Investigating complex molecular dynamics

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CUI THE HAMBURG CENTER FOR ULTRAFAST IMAGING

Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

CFEL SCIENCE
Controlled Molecule Imaging

DESY.

Acknowledgments

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CUI THE HAMBURG CENTER FOR ULTRAFAST IMAGING
UHH Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

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

MC-ITN MEDEA
MC-ITN ASPIRE

Alexander von Humboldt Stiftung/Foundation

Bundesministerium für Bildung und Forschung

HELMHOLTZ ASSOCIATION

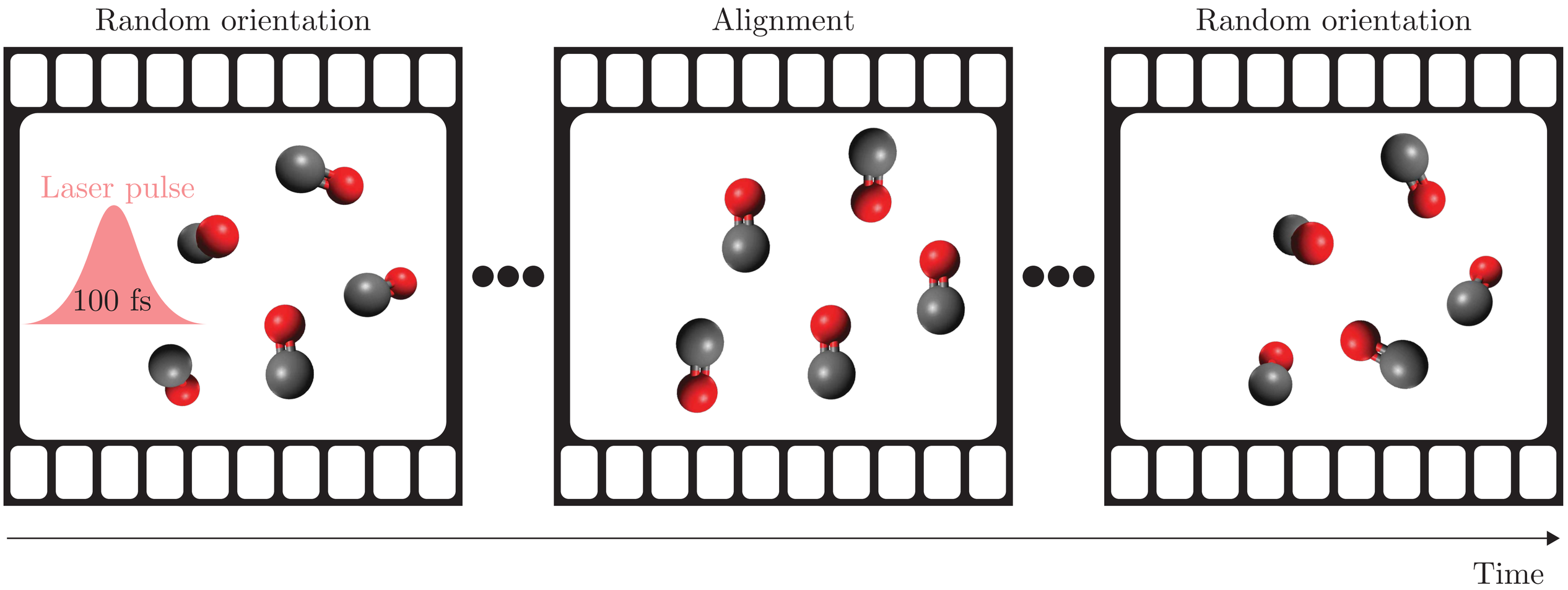
erc Collmotion European Research Council
Established by the European Commission

DESY.

Molecules

- What is a molecule?
- What does a molecule look like?
- The interaction of molecules with electromagnetic fields, including the interaction with light.

Alignment and orientation in various regimes
– an experimental molecular movie –



Karamatskos, *et int*, (13 authors) Rouzée, Küpper, *Nat. Comm.* **10**, 3365 (2019); arXiv:1802.06622 [physics]

Alignment and orientation in various regimes
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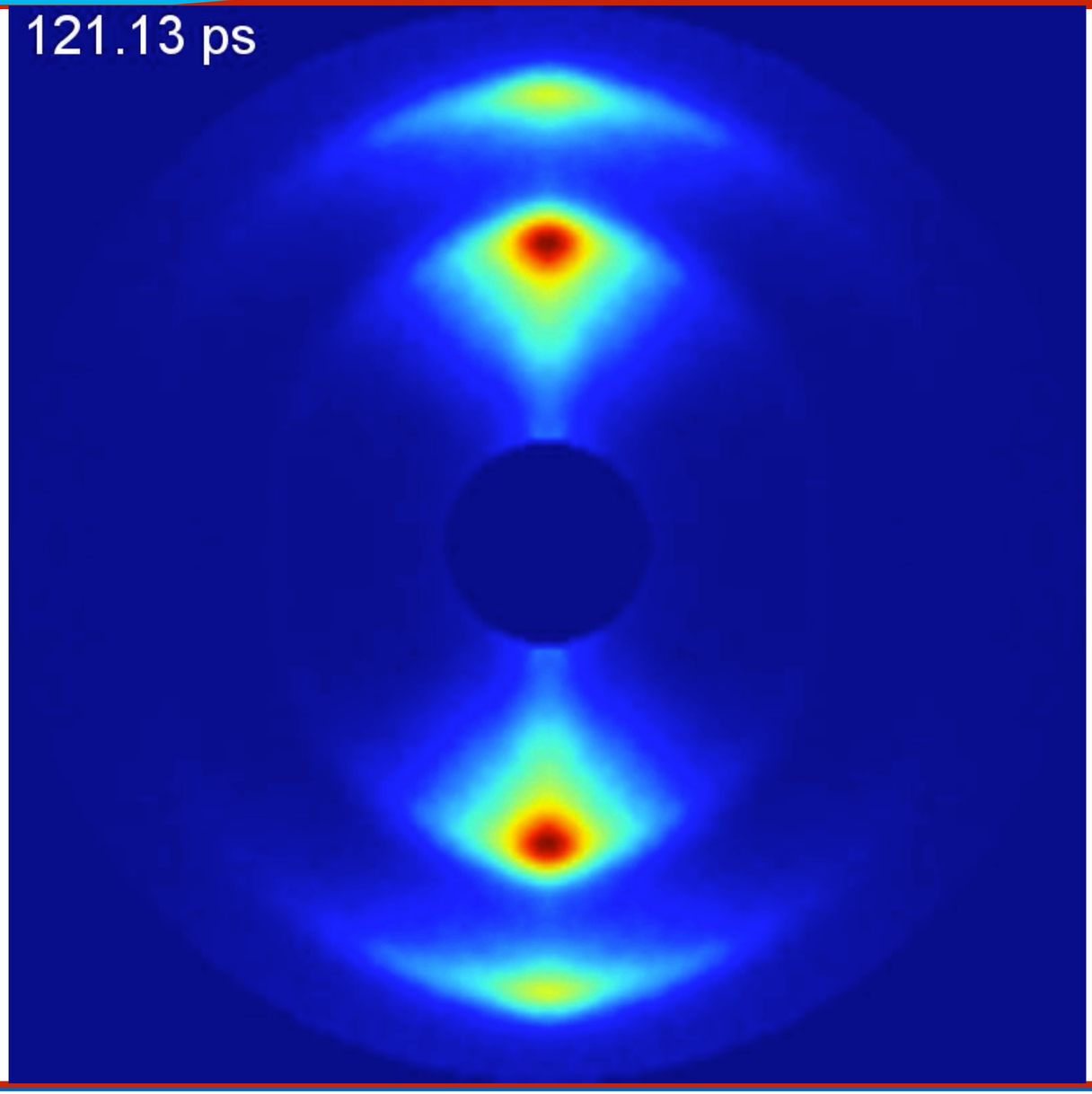
***M* = 0**

**Time-evolution
of a rotational wavepacket
displaying
quantum interference structure**



**“redish” colors show density distribution
of “S” end of OCS molecule**

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$\langle \cos^2 \theta \rangle_{3D} \geq 0.93$

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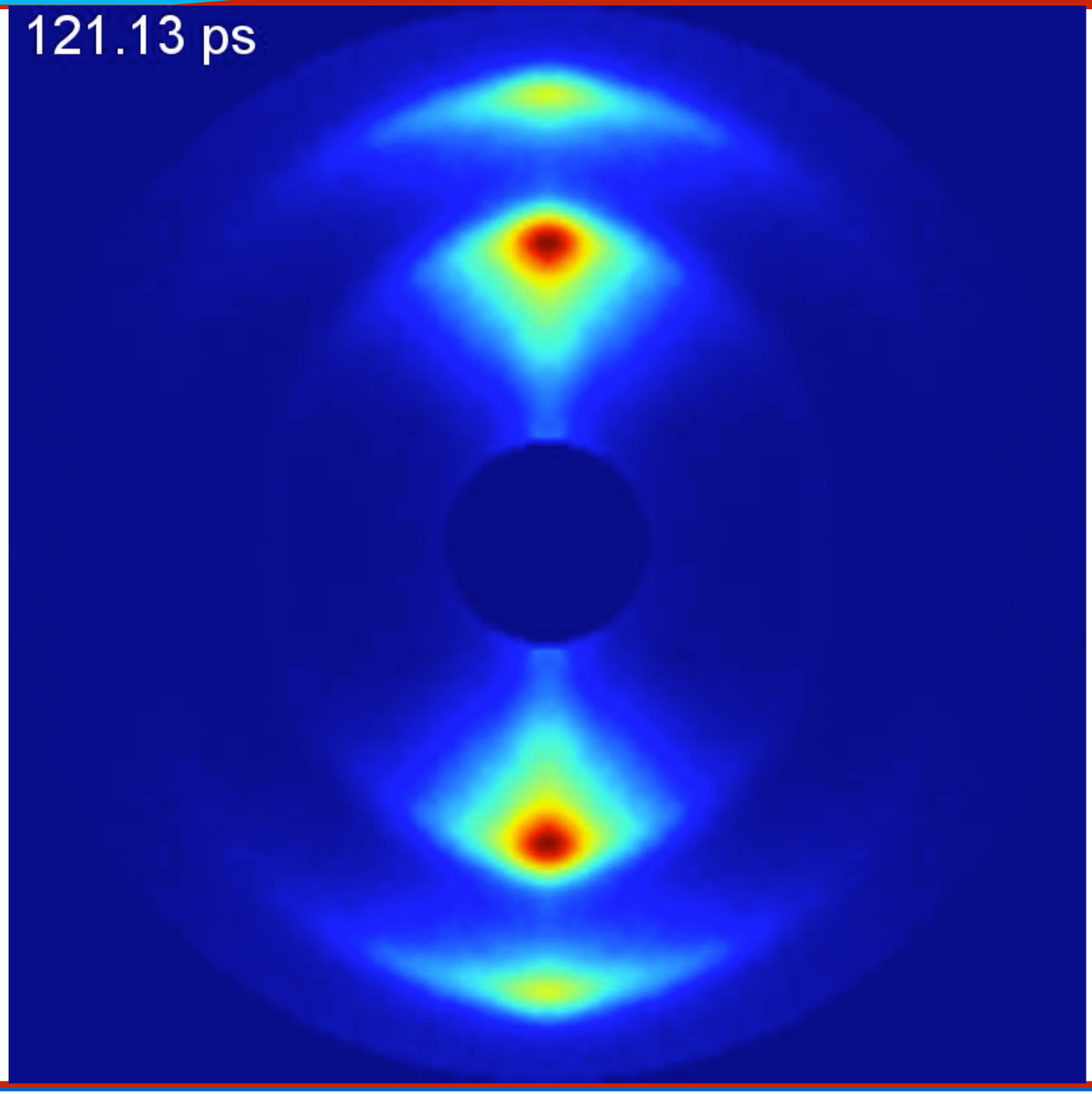

