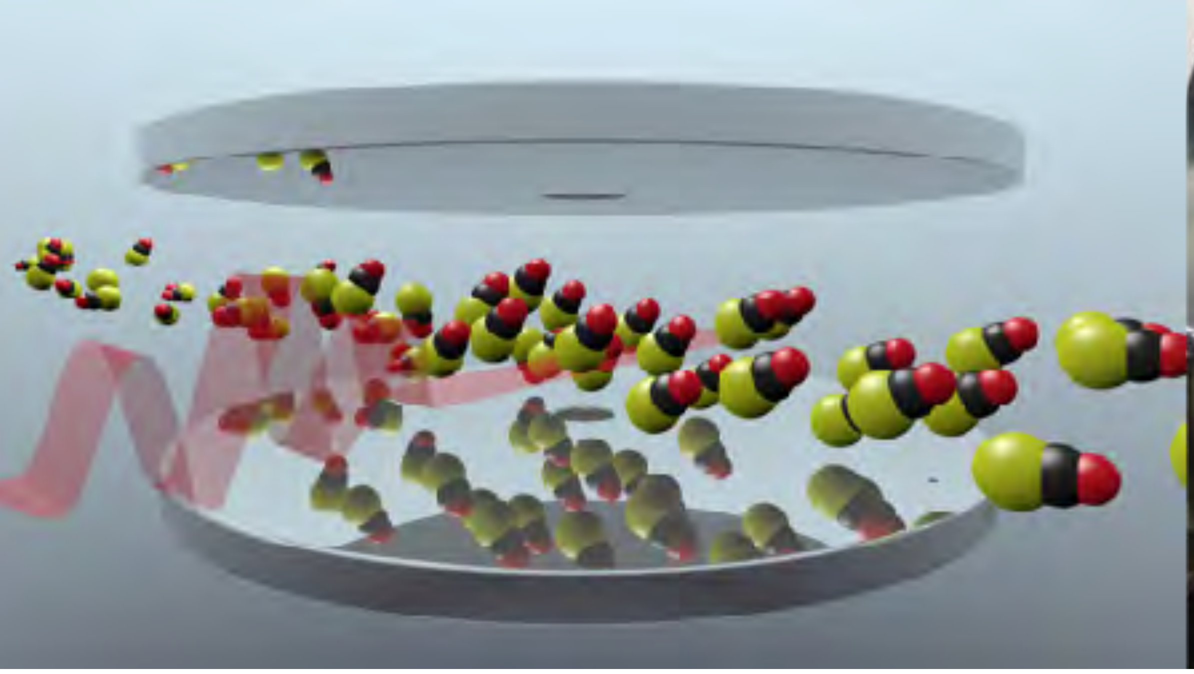
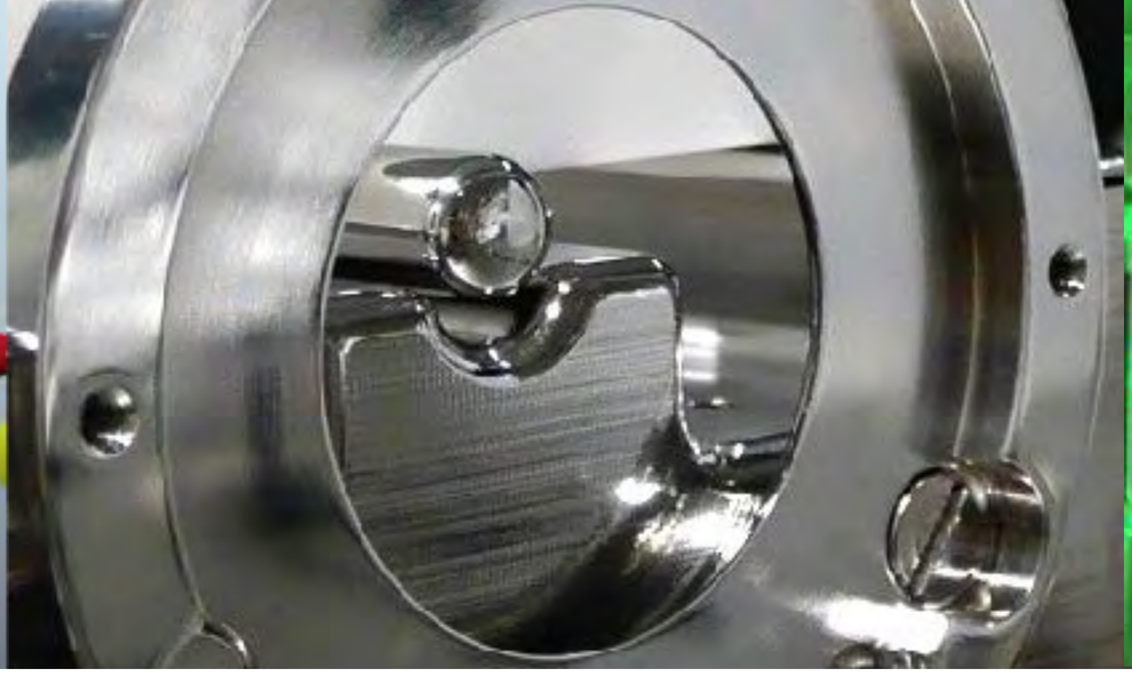
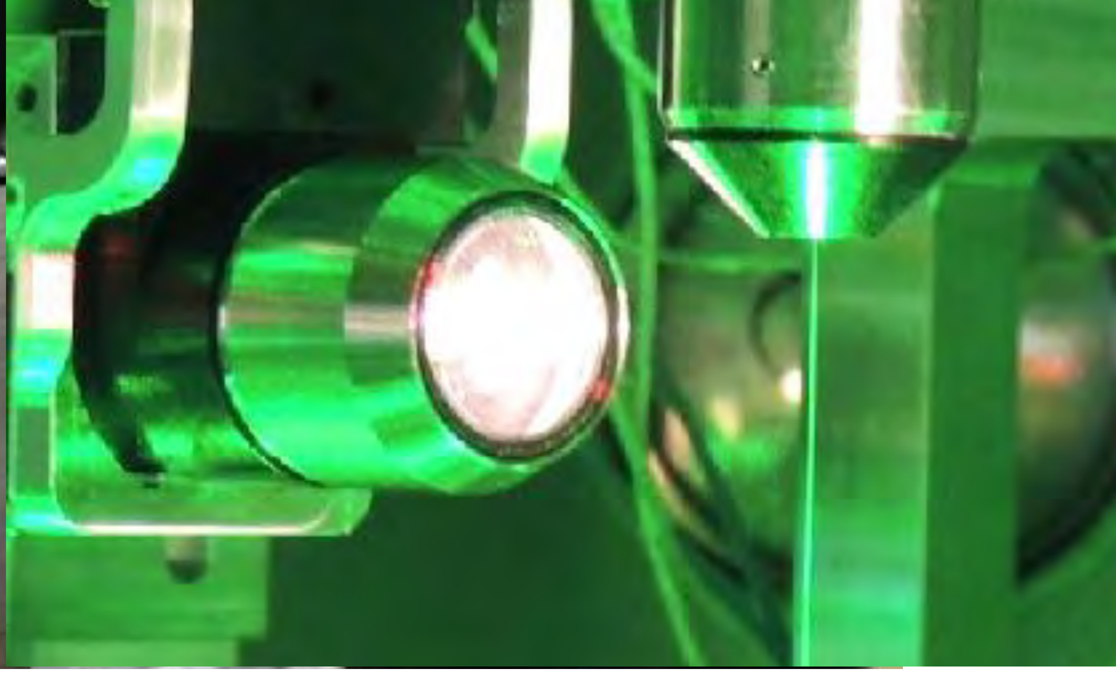




Molecular Sciences

Introduction of concepts and the basics of molecular physics

Jochen Küpper (Andrea Trabattoni)

Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg
Department of Physics & Department of Chemistry, Universität Hamburg
The Hamburg Center for Ultrafast Imaging, Universität Hamburg

3. & 7. August 2017

based on the UHH master module “The Basis of Modern Molecular Physics”

CUI THE HAMBURG CENTER FOR ULTRAFAST IMAGING

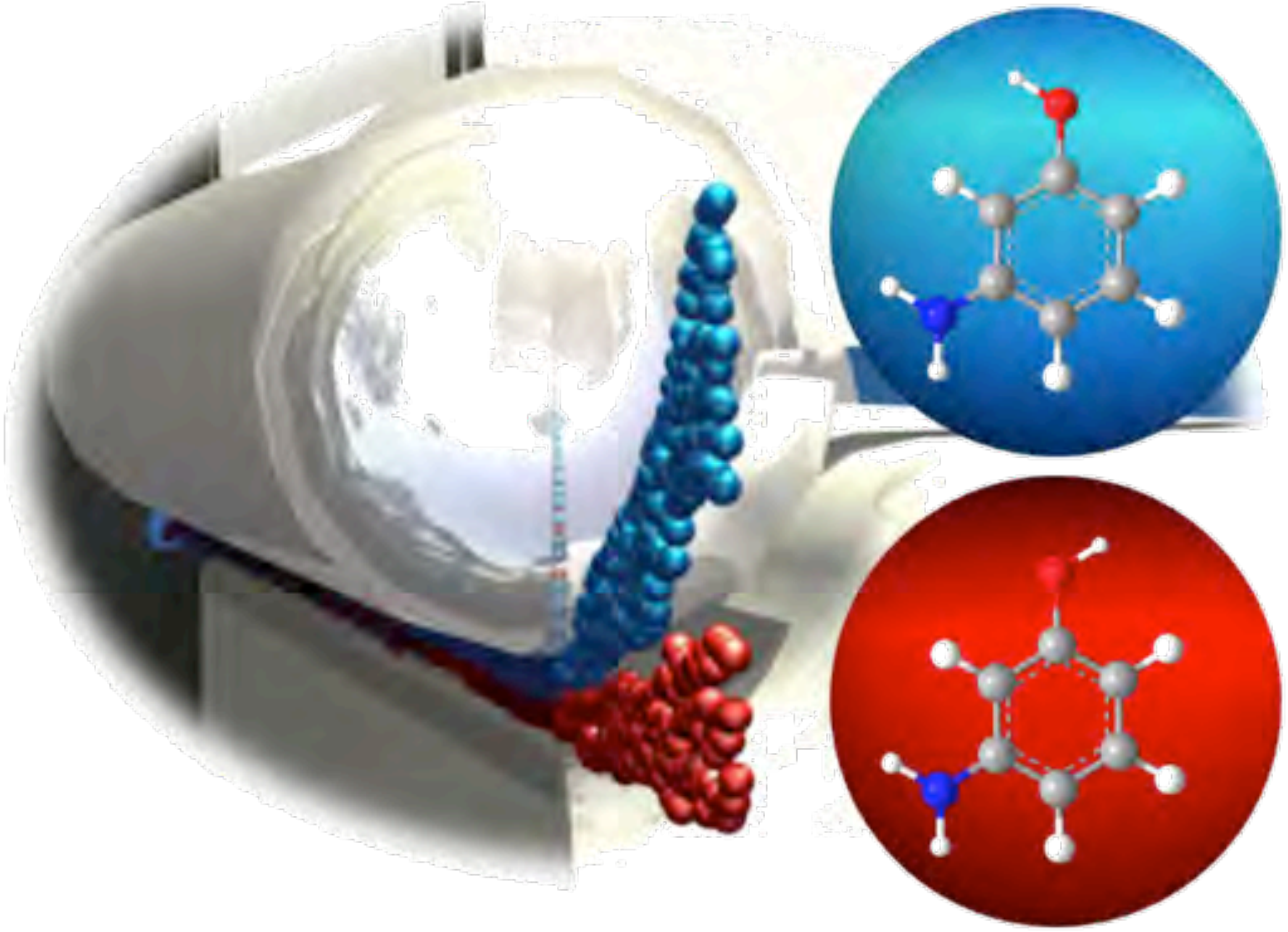
UHH Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

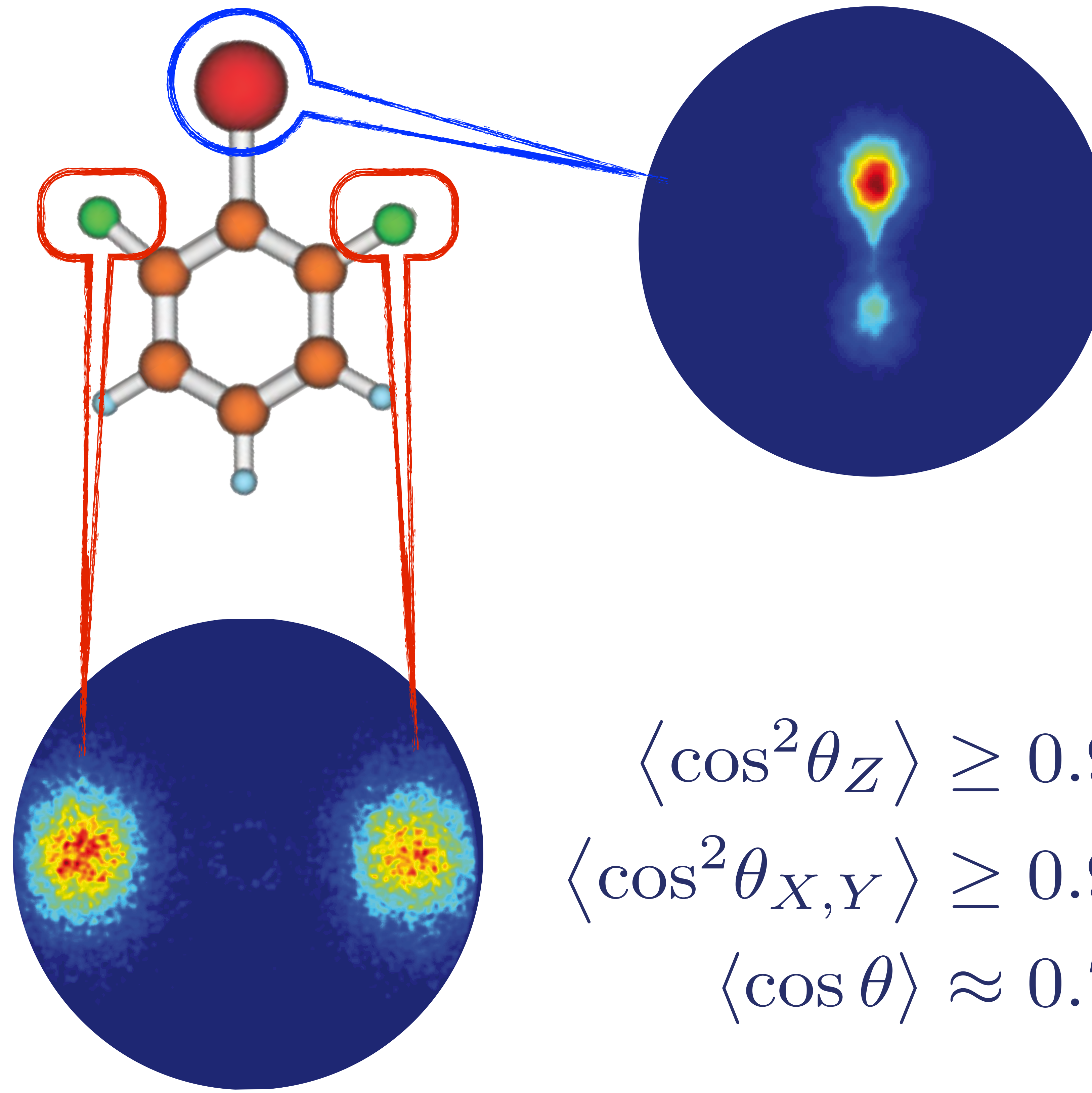
CFEL SCIENCE
Controlled Molecule Imaging

DESY

erc
CoMotion
European Research Council
Established by the European Commission

Molecules in fields
Manipulation of translational and rotational motion

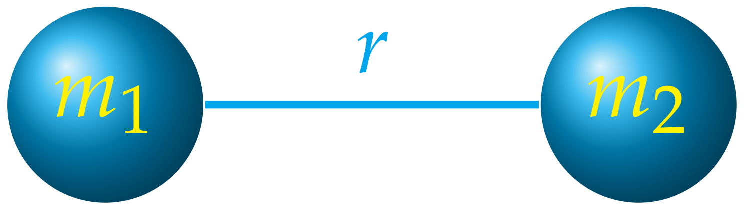




$$\langle \cos^2\theta_Z \rangle \geq 0.975$$
$$\langle \cos^2\theta_{X,Y} \rangle \geq 0.9$$
$$\langle \cos\theta \rangle \approx 0.7$$

Filsinger, Erlekam, von Helden, JK, Meijer, *Phys. Rev. Lett.* **100**, 133003 (2008)
Holmegaard, Nielsen, Nevo, Stapelfeldt, Filsinger, JK, Meijer, *Phys. Rev. Lett*. **102**, 023001 (2009)
Nevo, Holmegaard, Nielsen, Hansen, Stapelfeldt, Filsinger, Meijer, JK, *Phys. Chem. Chem. Phys*. **11**, 9912 (2009)

