Ultrafast dynamics in microsolvated biomolecules

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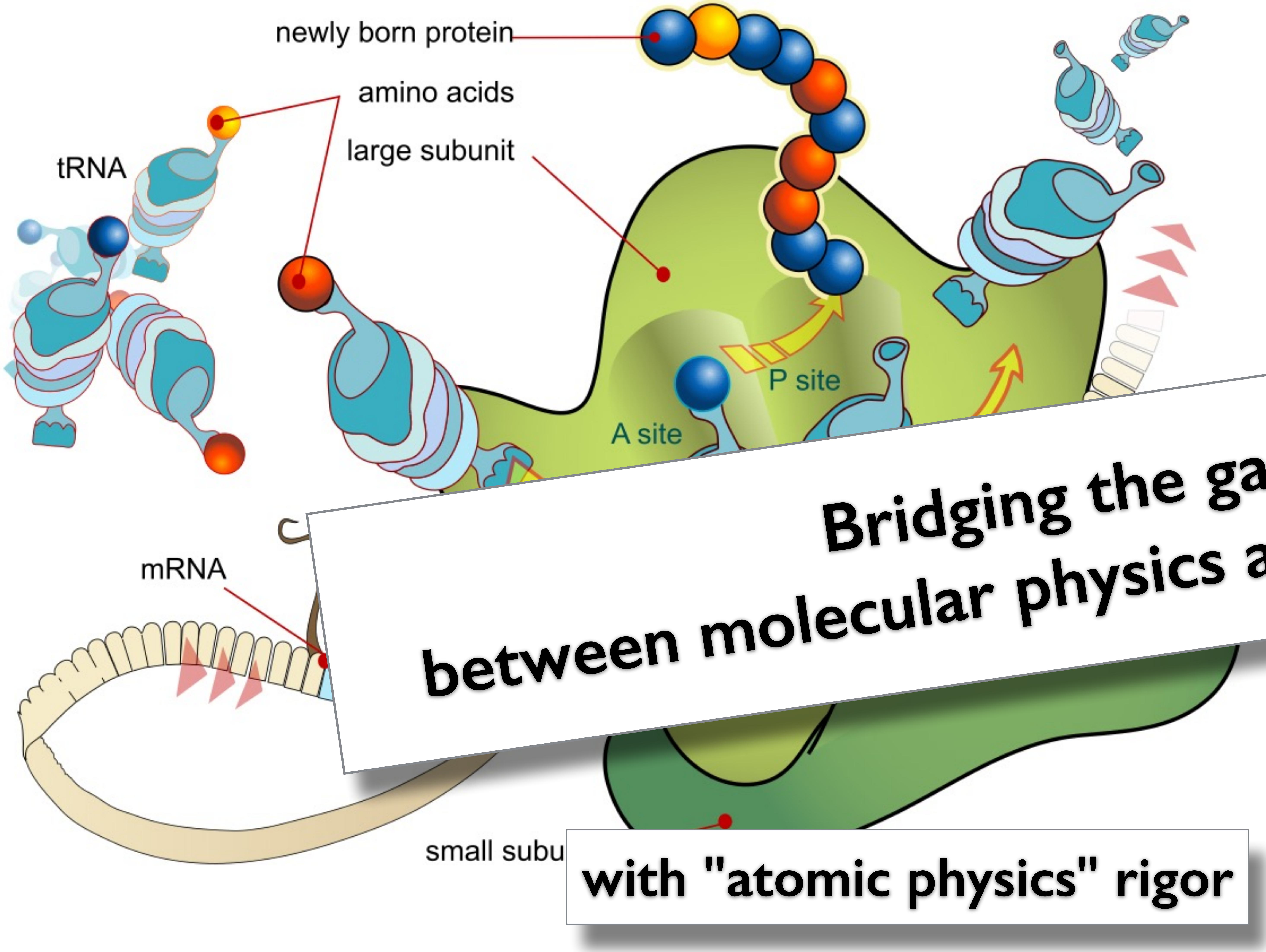
CUI THE HAMBURG CENTER FOR ULTRAFAST IMAGING

UHH Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

CFEL SCIENCE
Controlled Molecule Imaging

DESY.

Motivation: Unraveling elementary steps of (bio)chemical dynamics
Fun example: Ribosome, one complex molecular machine



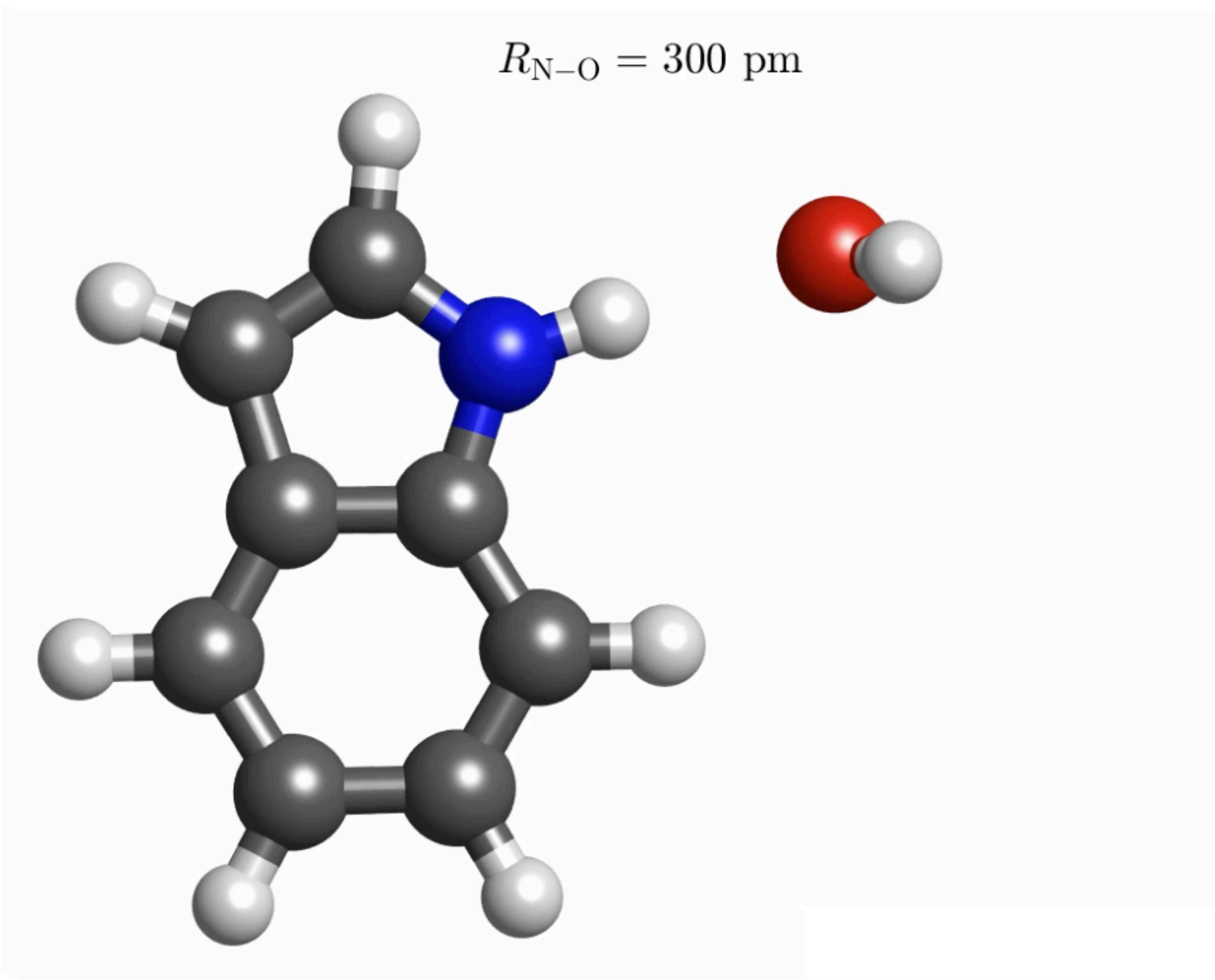
- molecular structure and structural recognition
- intermolecular interactions, hydrogen bonding, and the ... that allows ... nit rotation
- ...aking) of chemical bonds, incl. the peptide bond
- ***(how) can we understand the details (of the parts)?***

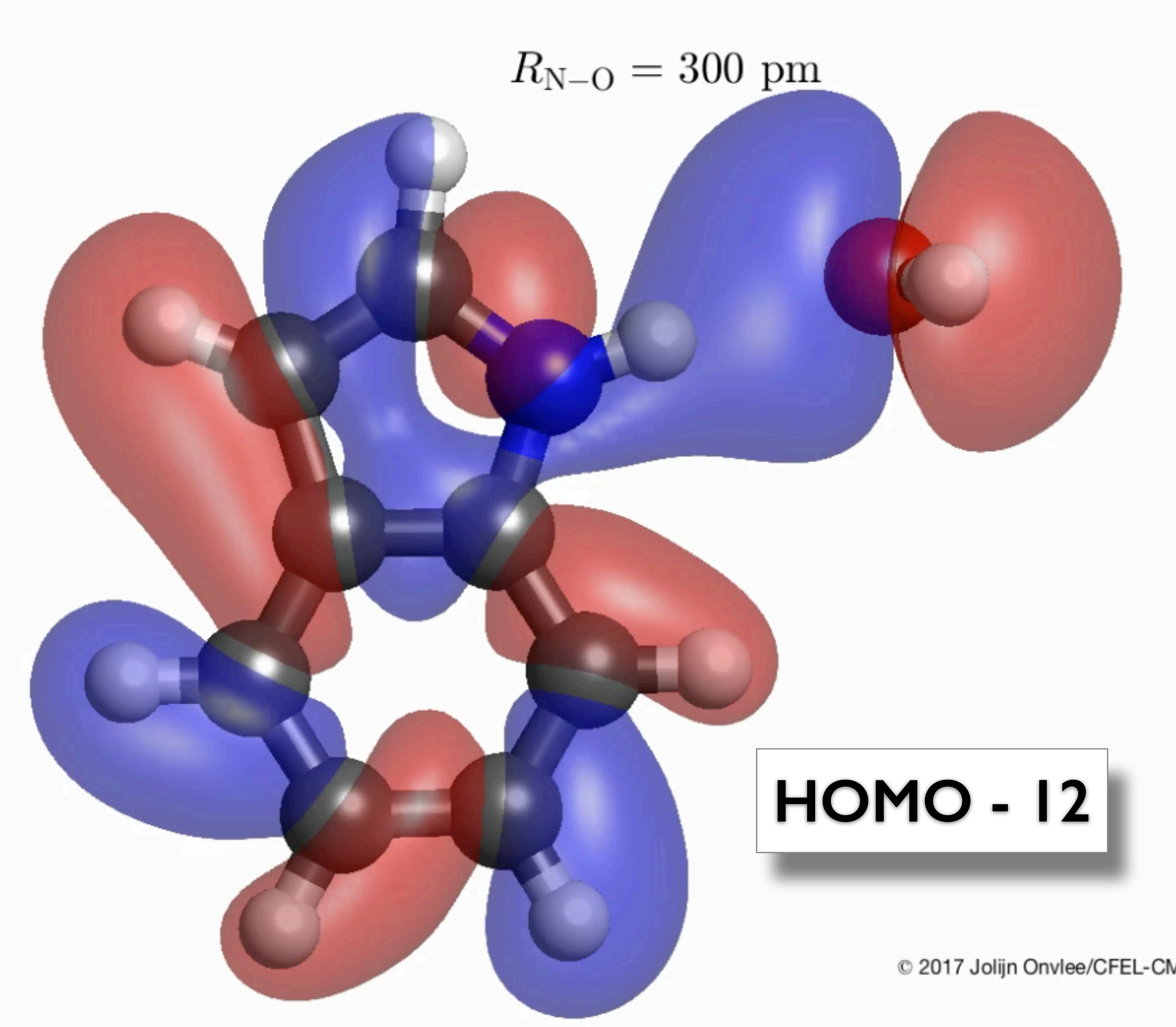
artists rendering (downloaded from Wikipedia, 2018)

Motivation: unraveling (bio)chemistry in real time and real space

SLAC website (2019)

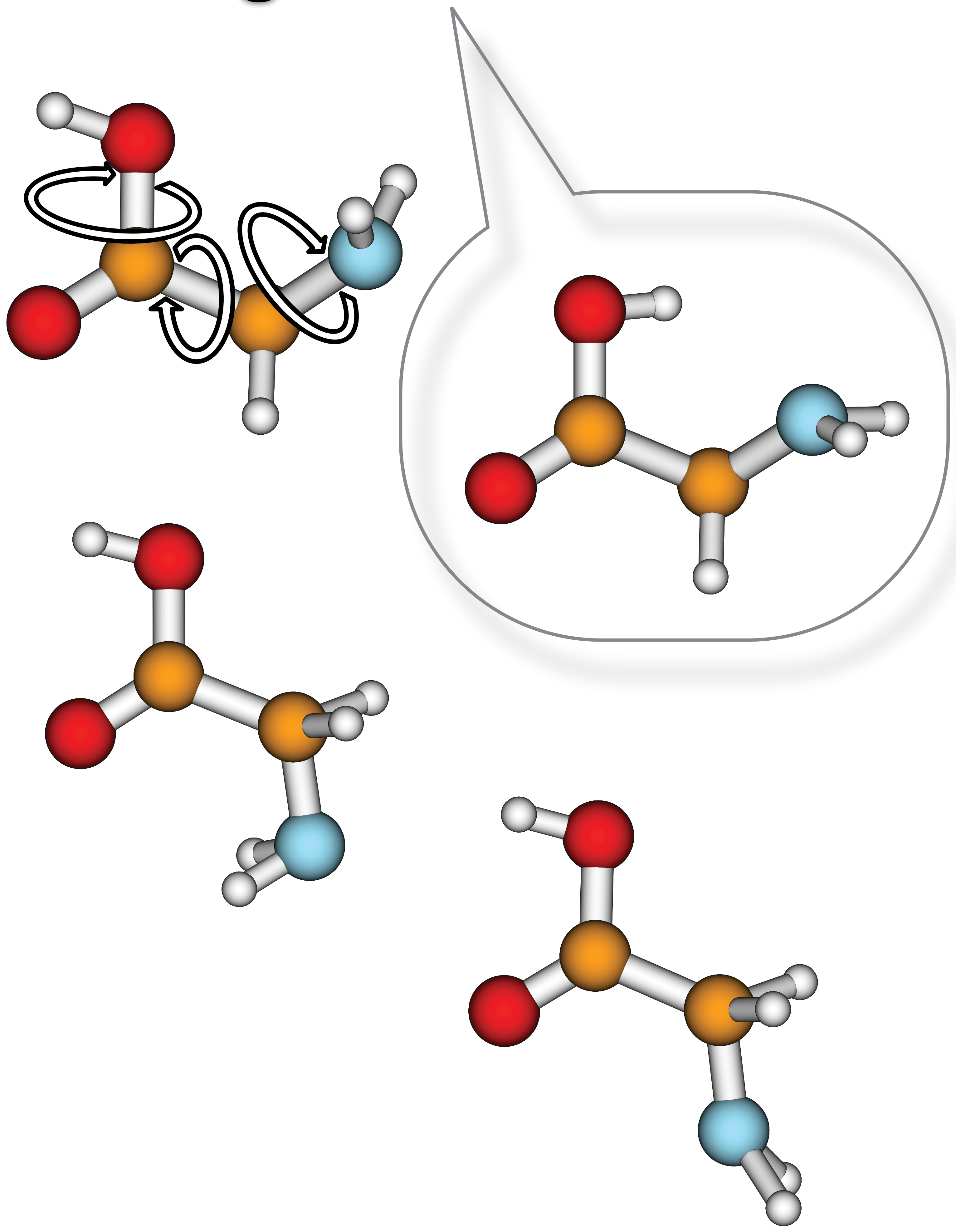
(Quantum) Molecular movie

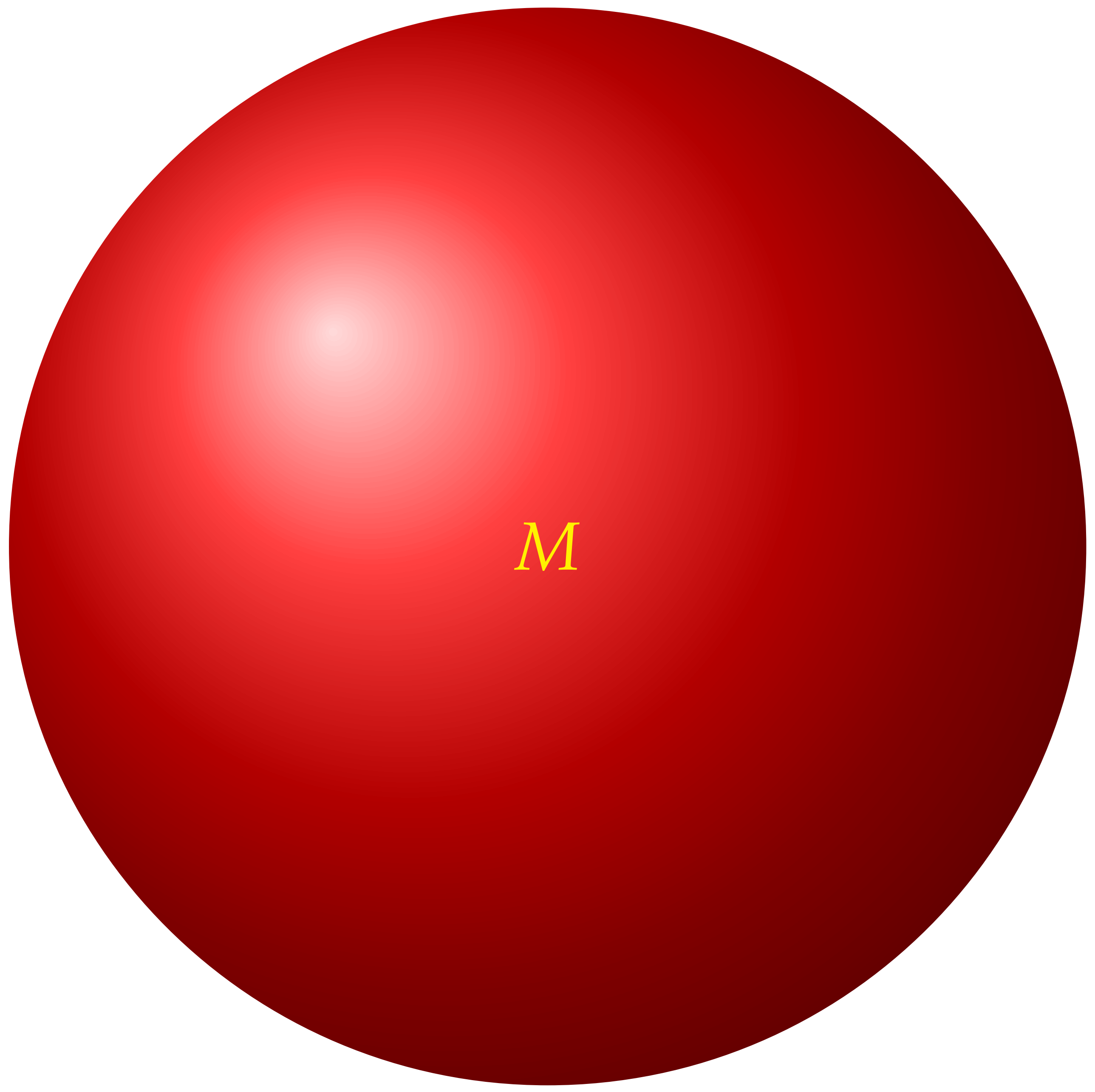




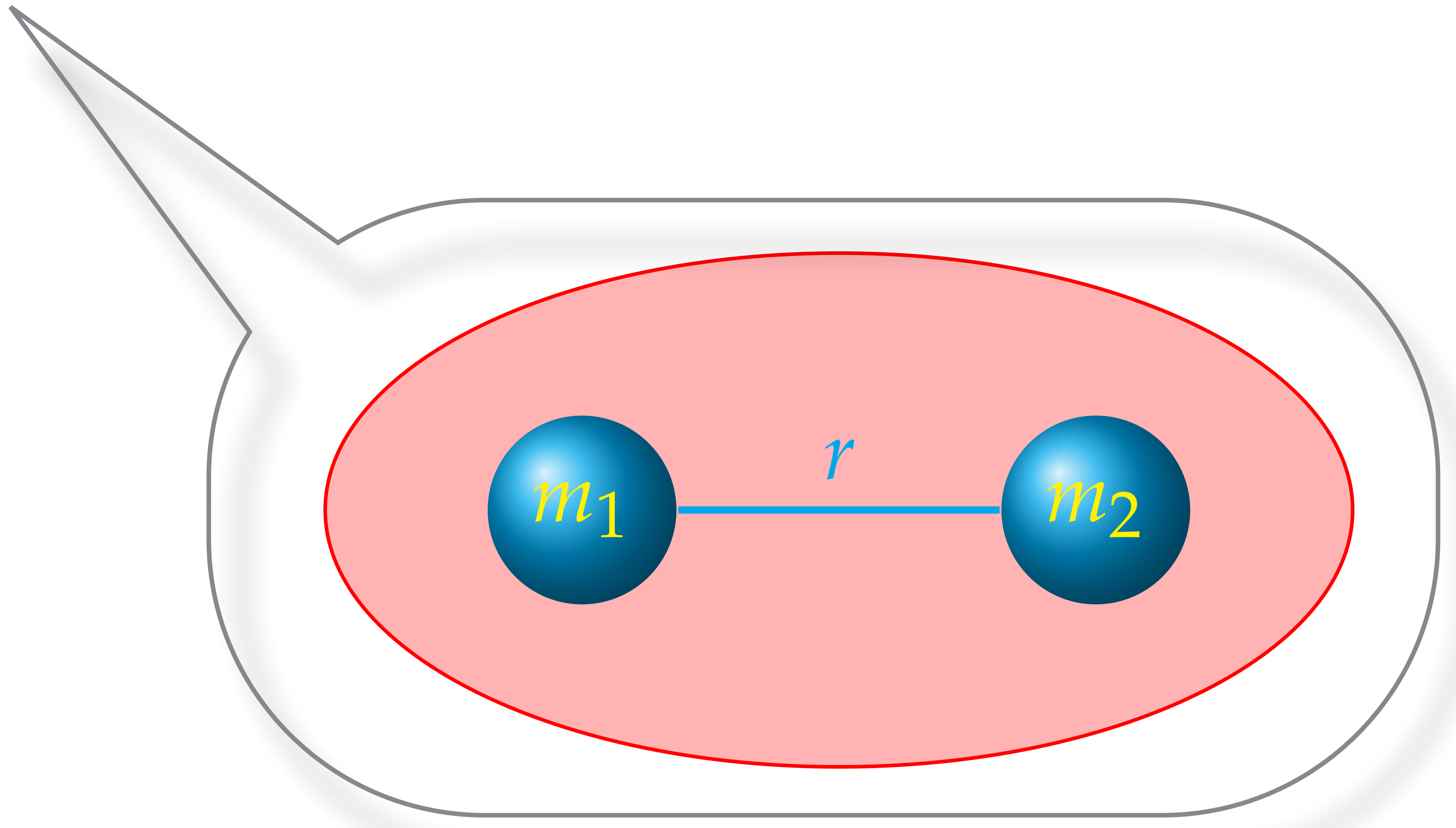
Control for high-fidelity imaging of complex molecules
What does a molecule (in free space) look like?