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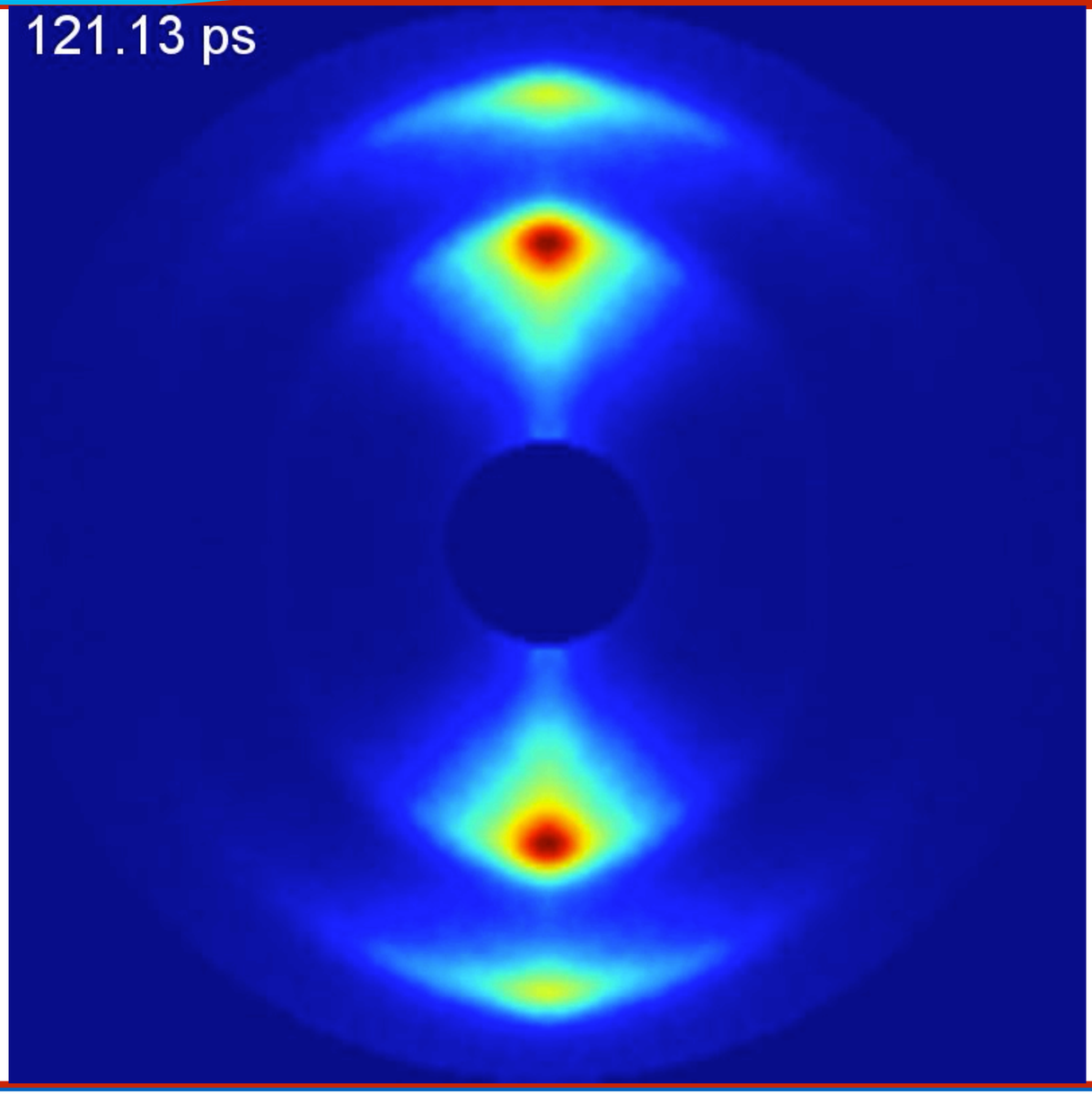

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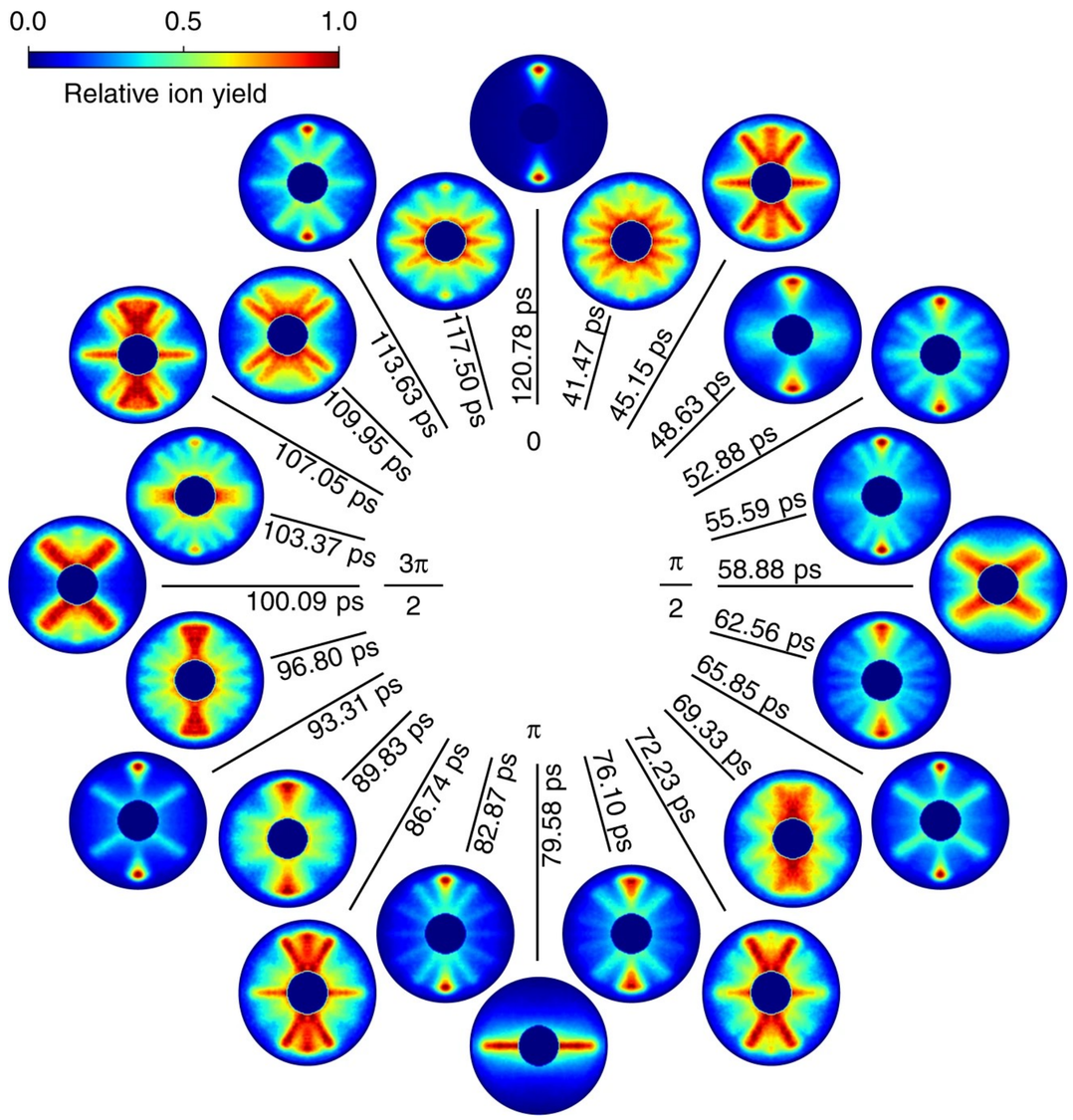

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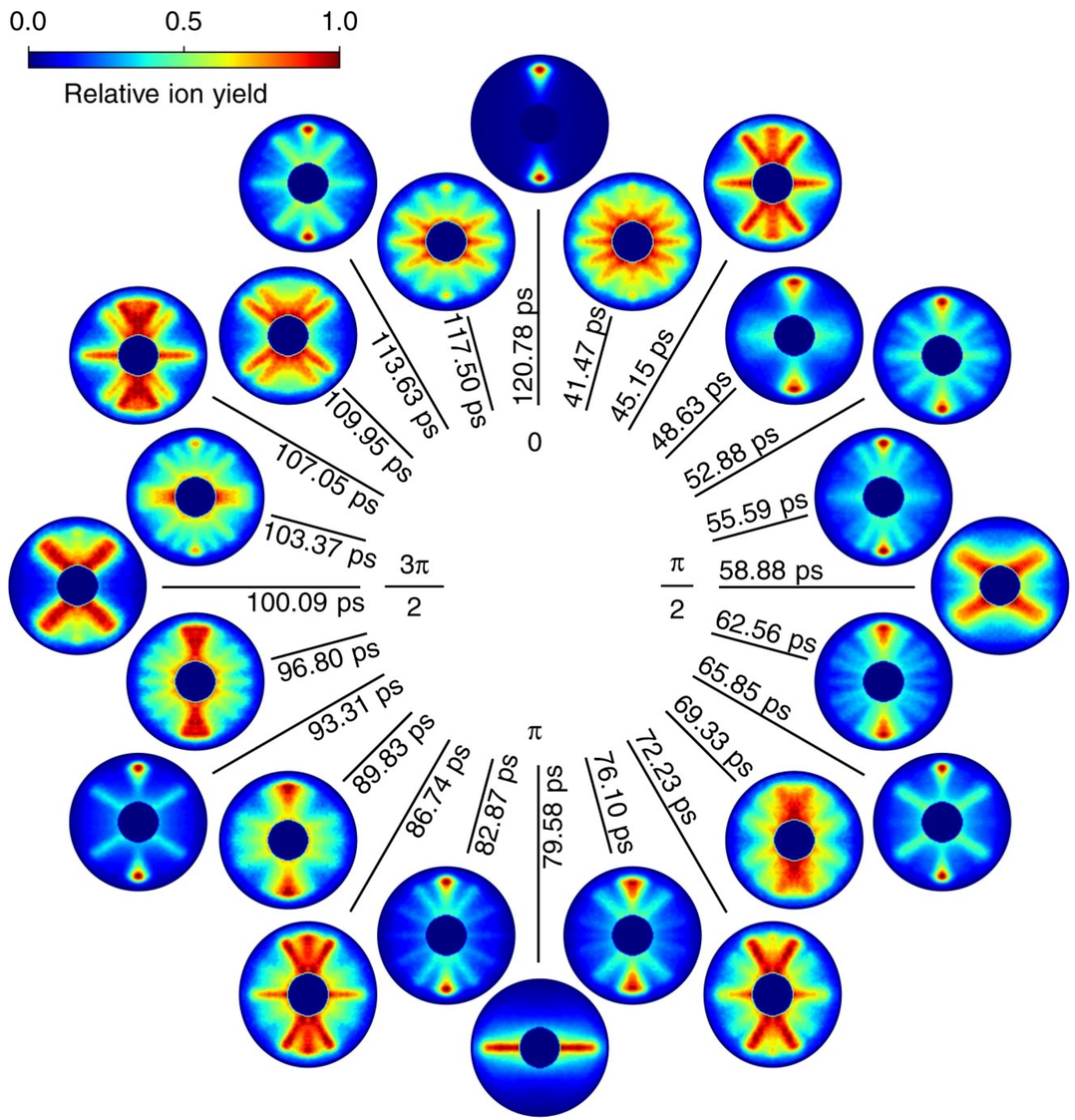