Rigid diatomic rotor



- classical energy:

$$E_r = \frac{1}{2} I \omega^2 \qquad \text{with } I = m_1 r_1^2 + m_2 r_2^2 \tag{8}$$

with the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and bond length $r = r_1 + r_2$ one obtains

$$E_r = \frac{1}{2} \mu r^2 \omega^2 \tag{9}$$

with $L = I\omega$ this yields

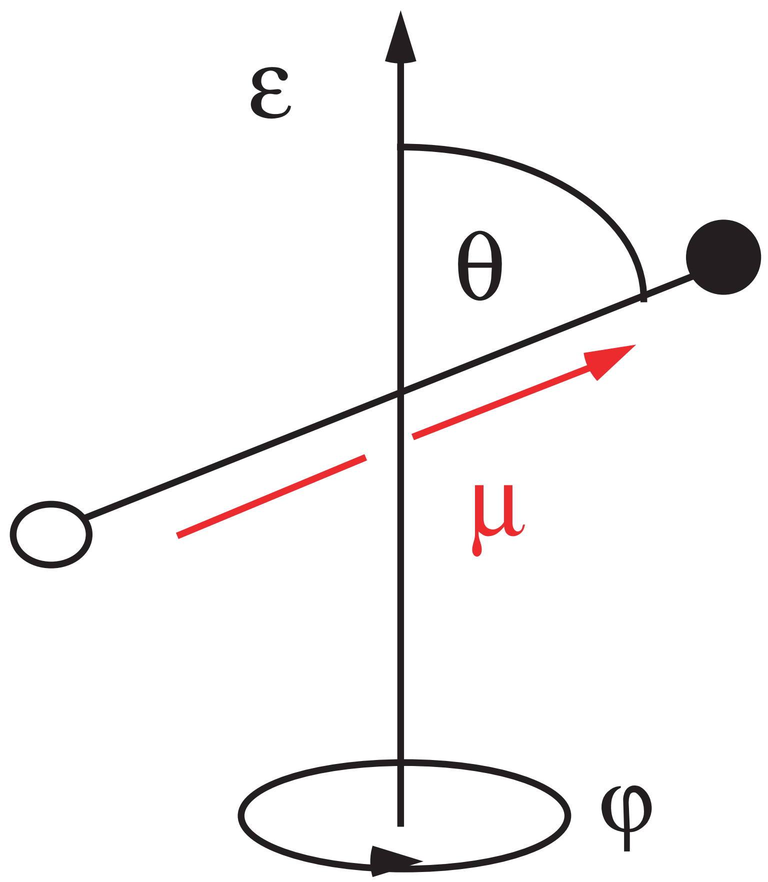
$$E_r = \frac{L^2}{2I} \tag{10}$$

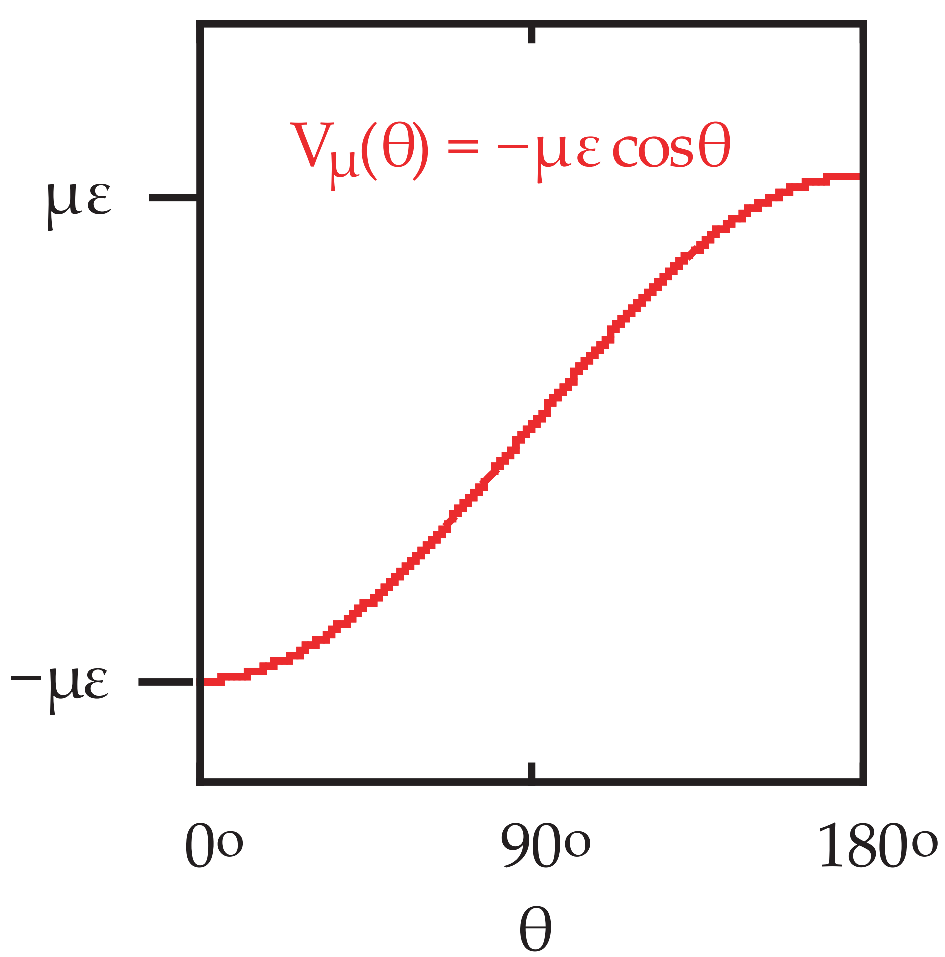
- quantum mechanical energy:

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \tag{11}$$

  - E_r is inversely proportional to I
  - E_r scales with rotational quantum number as $J(J+1)$

Orientation of a Permanent Dipole





- Hamiltonian

$$H = B\vec{J}^2 + V_\mu \tag{45}$$

- Dimensionless Hamiltonian

$$\frac{H}{B} = \vec{J}^2 - \frac{\mu\epsilon}{B}\cos\theta = \vec{J}^2 - \omega\cos\theta \tag{46}$$

- Dimensionless *interaction strenght* parameter

$$\omega = \frac{\mu\epsilon}{B} \tag{47}$$

- Mixing operator — couples states with equal M but J's differing by ±1

$$cos\theta \tag{48}$$

- Cylindrical symmetry around ϵ, therefore uniform in ϕ.

c.f. dimensional calculation in Y.-P. Chang et al, *Comp. Phys. Comm.* **185**, 339–349 (2014)

Schrödinger Equation

- Schrödinger Equation

$$\frac{H}{B}\psi = \left(\vec{J}^2 - \omega\cos\theta\right)\psi = \frac{E}{B}\psi \tag{49}$$

- Representation in the free rotor basis $|JK\rangle$

$$\psi = \left|\tilde{J}M\omega\right\rangle = \sum_{J=M}^{\infty} a_J^{\tilde{J}M}(\omega)\,|JM\rangle \tag{50}$$

- Matrix elements

$$\left\langle JM\left|\vec{J}\right|JM\right\rangle = J(J+1) \tag{51}$$

$$\langle JM\,|\cos\theta|\,J+1M\rangle = \sqrt{\frac{(J+M+1)(J-M+1)}{(2J+1)(2J+3)}} \tag{52}$$

$$\langle JM\,|\cos\theta|\,JM\rangle = 0 \tag{53}$$

$$\langle JM\,|\cos\theta|\,J-1M\rangle = \sqrt{\frac{(J+M)(J-M)}{(2J-1)(2J+1)}} \tag{54}$$

Energies and Wavefunctions

- Eigenfunctions are coherent linear superpositions of the field-free rotor basis functions: *hybridization*.
- Wavefunctions are of mixed parity (i. e., parity is different from ±1).
  With equation (50) and parity of basis functions $p_{J,M} = (-1)^J = p_J$, the parity of the mixed wavefunction is mixed as well:

$$p = \sum_J a_J \, p_J \tag{55}$$

- Parity conservation does not apply to state of indefinite parity. Such a state can be oriented and have a space-fixed electric dipole moment.
- In a state of definite parity, the space-fixed electric dipole moment is zero.

Example calculation

Group work "pendular states" (teams of 2, 15 min)

- set up the Hamiltonian matrix for fixed M and ω
- ensure convergence by using an appropriately sized Hamiltonian matrix
- okay, let's use $M = 0$ and $\omega = 1$, dimension (3×3) and the known matrix elements

$$H_{J,J+1} = \langle JM\,|\cos\theta|\,J+1M\rangle = \sqrt{\frac{(J+M+1)(J-M+1)}{(2J+1)(2J+3)}}$$

$$\langle JM\,|\cos\theta|\,JM\rangle = 0$$

$$H_{J,J-1} = \langle JM\,|\cos\theta|\,J-1M\rangle = \sqrt{\frac{(J+M)(J-M)}{(2J-1)(2J+1)}}$$

$$H_{J,J} = \left\langle JM\left|\vec{J}\right|JM\right\rangle = J(J+1)$$

- What can you say about the eigenstates under these conditions (numbers)?
- What is the energy of the ground state?
- What is the wavefunction of the ground state?
- What is the parity of the ground state?

Example Calculation I

Solution

- set up a matrix for fixed M and ω and a dimension that ensures convergence of eigenproperties obtained by diagonalization

$$\hat{H} = \begin{pmatrix} J_1(J_1+1) & -\omega\sqrt{\frac{(J_1+M+1)(J_1-M+1)}{(2J_1+1)(2J_1+3)}} & 0 \\ -\omega\sqrt{\frac{(J_2+M)(J_2-M)}{(2J_2-1)(2J_2+1)}} & J_2(J_2+1) & -\omega\sqrt{\frac{(J_2+M+1)(J_2-M+1)}{(2J_2+1)(2J_2+3)}} \\ 0 & -\omega\sqrt{\frac{(J_3+M)(J_3-M)}{(2J_3-1)(2J_3+1)}} & J_3(J_3+1) \end{pmatrix}$$

- for instance, for $M = 0$ and $\omega = 1$ get

$$\hat{H} = \begin{pmatrix} 0(0+1) & -1\sqrt{\frac{(0+0+1)(0-0+1)}{(2\cdot 0+1)(2\cdot 0+3)}} & 0 \\ -1\sqrt{\frac{(1+0)(1-0)}{(2\cdot 1-1)(2\cdot 1+1)}} & 1(1+1) & -1\sqrt{\frac{(1+0)(1-0)}{(2\cdot 1+1)(2\cdot 1+3)}} \\ 0 & -1\sqrt{\frac{(2+0)(2-0)}{(2\cdot 2-1)(2\cdot 2+1)}} & 2(2+1) \end{pmatrix}$$

Example Calculation II

Solution

- this yields the (numerical) Hamiltonian matrix

$$\hat{H} = \begin{pmatrix} 0 & -0.57735 & 0 \\ -0.57735 & 2 & -0.516398 \\ 0 & -0.516398 & 6 \end{pmatrix}$$

- Diagonalization yields the eigenvalues and eigenvectors

$$\lambda_1 = -0.157653 \qquad C_1 = (0.964446, 0.2639998, 0.01215001) \tag{56}$$

$$\lambda_2 = 2.09118 \qquad C_2 = (-0.264, 0.956214, 0.126326) \tag{57}$$

$$\lambda_3 = 6.06648 \qquad C_3 = (0.01215, -0.127666, 0.991743) \tag{58}$$

- This calculation defines the ground state with sufficient accuracy:

$$E(\tilde{J} = 0, M = 0)_{\omega=1} = -0.157653 \cdot B \tag{59}$$

$$\left|\tilde{J} = 0, M = 0\right\rangle_{\omega=1} = 0.964446 \left|J = 0, M = 0\right\rangle + 0.2639998 \left|J = 1, M = 0\right\rangle + 0.01215001 \left|J = 1, M = 0\right\rangle \tag{60}$$

- The eigenfunctions of the Hamiltonian are the coherent linear superpositions of the field-free-rotor basis functions

Example Calculation III
Solution

- we speak of *hybridization* of the wavefunctions (basis functions)
- For our ground state we get the parity

$$\begin{aligned} p = \sum_J a_j p_j &= 0.964446 \cdot (-1)^0 + 0.2639998 \cdot (-1)^1 + 0.01215001 \cdot (-1)^2 \\ &= 0.712 \\ &\neq \pm 1 \end{aligned} \tag{61}$$

Since the parity is not defined, such a state can be (is) oriented.
The system in this state has a space-fixed dipole moment!

Effective Dipole Moment

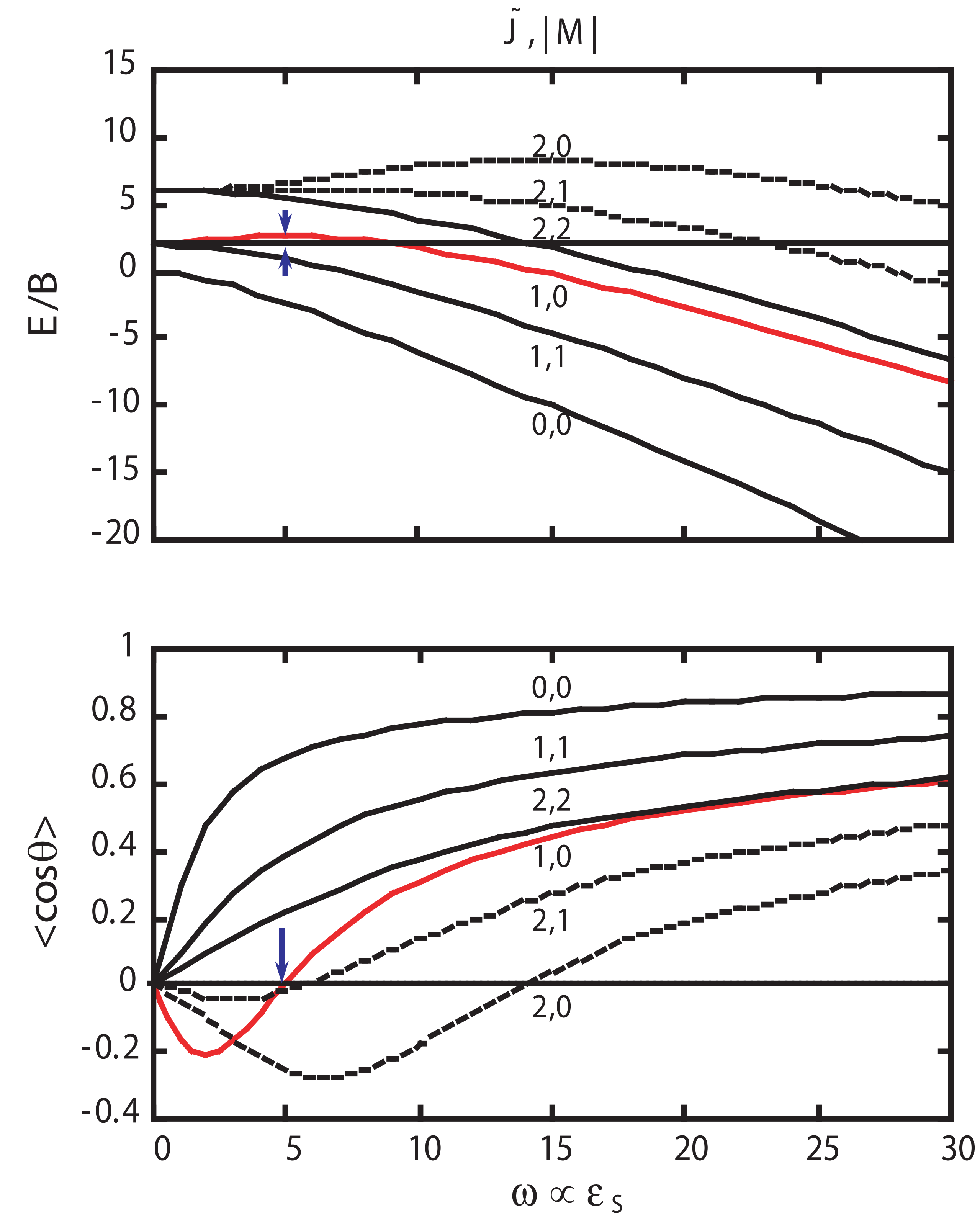
The (negative) derivative of the energy with respect to the field strength is the effective dipole moment of the quantum state:

$$\langle\cos\theta\rangle = -\frac{\partial E/B}{\partial\omega} \tag{62}$$

$$\theta_{\text{max}} = \arccos\langle\cos\theta\rangle \tag{63}$$

low field seeker E *increases* with increasing ϵ.

high field seeker E *decreases* with increasing ϵ.



Molecules in fields
Selection of quantum states and species

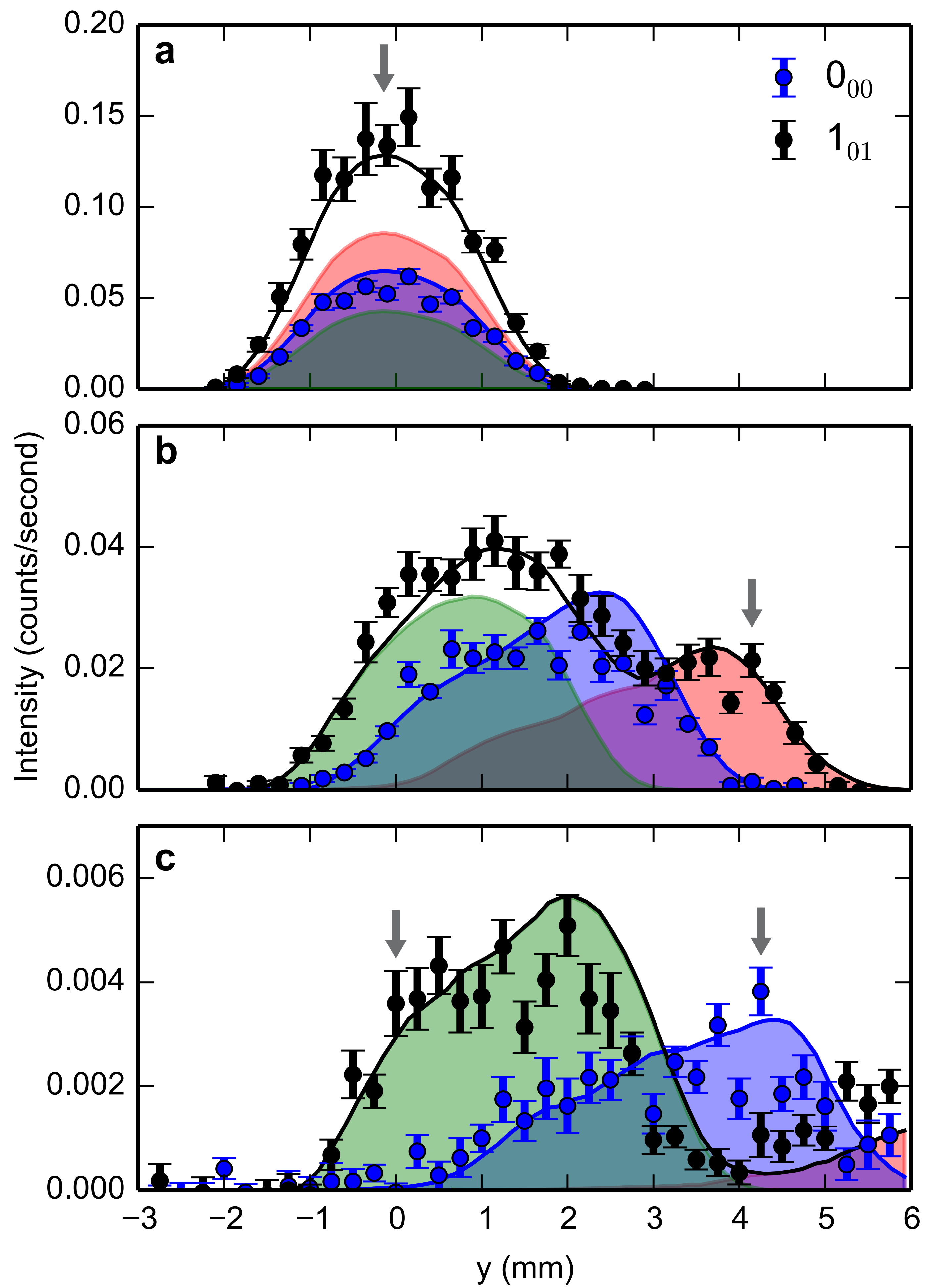
$$U_{Stark} = -\frac{1}{2}E^2(\Delta\alpha cos^2\theta + \alpha_\perp) - \mu E cos\theta$$

$$U_{Stark} = -\vec{\mu} \cdot \vec{E}$$

$$\vec{F}_{Stark} = -\vec{\nabla} U_{Stark}$$

$$f(\mu, \vec{\nabla} E) \longrightarrow v_z = -\frac{1}{M}\int_{-\infty}^{\infty} \left(\vec{\nabla} U\right)_z dt,$$

Understanding and controlling the dynamics of highly excited molecular systems
Separating para and ortho water