Selecting individual molecular species

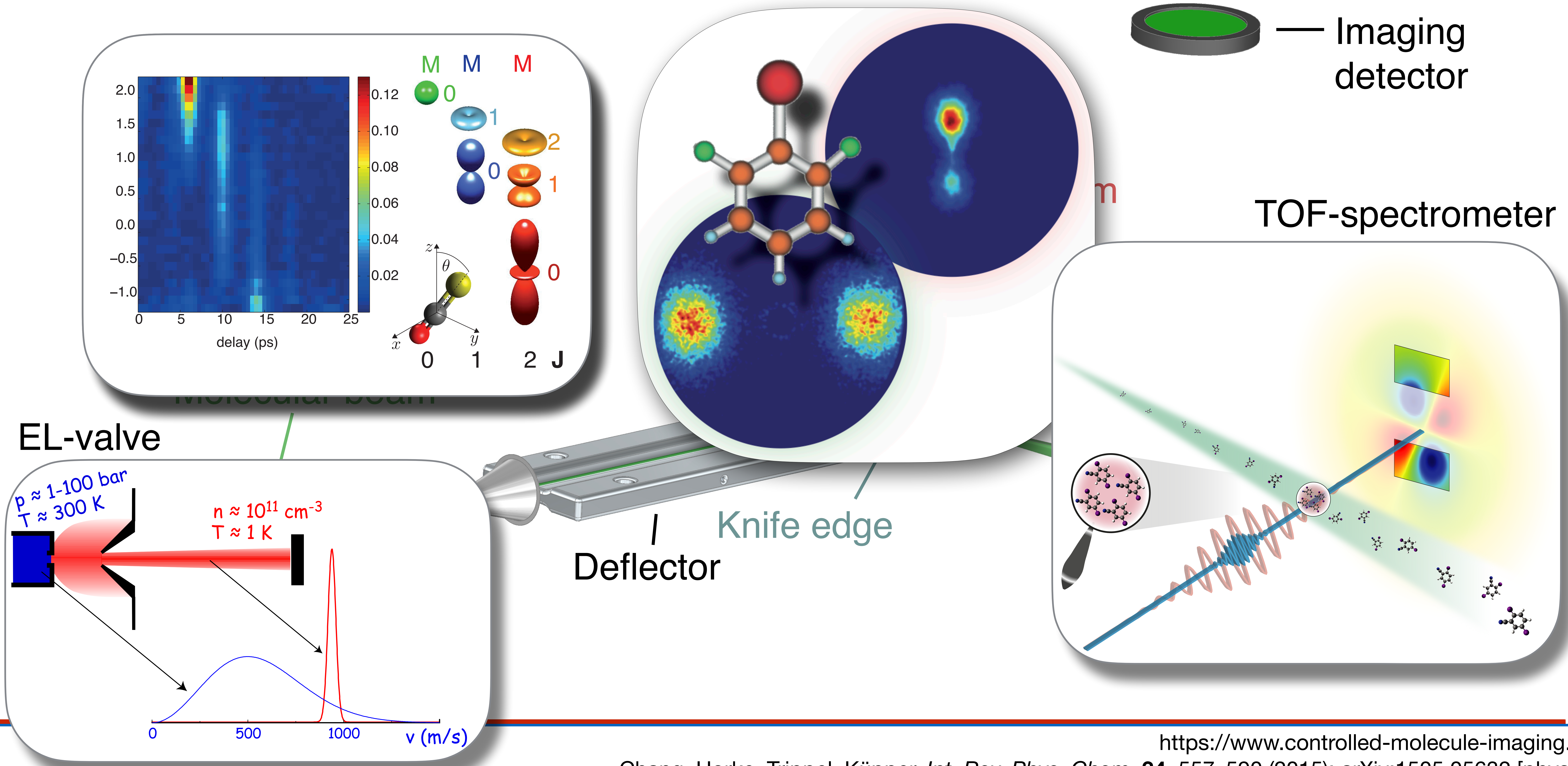




Alignment and orientation



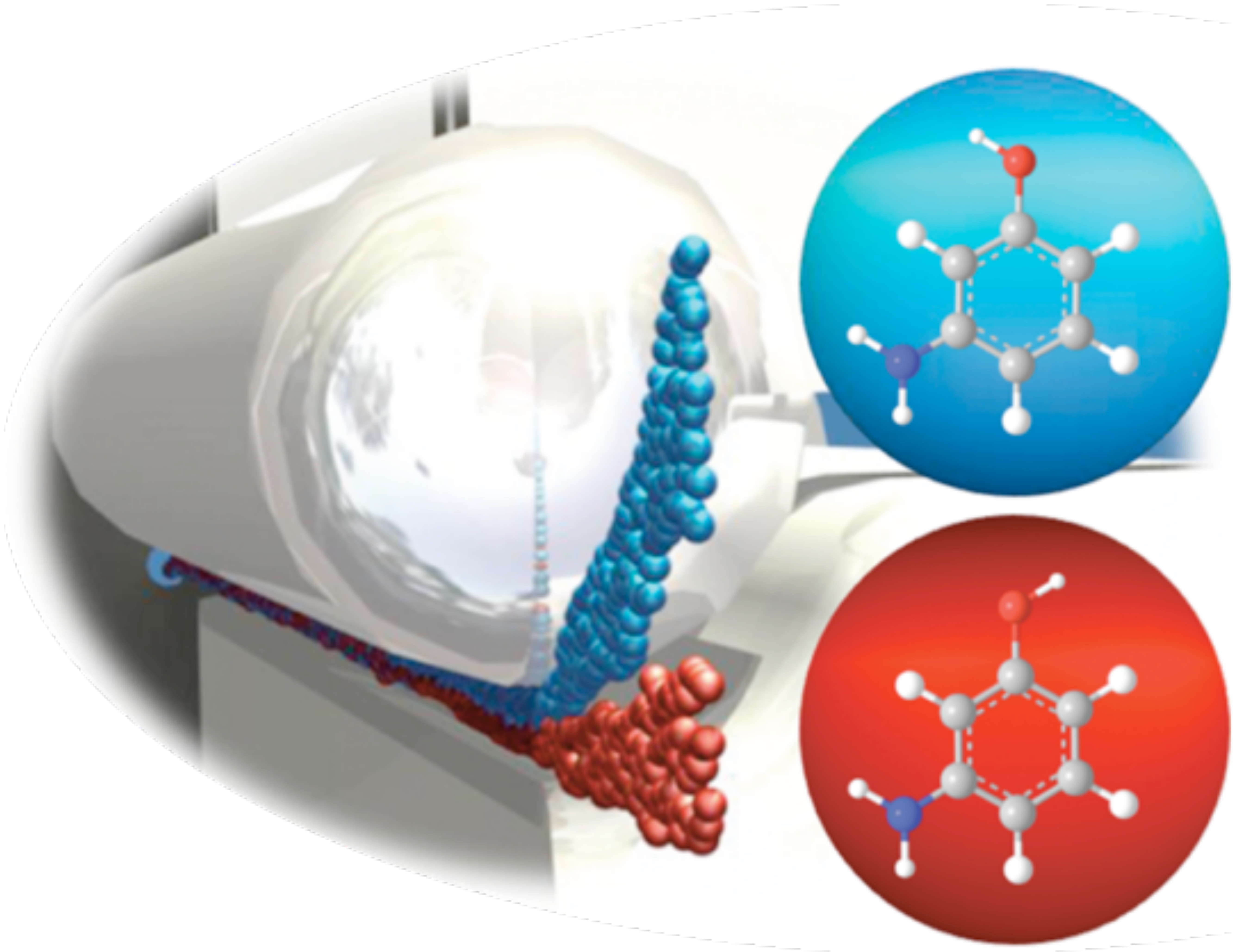
Experimental approach

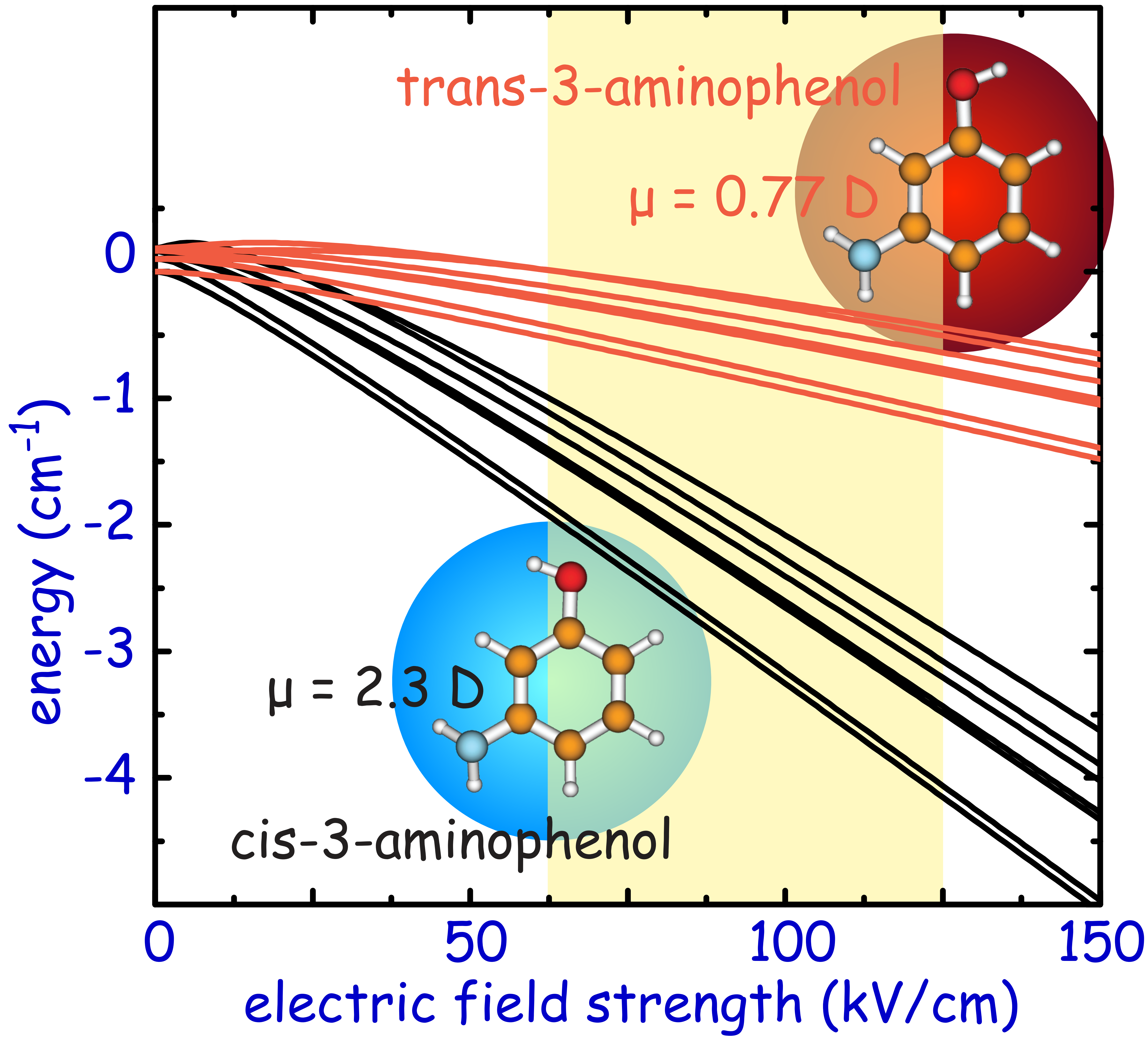


https://www.controlled-molecule-imaging.org

Chang, Horke, Trippel, Küpper, *Int. Rev. Phys. Chem.* **34**, 557–590 (2015); arXiv:1505.05632 [physics]

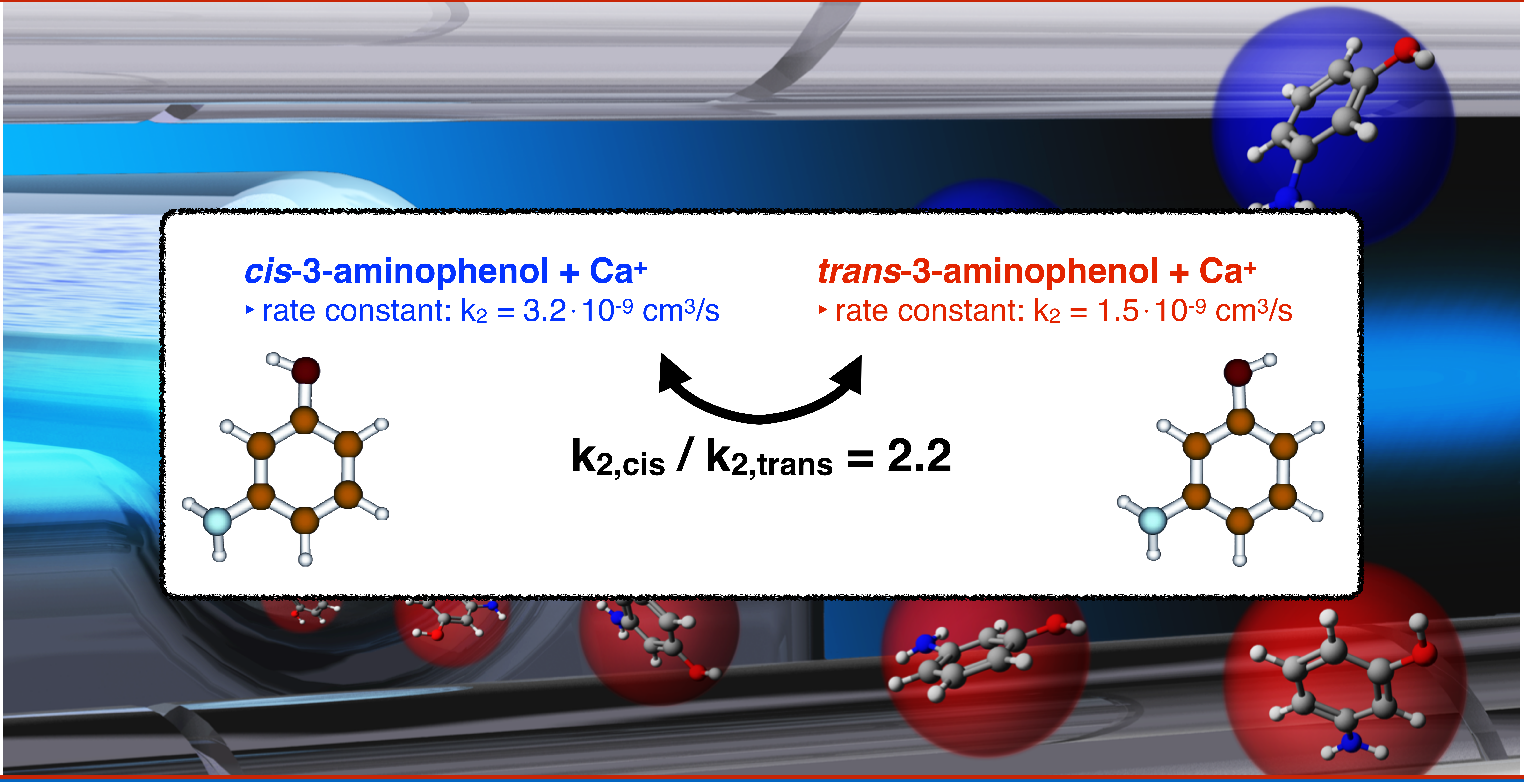
Spatial separation of conformers using electric fields





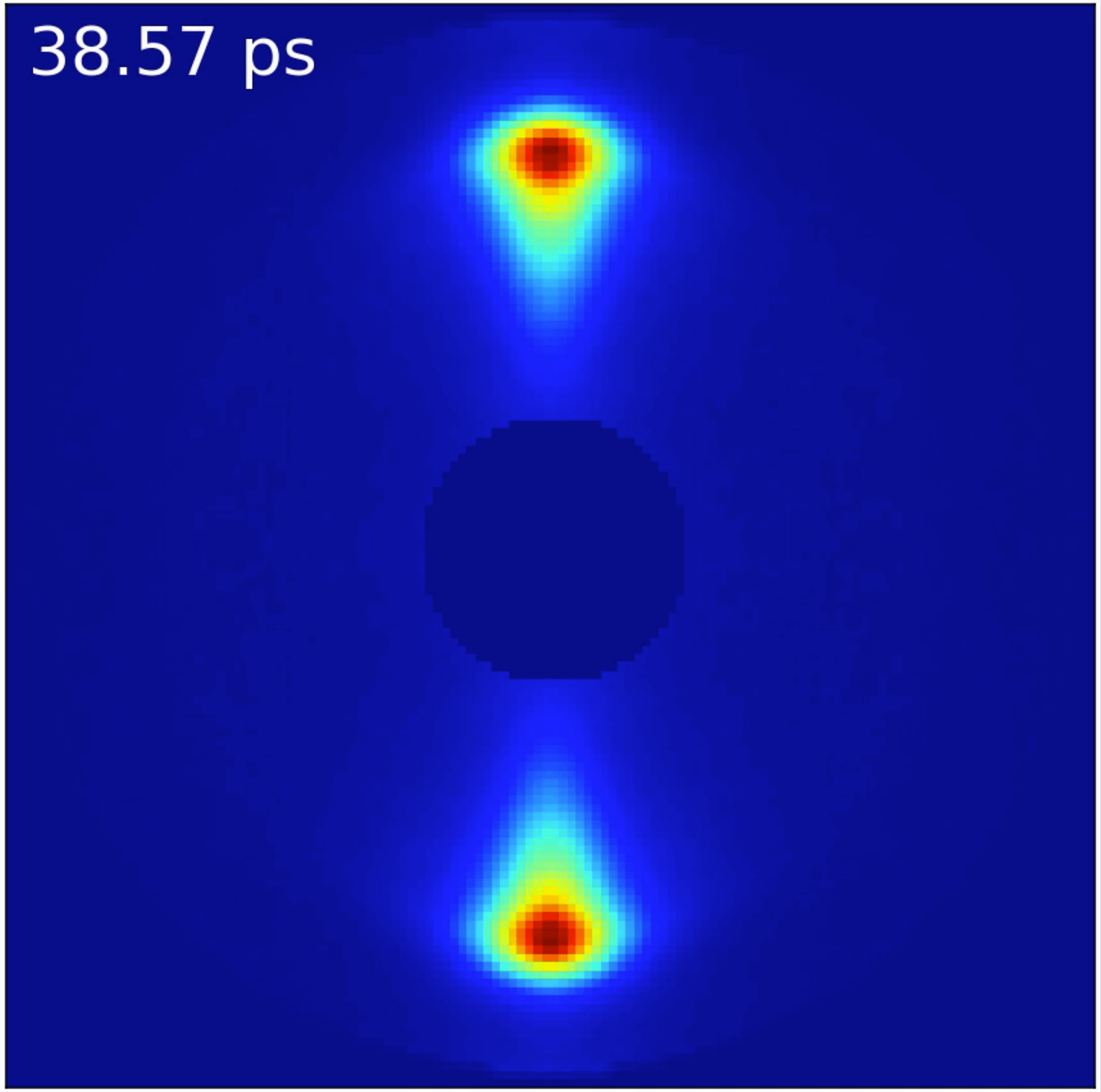
Filsinger, Erlekam, von Helden, Küpper, Meijer, *Phys. Rev. Lett.* **100**, 133003 (2008); arXiv:0802.2795 [physics]
Filsinger, Küpper, Meijer, Hansen, Maurer, Nielsen, Holmegaard, Stapelfeldt, *Angew. Chem. Int. Ed*. **48**, 6900 (2009)
Chang, Horke, Trippel, Küpper, *Int. Rev. Phys. Chem.* **34**, 557–590 (2015); arXiv:1505.05632 [physics]

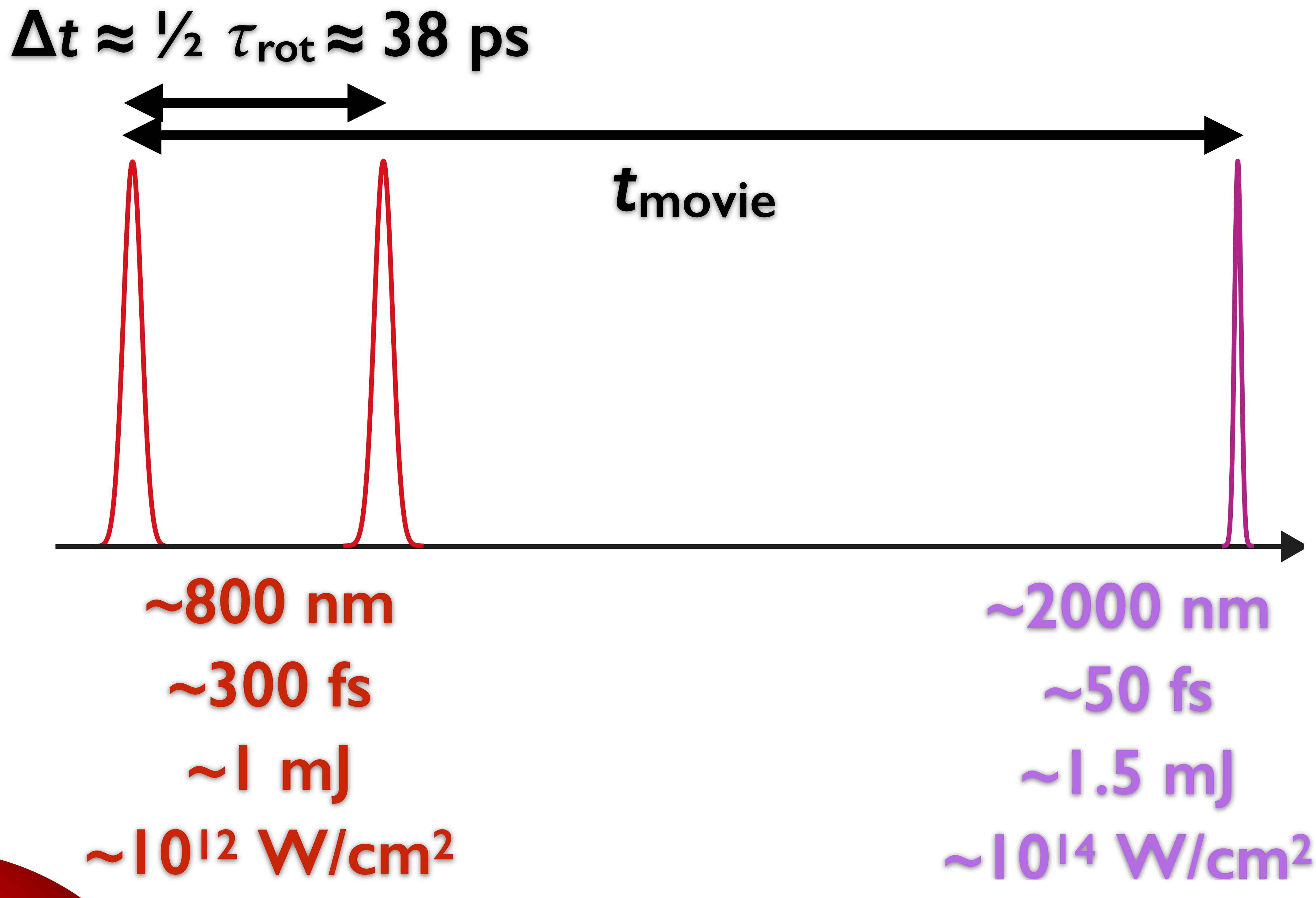
Conformer-specific reactivity
The structure-function relationship in chemistry