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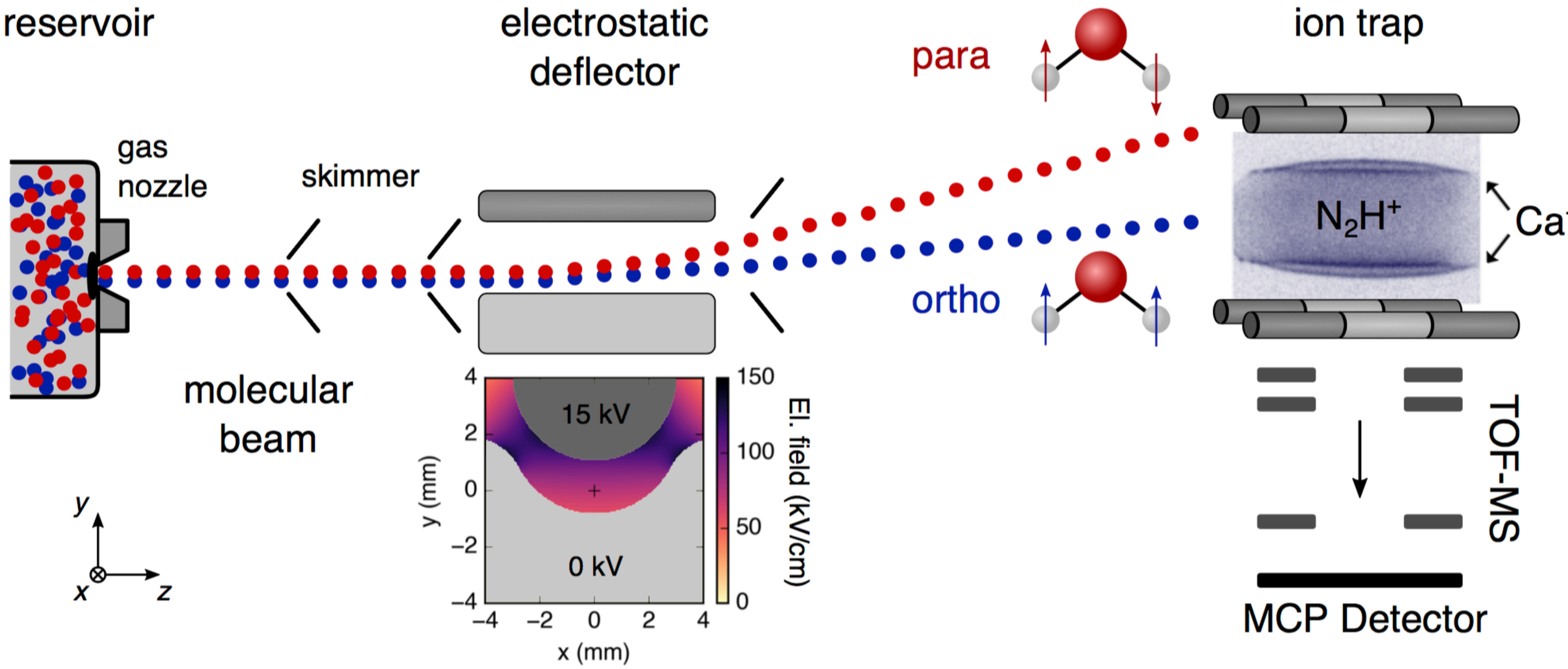
Specific chemical reactions of *para* and *ortho* water



Kilaj, Gao, Rösch, Rivero, JK, Willitsch, *Nat. Comm.* **9**, 2096 (2018)

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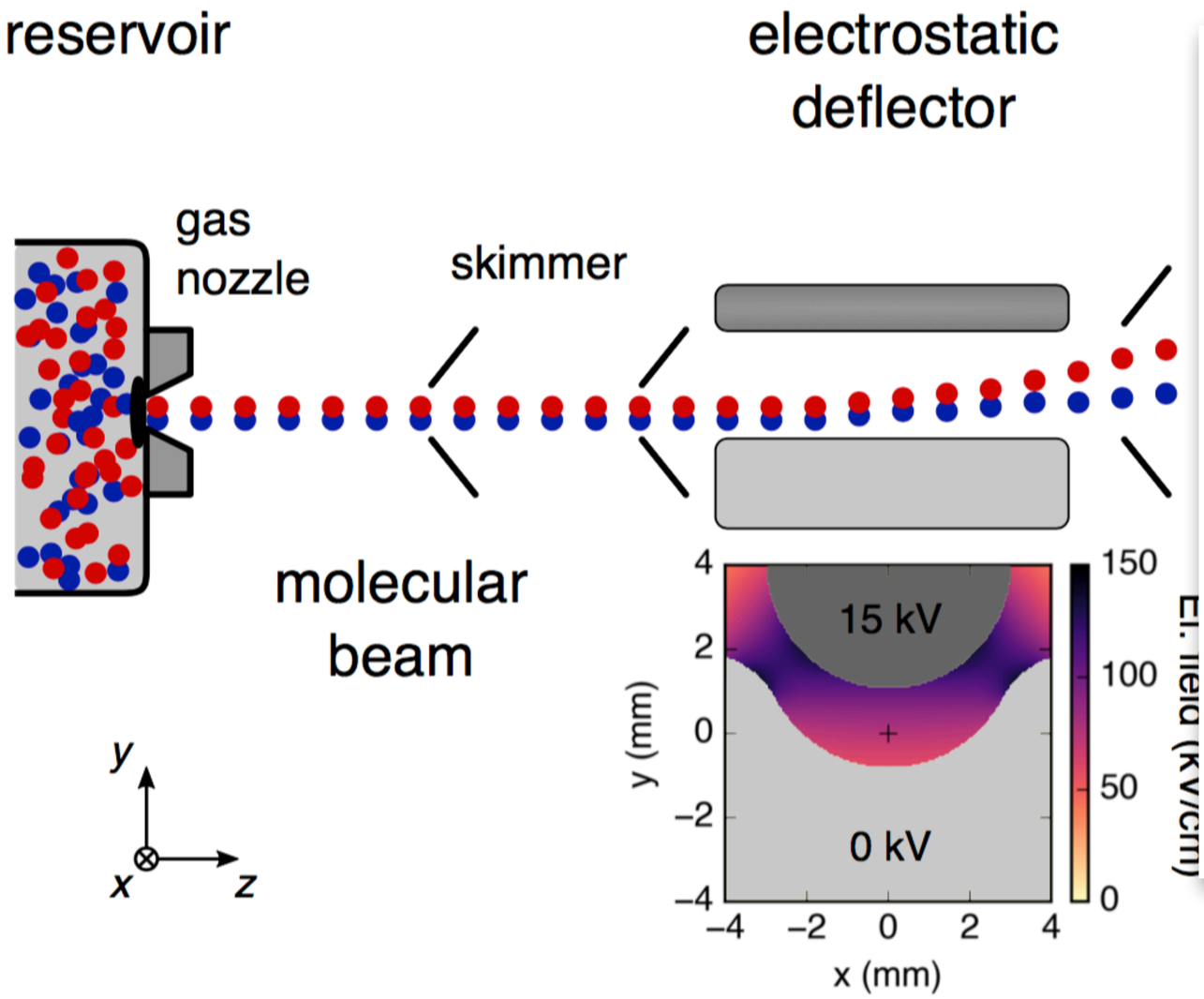