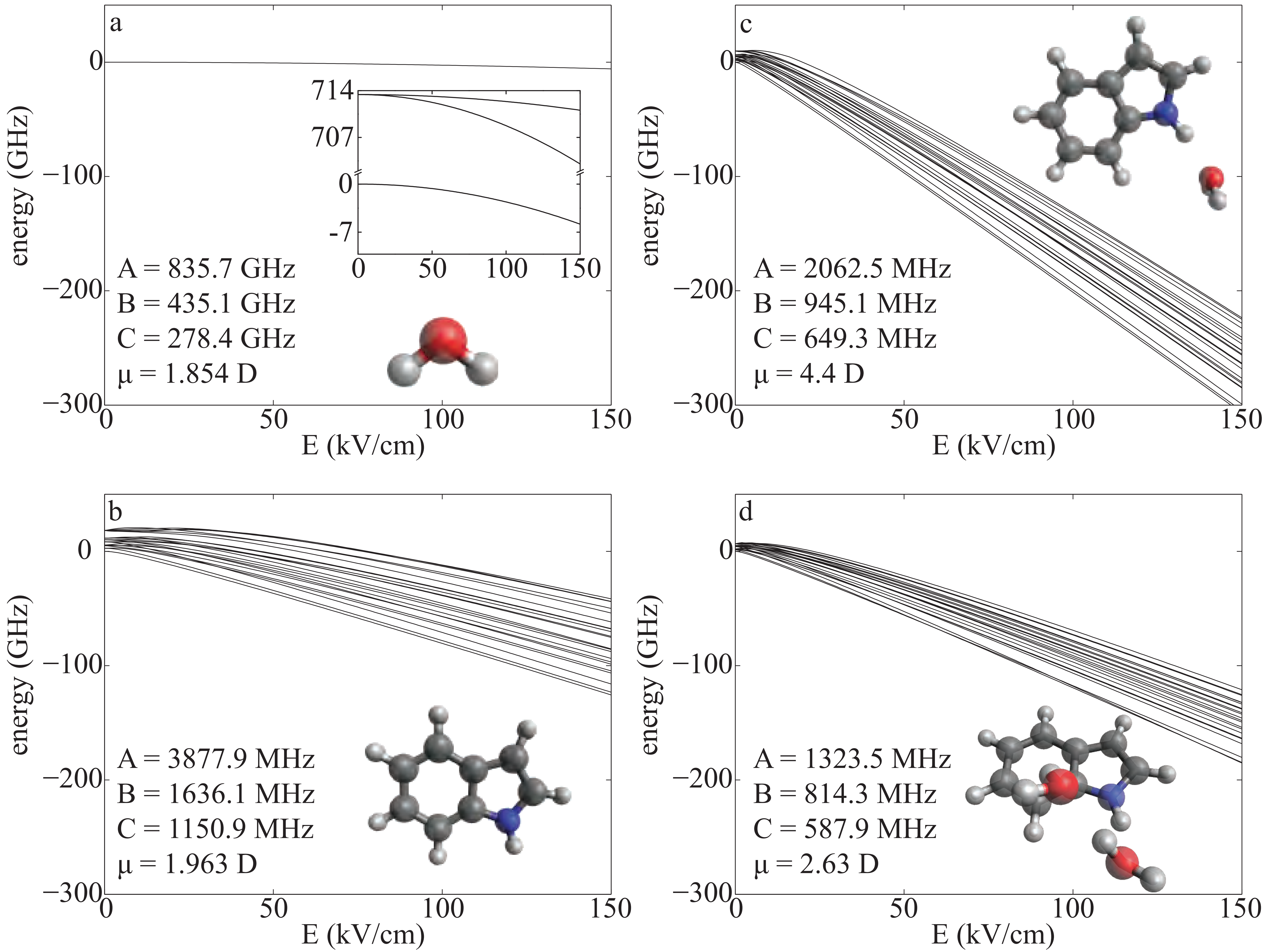
$$\vec{F}_{Stark} = 0$$

$$\vec{F}_{Stark1}$$

$$\vec{F}_{Stark2}$$

Horke, Chang, Długołęcki, JK, *Angew. Chem. Int. Ed.* **53,** 11965 (2014, *VIP*)

Spatial separation of neutral clusters using the m/μ deflector: pure samples of indole-water (indole-$(H_2O)_1$)



Trippel, Chang, Stern, Mullins, Holmegaard, JK, *Phys. Rev. A* (2012)

Spatial separation of neutral clusters using the m/μ deflector
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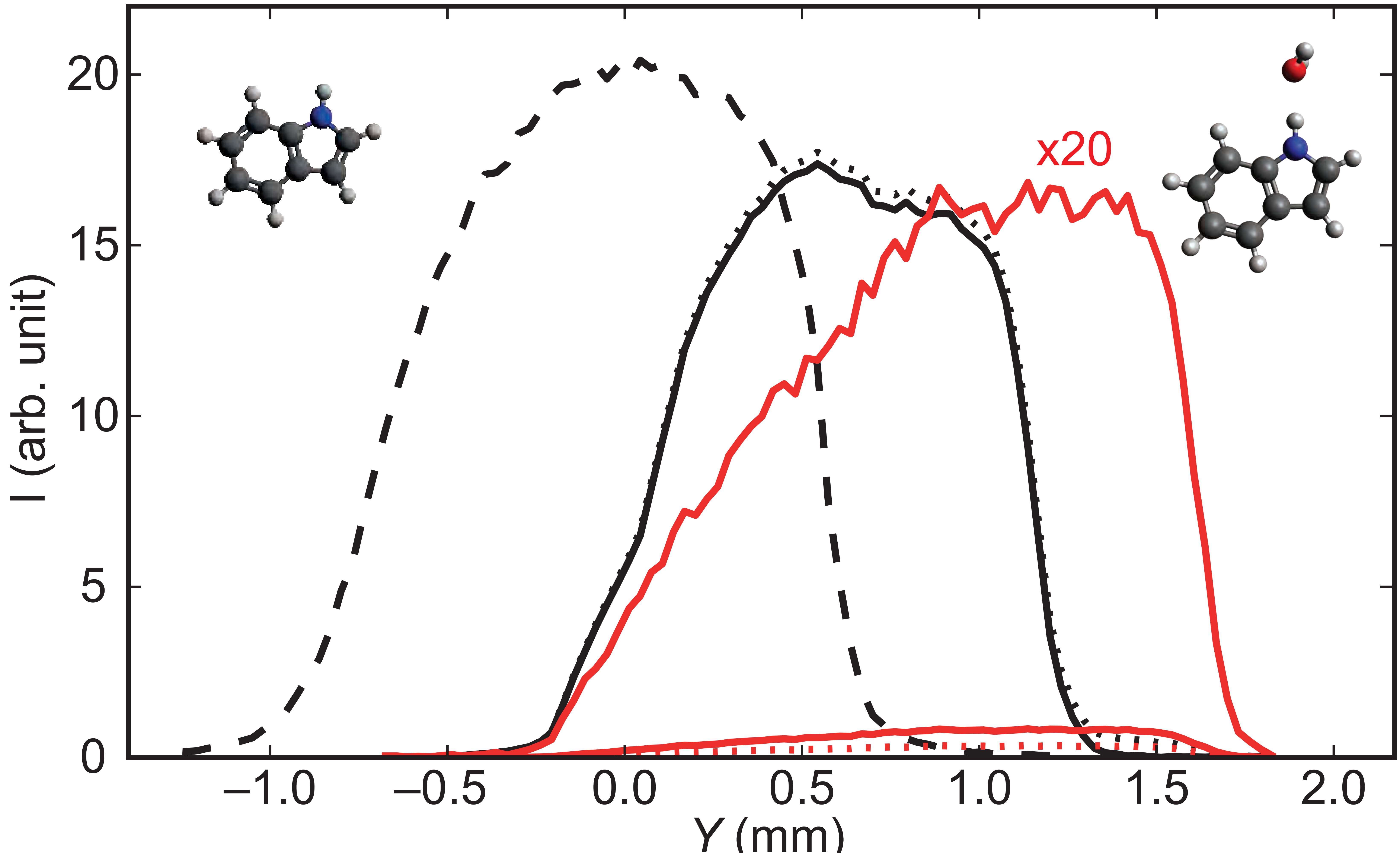
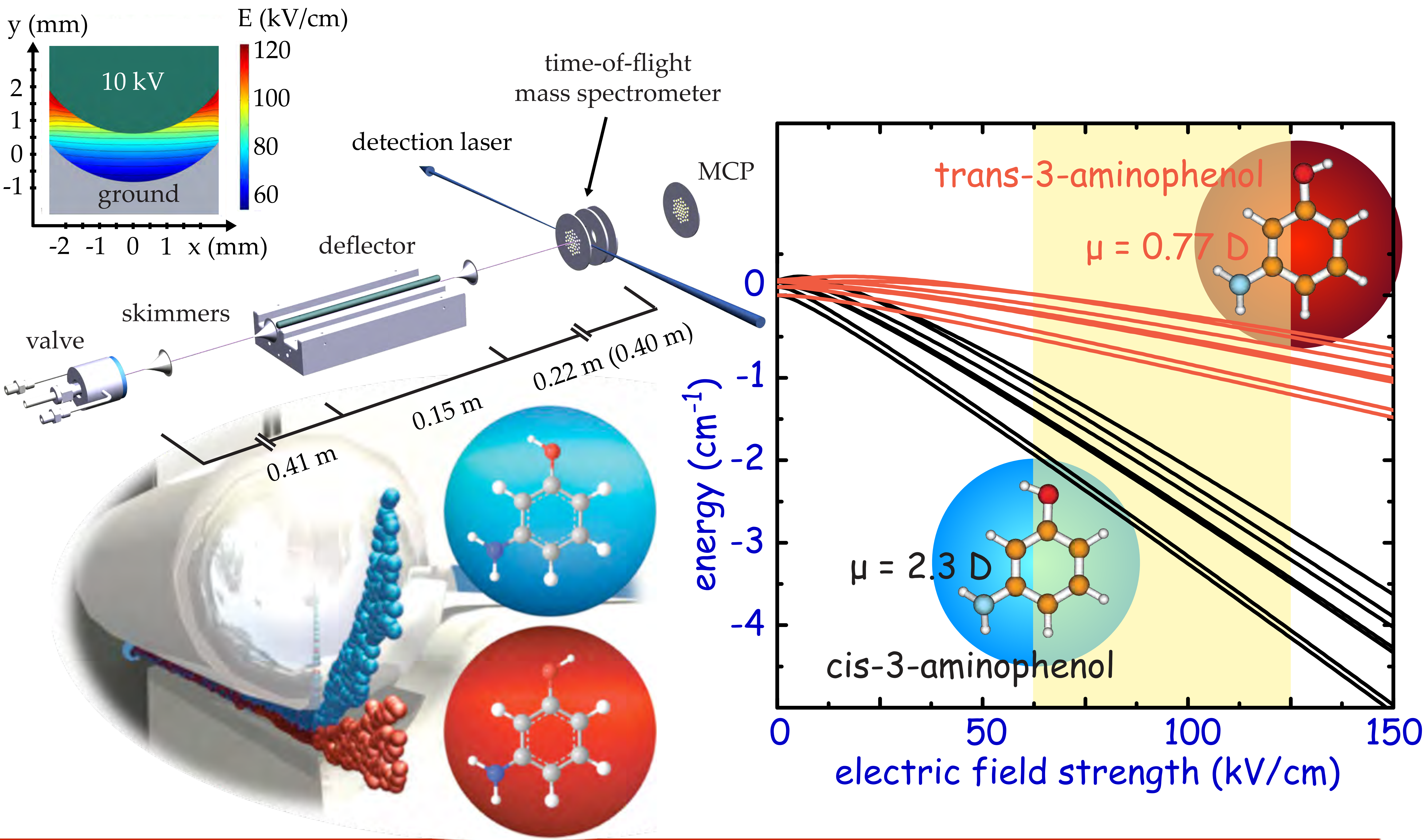


Trippel, Chang, Stern, Mullins, Holmegaard, JK, Phys. Rev. A 86, 033202 (2012)
Chang, Horke, Trippel, JK, Int. Rev. Phys. Chem. 34, 557–590 (2015)

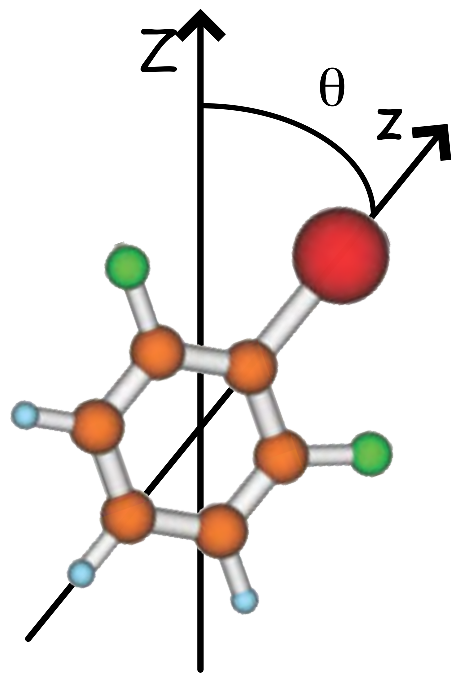
Conformer selection with the m/μ deflector



Filsinger, Erlekam, von Helden, JK, Meijer, *Phys. Rev. Lett.* ***100***, 133003 (2008)
Filsinger, JK, Meijer, Hansen, Maurer, Nielsen, Holmegaard, Stapelfeldt, *Angew. Chem. Int. Ed.* **48**, 6900 (2009)

Molecules in fields
Alignment and orientation with electric fields

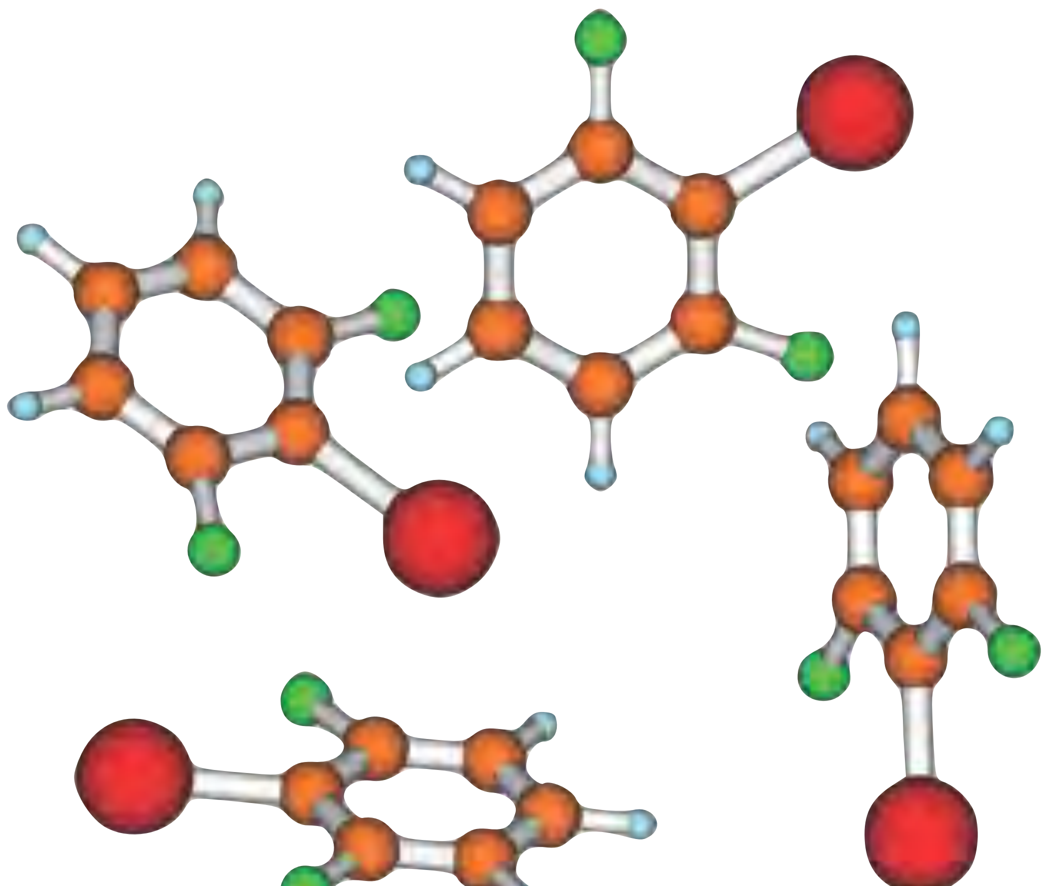
Molecular alignment and orientation
Connecting molecular and laboratory frame