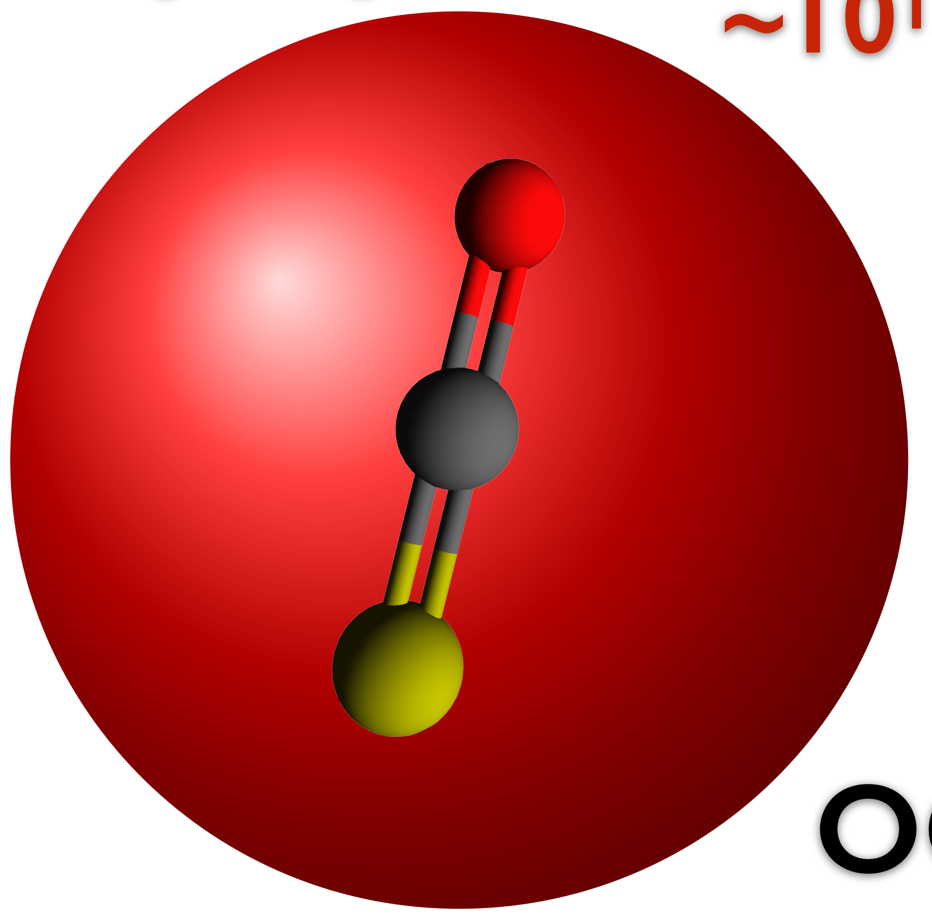
Fragmentation of ionized water dimer $(H_2O)_2$
Exploiting a new transportable endstation with everything implemented

Molecular movies: Imaging quantum “rotational” dynamics
Two-pulse alignment of absolute-ground-state-selected OCS





$t = 0$

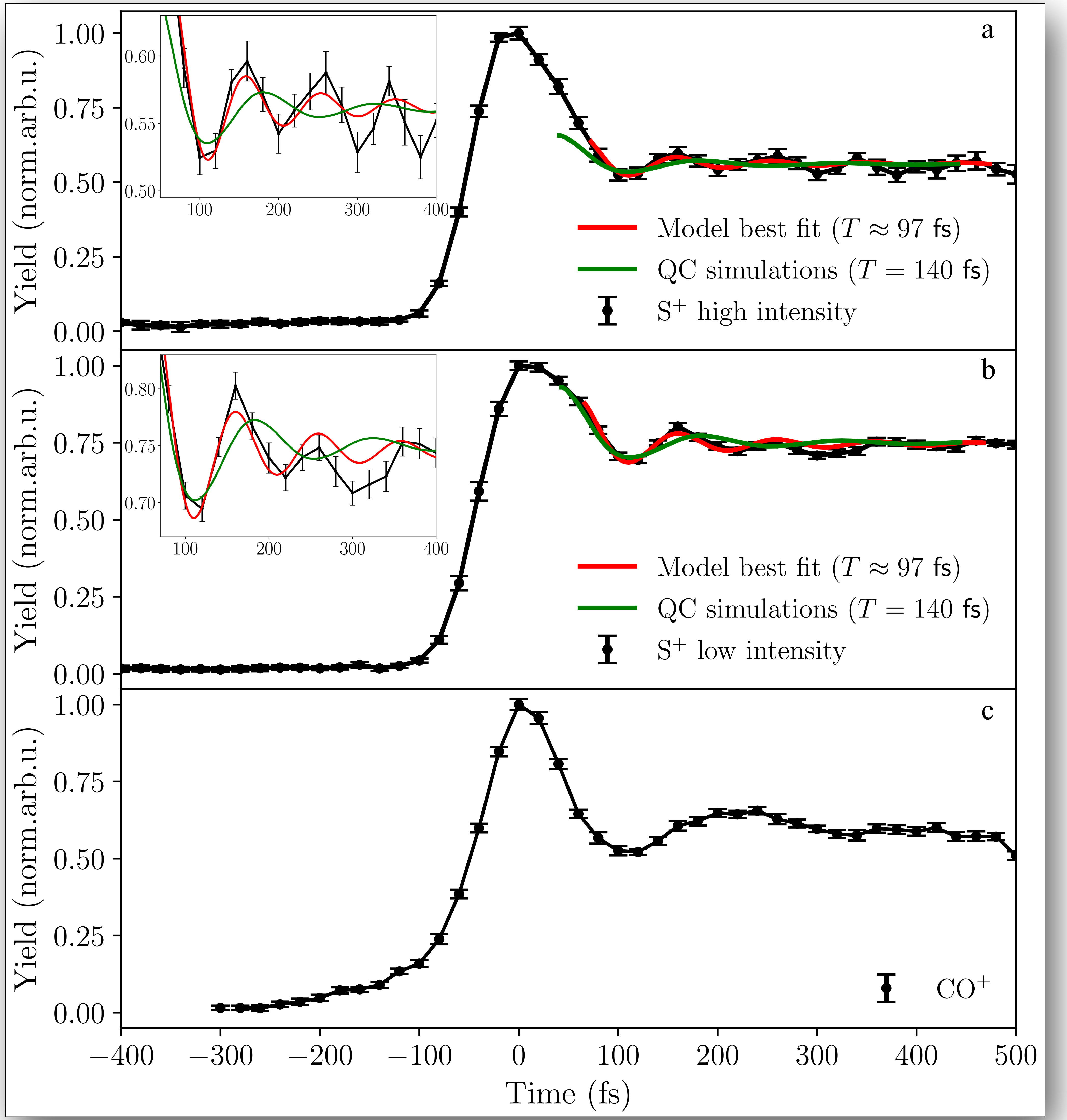


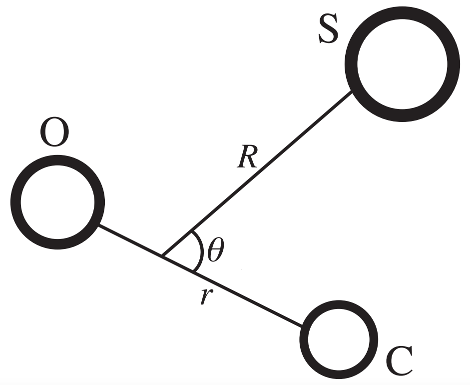
$$\langle \cos^2\theta \rangle = 0.94$$
$$\theta_m \approx 14^\circ$$

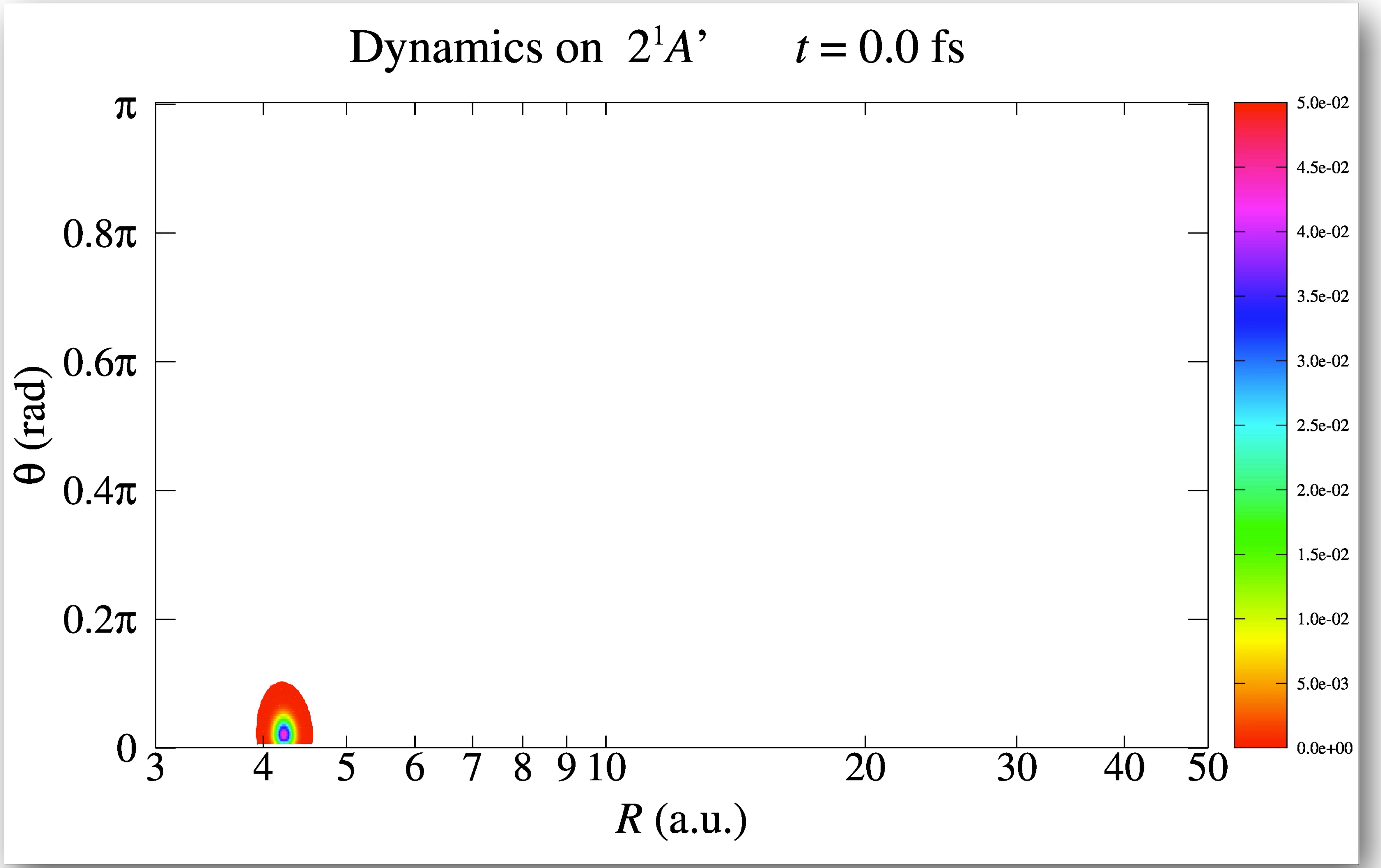
OCS ^1X, v = 0, J = 0

Karamatskos, *et int* (13 authors), Rouzée, Küpper, *Nat. Comm.* **10**, 3364 (2019); arXiv:1802.06622 [physics]

The *real-time* dissociation dynamics of ultraviolet (UV) excited OCS
Getting started … time-dependent experimental ion yields

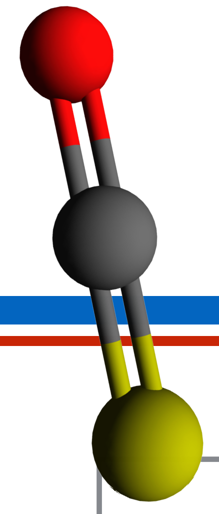






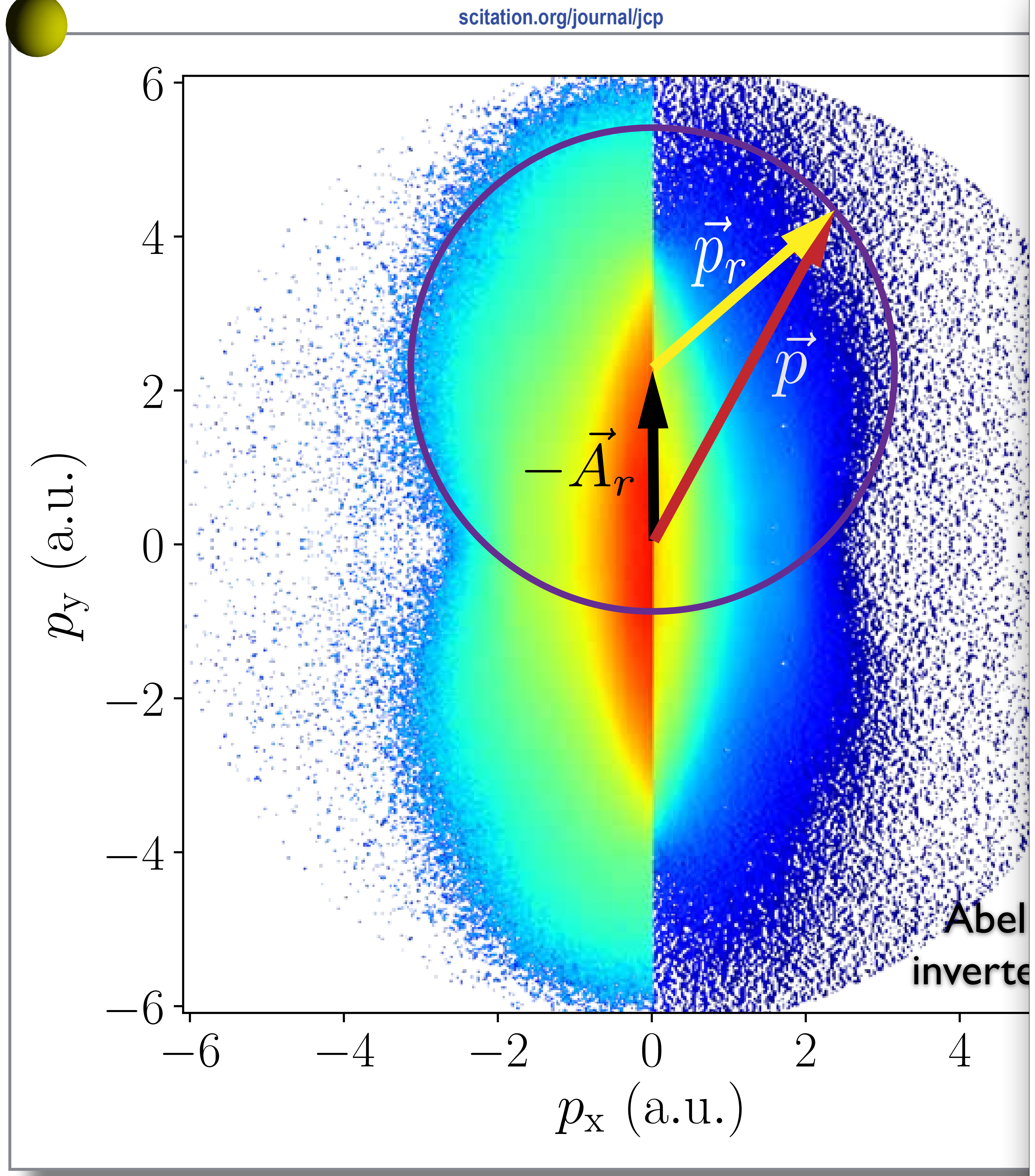
Karamatskos, Yarlagadda, Patchkovskii, Vrakking, Welsch, Küpper, Rouzée, *Faraday Discusssions* (2020), DOI: 10.1039/d0fd00119h

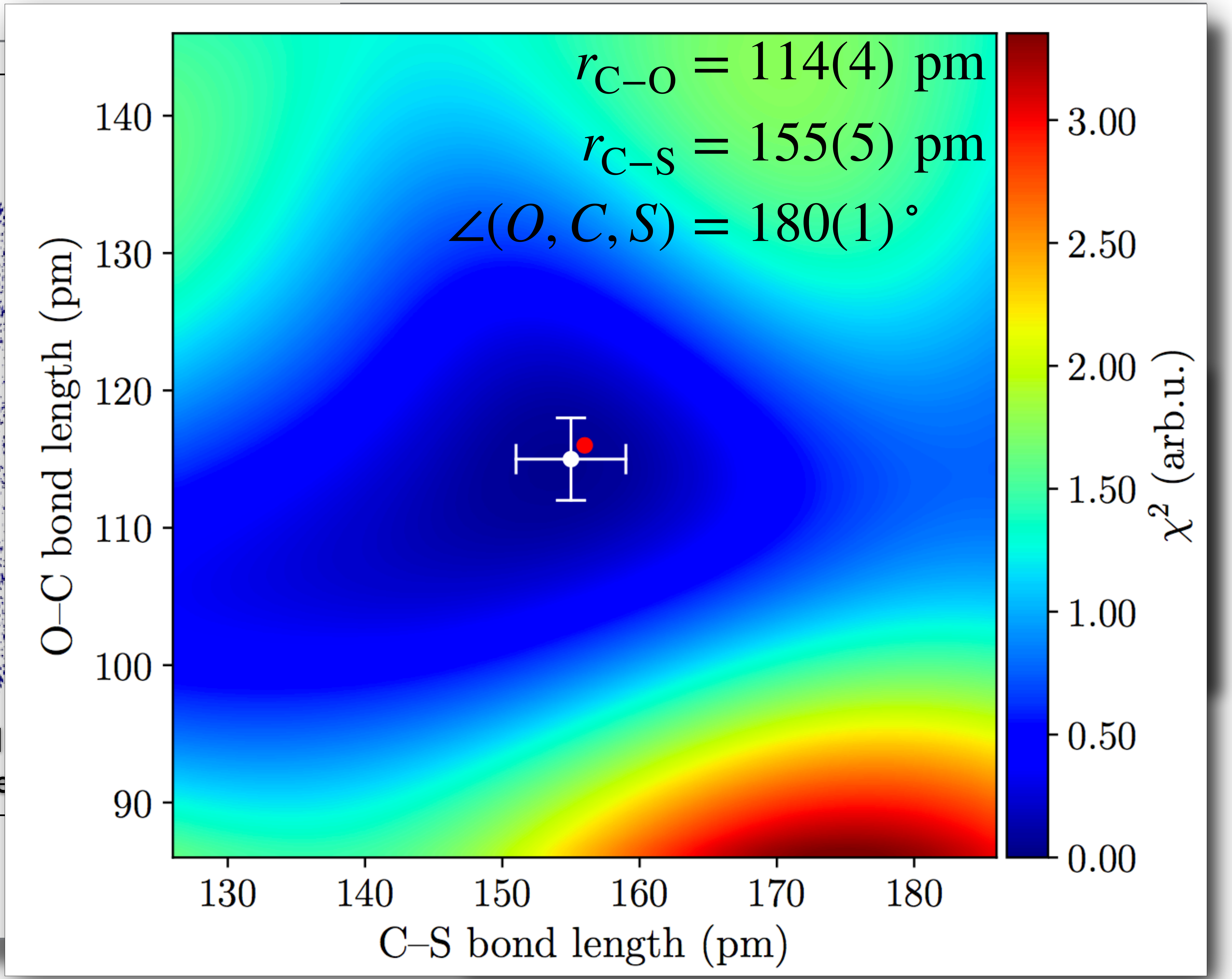
Atomic-resolution imaging
Laser-induced electron diffraction of OCS