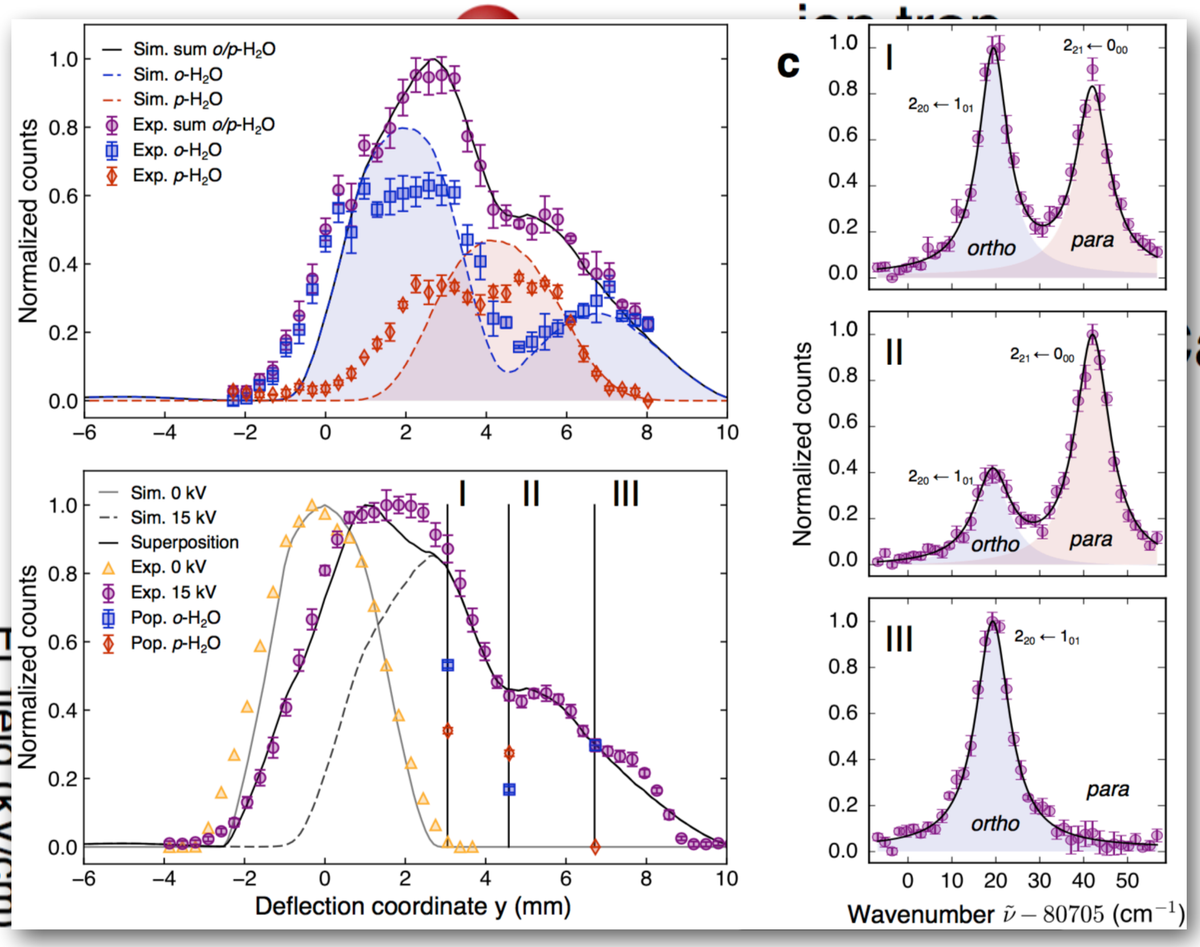

MCP Detector

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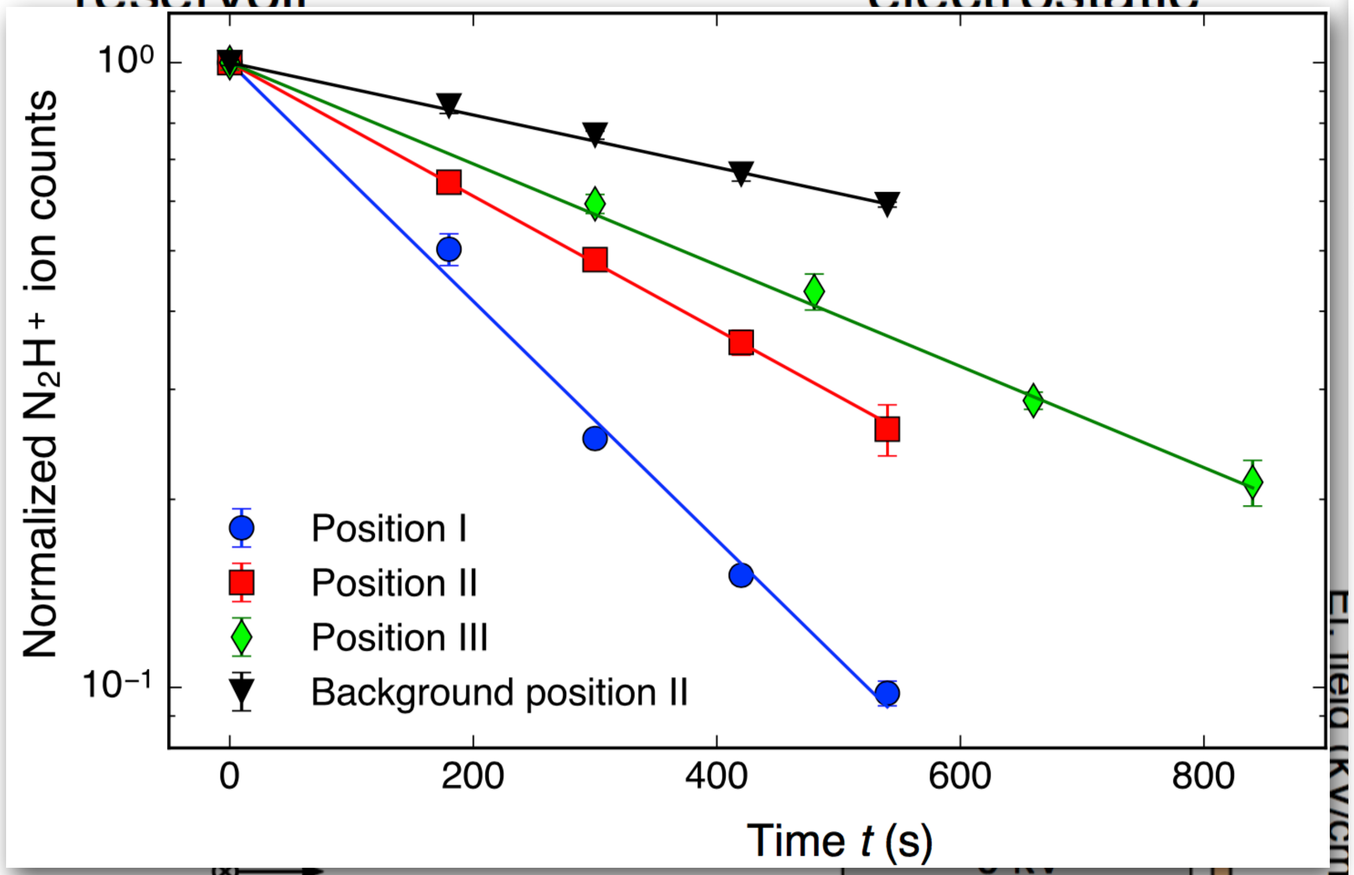