$\langle \cos\theta \rangle$ orientation

$\langle \cos^2\theta \rangle$ alignment

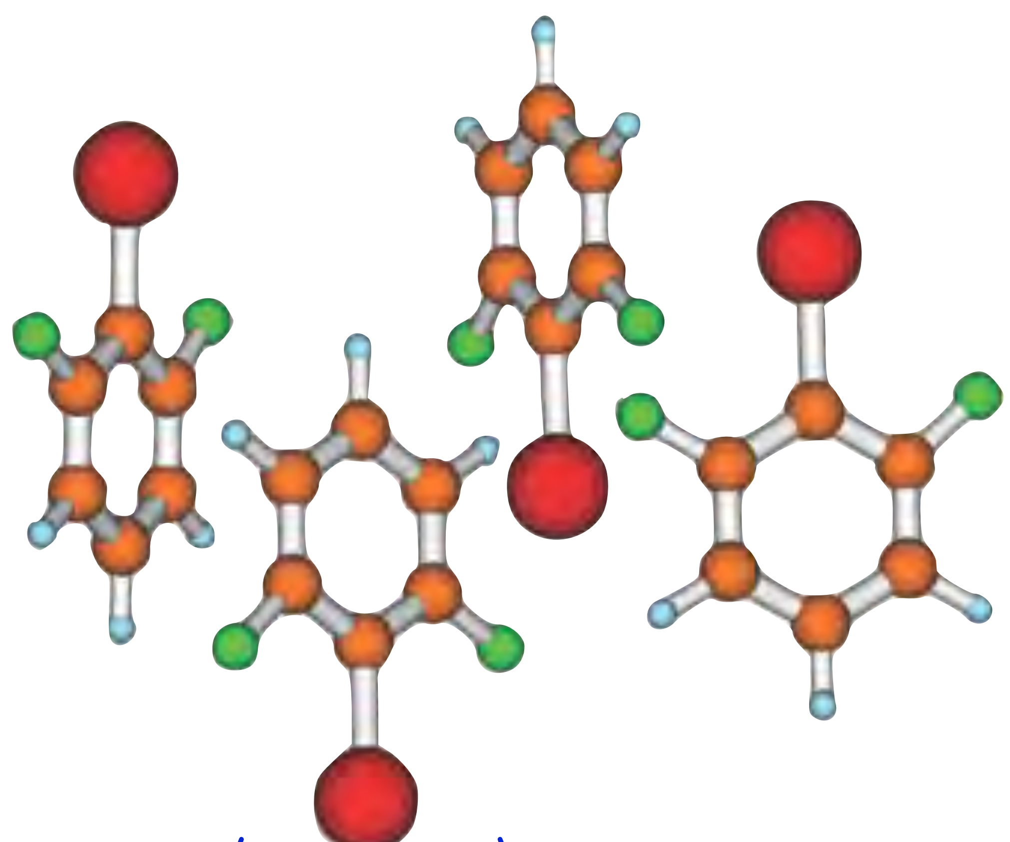
isotropic



$$\langle \cos\theta \rangle = 0$$

$$\langle \cos^2\theta \rangle = 1/3$$

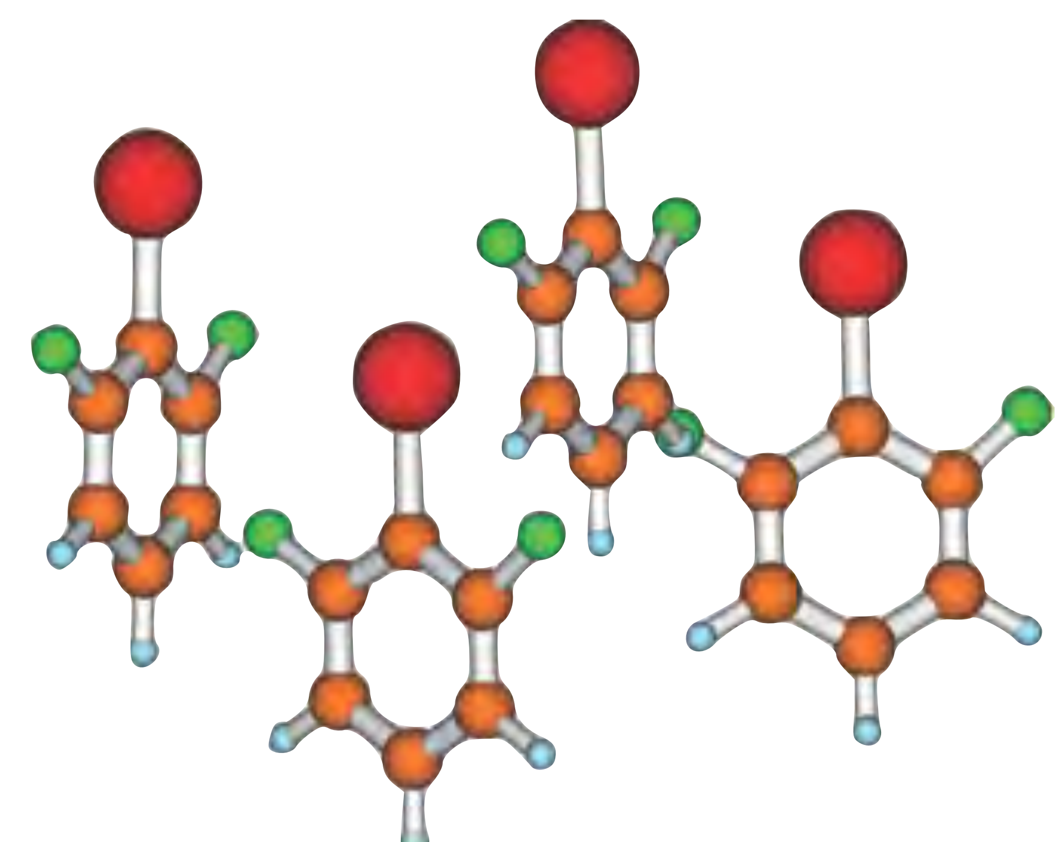
aligned



$$\langle \cos\theta \rangle = 0$$

$$\langle \cos^2\theta \rangle > 1/3$$

oriented



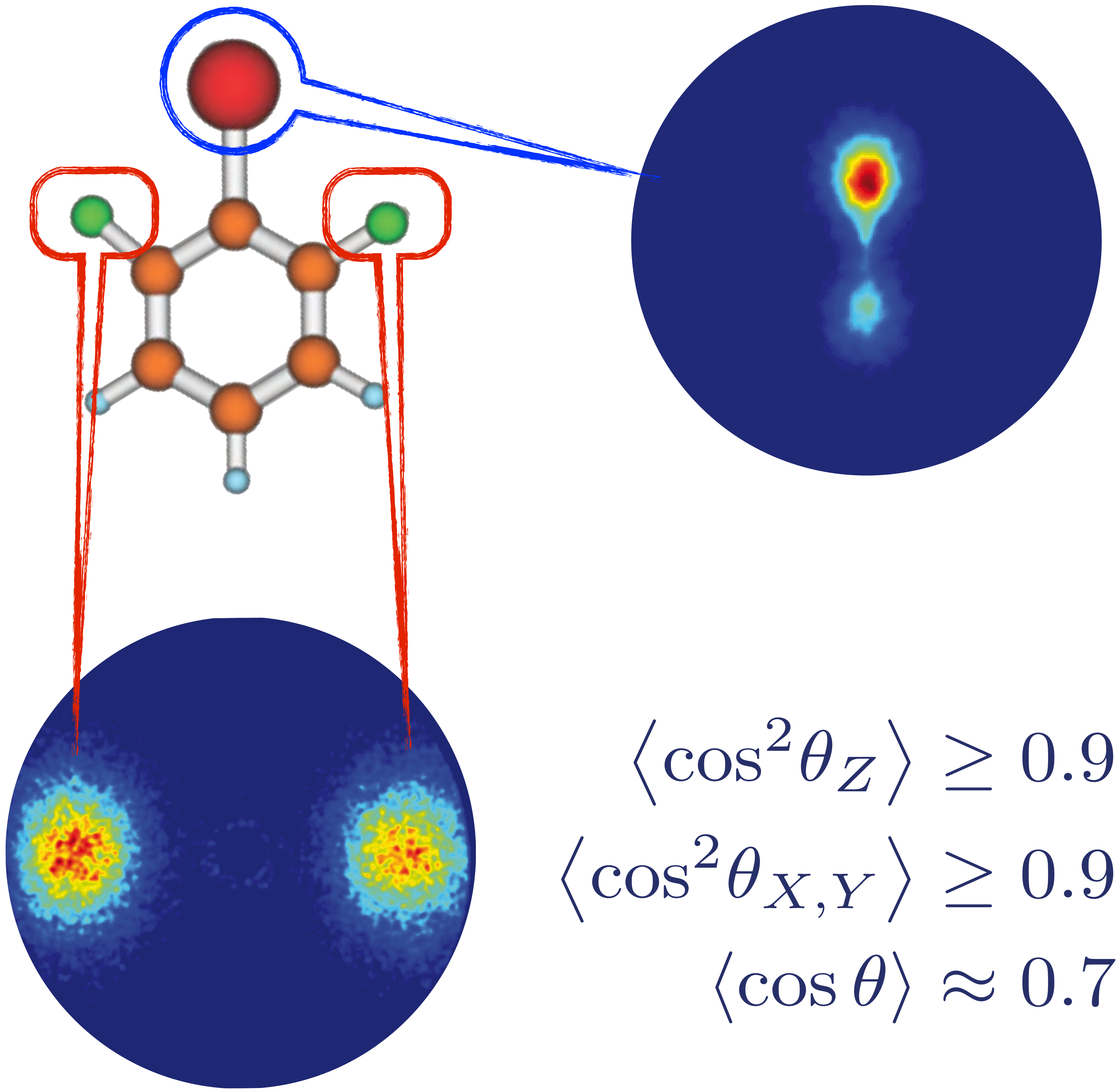
$$\langle \cos\theta \rangle > 0$$

$$\langle \cos^2\theta \rangle > 1/3$$

3D alignment: Larsen, Hald, Bjerre, Stapelfeldt, Seideman, *Phys. Rev. Lett*. **85**, 2470 (2000)

3D orientation: Nevo, Holmegaard, Nielsen, Hansen, Stapelfeldt, Filsinger, Meijer, JK, *Phys. Chem. Chem. Phys*. **11**, 9912 (2009)

Molecular alignment and orientation
Connecting molecular and laboratory frame



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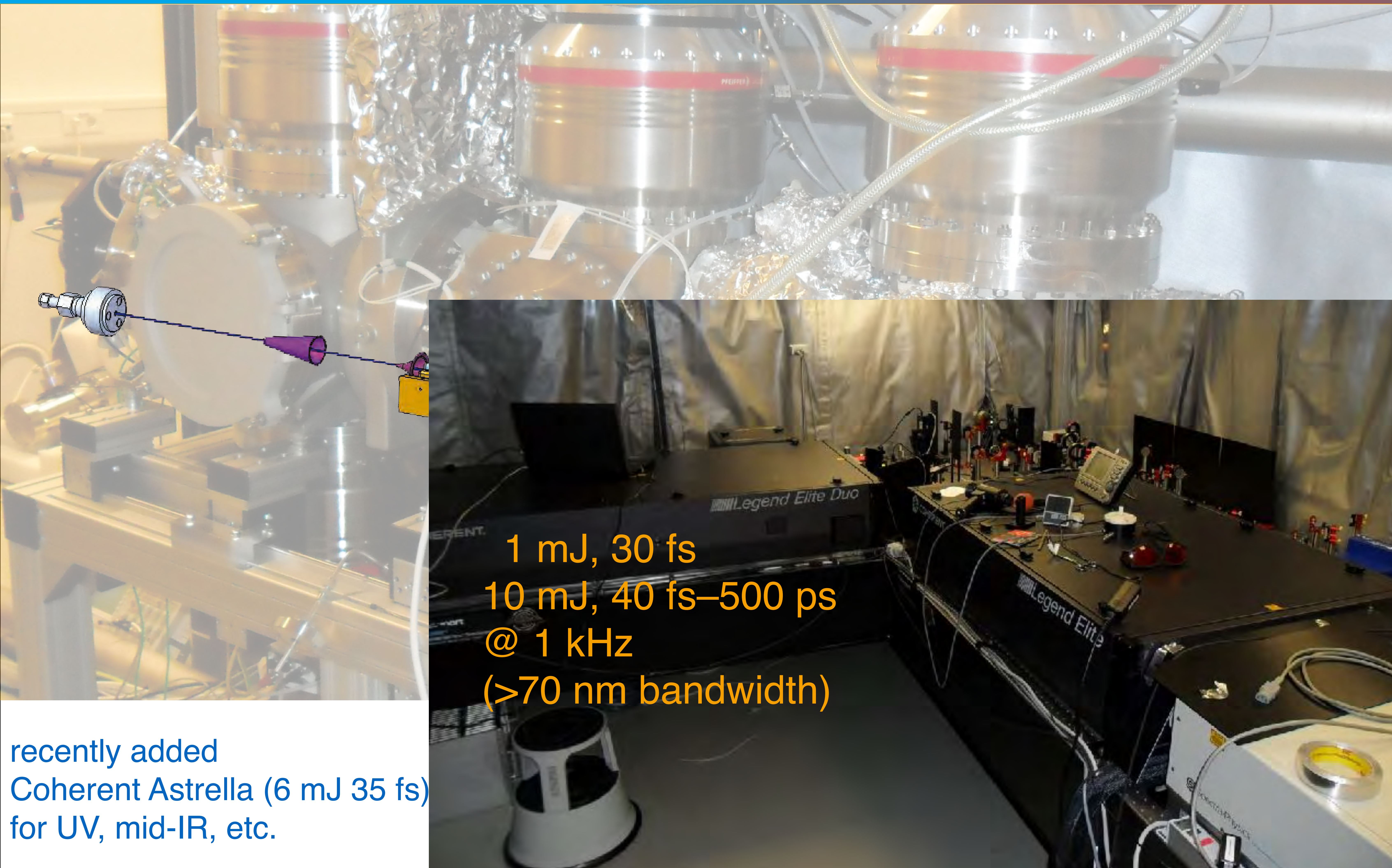
Holmegaard, Nielsen, Nevo, Stapelfeldt, Filsinger, JK, Meijer, *Phys. Rev. Lett.* **102**, 023001 (2009)
Nevo, Holmegaard, Nielsen, Hansen, Stapelfeldt, Filsinger, Meijer, JK, *Phys. Chem. Chem. Phys.* **11**, 9912 (2009)

Toward time-resolved *imaging of chemical dynamics*
kHz-rate manipulation experiments

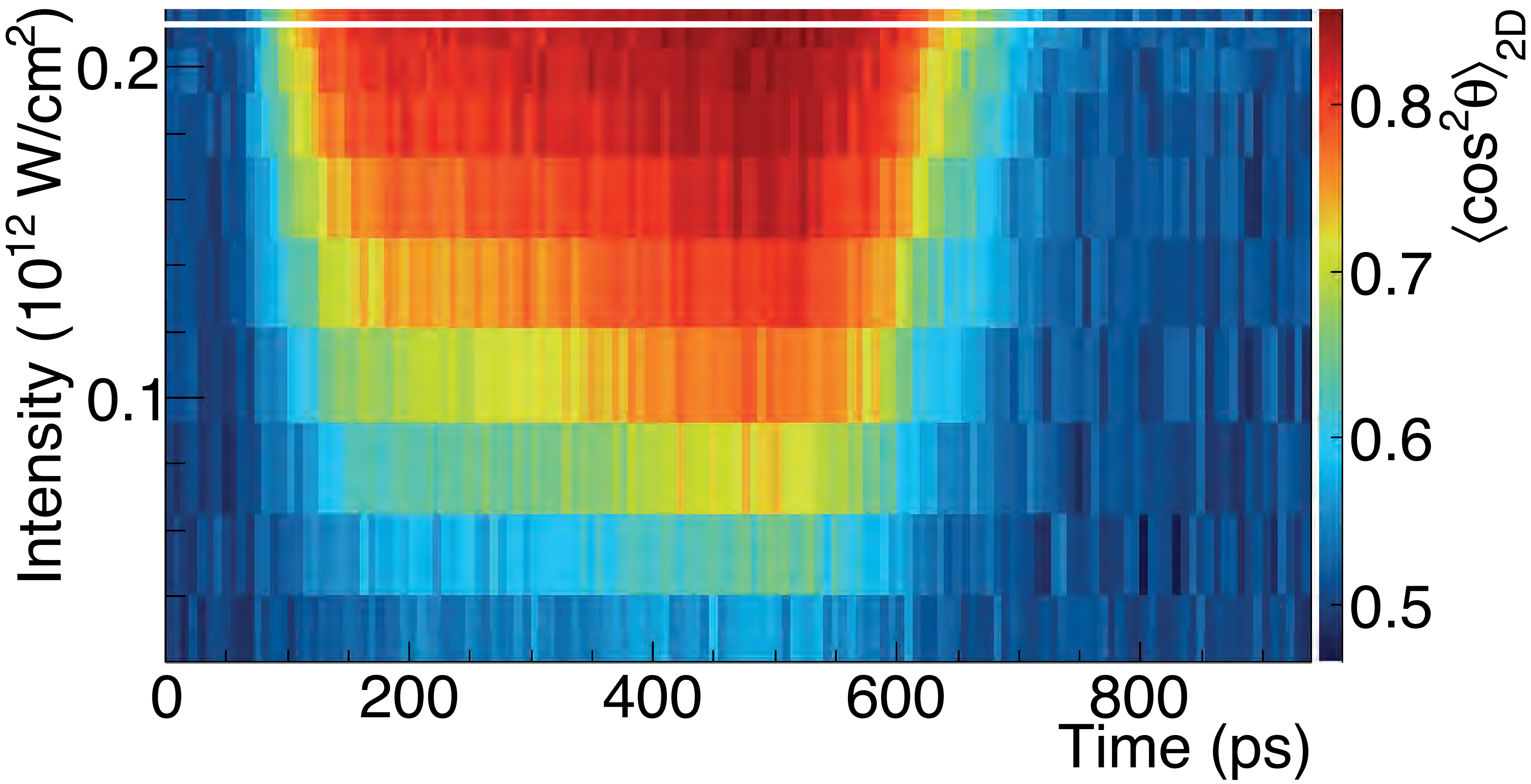


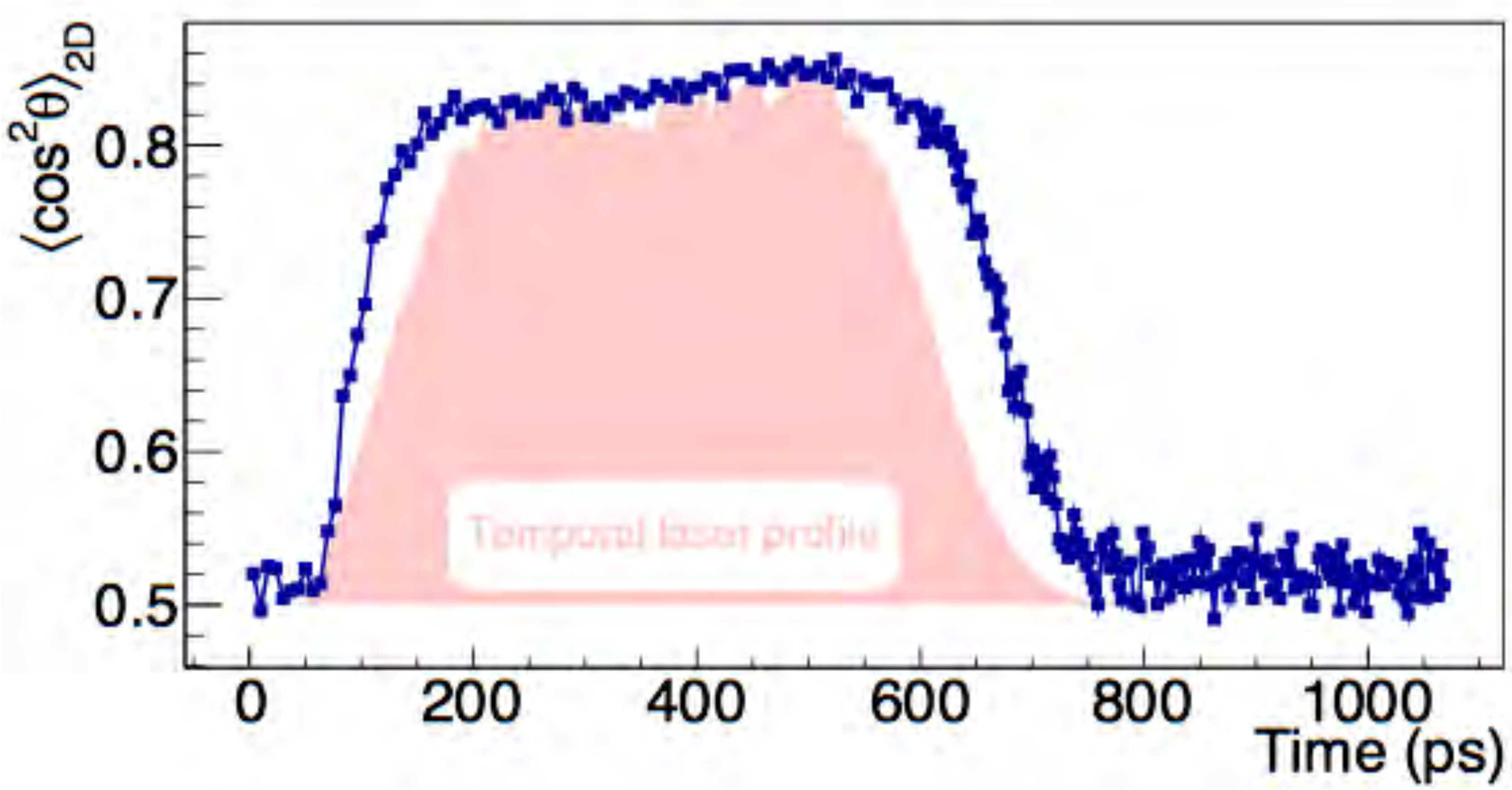
1 mJ, 30 fs
10 mJ, 40 fs–500 ps
@ 1 kHz
(>70 nm bandwidth)

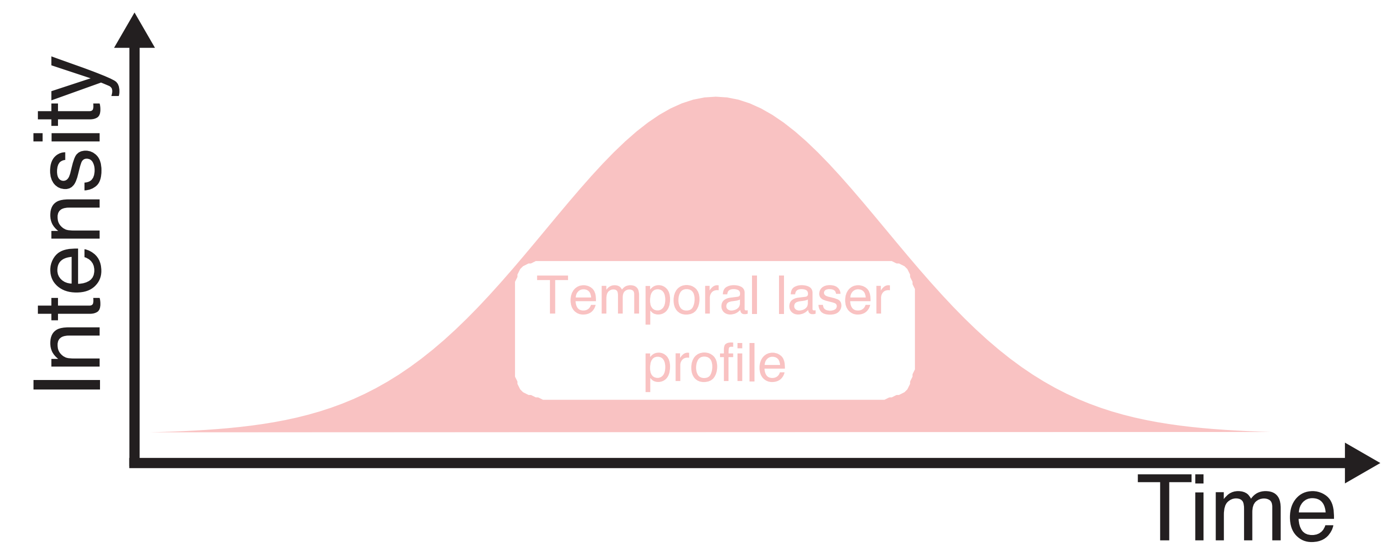
recently added
Coherent Astrella (6 mJ 35 fs)
for UV, mid-IR, etc.