The Journal of Chemical Physics

AIP Publishing

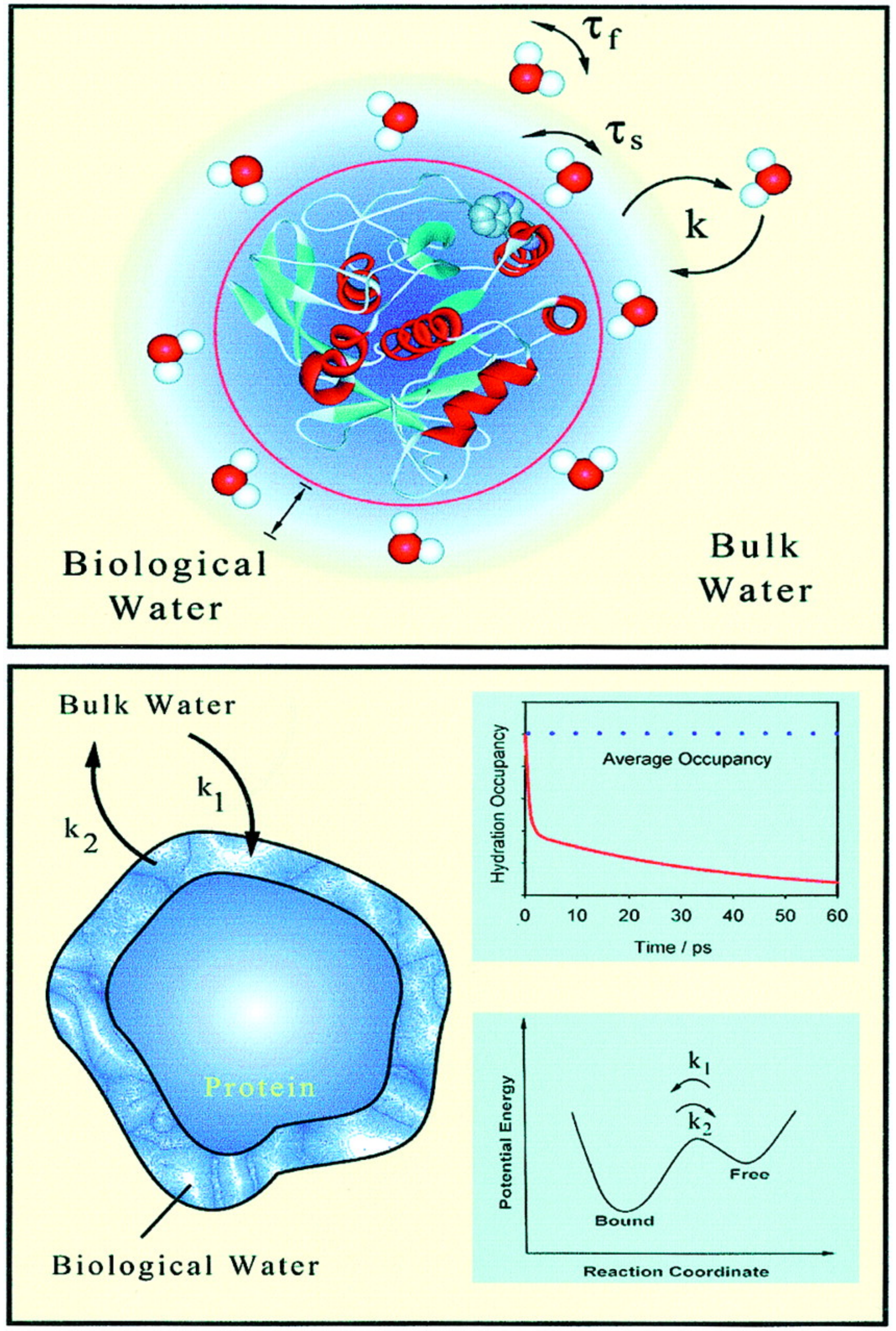


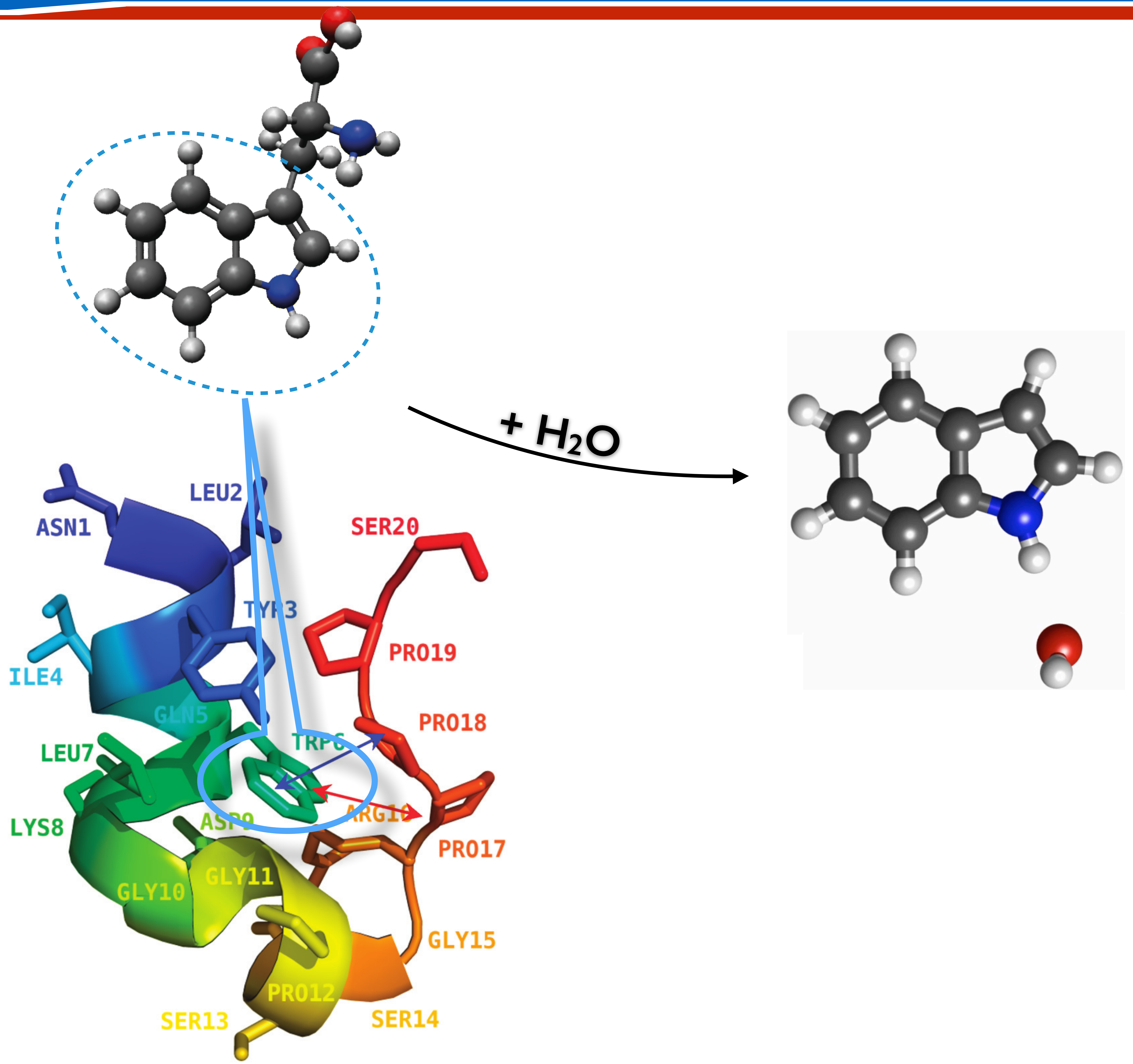


Trabattoni, Wiese, De Giovannini, Olivieri, Mullins, Onvlee, Son, Frusteri, Rubio, Trippel, Küpper, Nat. Comm 11, 2546; arXiv:1802.06622 [physics]

Karamatskos, Goldsztejn, Raabe, Stammer, Mullins, Trabattoni, Johansen, Stapelfeldt, Trippel, Vrakking, Küpper, Rouzée, *J. Chem. Phys.* **150**, 244301 (2019); arXiv:1905.03541 [physics]

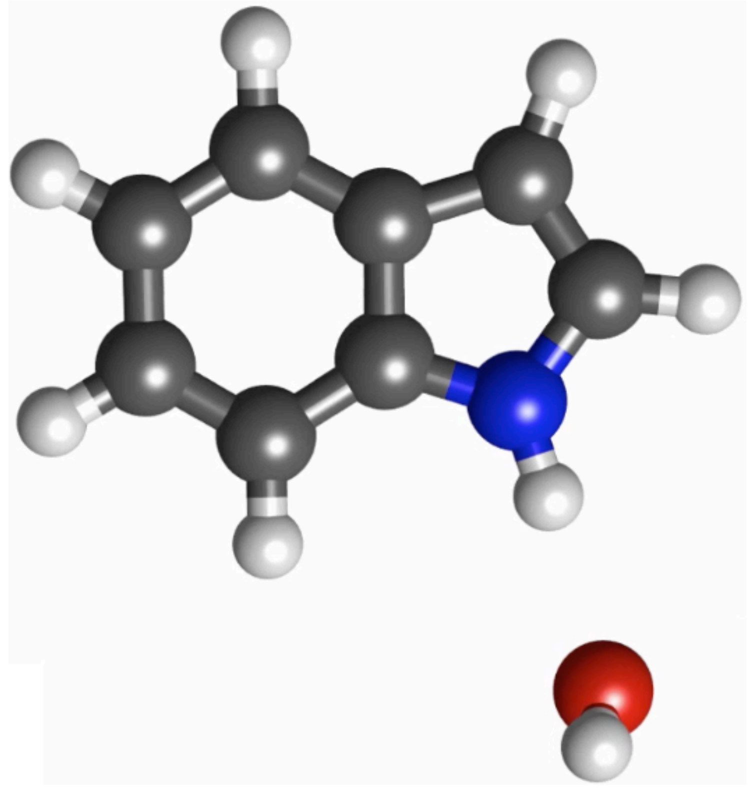
Biological molecules in solvation
From proteins to precision studies of model systems



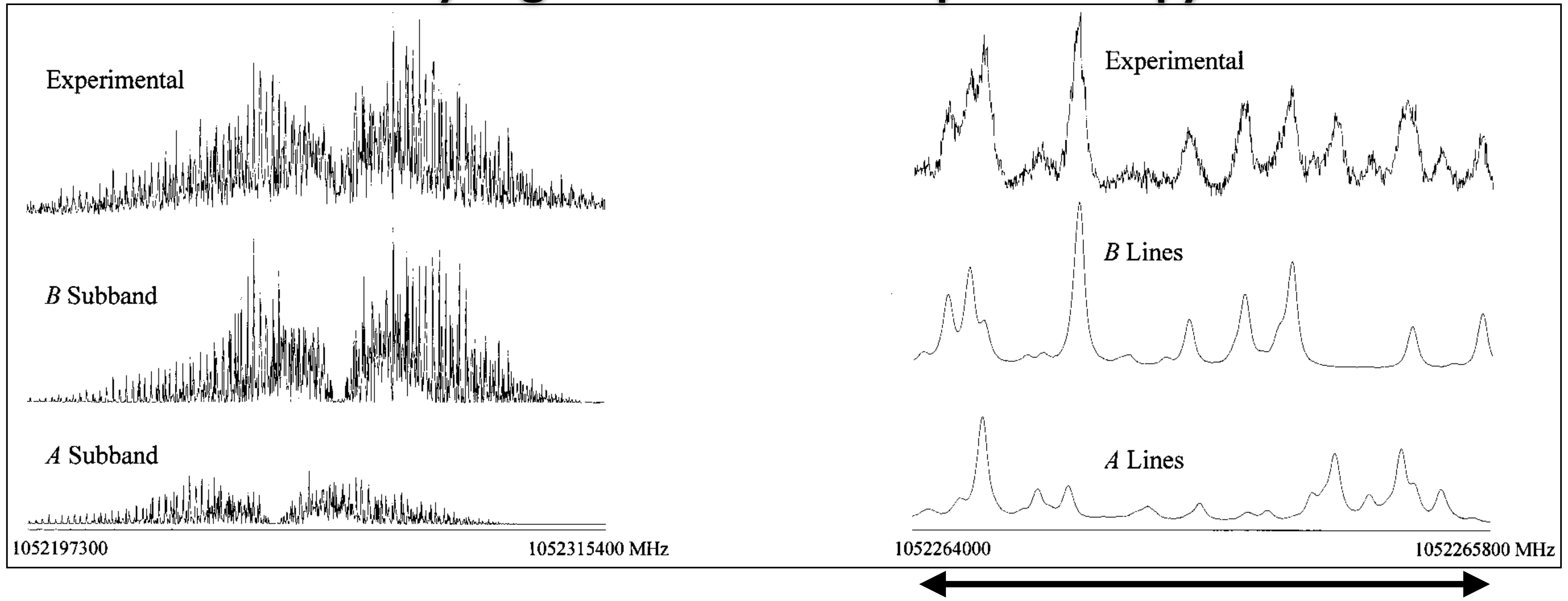


Pal, Peon, Zewail, *PNAS* **99**, 1763 (2002

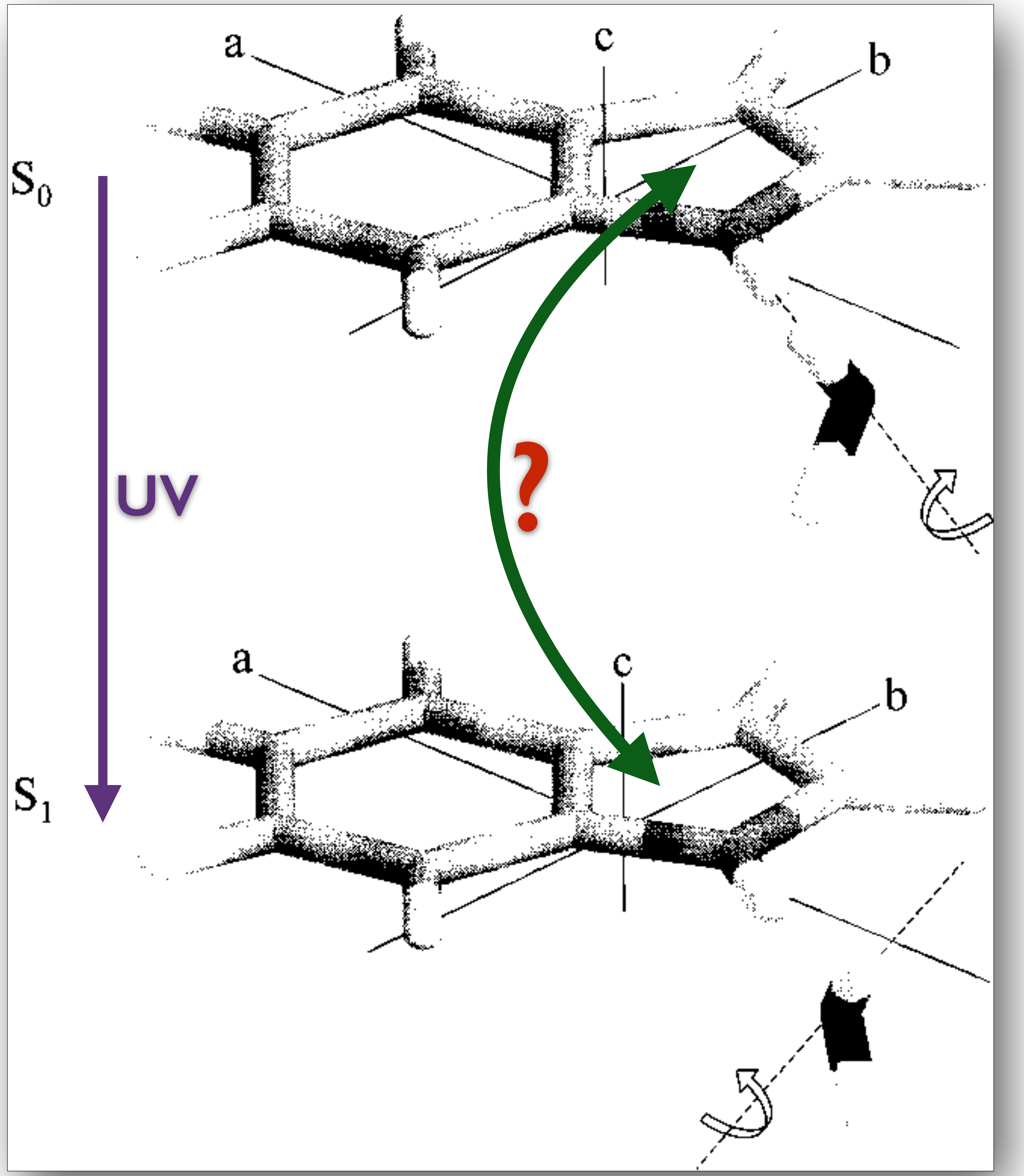
High-resolution UV spectroscopy: Structure determination of gas phase molecules



Very-high-resolution UV spectroscopy



6 GHz ≈ 0.2 cm^{-1} ≈ 0.25 meV

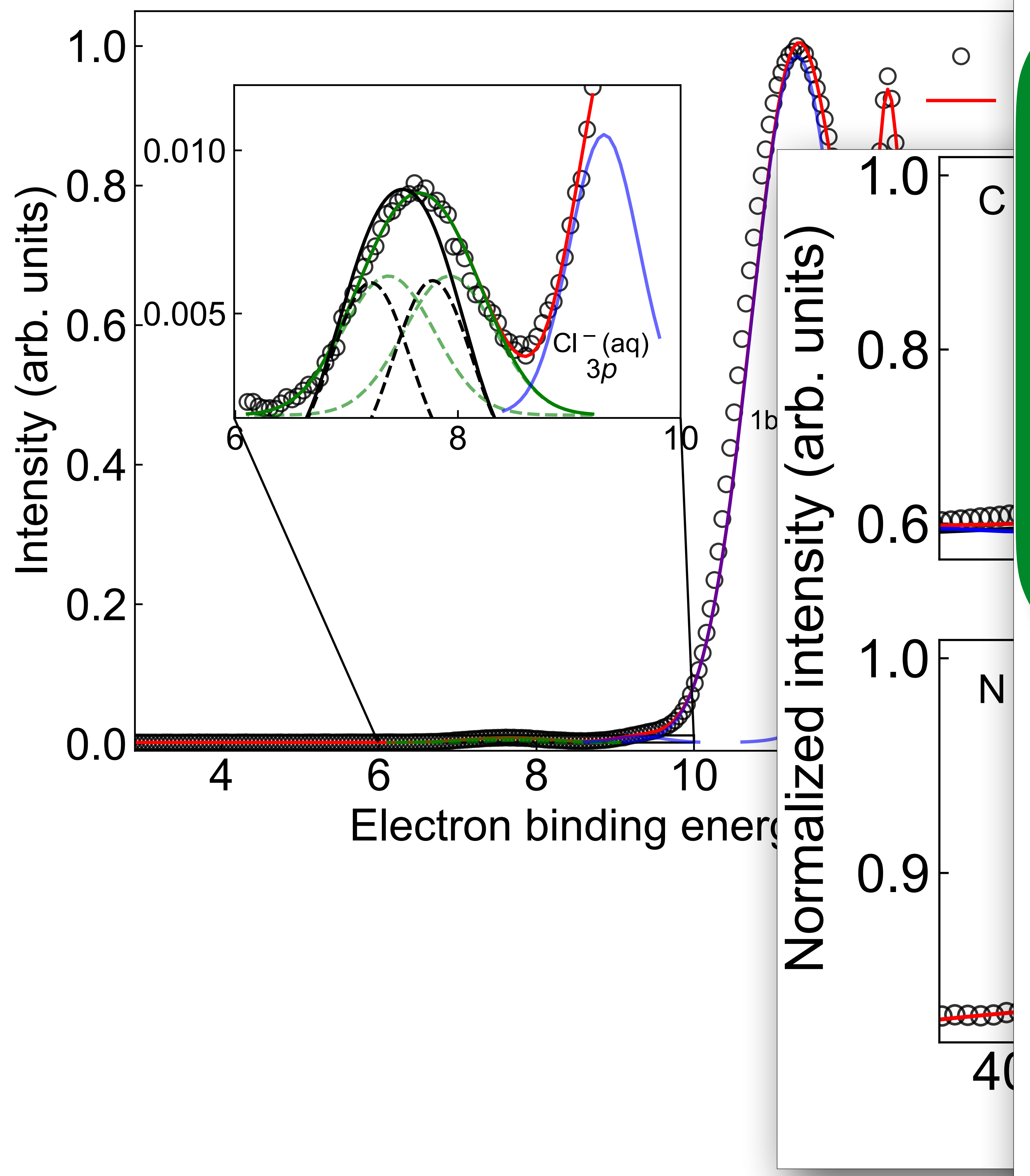


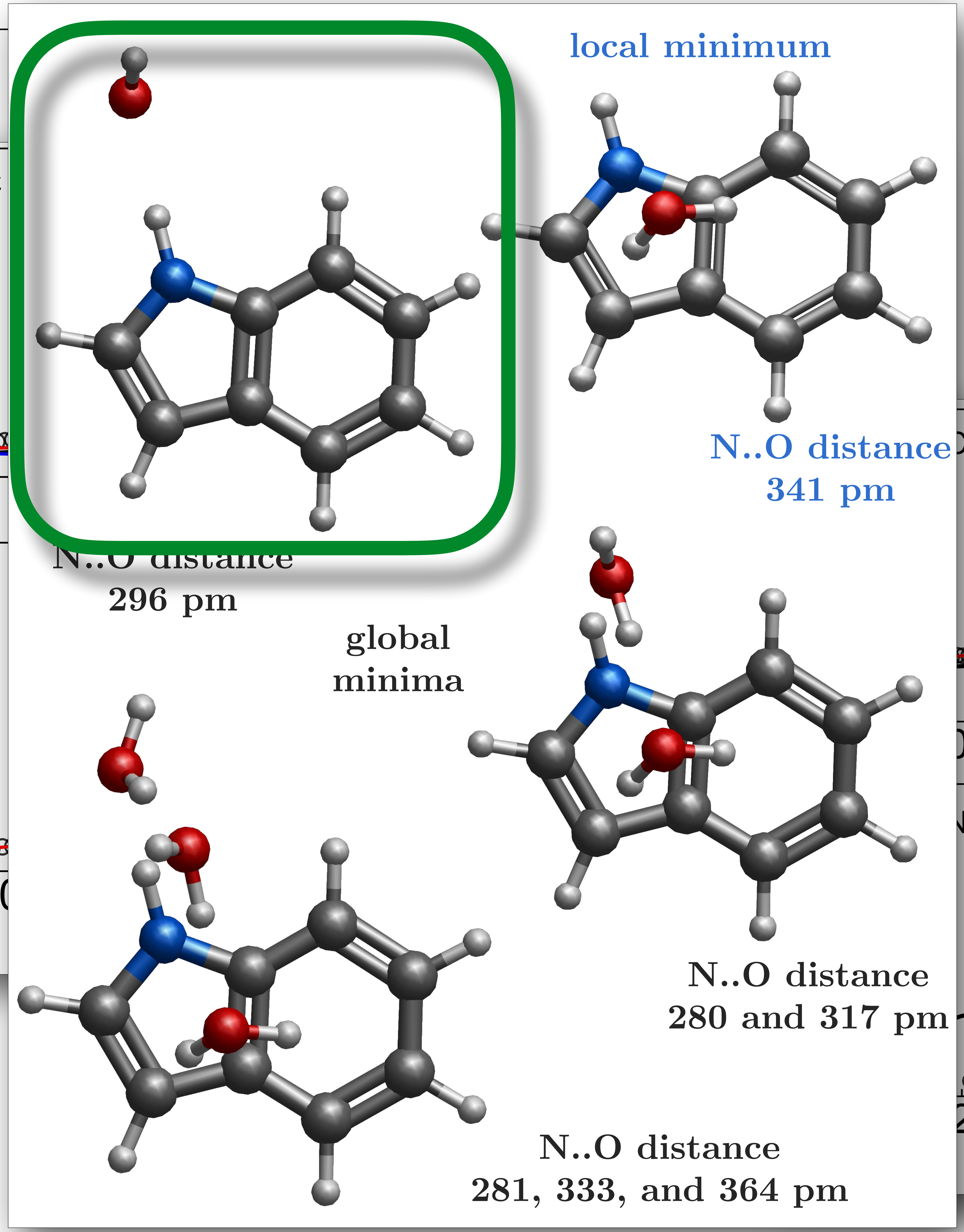
Solvent Reorganization in the Electronically Excited State

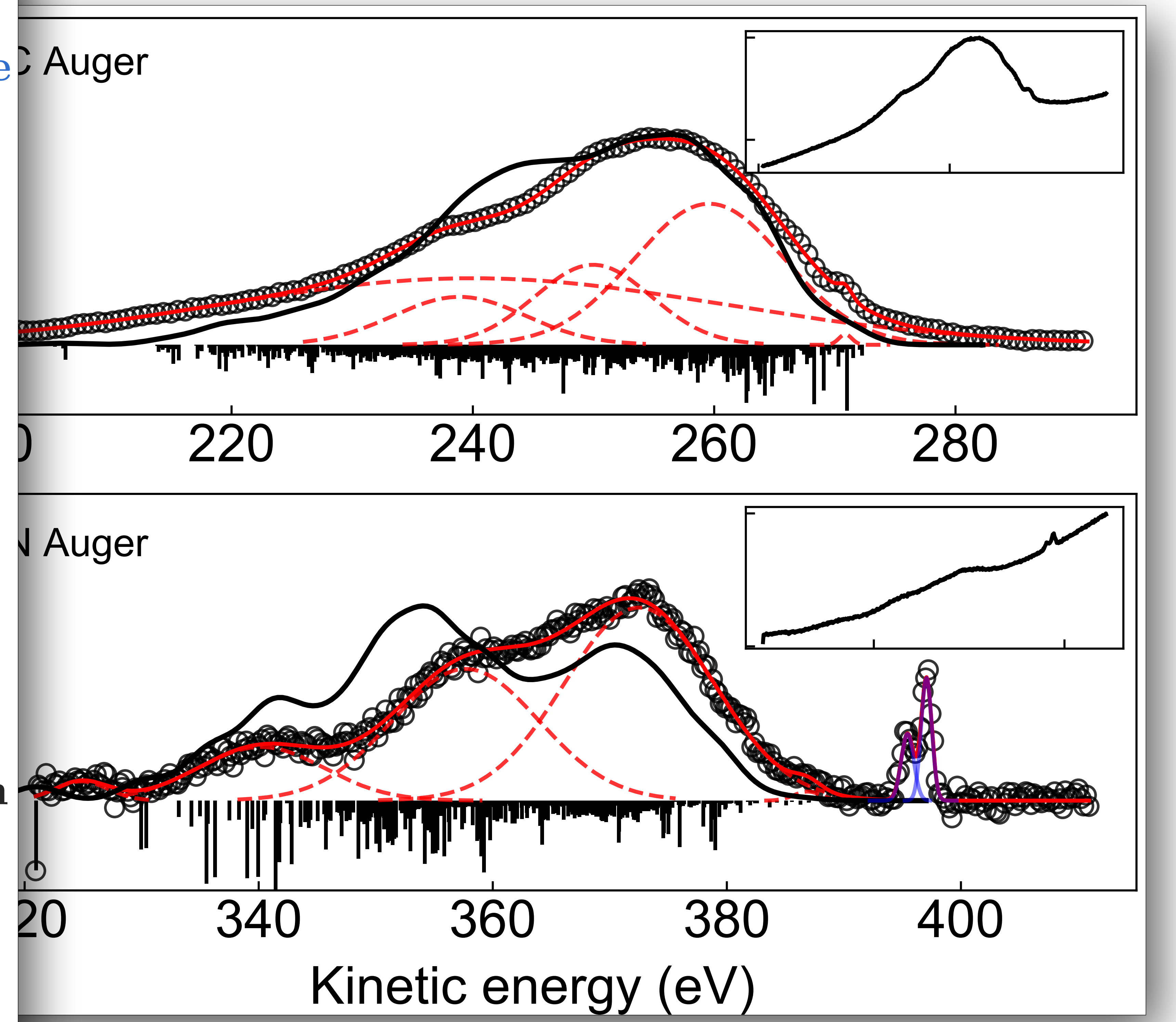
First experimental structure of indole-water: Korter, Pratt, Küpper, *J. Phys. Chem.* A **102**, 7211 (1998)

cf. complete sub-picometer atomic structure of ground-state and electronically-excited phenol: Ratzer, Küpper, Spangenberg, Schmitt, *Chem. Phys.* **283**, 153 (2002)