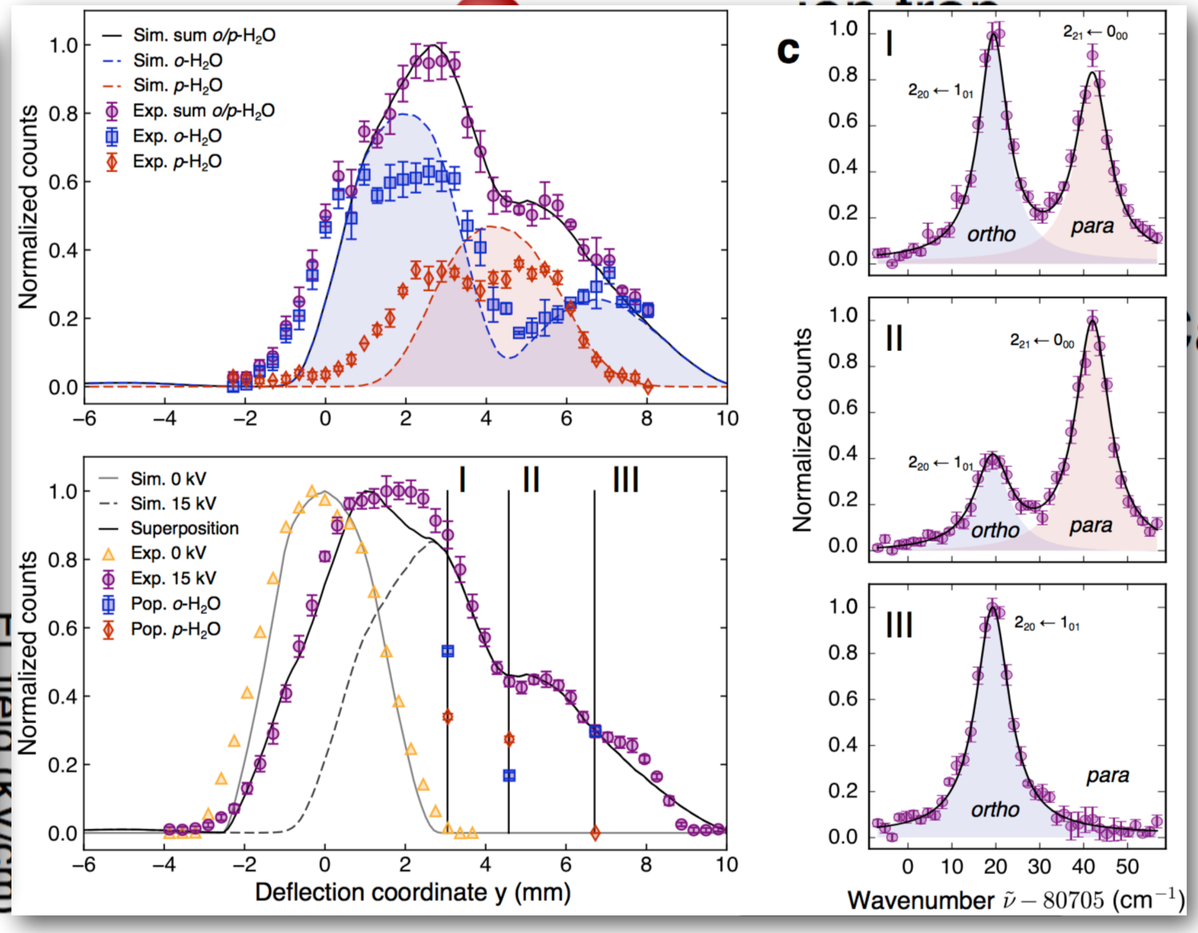

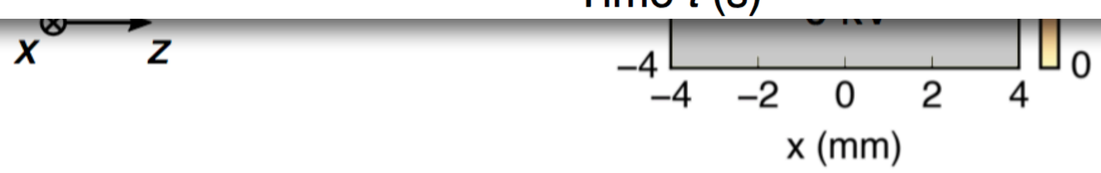

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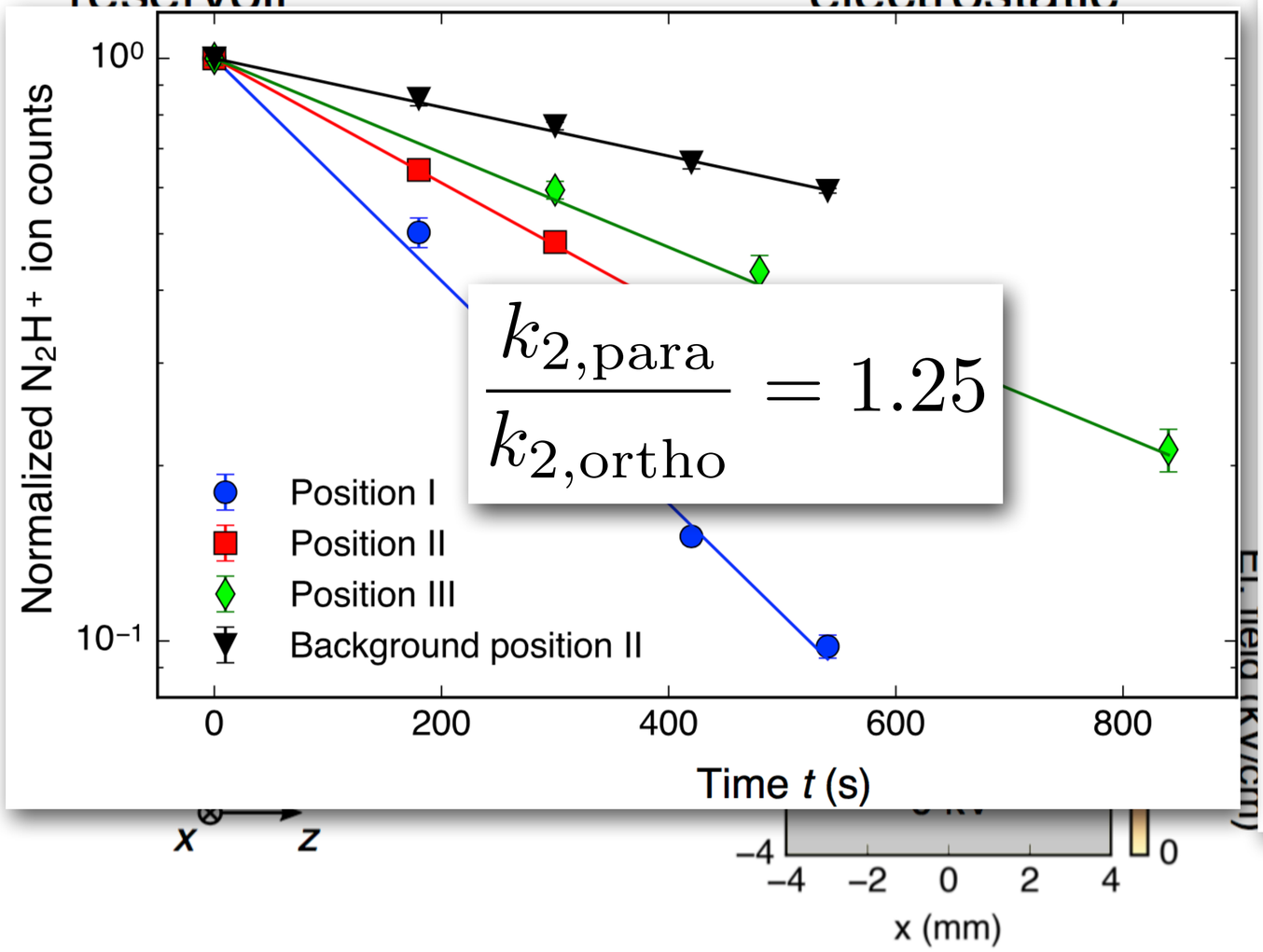

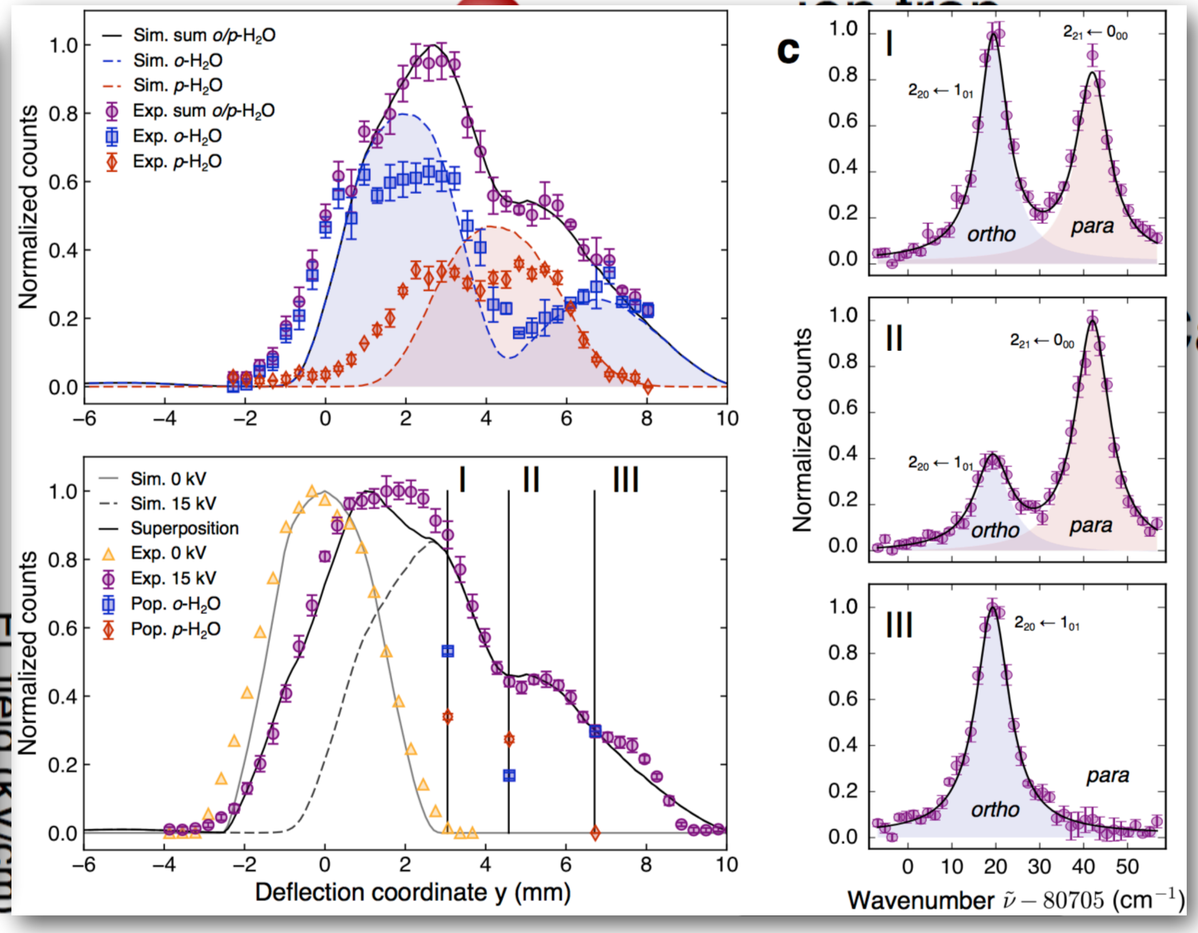

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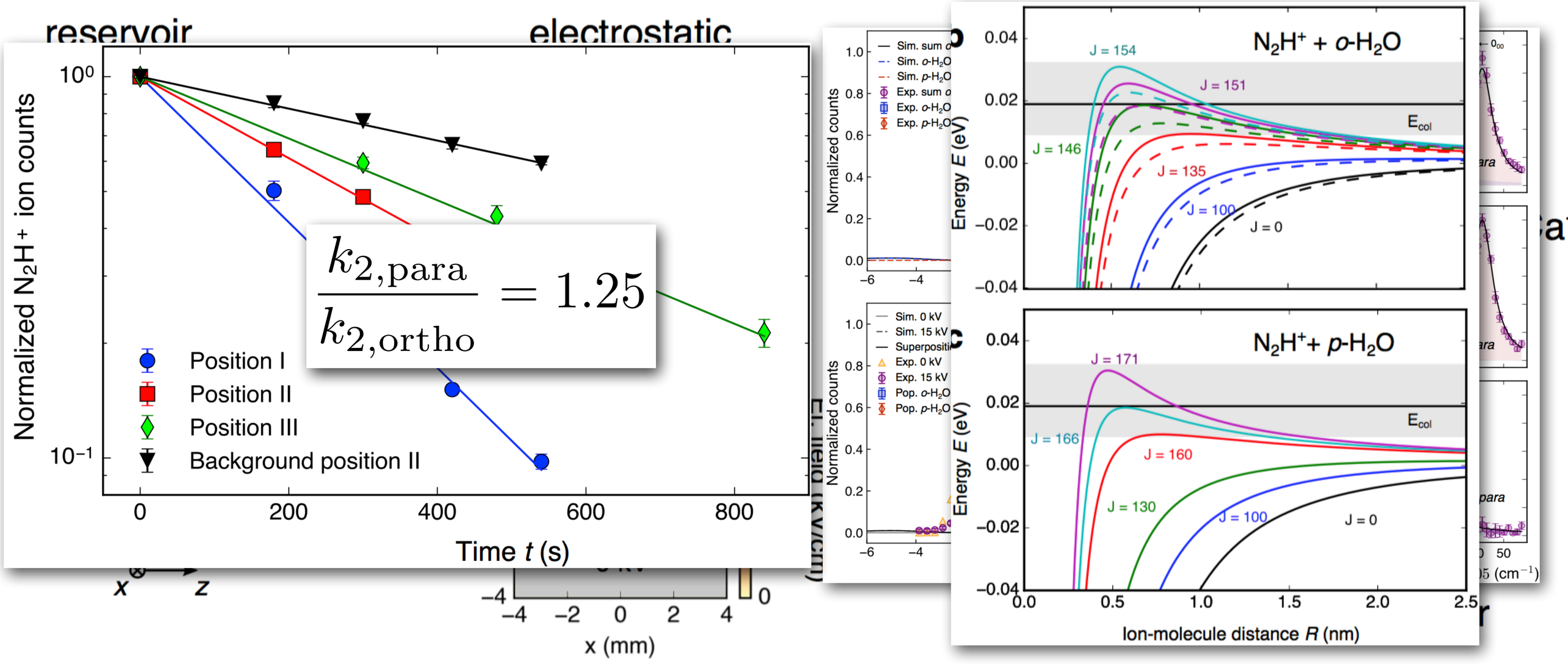