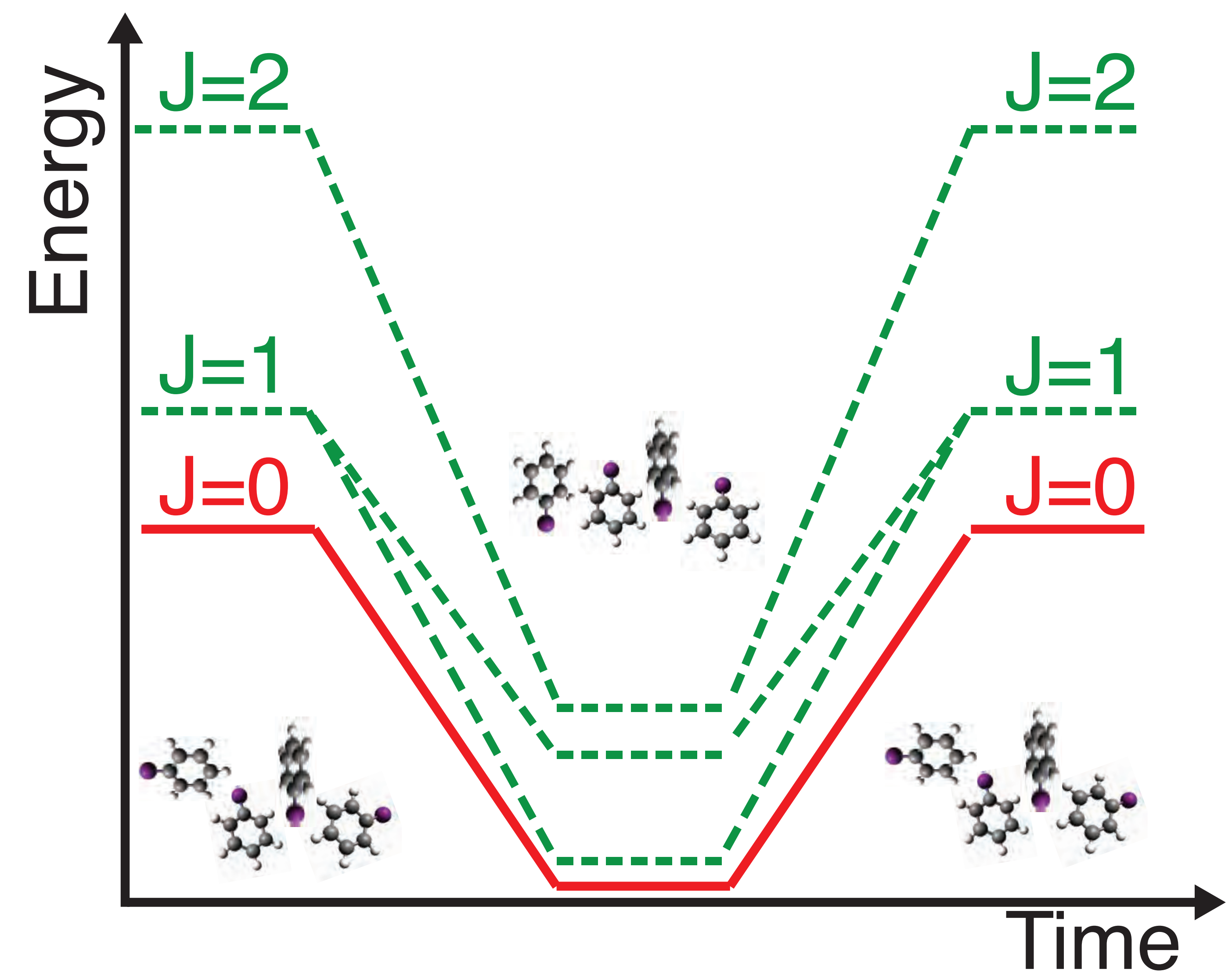
Trippel, Mullins, Müller, Kienitz, Długołęcki, JK, *Mol. Phys.* **111**, 1738-1743 (2013, Bretislav Friedrich Festschrift)

Scenarios of rotational dynamics in OCS (X, v=0, J=0)
Adiabatic alignment with a 485 ps pulse



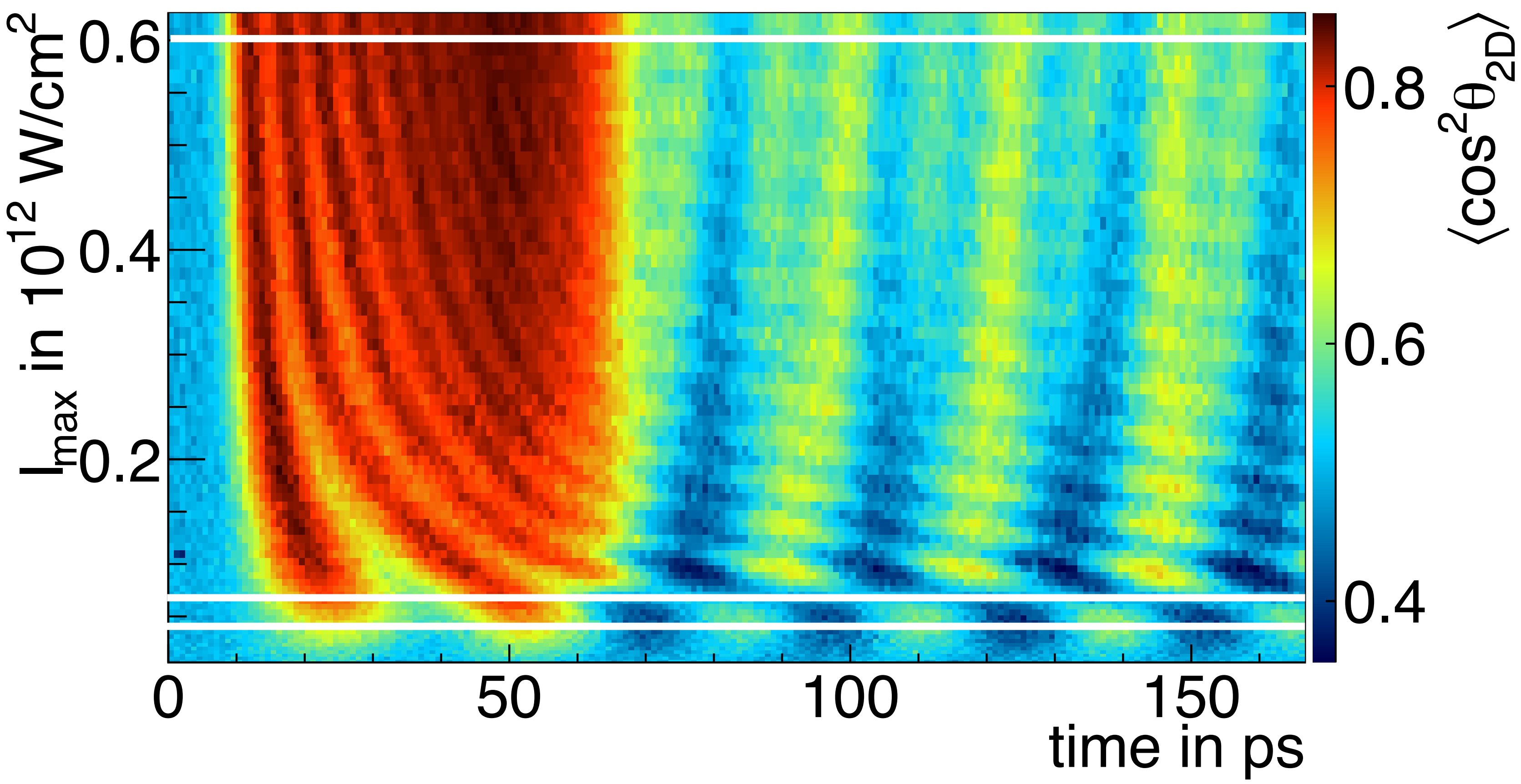


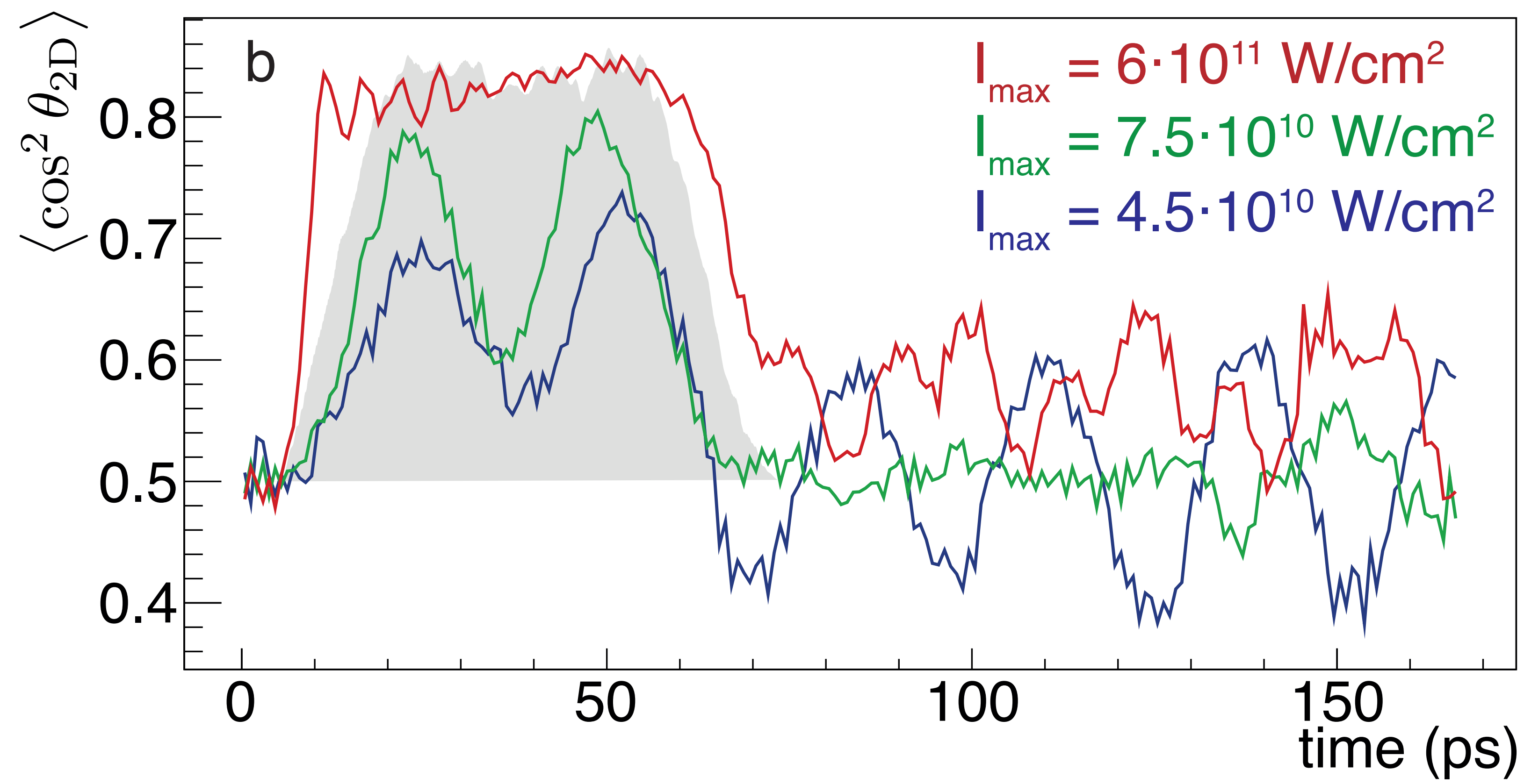




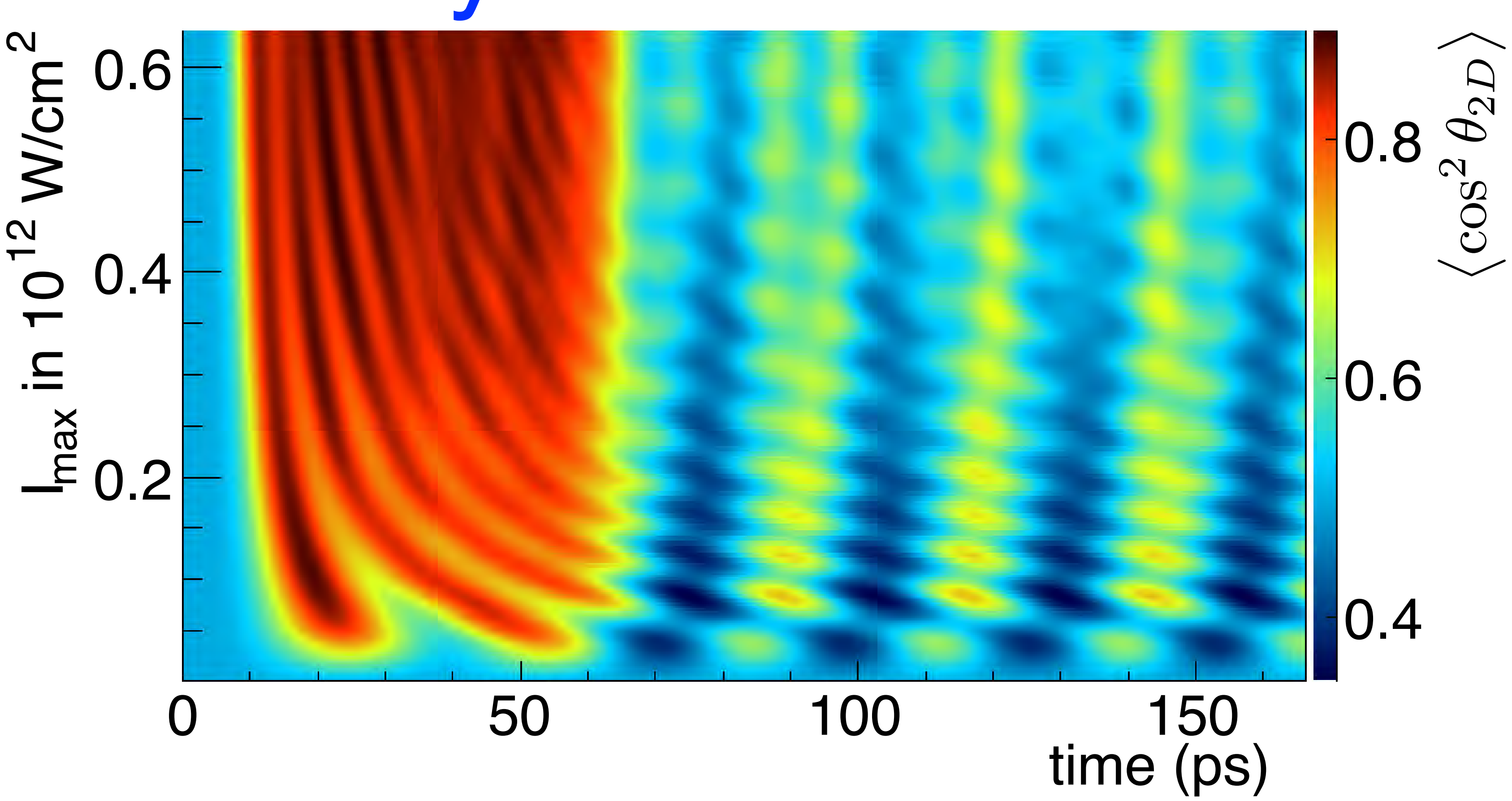
Scenarios of rotational dynamics in OCS (X, v=0, J=0)
Intermediate-case alignment with a 50 ps pulse

experiment





theory

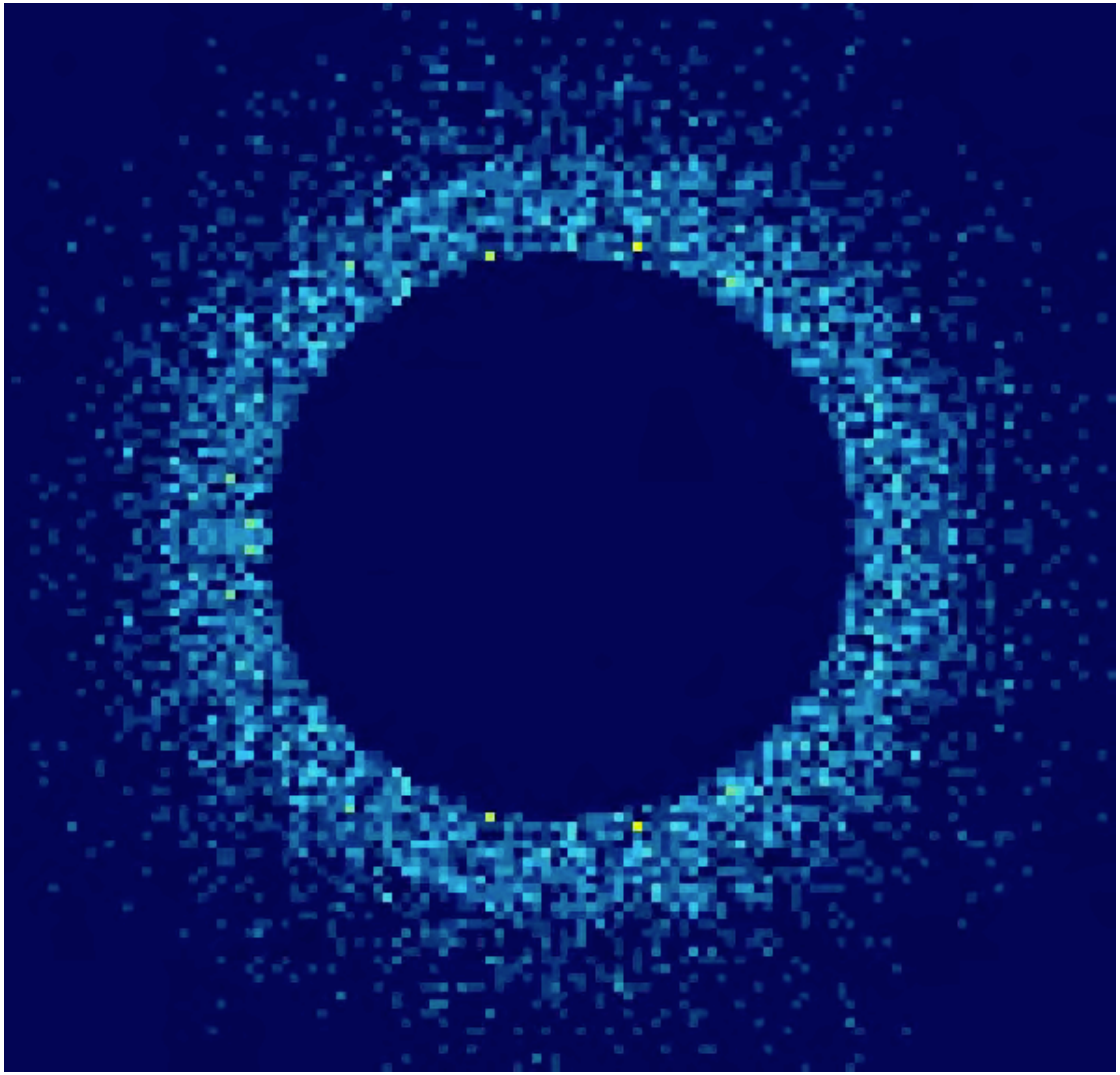


A simple two state wave packet,
a working coherent-control experiment
and a strongly-driven quantum pendulum

Achievable degree of alignment
is comparable to adiabatic case!