Molecular interactions of indole in aqueous solution
x-ray (600 eV) photoelectron spectroscopy of indole in an aqueous liquid jet







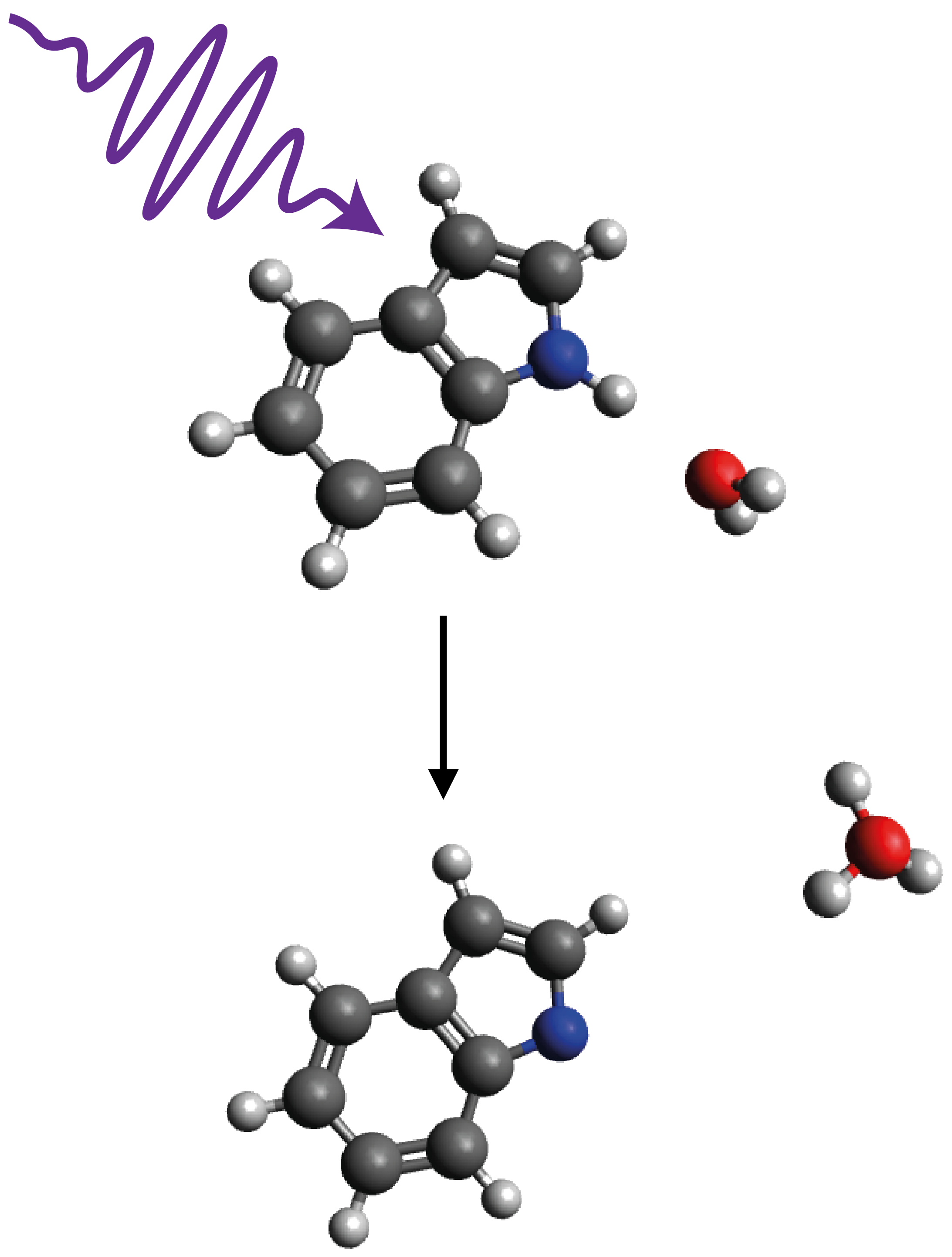
He, Malerz, Trinter, Trippel, Tomaník, Belina, Slavíček, Winter, Küpper, *J. Phys. Chem. Lett.* accepted (2023); arXiv:2205.08217 [physics]

Water molecule as “molecular sunscreen”
Dynamics of bond-breaking in electronically excited indole-water

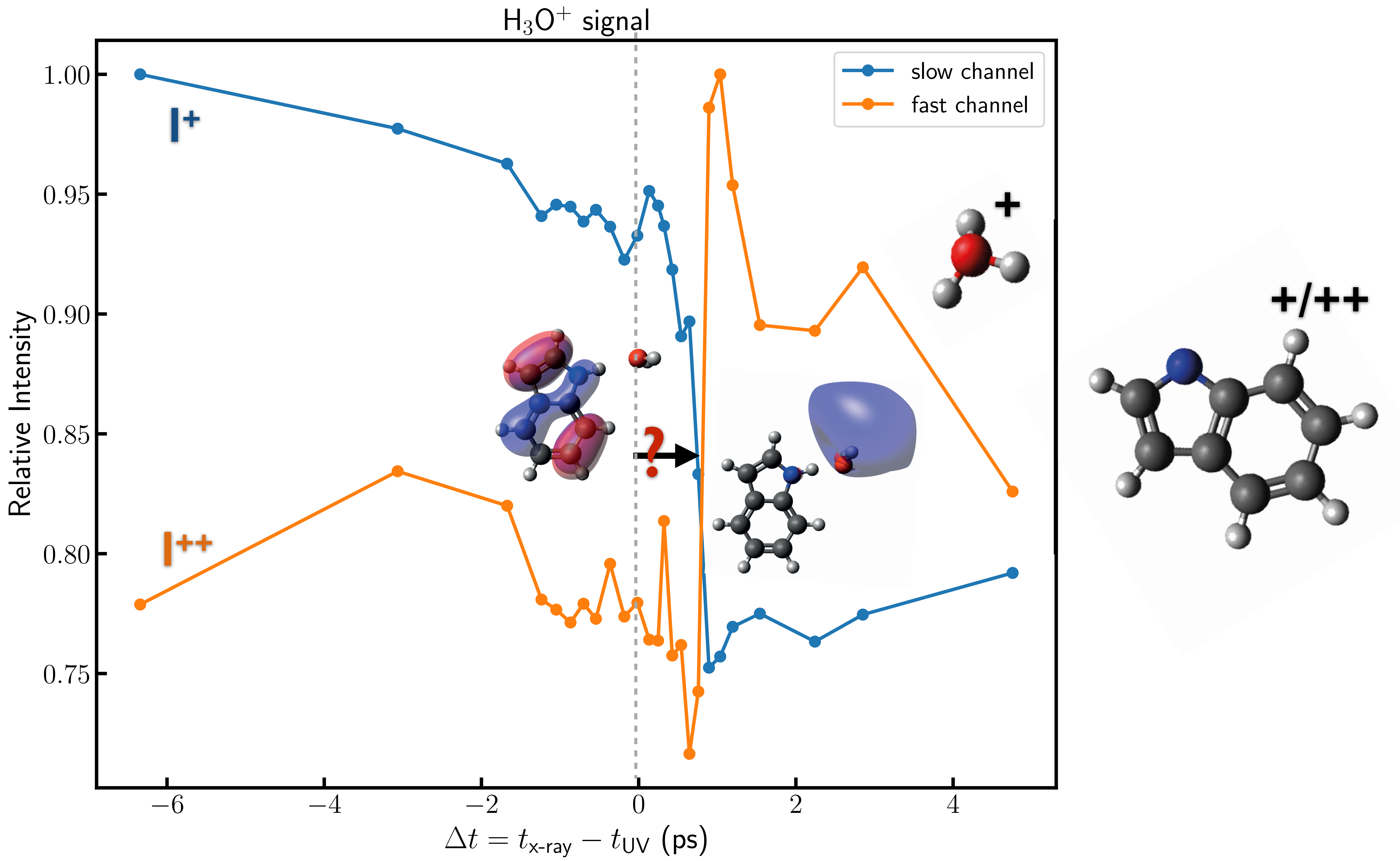
Onvlee, Trippel, Küpper, *Nat. Comm.* **13**, 7462 (2022); arXiv:2103.07171 [physics]

Observing the timescale of the formation of the dipole-bound electron?

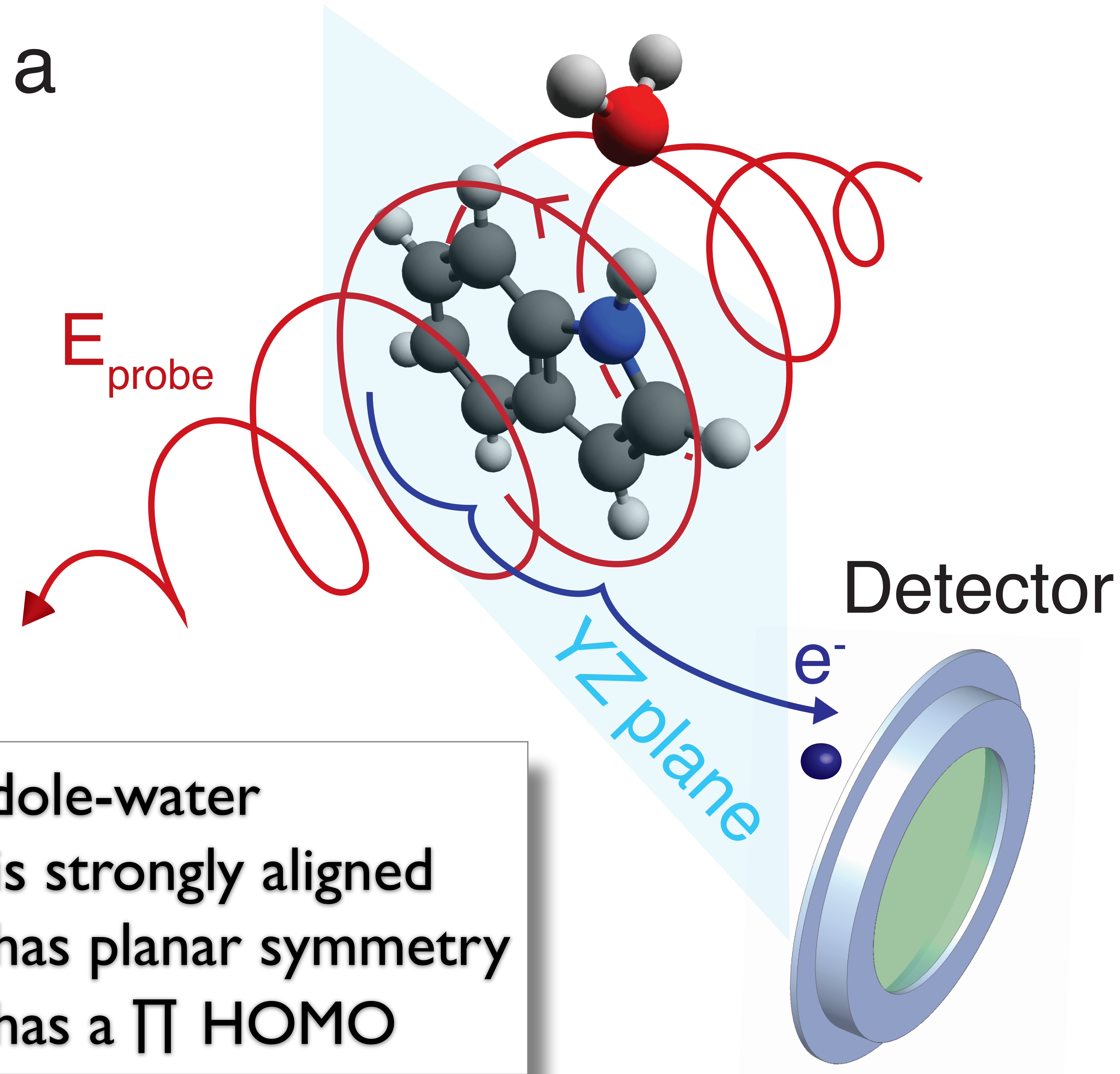
Pump: UV 266 nm



Probe: x-ray ~500 eV

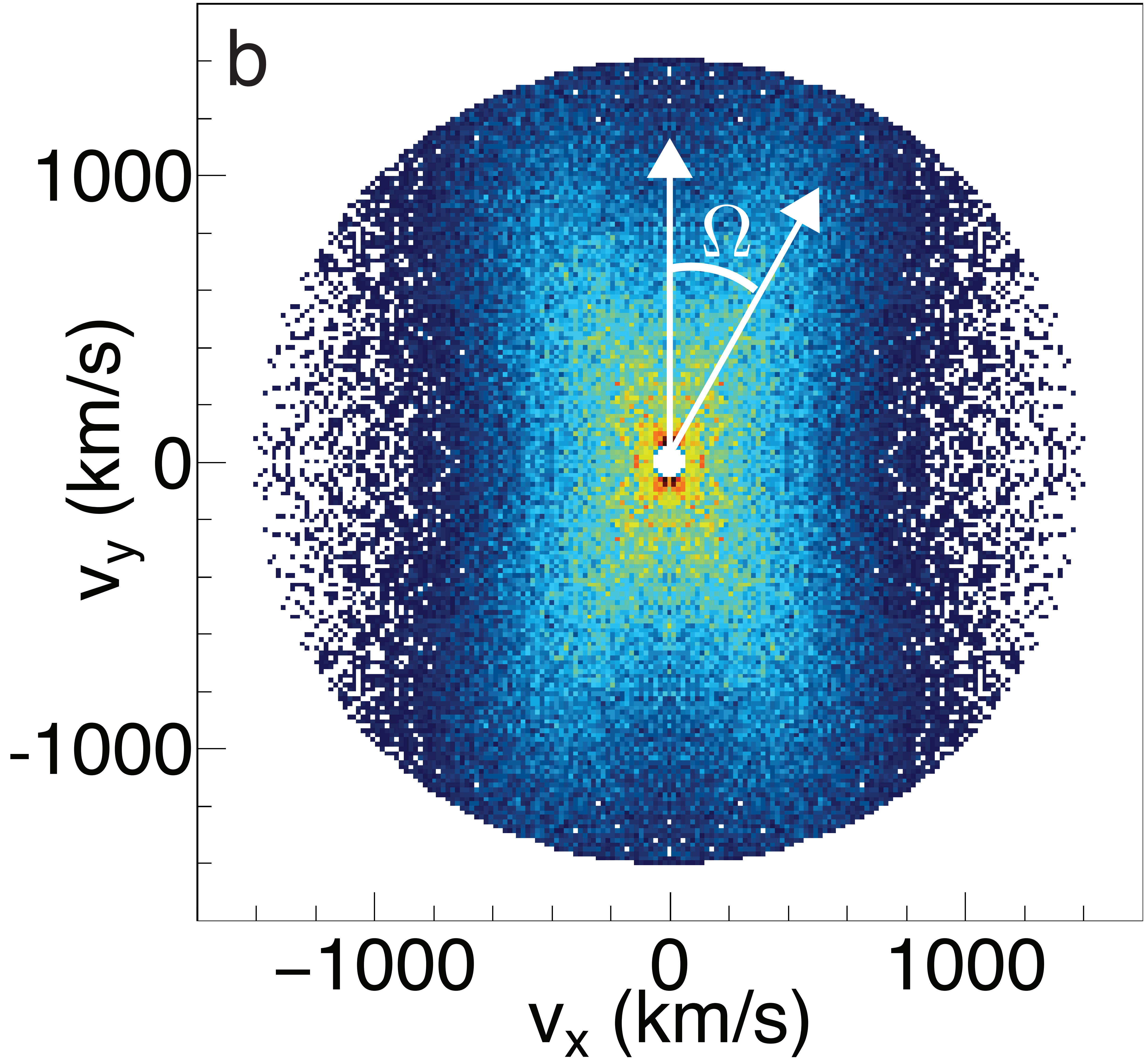


Molecular frame photoelectron angular distributions of the 3D-aligned indole-water complex



Indole-water

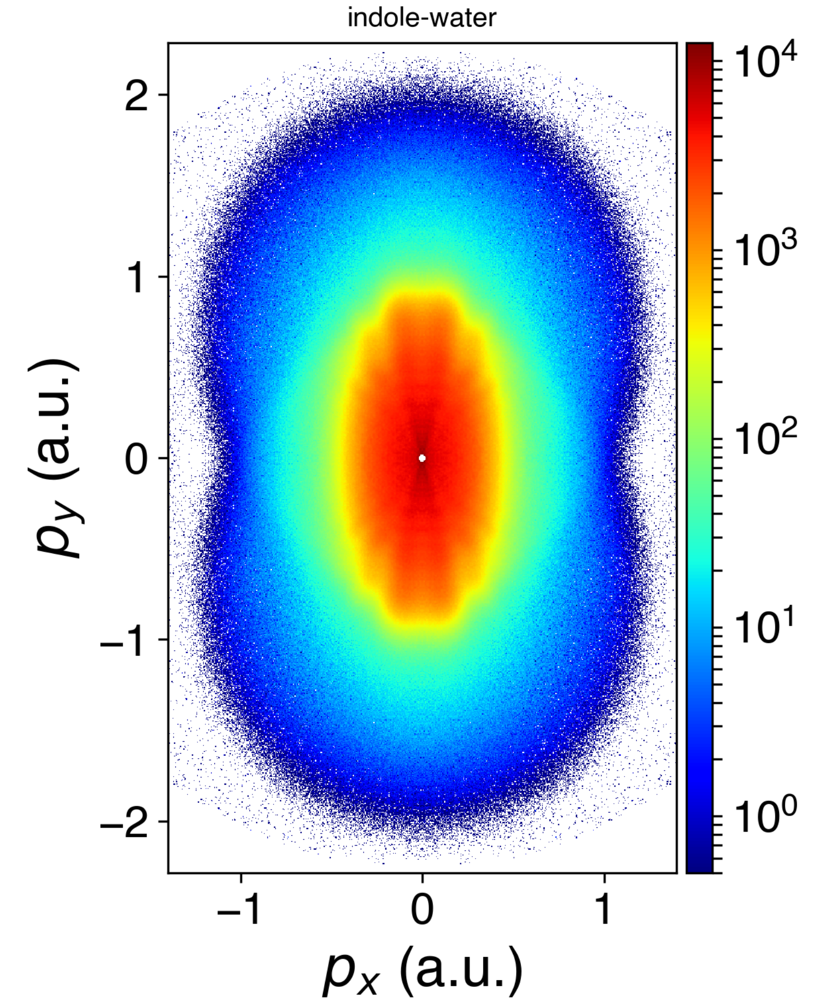
- is strongly aligned
- has planar symmetry
- has a π HOMO

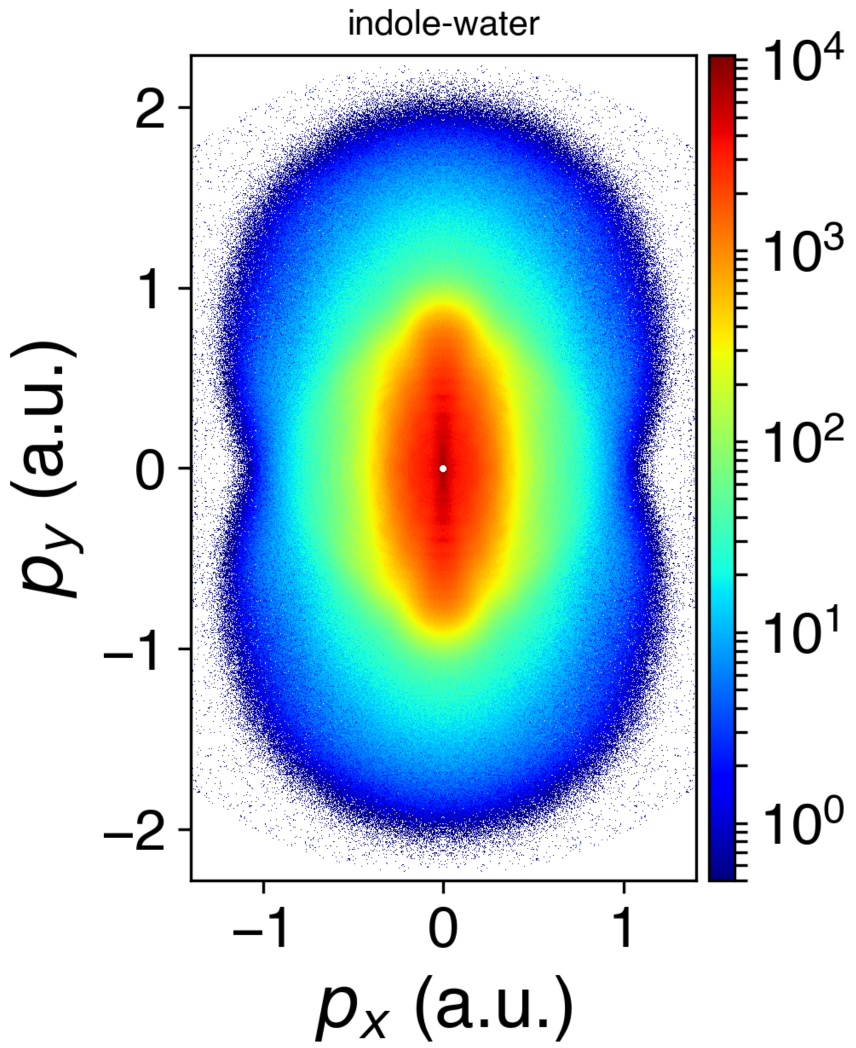


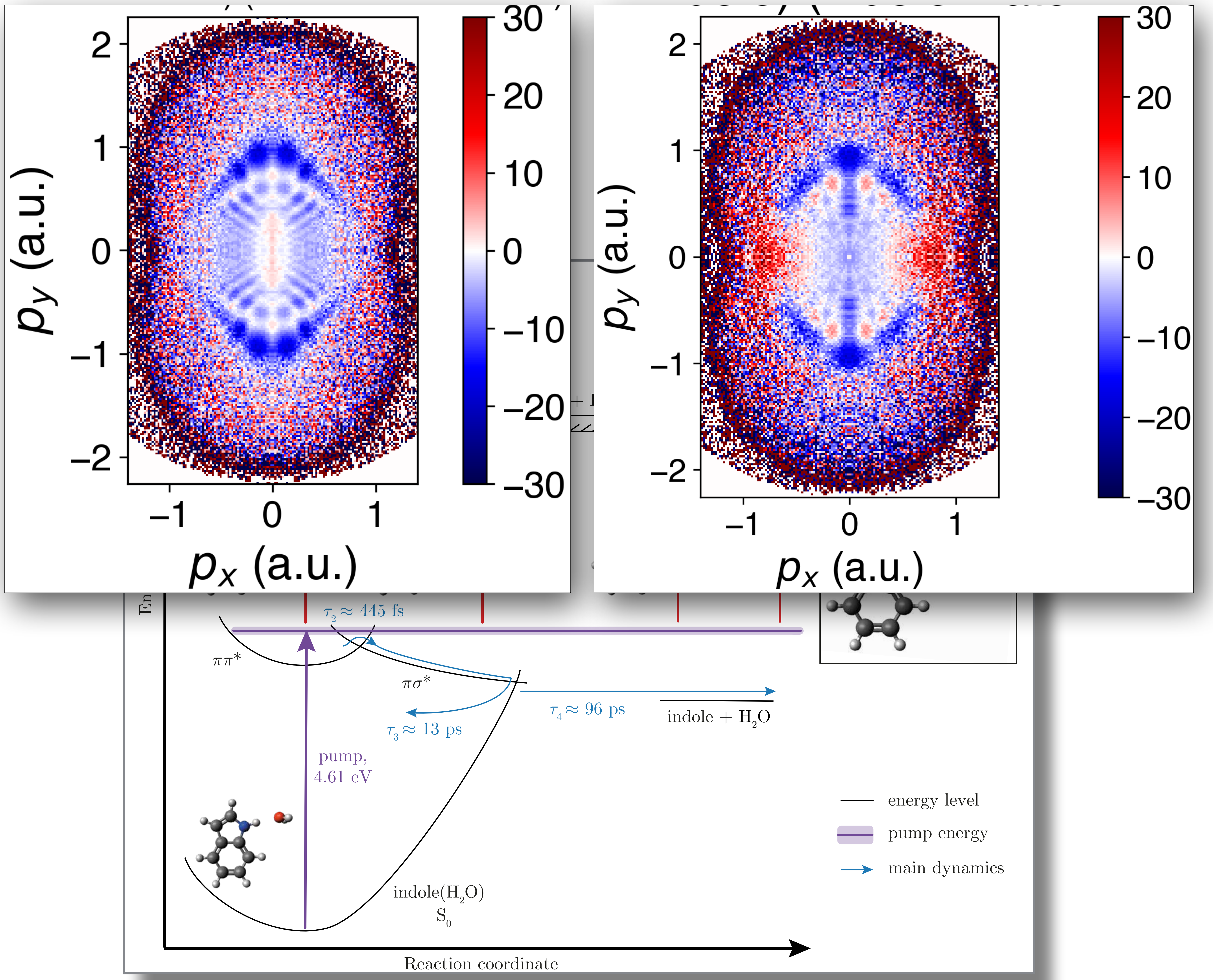
Holmegaard, Hansen, Kalhøj, Kragh, Stapelfeldt, Filsinger, Küpper, Meijer, Dimitrovski, Abu-samha, Martiny, Madsen, *Nature Phys.* **6**, 428 (2010); arXiv:1003.4634 [physics]
Trippel, Wiese, Mullins, Küpper, *J. Chem. Phys.* **148**, 101103 (2018); arXiv:1801.08789 [physics]