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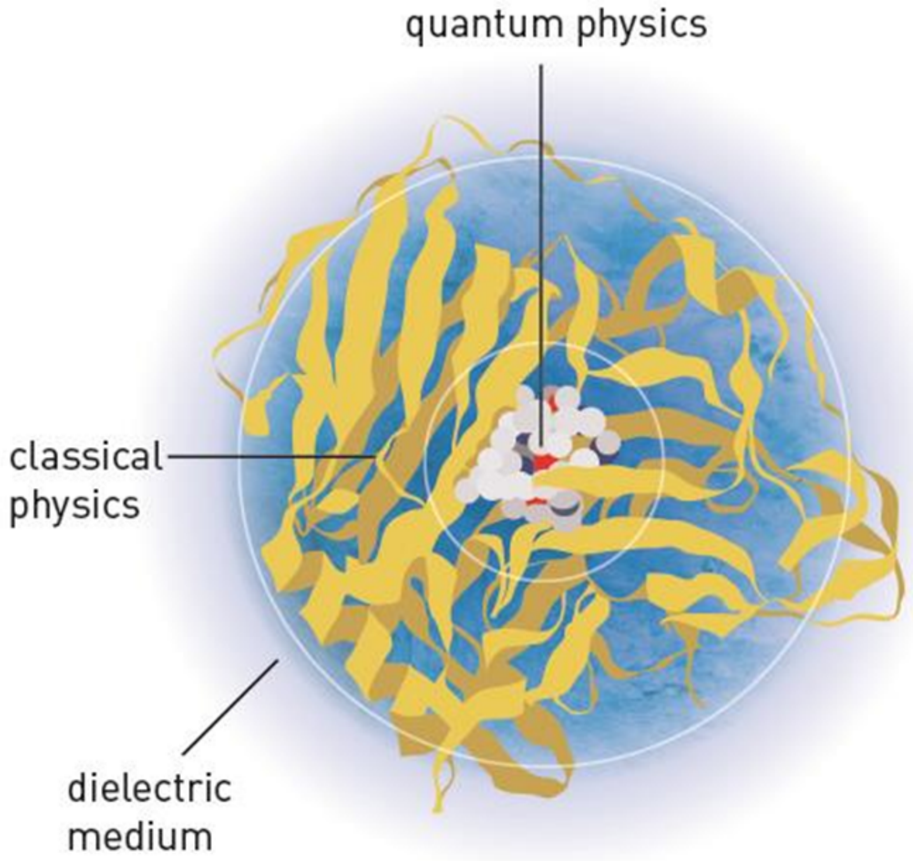
The Nobel Prize in Chemistry 2013
Multiscale models for complex chemical systems

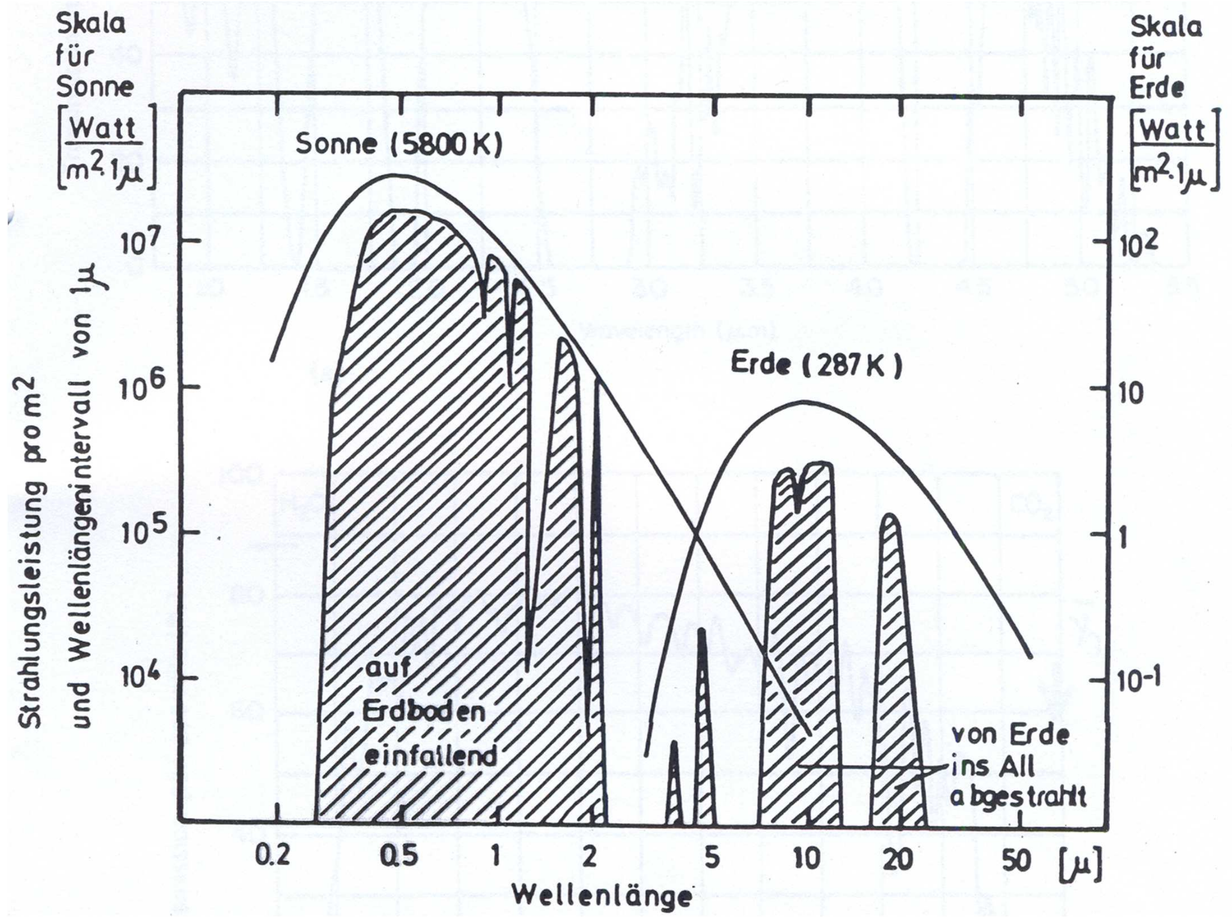


kindly provided by Professor Ulf Ryde
(Division of Theoretical Chemistry, Lund University)

http://nobelprize.org/nobel_prizes/chemistry/laureates/2013/index.html

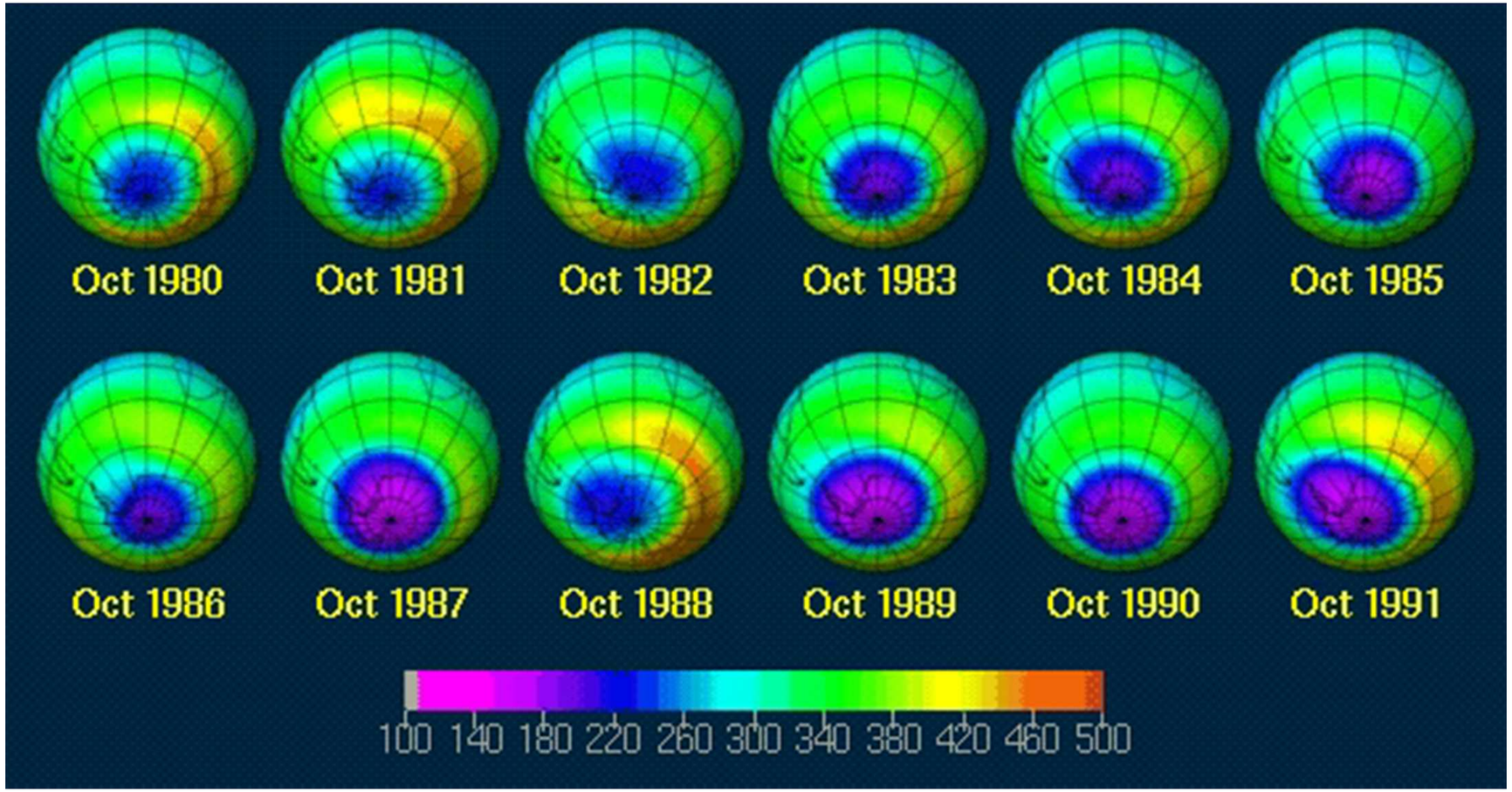
Importance of molecular structure

- Black-body radiation of sun and earth → greenhouse effect
- Absorption of water vapor, carbon dioxide, methane, ozone