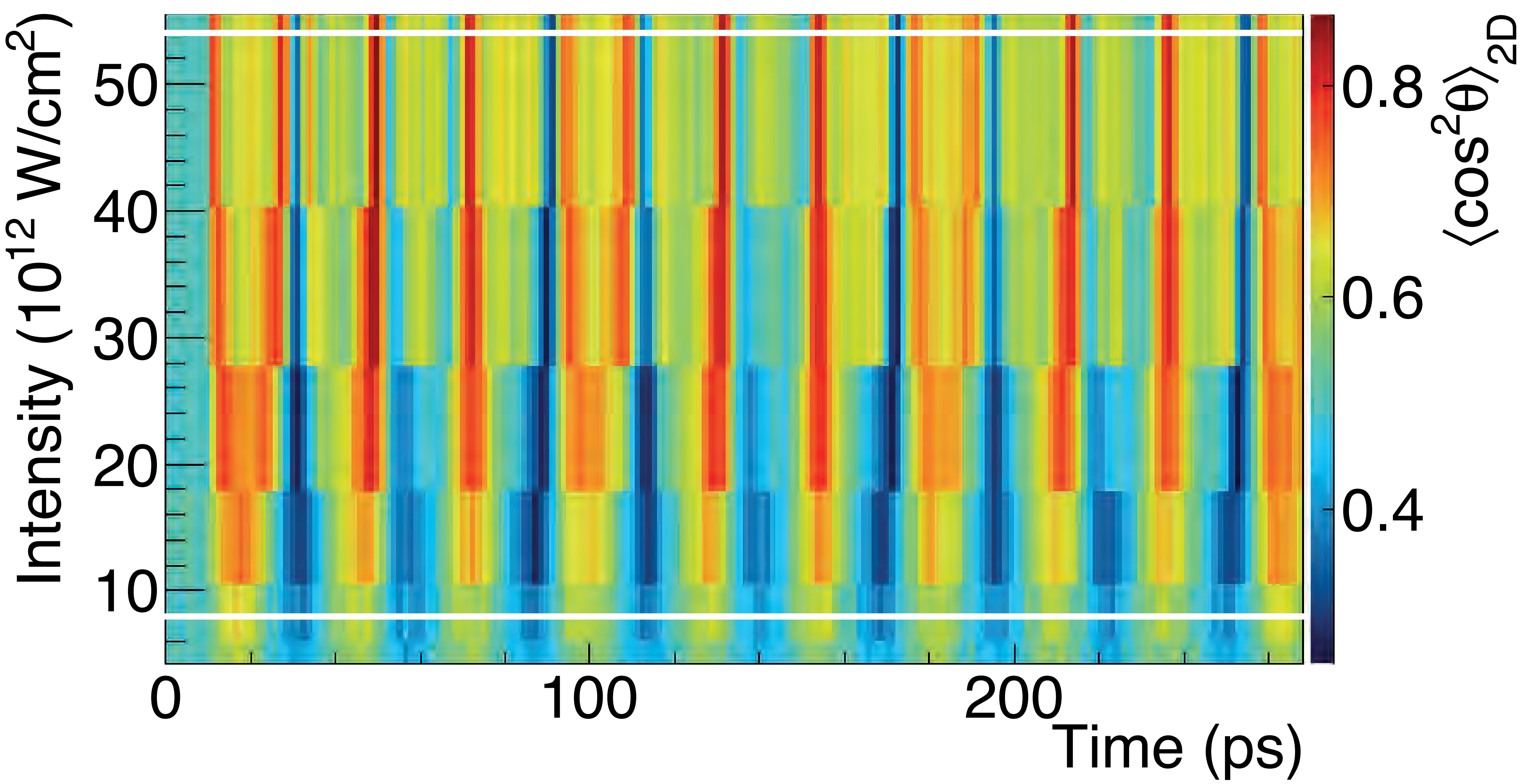
Trippel, Mullins, Müller, Kienitz, Omiste, Stapelfeldt, González Férez, JK, *Phys. Rev.* A **89**, 051401(R) (2014)

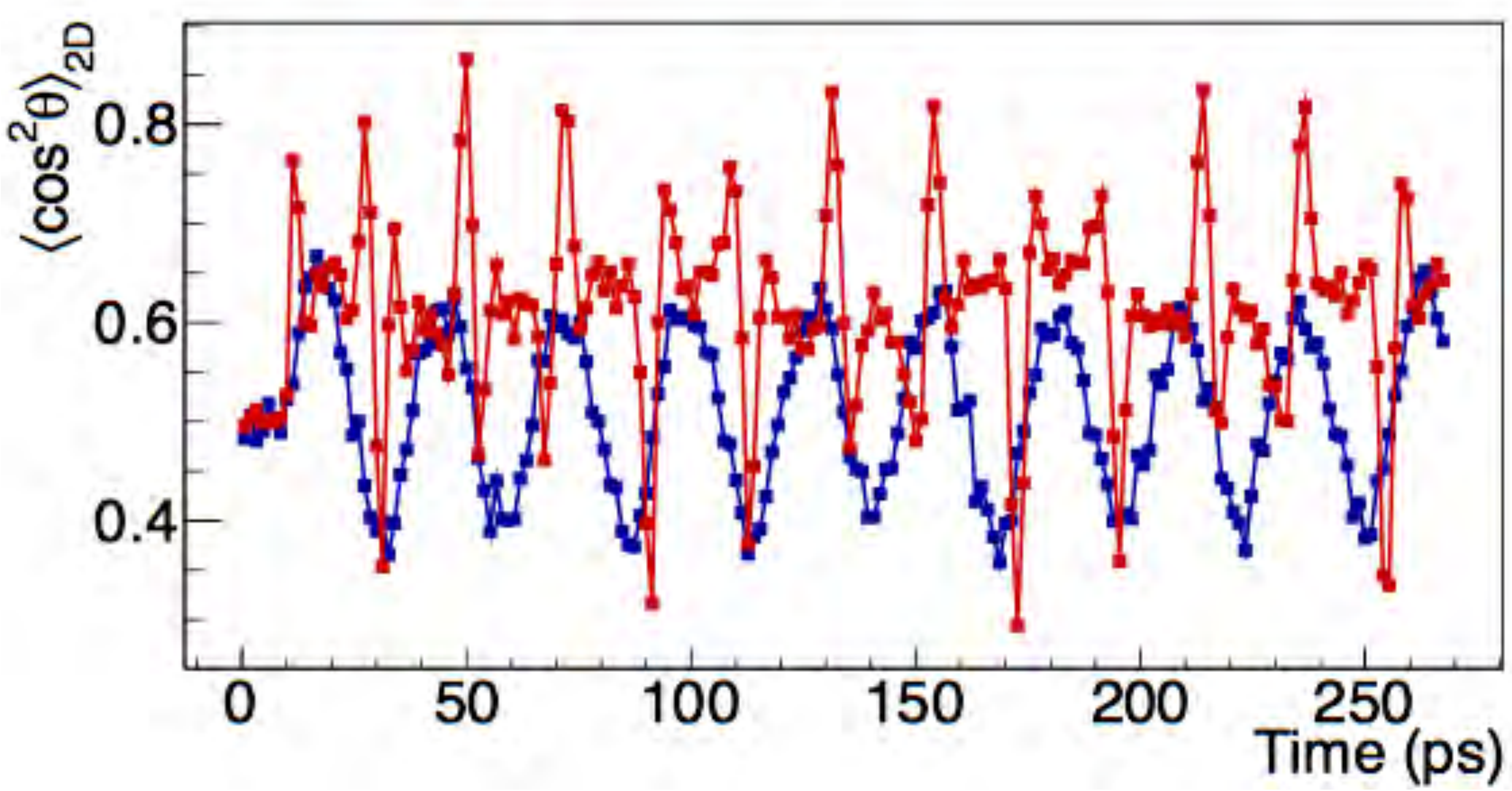
Scenarios of rotational dynamics in OCS (X, v=0, J=0)
Intermediate-case alignment with a 50 ps pulse

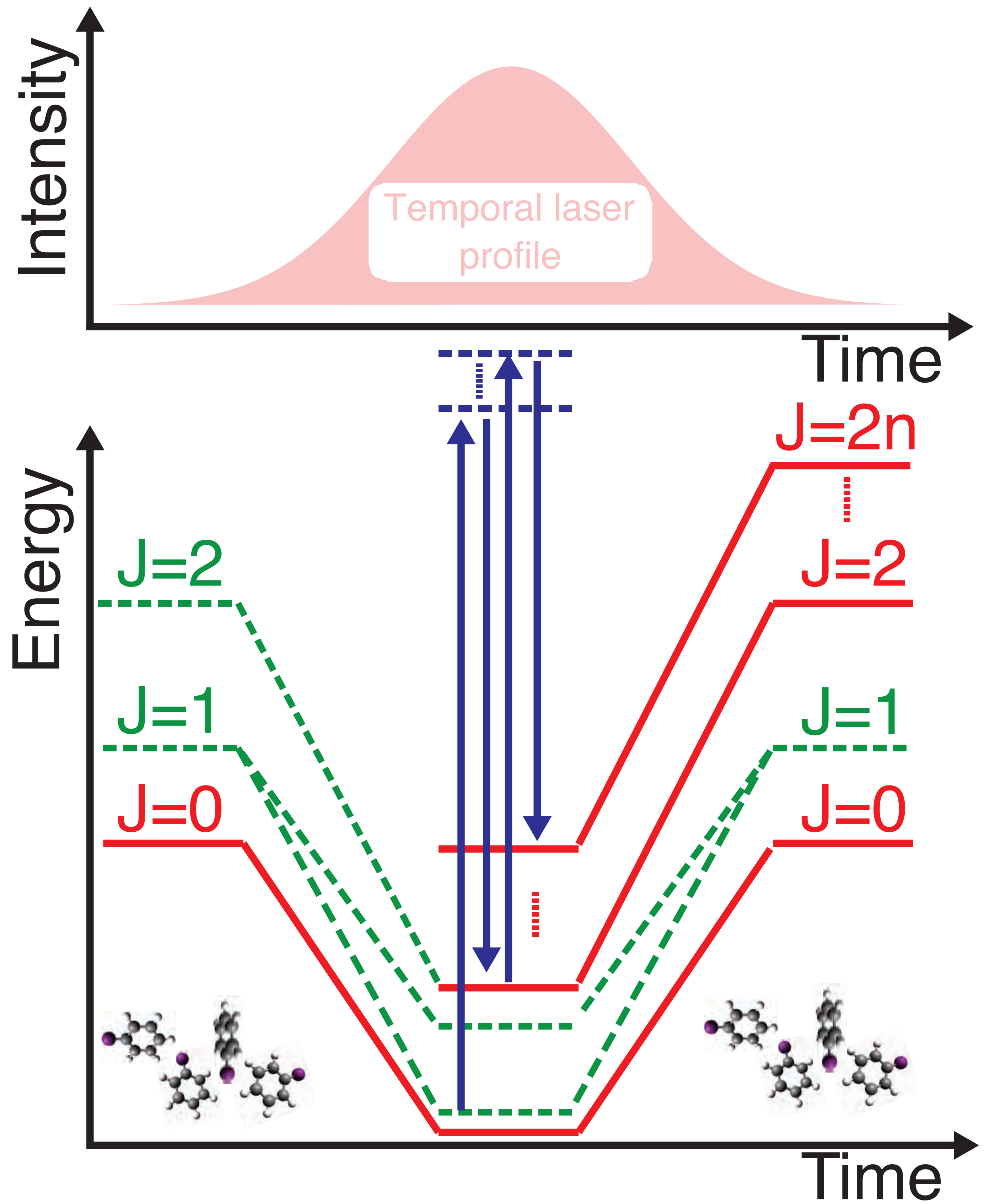


A “molecular movie” at 10^{12} slowdown (80 ps in 80 s)

Scenarios of rotational dynamics in OCS (X, v=0, J=0)
Impulsive alignment with a 50 fs pulse

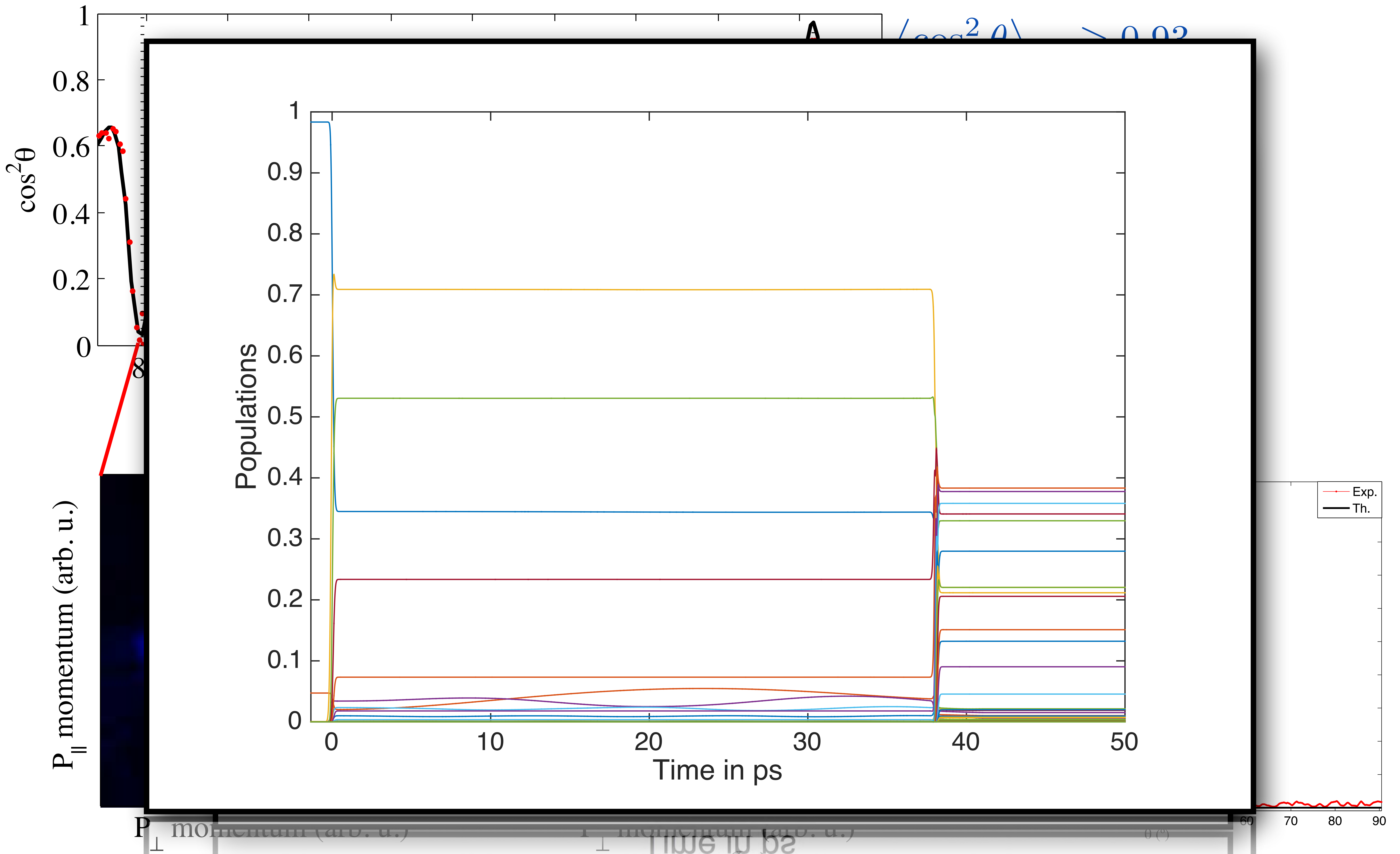






Trippel, Mullins, Müller, Kienitz, Omiste, Stapelfeldt, González Férez, JK, Phys. Rev. A 89, 051401(R) (2014)