Toward atomic-resolution imaging of the radiation-protection effect
Watching the changes from reactants to products

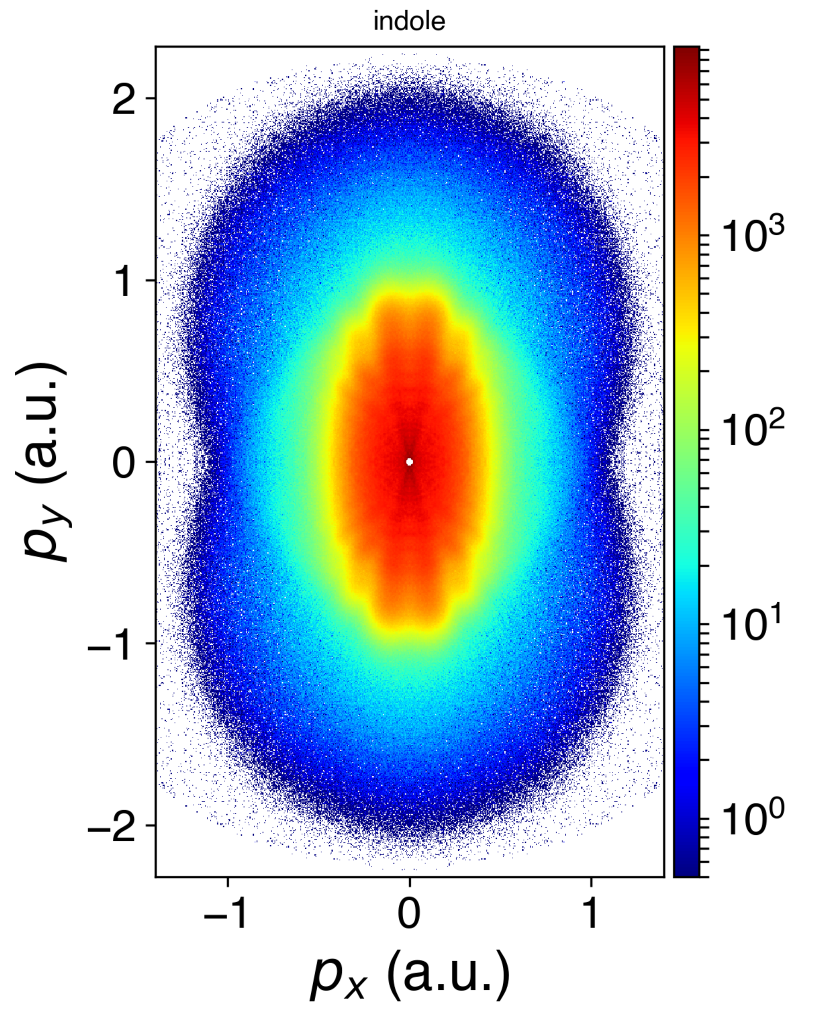
t = 0

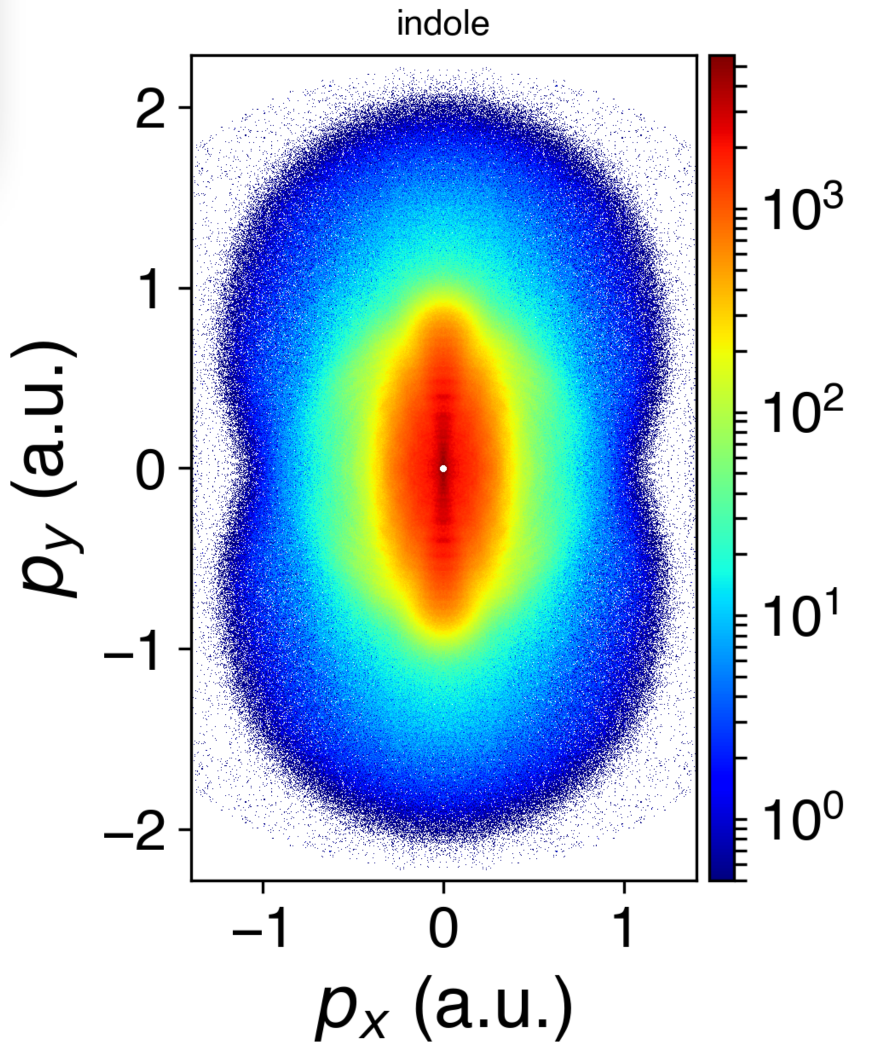






t = ∞

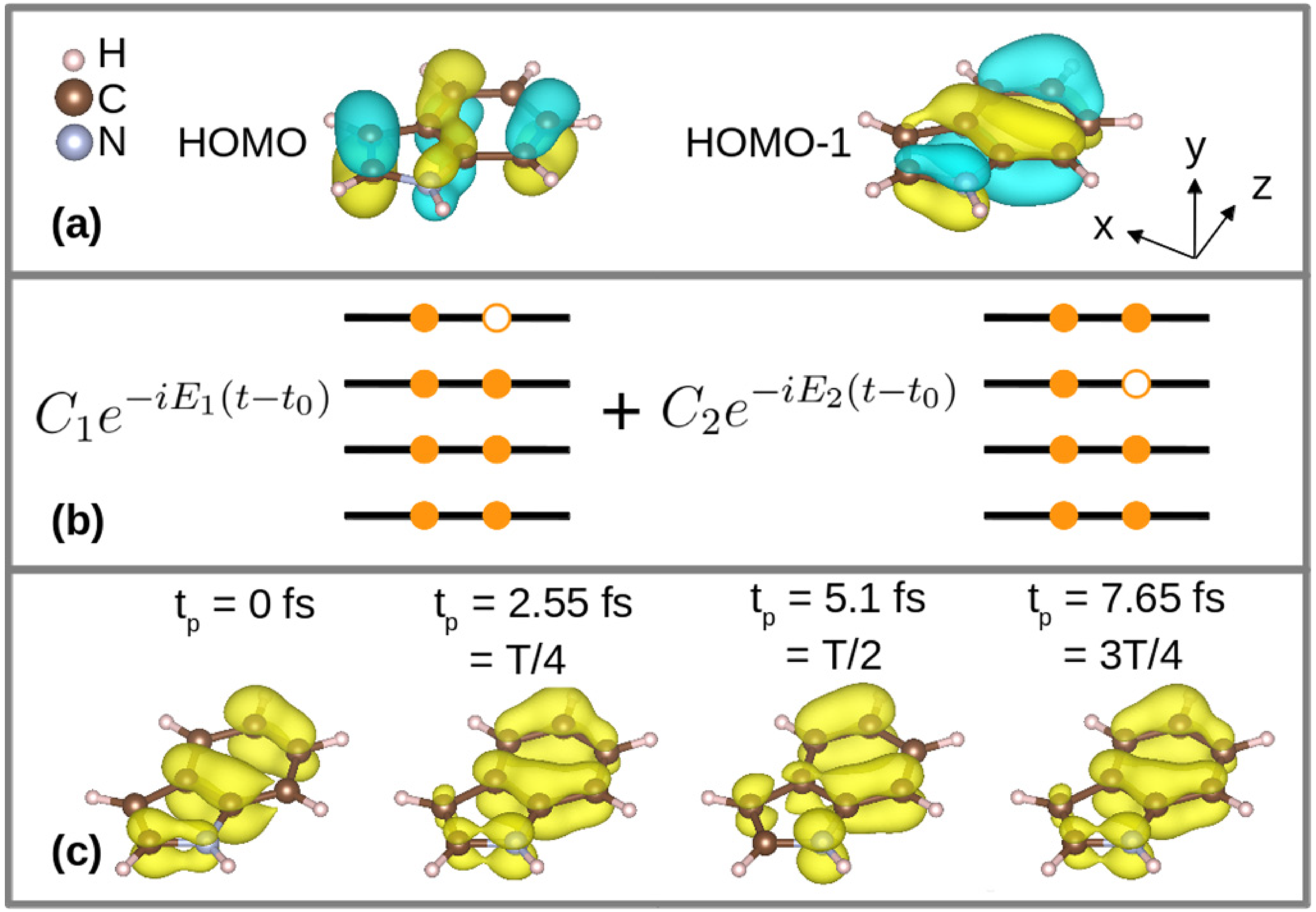




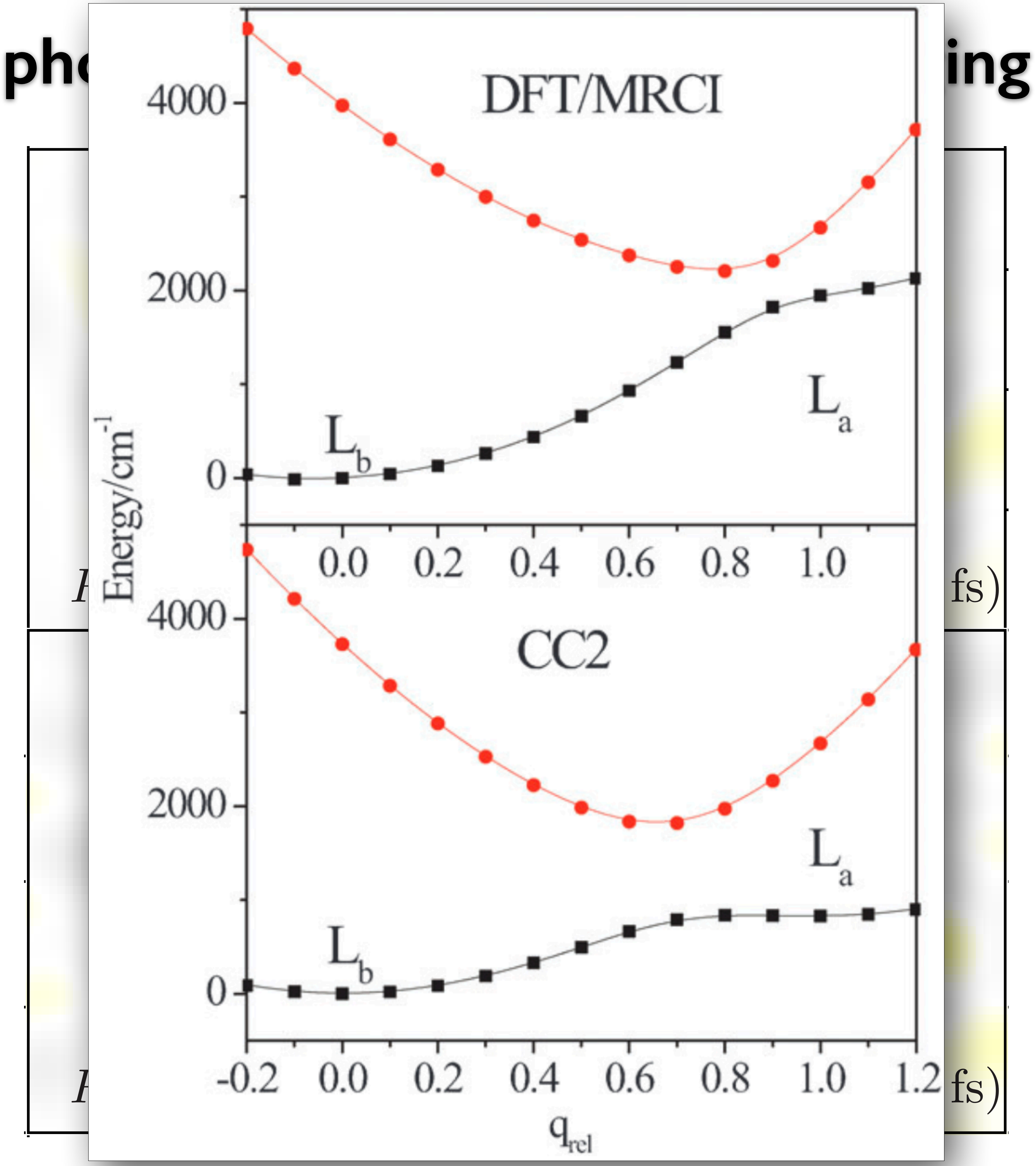
Wiese, Onvlee, Küpper, *in preparation* (2022)

Influence of solvation on ultrafast electron dynamics?
Electronic L_a-L_b dynamics in indole

outer-valence wavepacket

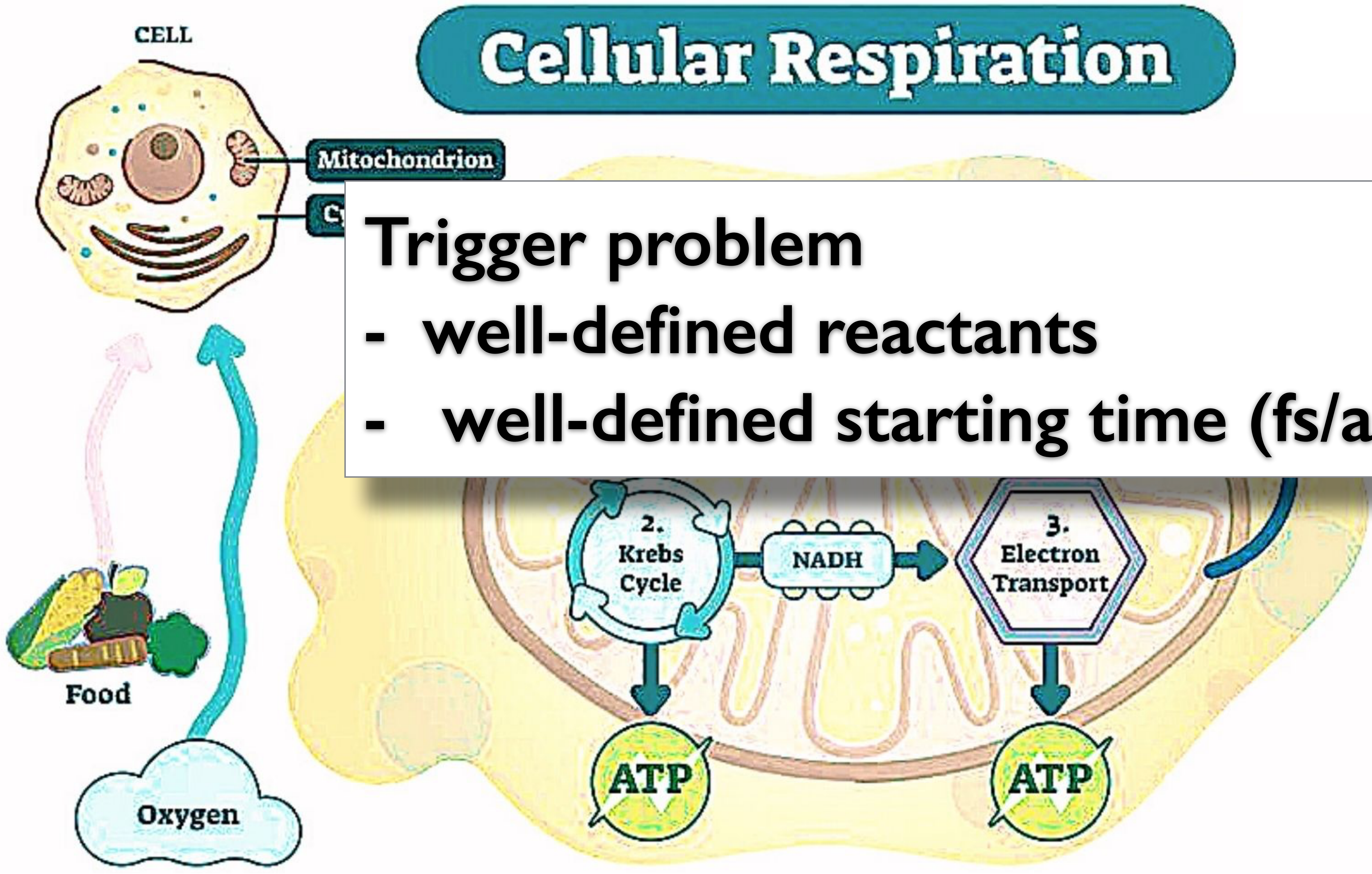


ph… ing



Küpper, Pratt, Meerts, Brand, Tatchen, Schmitt, *PCCP* **12**, 4980 (2010)
Popova-Gorelova, Küpper, Santra, *Phys. Rev.* A **94**, 013412 (2016); arXiv:1607.01322 [physics]

Next challenge:
Imaging the elementary ultrafast steps of thermal-energy dynamics



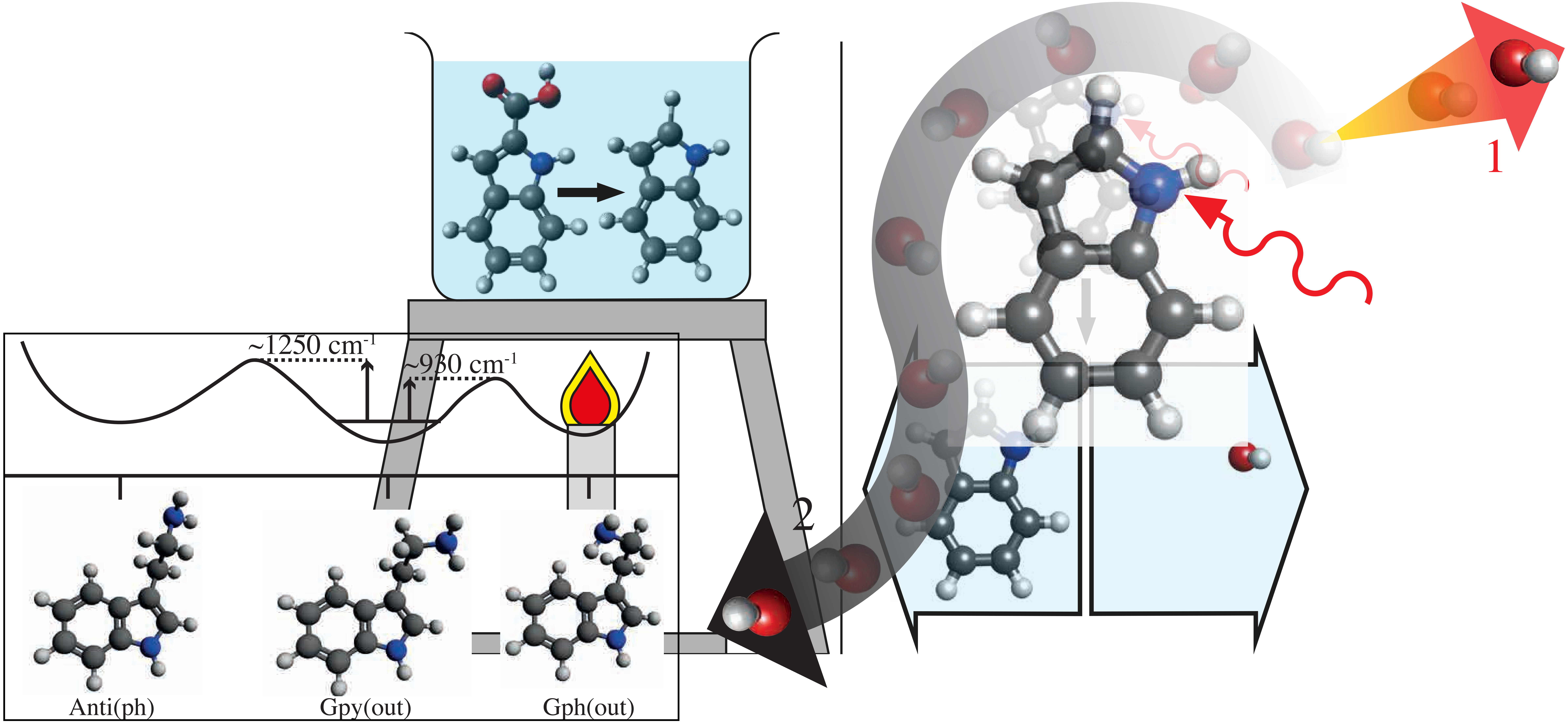
Trigger problem

- well-defined reactants
- well-defined starting time (fs/as scale)

https://www.biologyonline.com/dictionary/krebs-cycle.