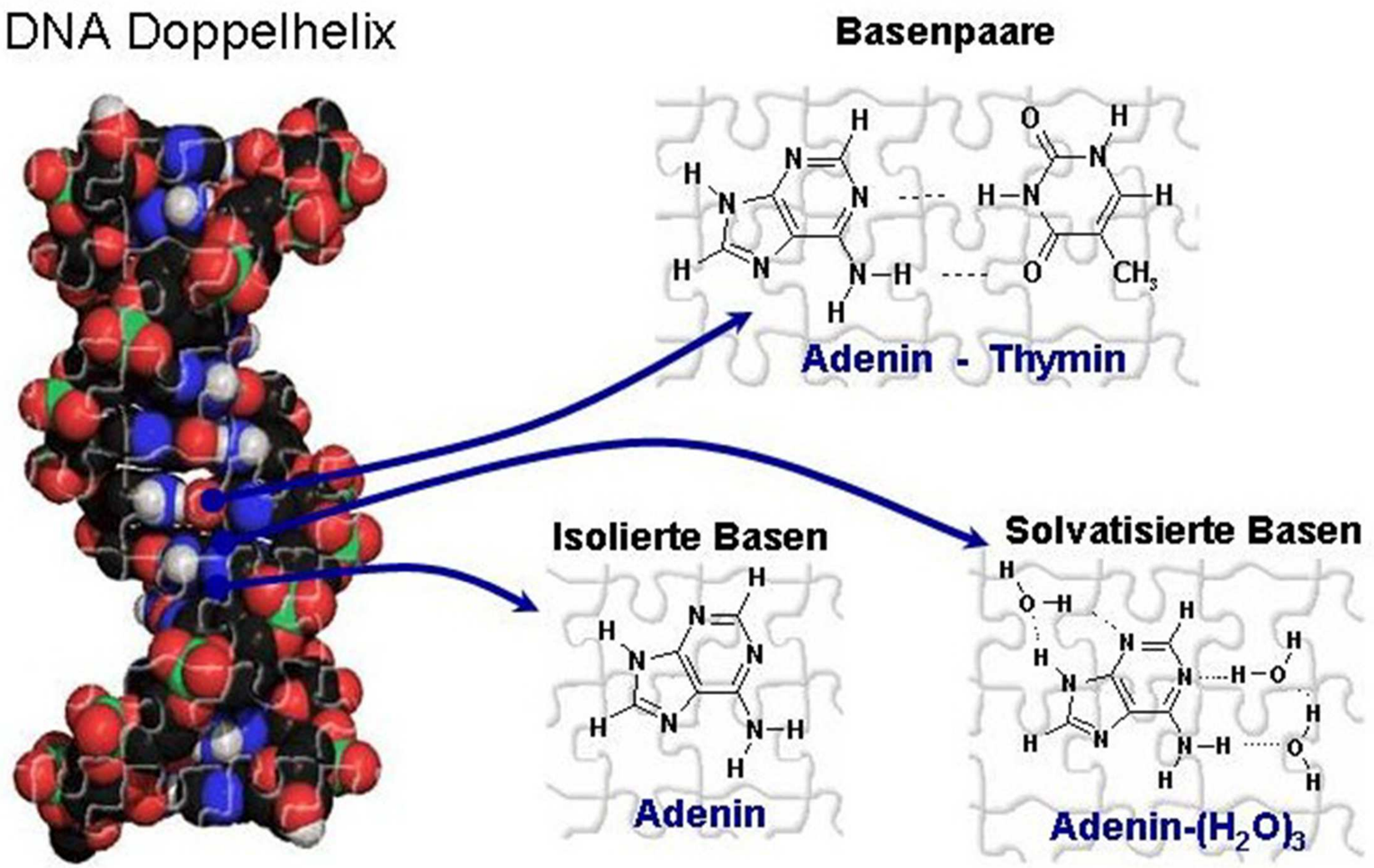
Importance of molecular structure

- Catalytic destruction of ozone by atomic halogens → ozone depletion
- Source of halogen atoms is photodissociation of man-made halocarbon refrigerants (chlorofluorocarbons,...)



Importance of molecular structure

- Efficient absorption of UV radiation by ozone
- But, ozone was generated in the atmosphere AFTER oxygen production had started (photosynthesis)!
- How did the first animals survive?



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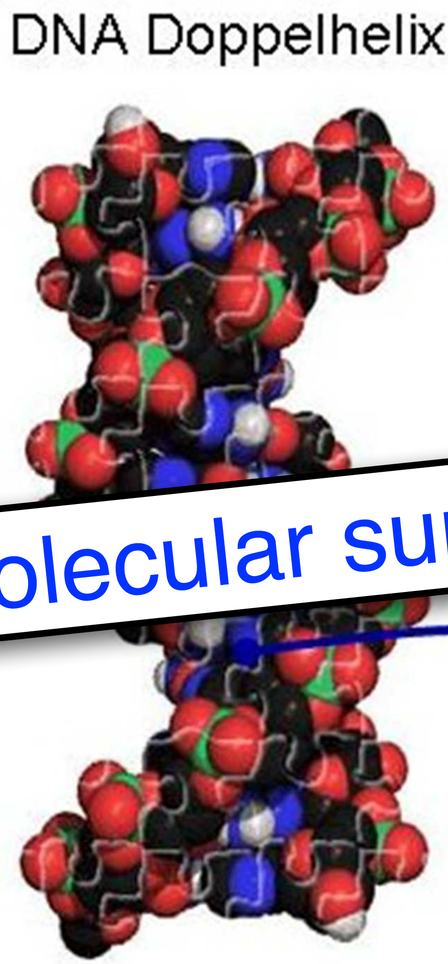
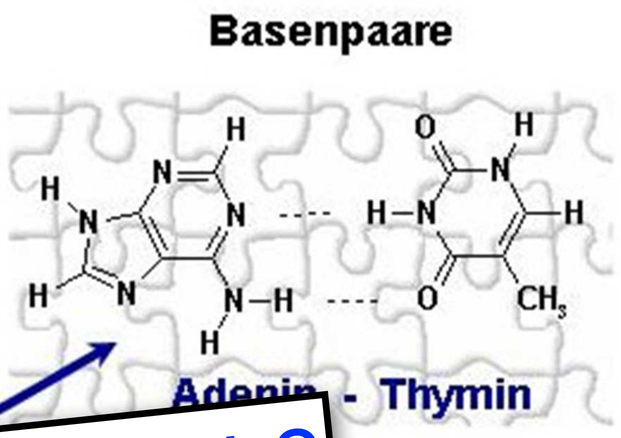
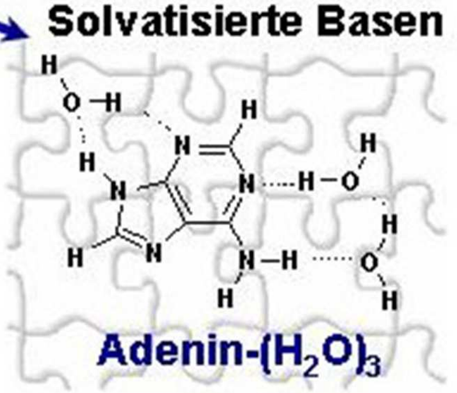
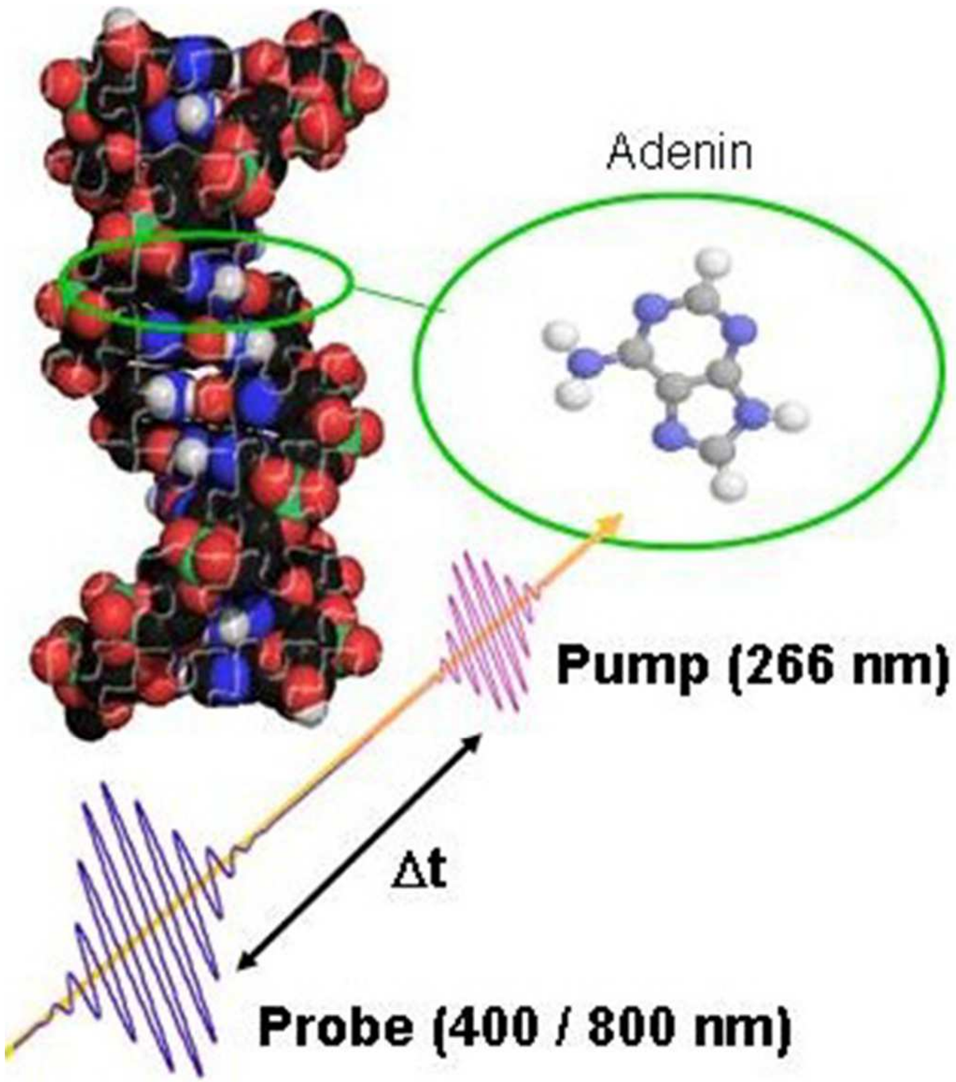


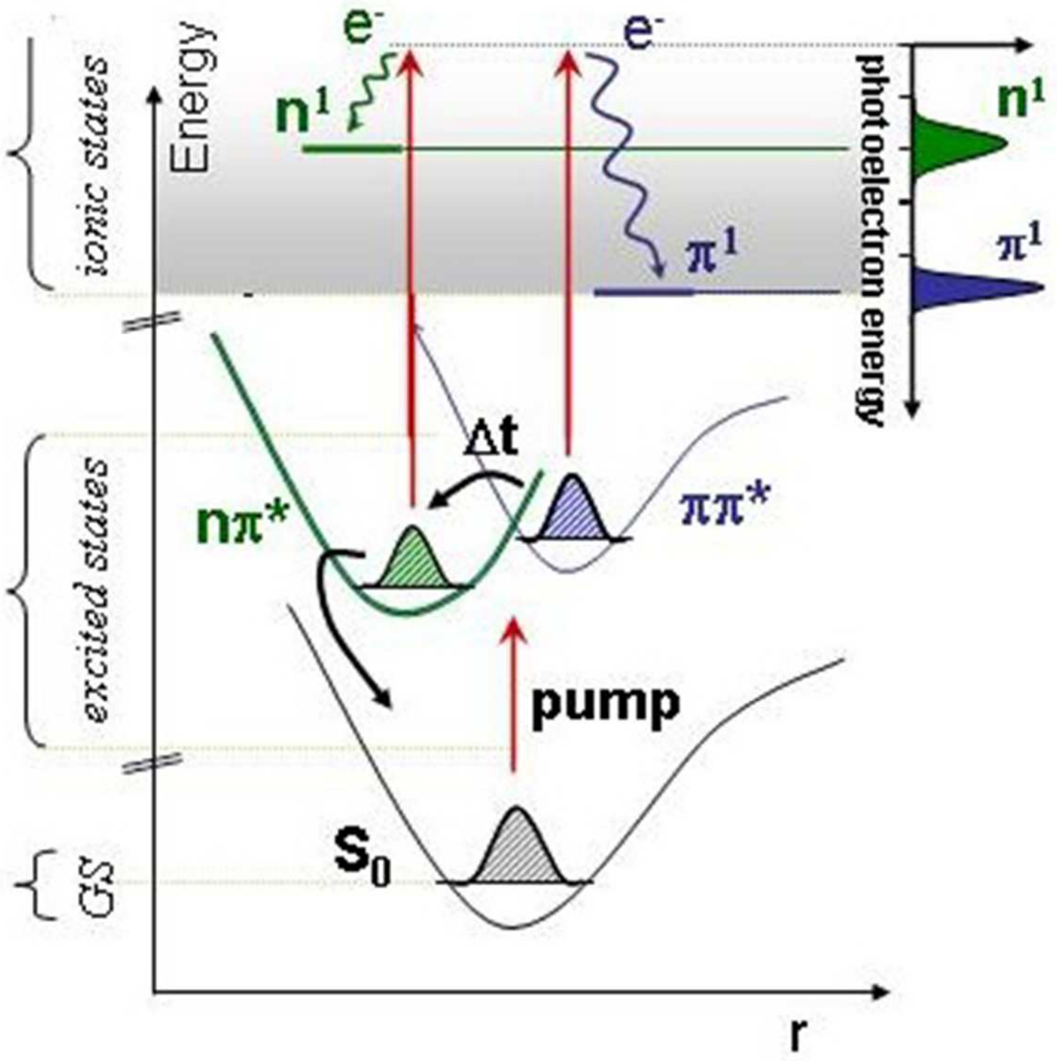


How does molecular sunscreen work?