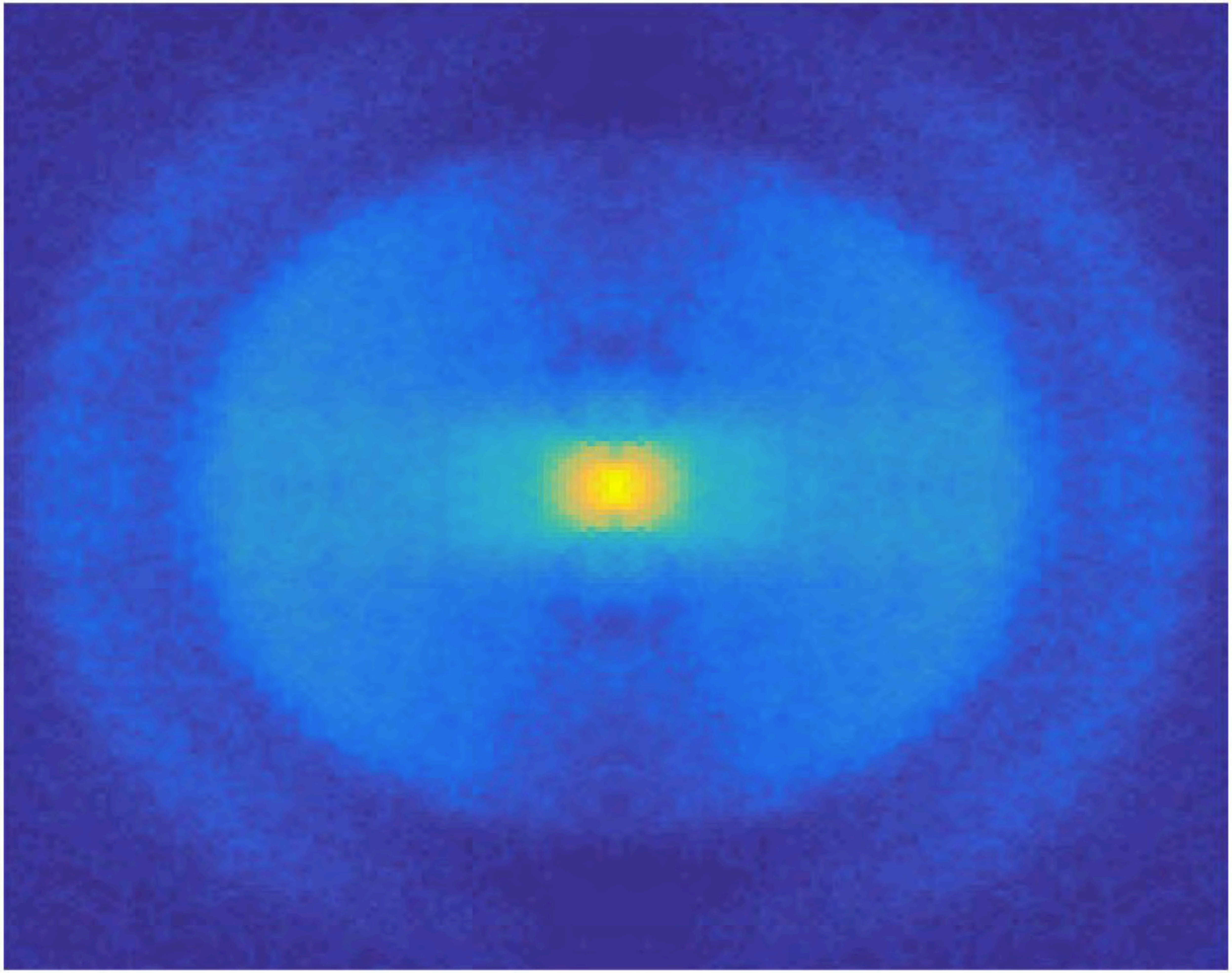
Scenarios of rotational dynamics in OCS (X, v=0, J=0)
Very strong alignment using two short pulses



with Arnaud Rouzée, MBI Berlin

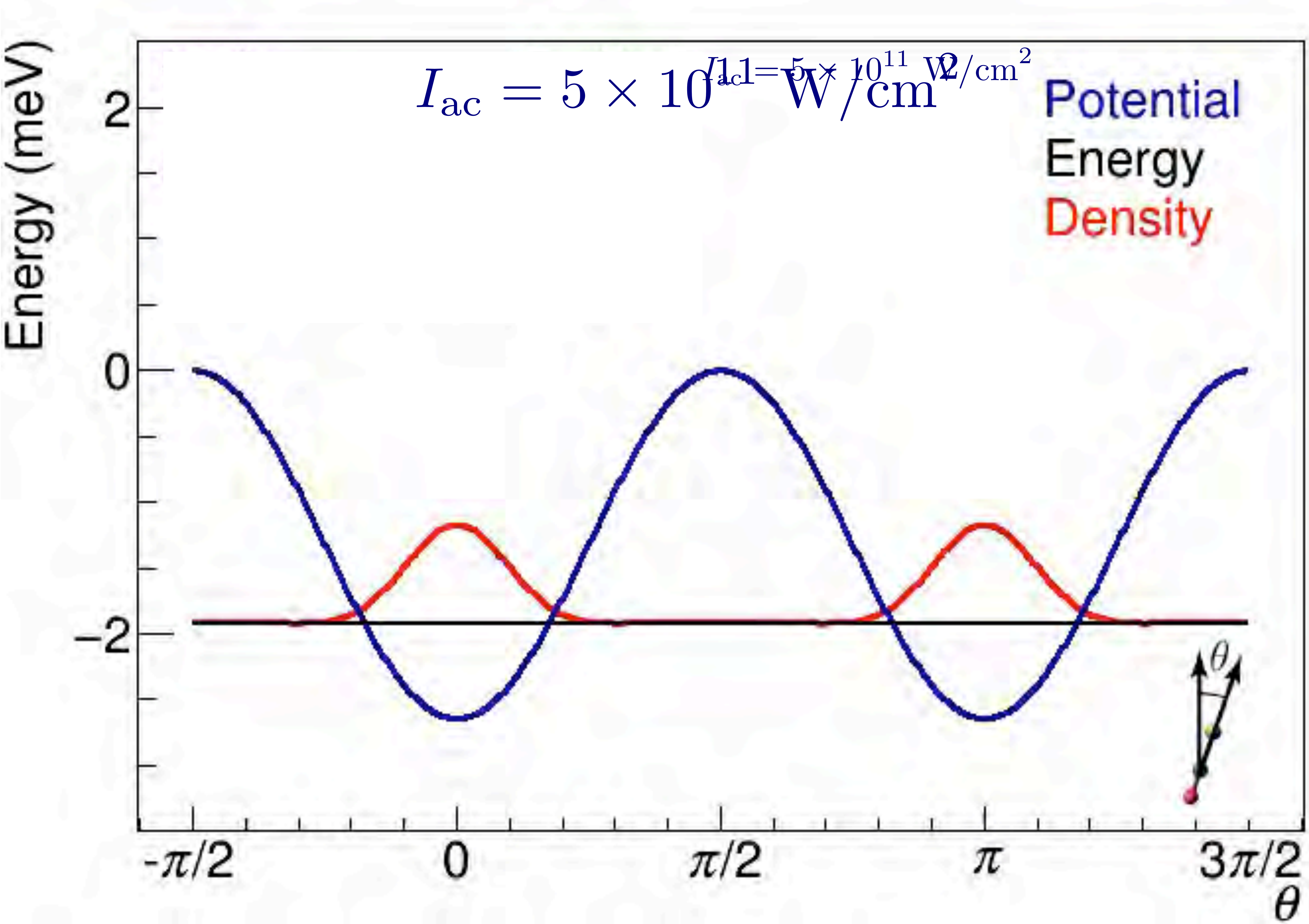
Scenarios of rotational dynamics in OCS (X, v=0, J=0)
Imaging quantum-revivals

-0.75355 ps

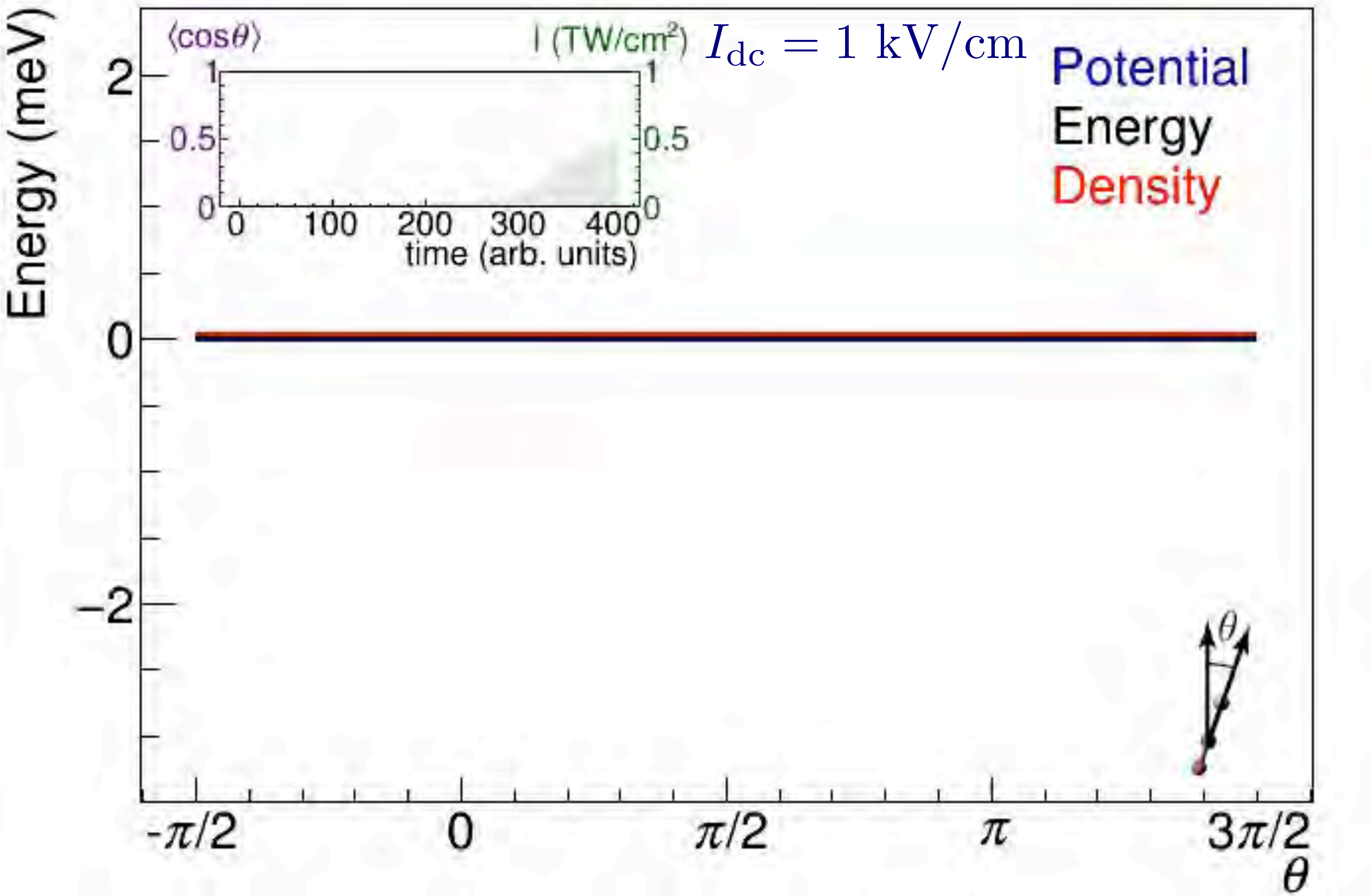


with Arnaud Rouzée, MBI Berlin

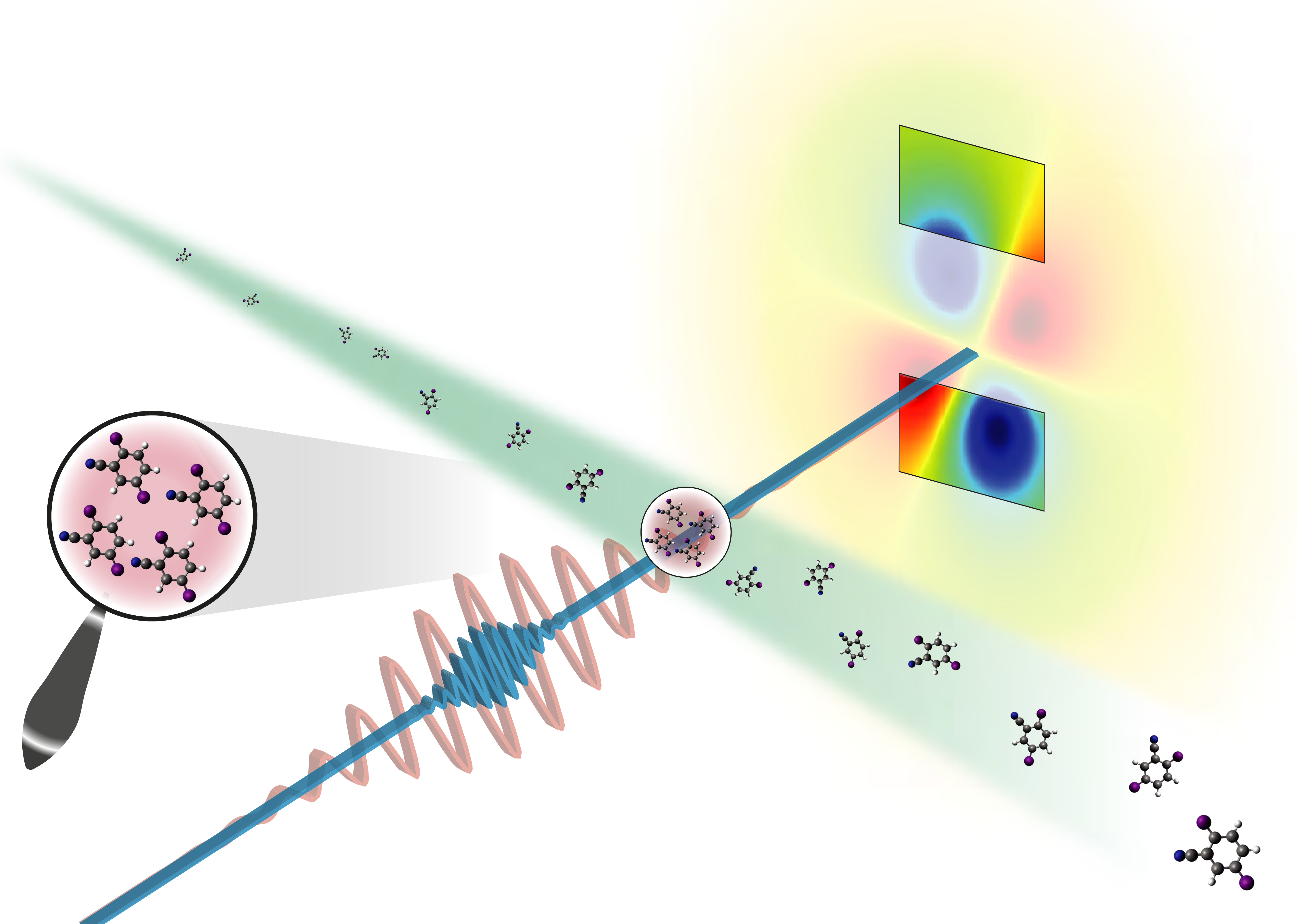
Mixed-field orientation: *The flea on Schrödinger's cat* or how tiny perturbations localize the wave function



Building a double-minimum potential with pertinent asymmetry

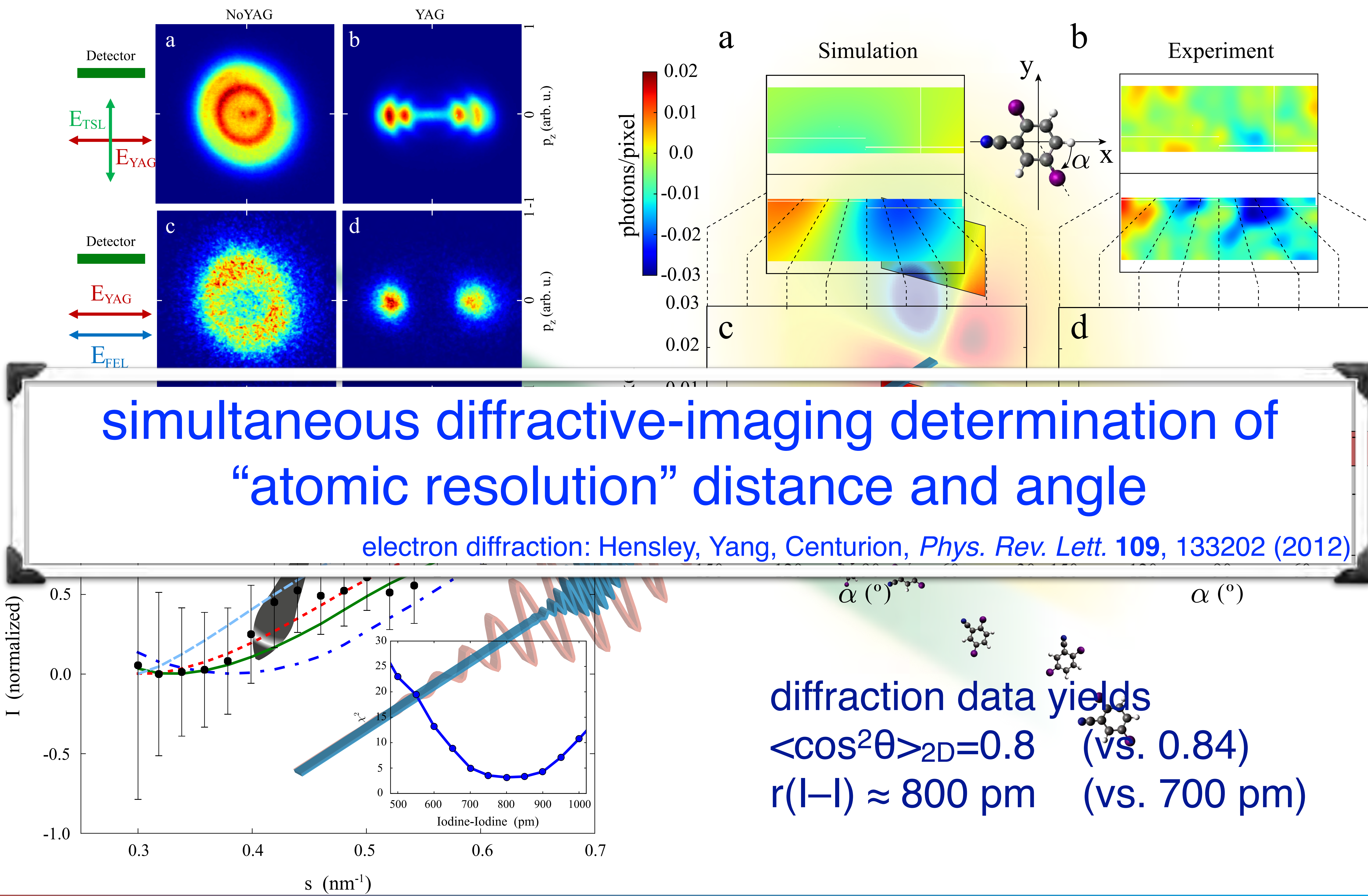


Imaging molecular dynamics with controlled molecules



JK, et al (53 authors), *Phys. Rev. Lett.*, **112**, 083002 (2014)

Coherent diffractive imaging of isolated molecules
100 pm precision from 0.5 nm^{-1} diffraction (λ = 620 pm)



simultaneous diffractive-imaging determination of "atomic resolution" distance and angle

electron diffraction: Hensley, Yang, Centurion, *Phys. Rev. Lett.* **109**, 133202 (2012)