Robinson, Küpper, submitted (2023); arXiv:2308.09602 [physics]

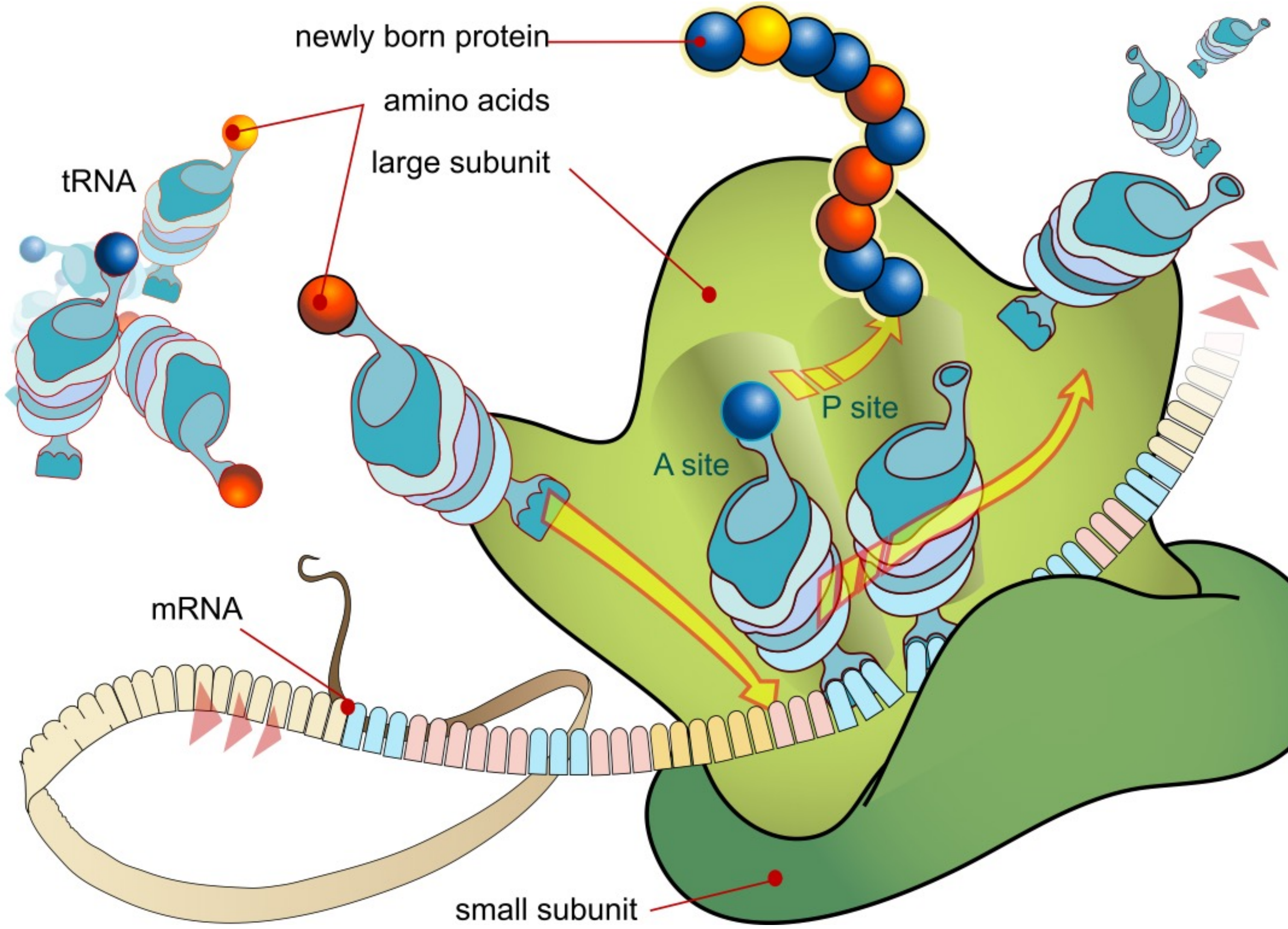
Imaging ultrafast elementary steps of thermal-energy chemistry



cf. Dian, Clarkson, Zwier, *Science* 303, 1169 (2004)

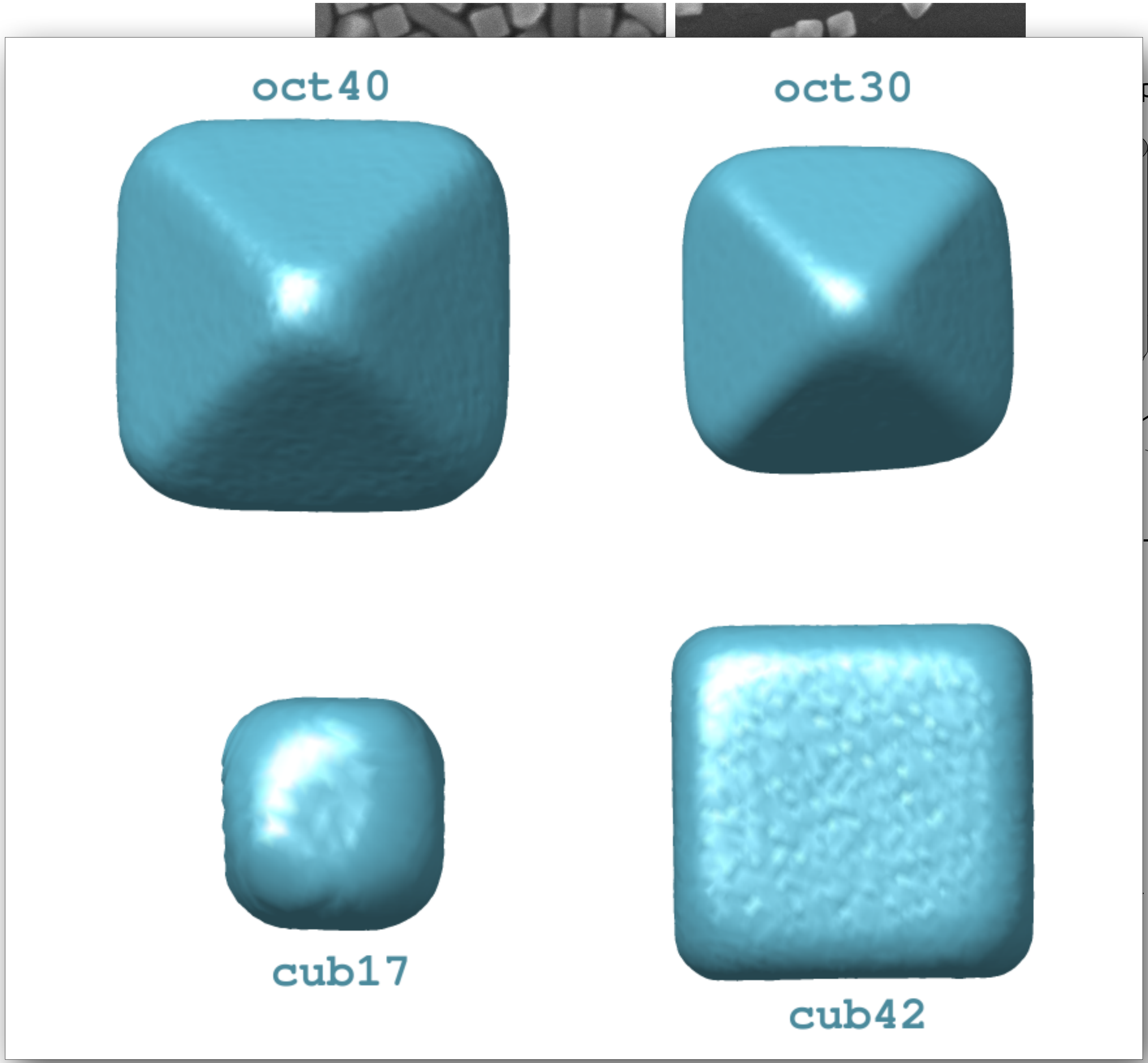
Robinson, Küpper, submitted (2023); arXiv:2308.09602 [physics]

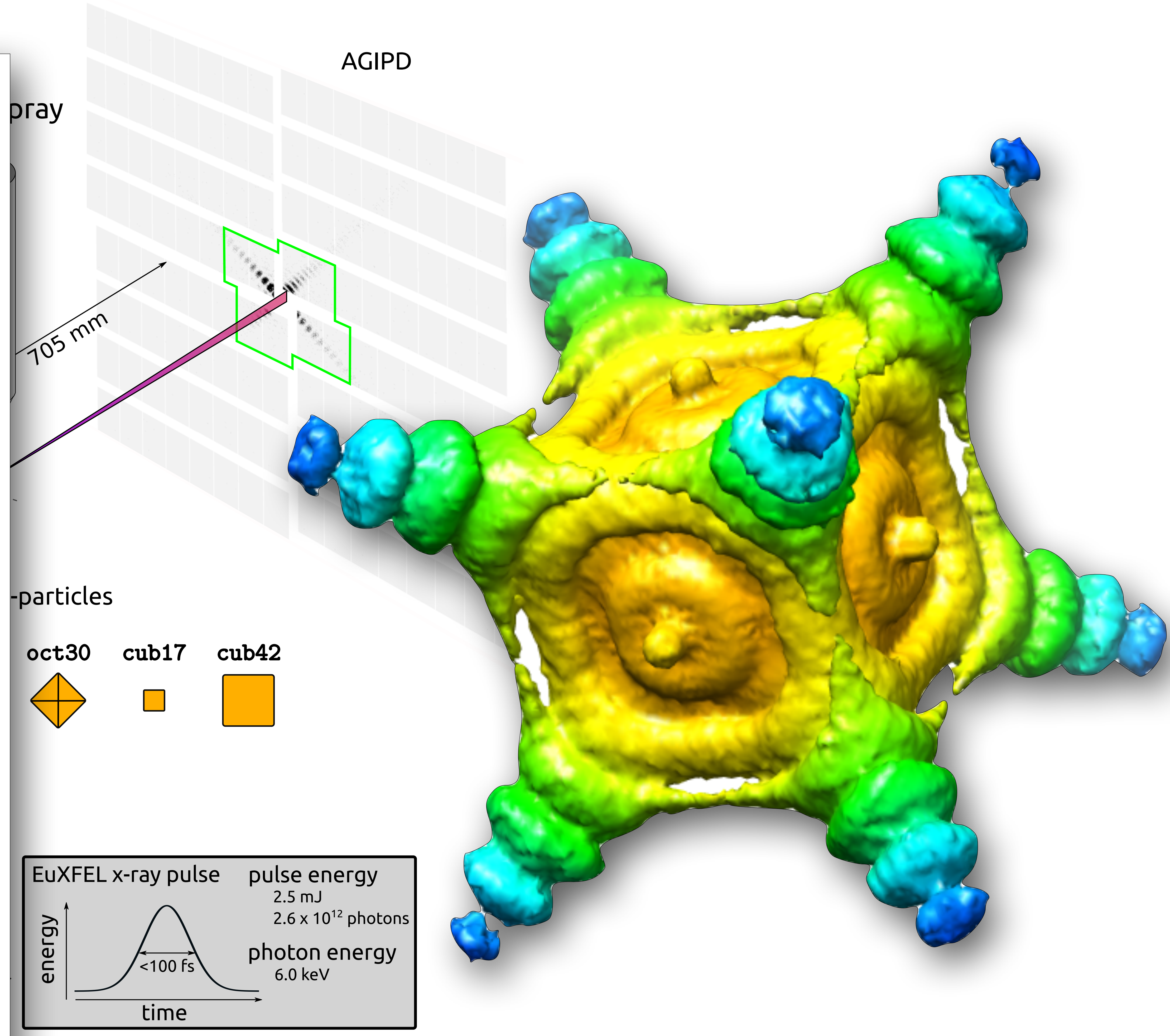
Tackling biological macromolecules directly



artists rendering (downloaded from Wikipedia, 2018)

Benchmarking single-particle imaging and creating an extended dataset
The million pattern gold standard

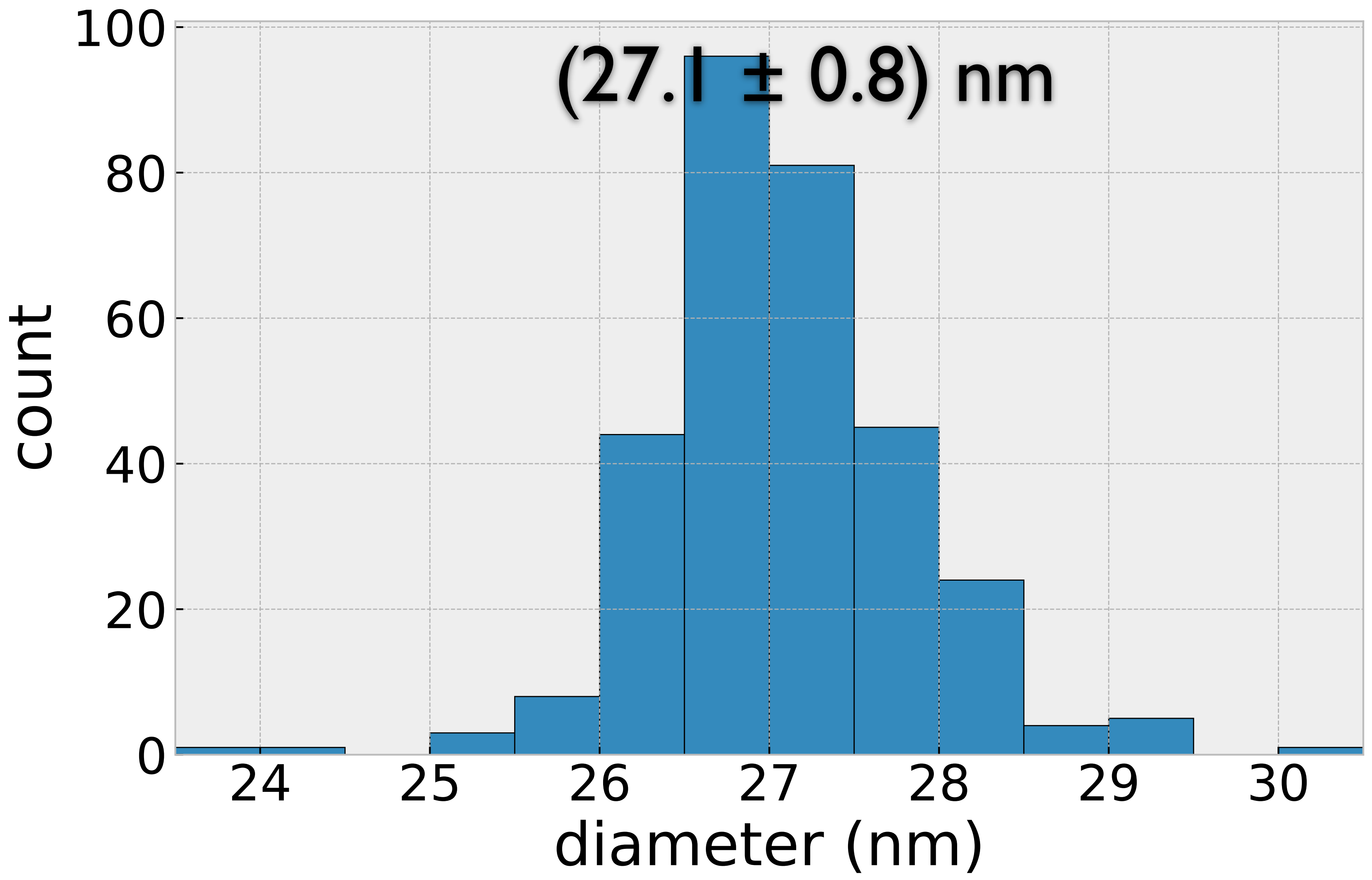


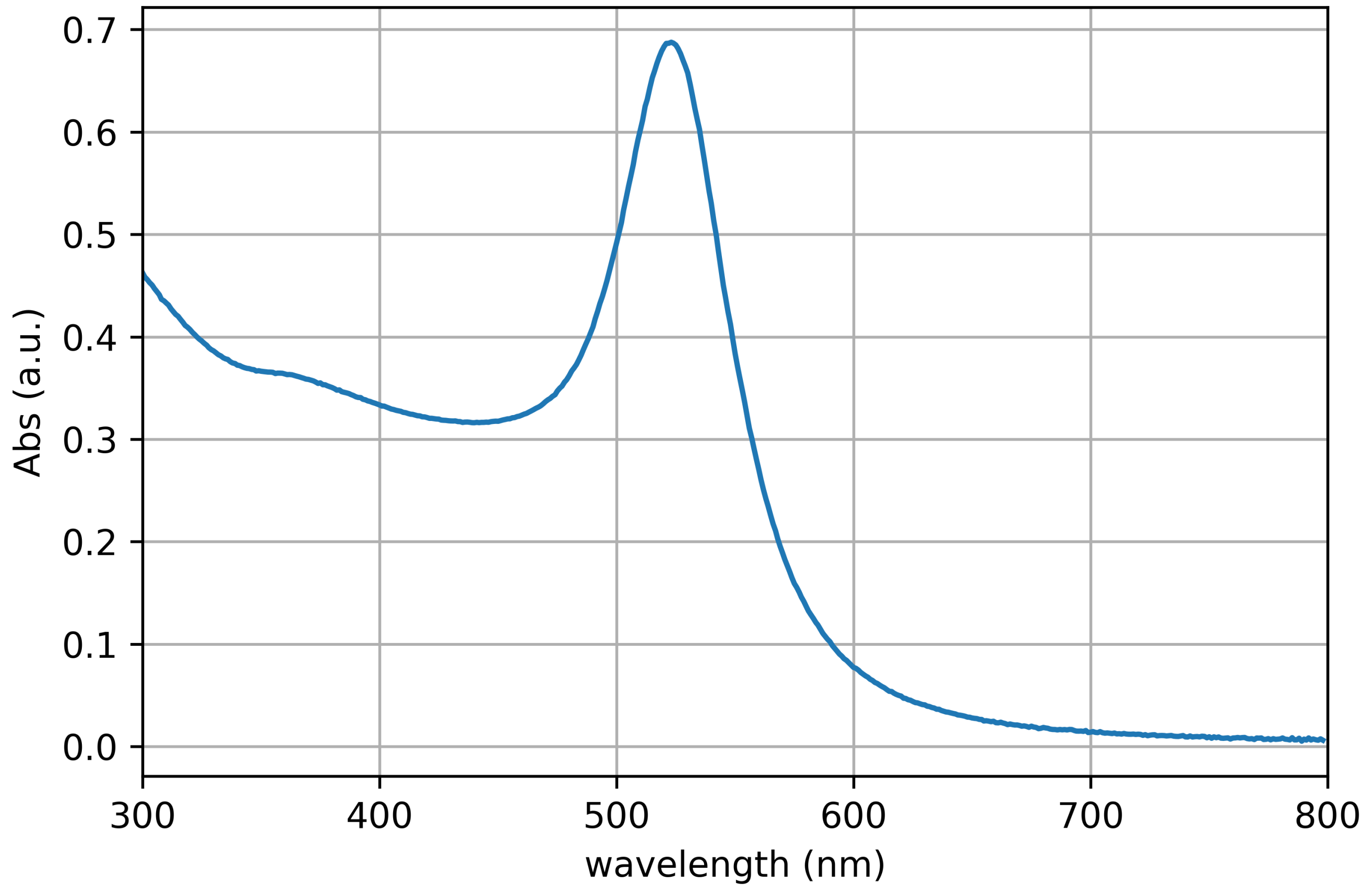


Ayyer, Lourdu, Bielecki, *et int* (34 authors), Küpper, Loh, Mancuso, Chapman, *Optica* **8**, 15 (2020); arXiv:2007.13597 [physics]

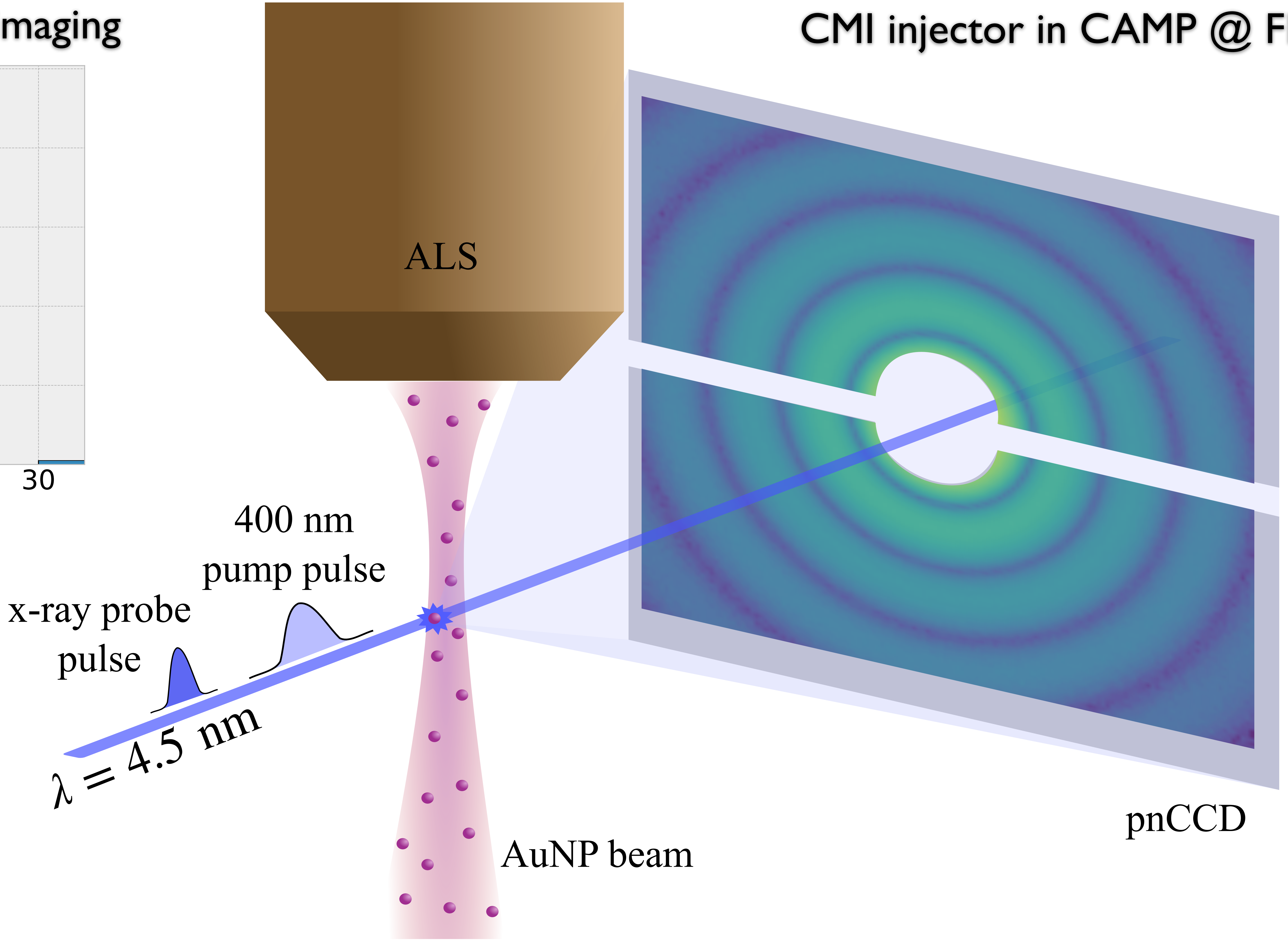
Recording the "Molecular Movie"
Electron-phonon-coupling in gold nanoparticles

Particle size distribution from TEM imaging





CMI injector in CAMP @ FLASH



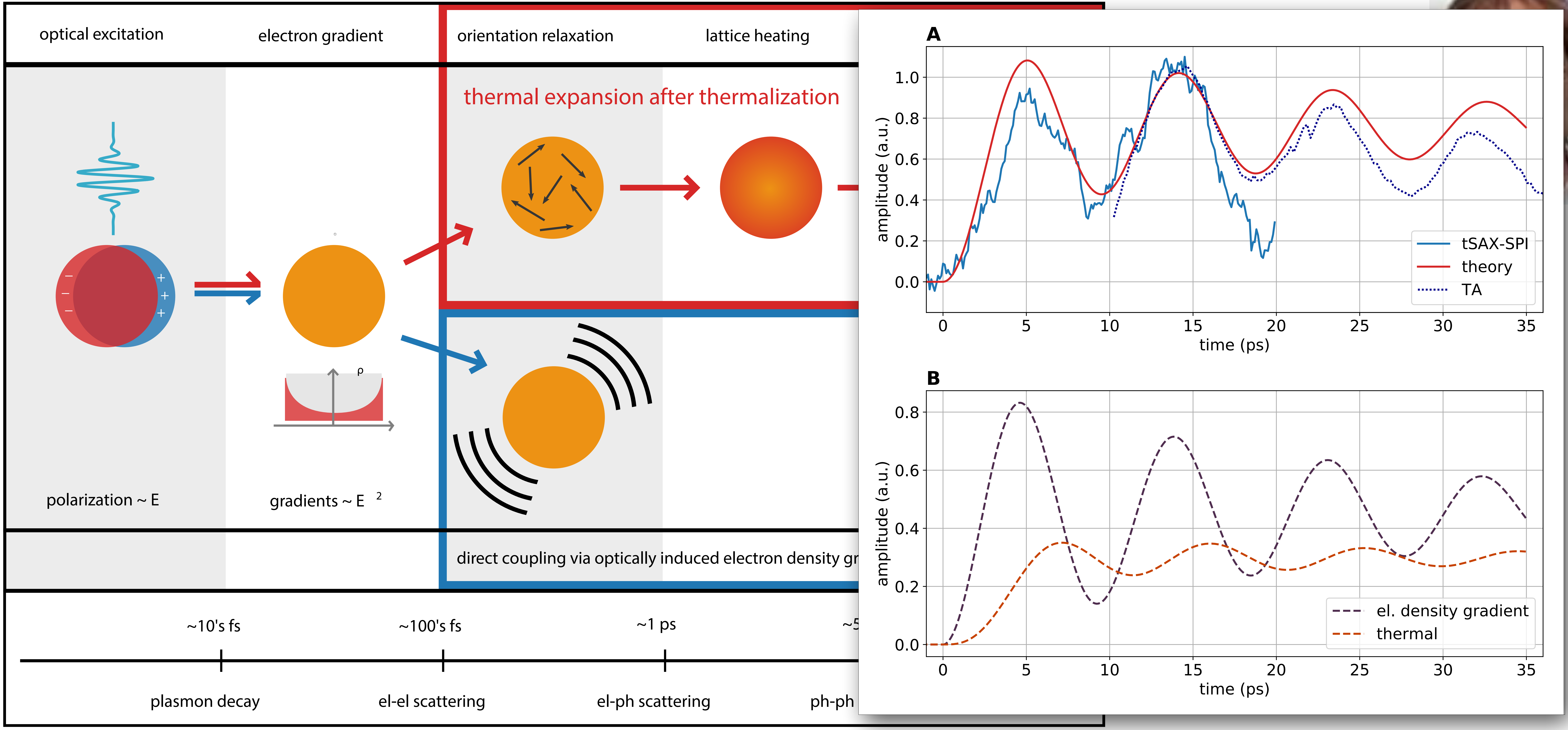
Höing, Salzwedel, Worbs, et int. (15 authors), Knorr, Ayyer, Küpper, Lange, *Nano Lett.* **23**, 5943–5950 (2023); https://arxiv.org/abs/2303.04513 [physics]

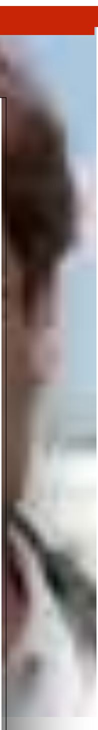
transient-SAXS imaging of AuNP structure (size) and the necessary new concept for electron–phonon coupling

supported by time-resolved transient-absorption spectroscopy

Höing, Salzwedel, Worbs, et int. (15 authors), Knorr, Ayyer, Küpper, Lange, *Nano Lett.* **23**, 5943–5950 (2023); https://arxiv.org/abs/2303.04513 [physics]

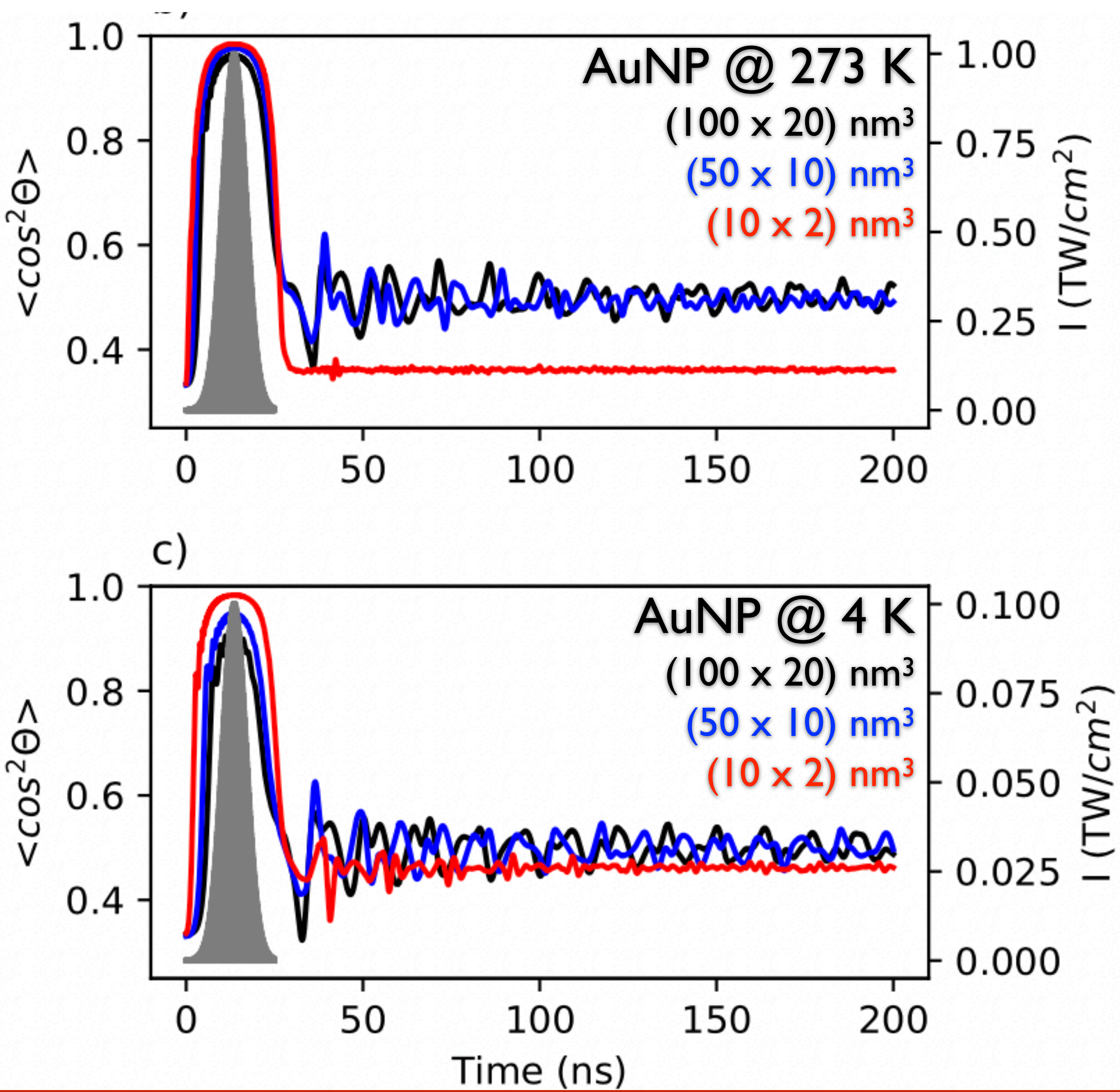
Relaxation dynamics in plasmonic nanoparticles
From traditional scattering concepts to direct field-driven coupling



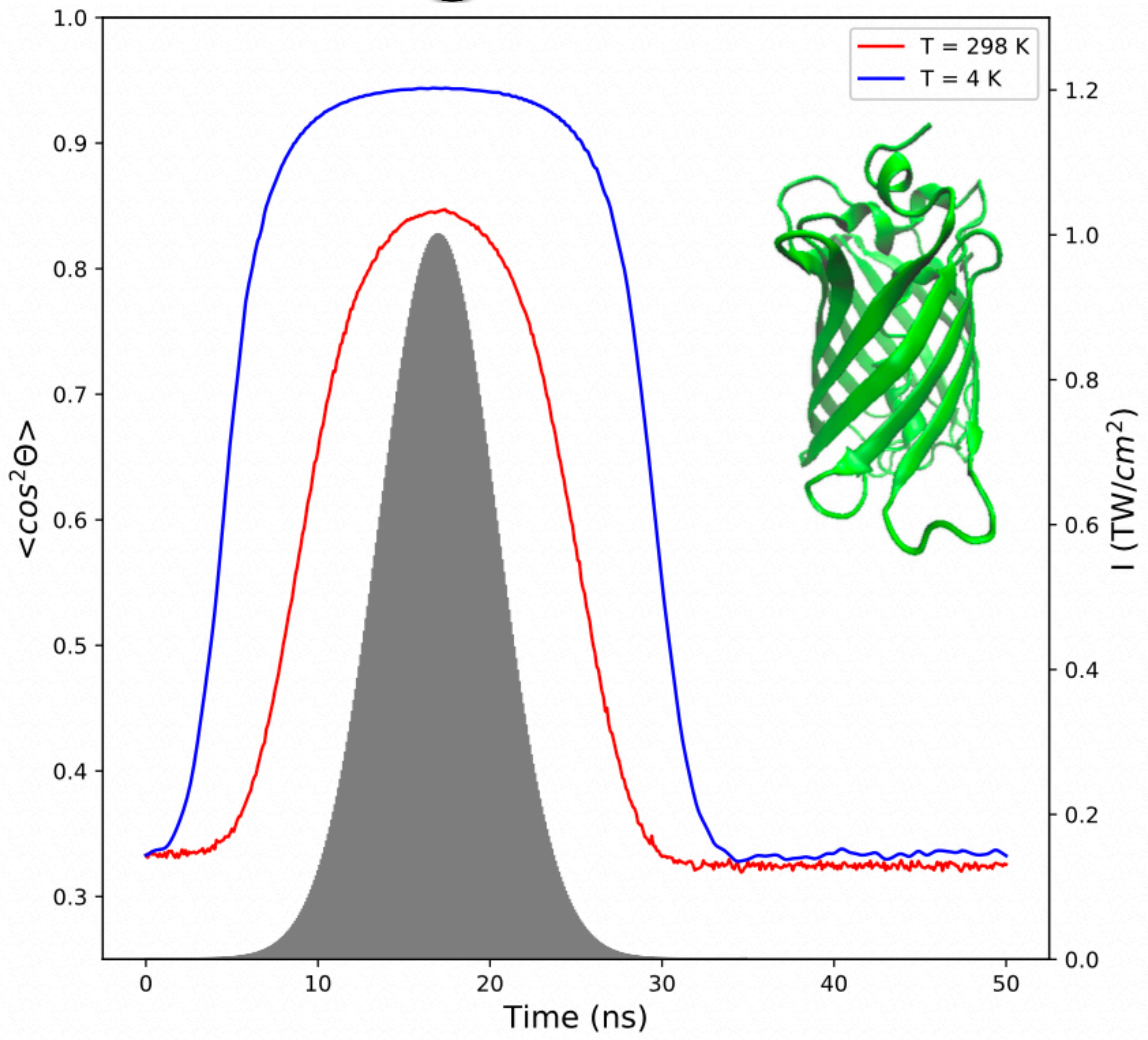


Höing, Salzwedel, Worbs, et int. (15 authors), Knorr, Ayyer, Küpper, Lange, *Nano Lett.* **23**, 5943–5950 (2023); arxiv.org:2303.04513 [physics]

Modeling of laser-induced alignment using classical-mechanics simulations

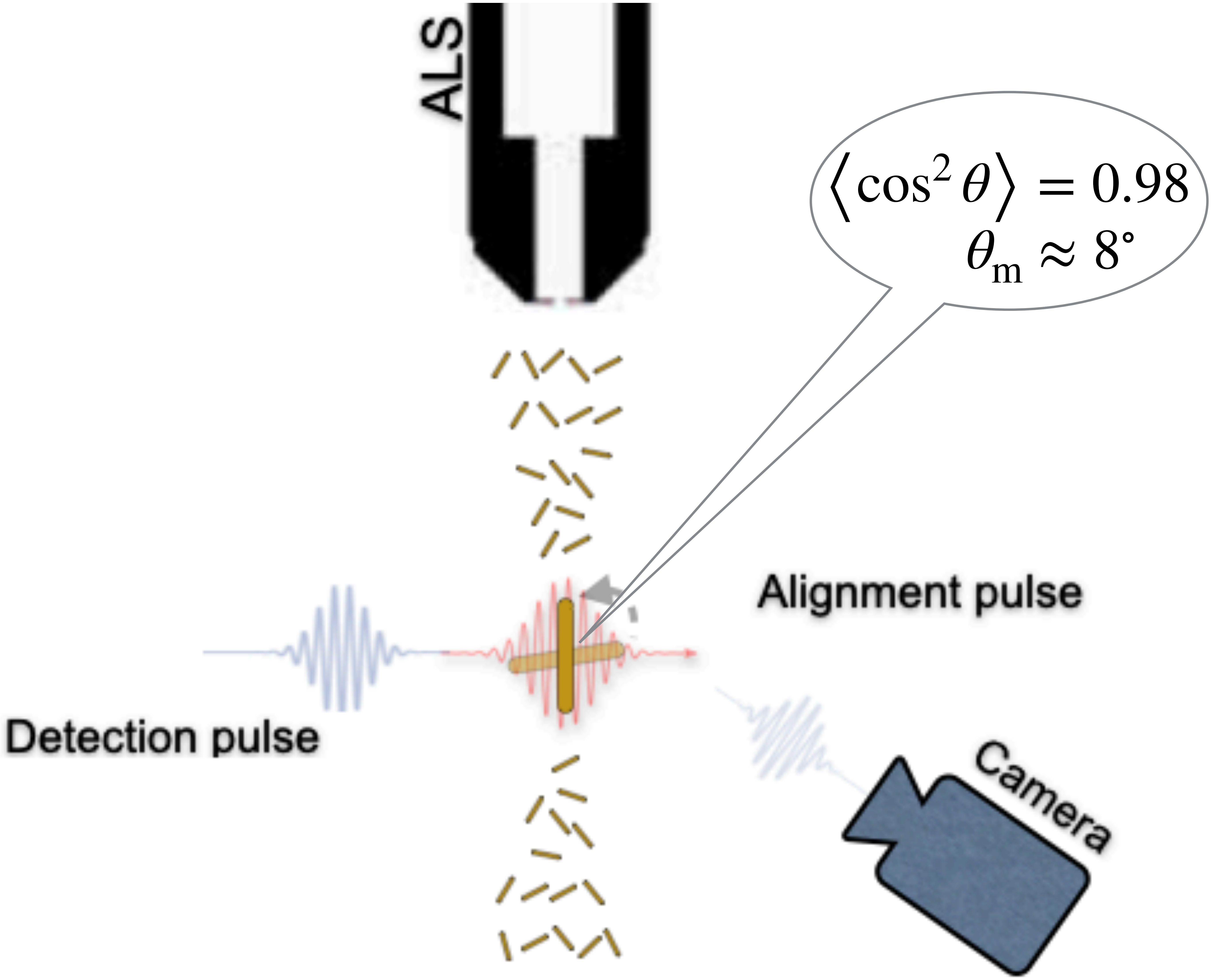


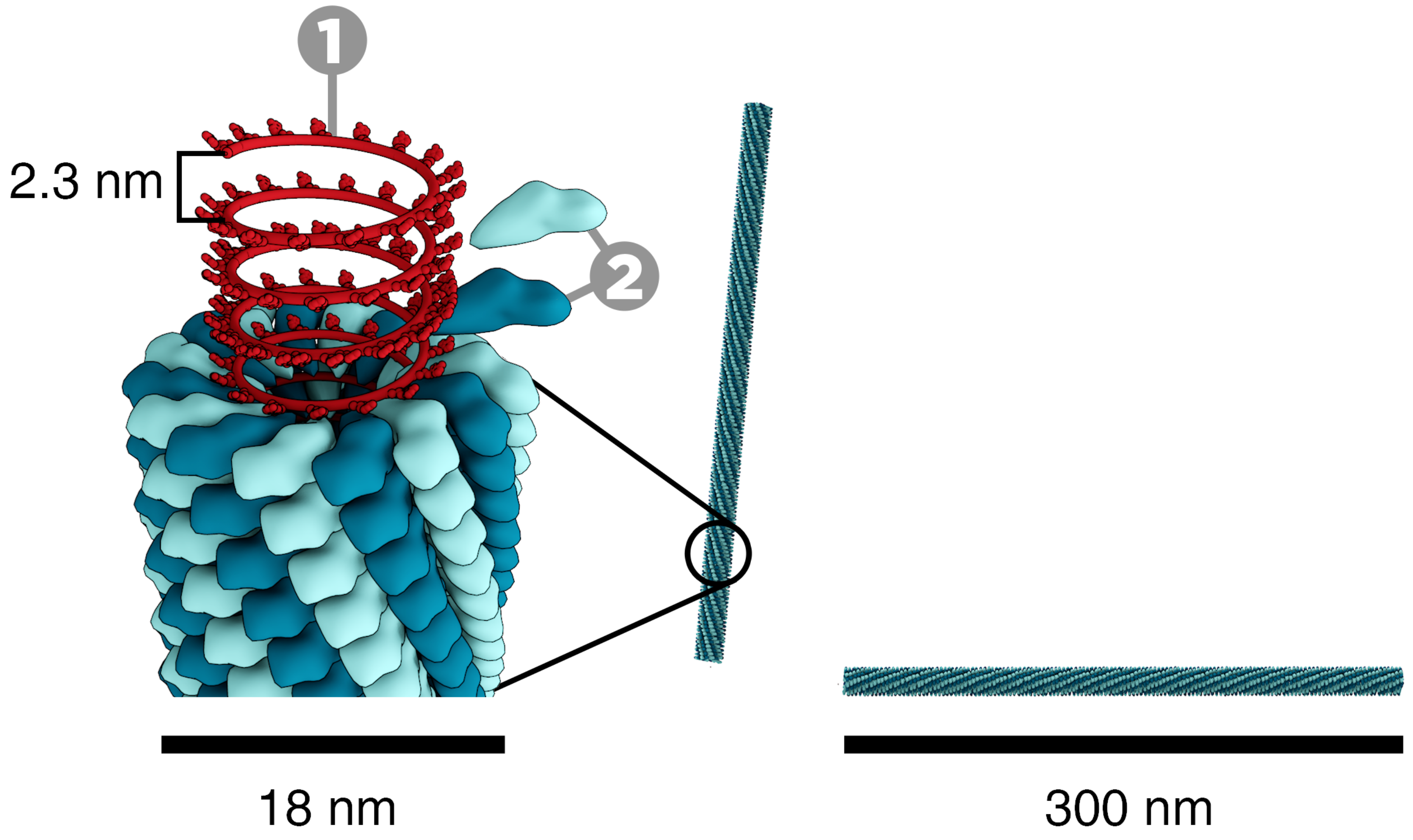
GFP @ 4 K & 273 K



Amin, Hartmann, Samanta, Küpper, submitted (2023); arXiv:2306.05870 {physics]
https://github.com/CMIclassirot

Experimental realization of laser-induced alignment and detection





theory: Amin, Hartmann, Samanta, Küpper, submitted (2023); arXiv:2306.05870 {physics}
Haas, Cheng, Amin, Samanta, Küpper, in preparation, (2023)

Summary

- Electric fields allow for strong control of molecules and nanoparticles
  - separating molecular species: quantum states, conformers, (microsolvated) aggregates, …
  - fixing molecules in space: one- and three-dimensional alignment and orientation
  - (control of chirality is feasible)
- Appropriate control schemes allow to **disentangle the *ultrafast dynamics of molecular systems*** in specific detail
  - directly connected to radiation damage processes in biological matter:
    - low-energy ionization of molecule-water complexes demonstrates specific protection effect
    - UV-induced initial electronic and dissociation dynamics of indole-water
- Imaging ultrafast elementary steps of thermal-energy (bio)chemistry
- Diffractive imaging unravels gas-phase molecular structures down to *few-picometer spatial resolution* (on femtosecond timescales)
- Imaging nanoscale-particle structural dynamics provides novel insight into energy-transfer processes and time-resolved structural biology

Acknowledgments
CFEL Controlled Molecule Imaging Group

CUI THE HAMBURG CENTER FOR ULTRAFAST IMAGING

UHH Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

DFG DASHH

EXC Center for Ultrafast Imaging
EXC Advanced Imaging of Matter
SPP 1840 Quantum Dynamics in Tailored Light Fields

Röntgen Ångström Cluster UDIET

HELIOS Helmholtz-Lund International Graduate School

CMWS Centre for Molecular Water Science

Alexander von Humboldt Stiftung/Foundation

Bundesministerium für Bildung und Forschung

HELMHOLTZ ASSOCIATION

erc European Research Council
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Acknowledgments
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CUI THE HAMBURG CENTER FOR ULTRAFAST IMAGING
UHH Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

DFG DASHH
EXC Center for Ultrafast Imaging
EXC Advanced Imaging of Matter
SPP 1840 Quantum Dynamics in Tailored Light Fields

Röntgen Ångström Cluster
UDIET

HELIOS
Helmholtz-Lund International Graduate School

CMWS Centre for Molecular Water Science

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CFEL SCIENCE
Controlled Molecule Imaging

Join us on *Science Campus Hamburg-Bahrenfeld*…

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We are looking for motivated colleagues at all career levels, please see https://www.controlled-molecule-imaging.org/careers or contact me directly.

Open positions at Master-student, doctoral, and postdoctoral level

- Disruptive sample-delivery approaches for atomic-resolution cryo-EM
- Solvent effects in the ultrafast dynamics of (bio)molecules
- Single-particle imaging of cryogenically cooled and controlled beams of (bio-) nanoparticles