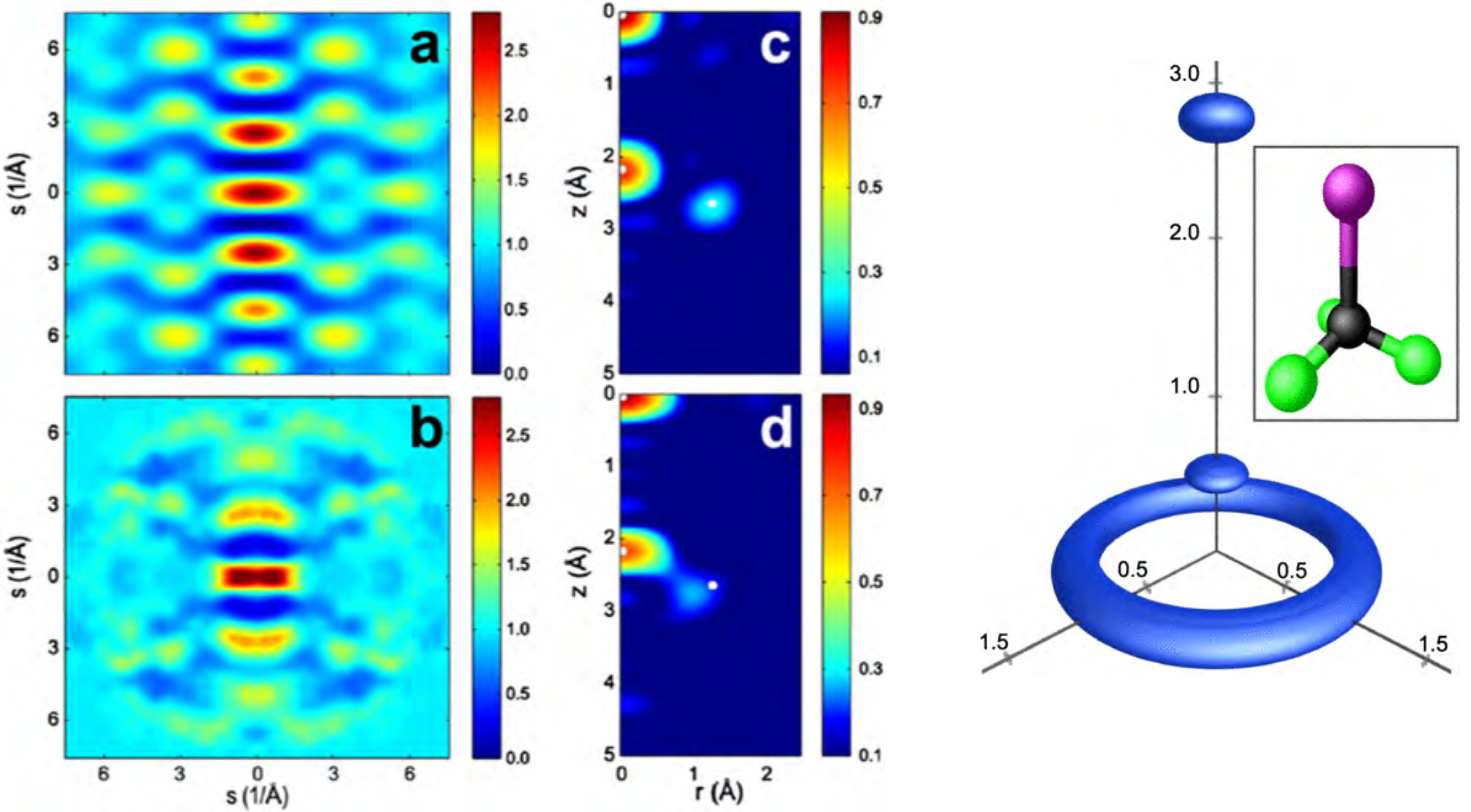
diffraction data yields

$<\cos^2\theta>_{2D}$=0.8 (vs. 0.84)

r(I–I) ≈ 800 pm (vs. 700 pm)

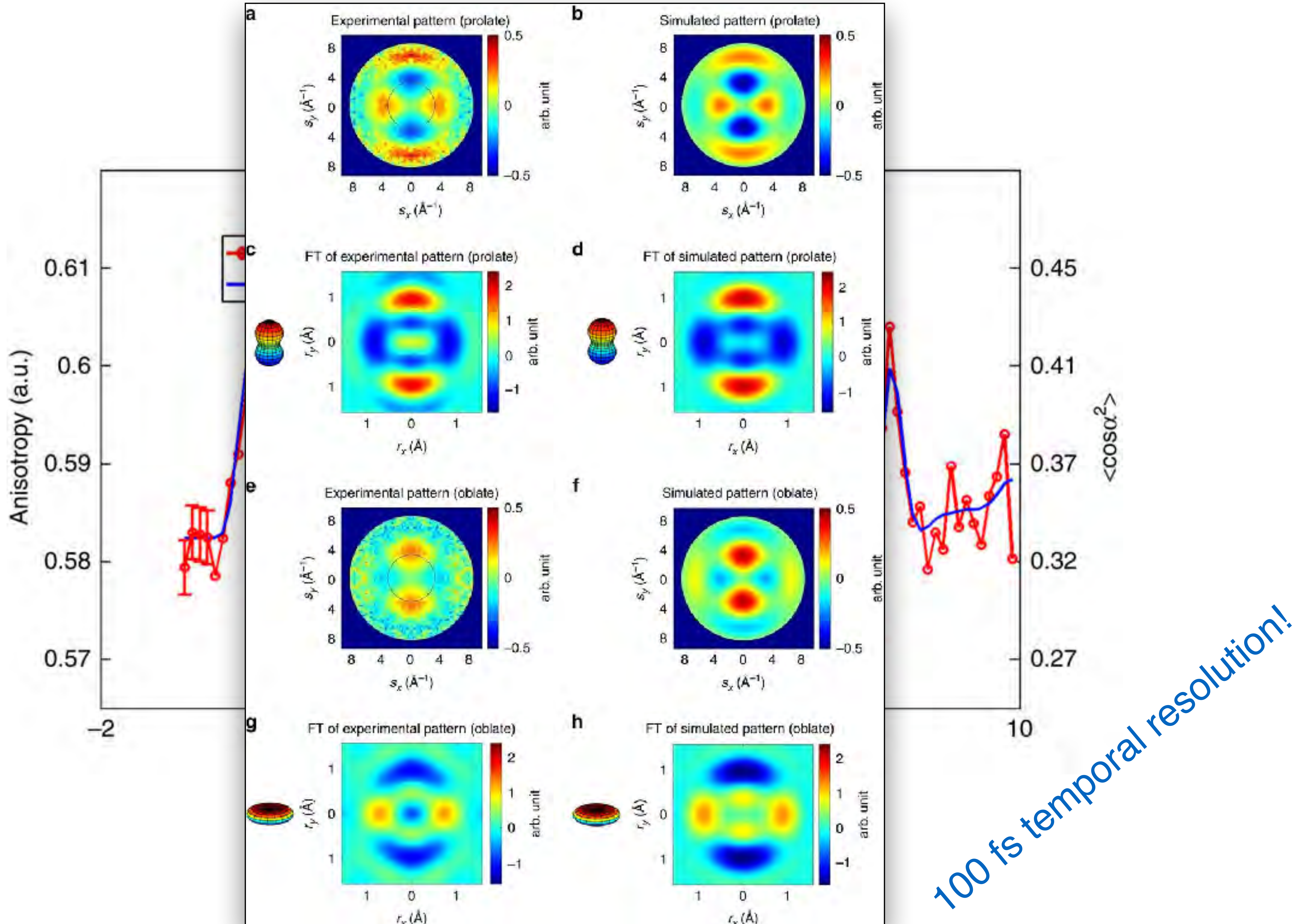
JK, et al (53 authors), *Phys. Rev. Lett.*, **112**, 083002 (2014)

Imaging of Isolated Molecules with Ultrafast Electron Pulses



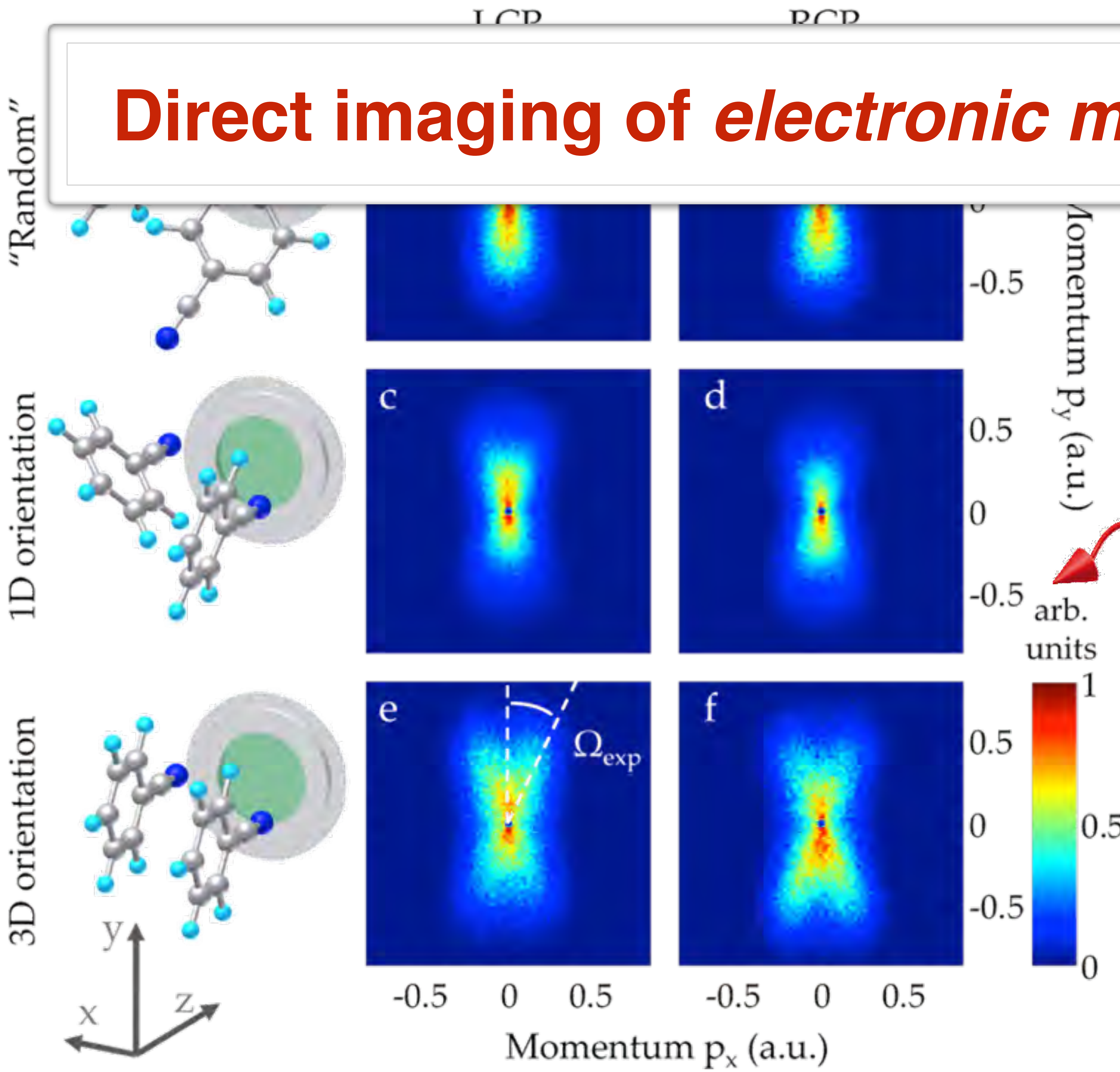
Hensley, Yang, Centurion, *Phys. Rev. Lett.* **109**, 133202 (2012)
Centurion, *J. Phys.* B **49**, 062002 (2016)

Diffractive imaging of (rotational) dynamics

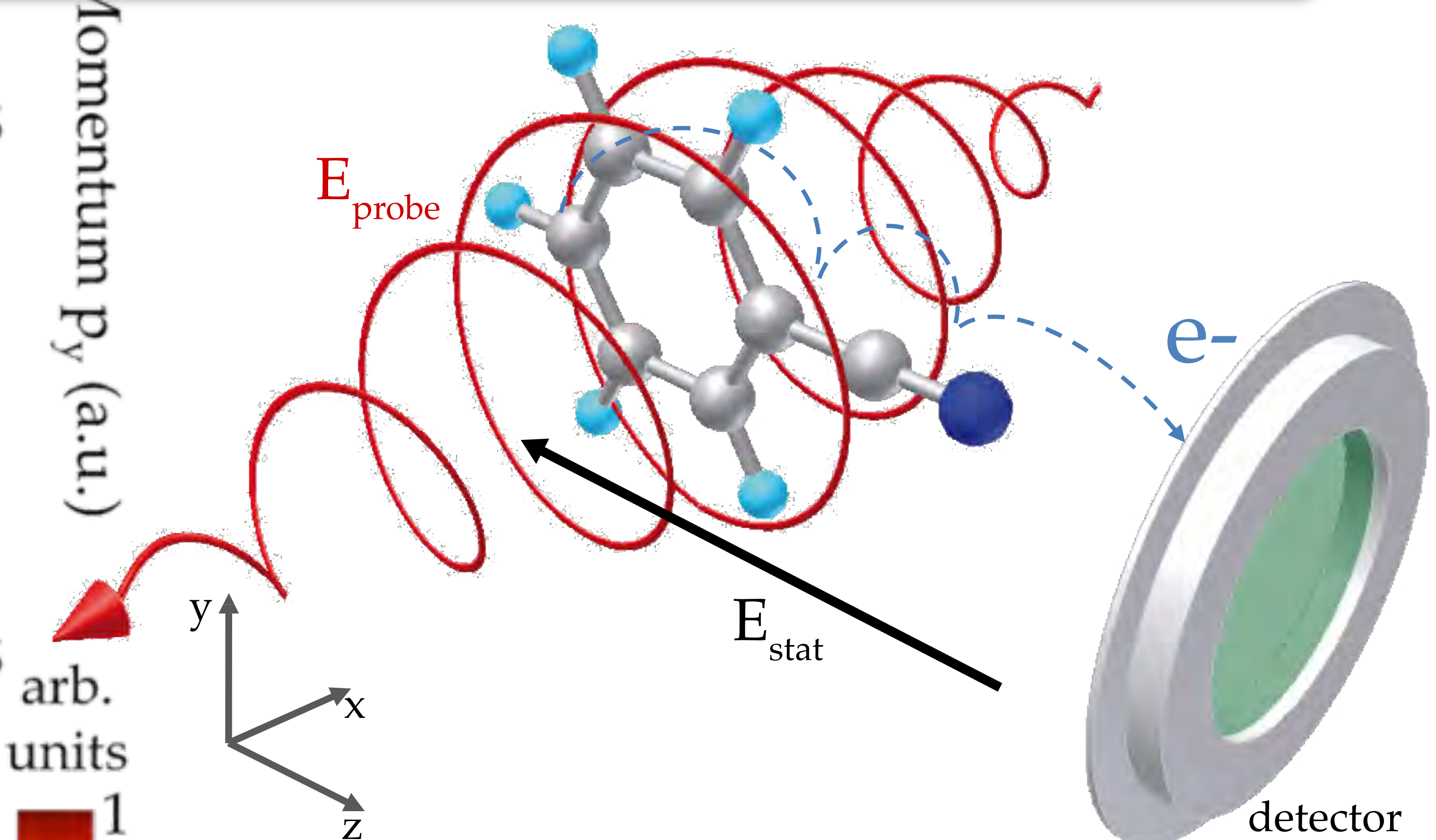


Gühr, Centurion, Wang, et al (23 authors), *Nat. Comms.* **7**, 11232 (2016)

Molecular frame photoelectron angular distributions of 3D-oriented benzonitrile molecules



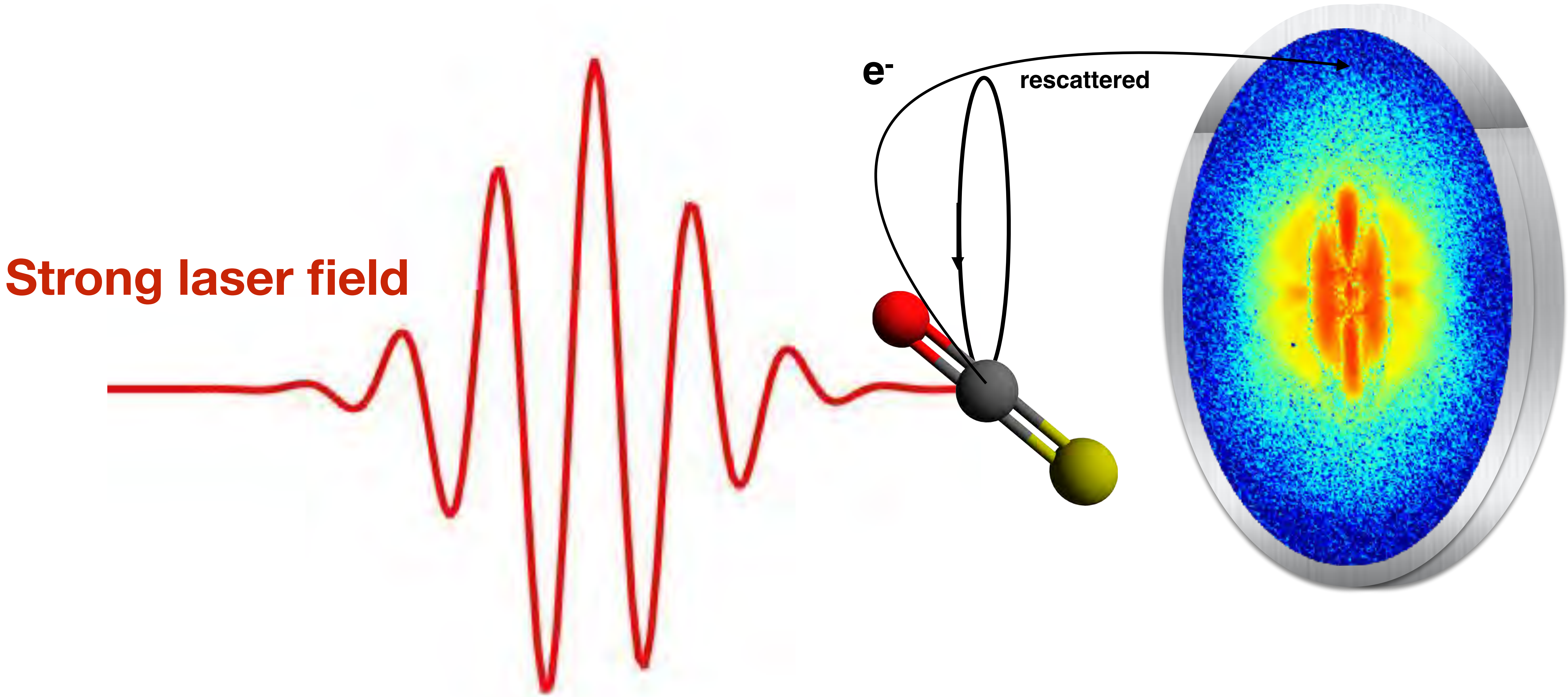
Direct imaging of *electronic molecular structure*



E_{stat} = 467 V/cm
$E_{control}$ = 7 × 10^{11} W/cm^2
E_{probe} = 1.2 × 10^{14} W/cm^2

Holmegaard, Hansen, Kalhøj, Kragh, Stapelfeldt, Filsinger, JK, Meijer, Dimitrovski, Abu-samha, Martiny, Madsen, *Nature Phys*. **6**, 428 (2010)

Laser induced electron diffraction



Direct imaging of *nuclear molecular structure*

“game”: electron trajectories in an external field