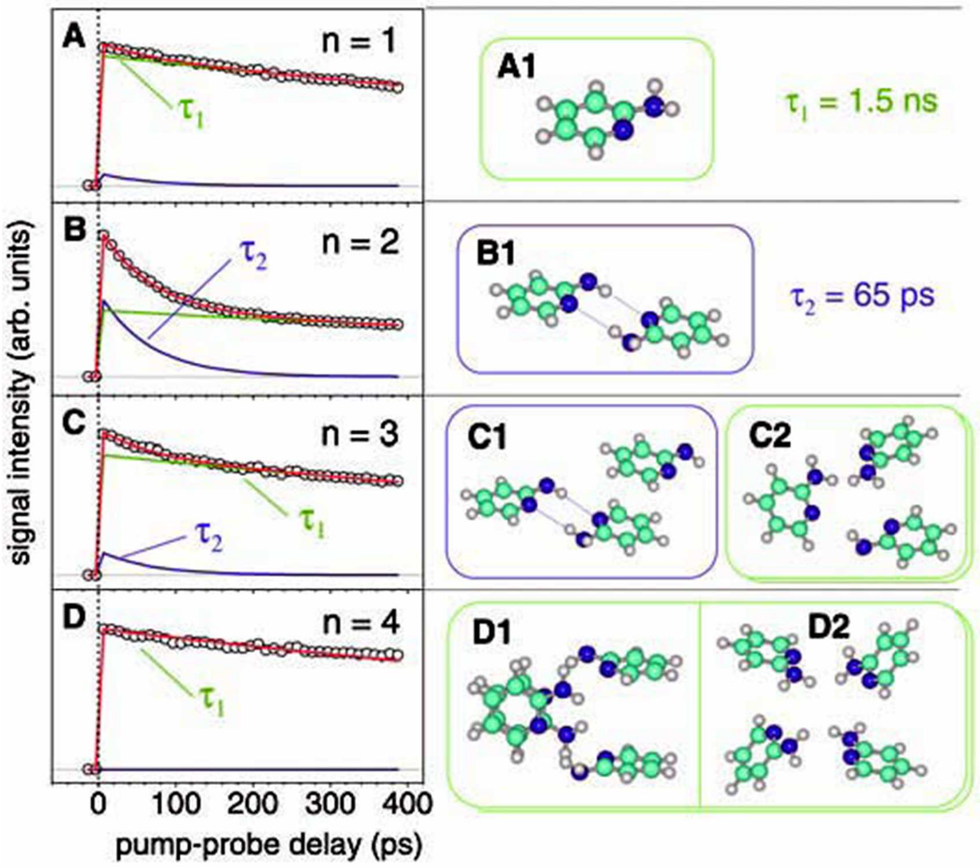
Relation between molecular structure, function and dynamics

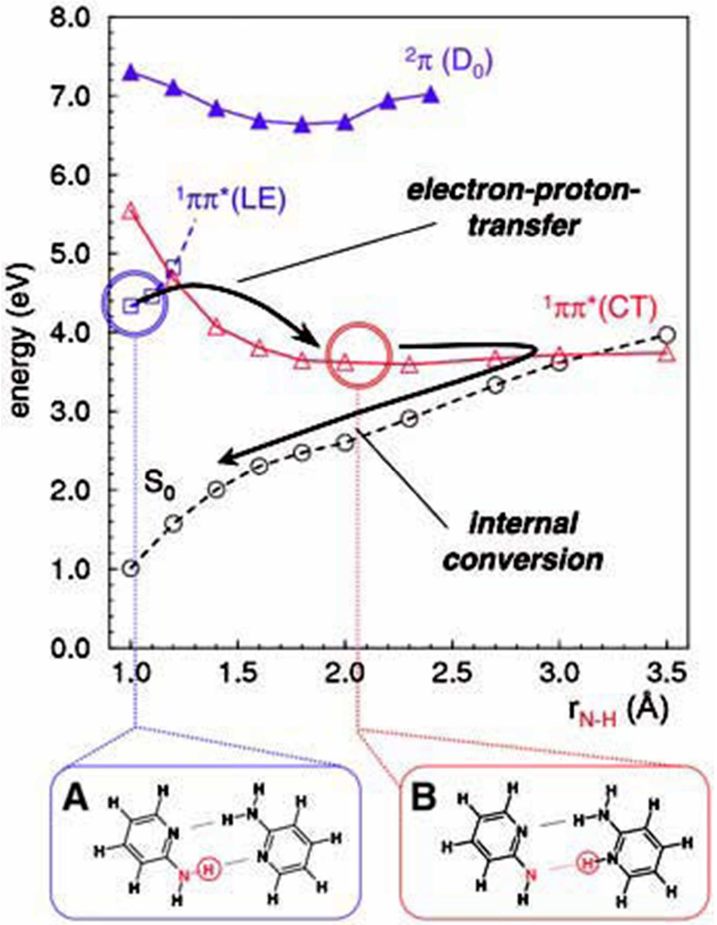




Relation between molecular structure, function and dynamics

- Femtosecond pump-probe spectroscopy on the aminopyridine model system



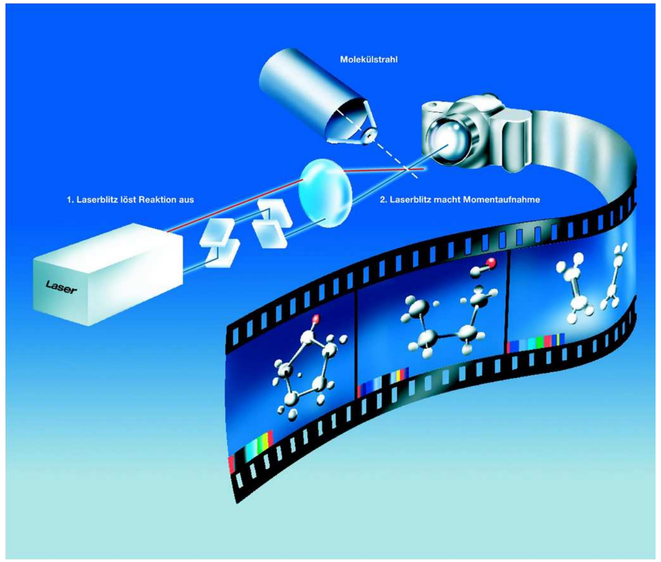


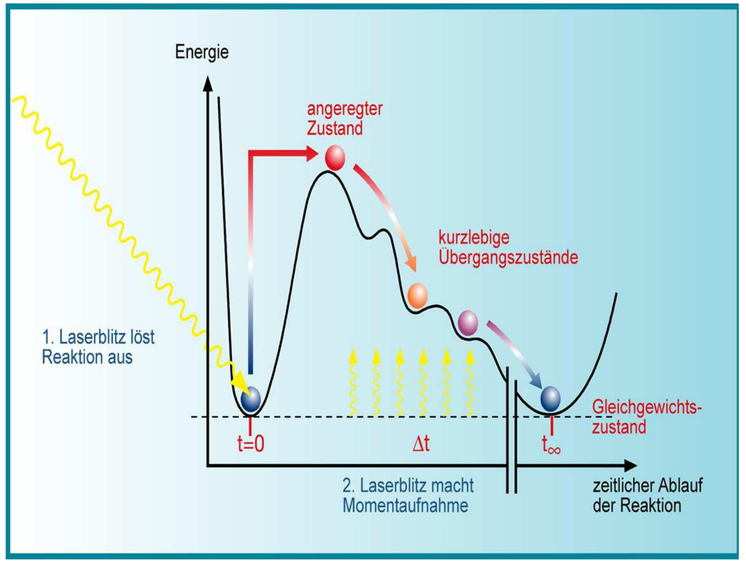
- **Only the dimer shows ultrafast relaxation!**

T. Schultz et al., Science 306, 1765 (2004)

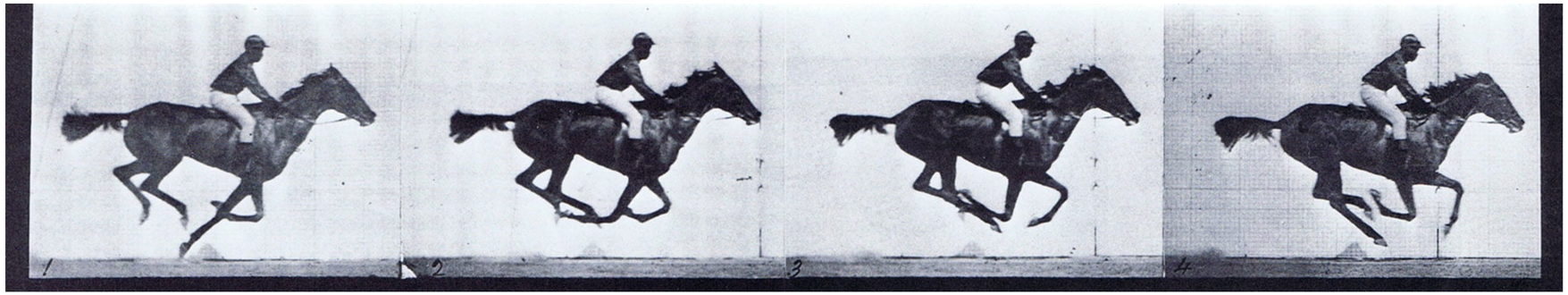
Recording the molecular movie - the ultimate dream

- Imaging of chemical reactions of single molecules

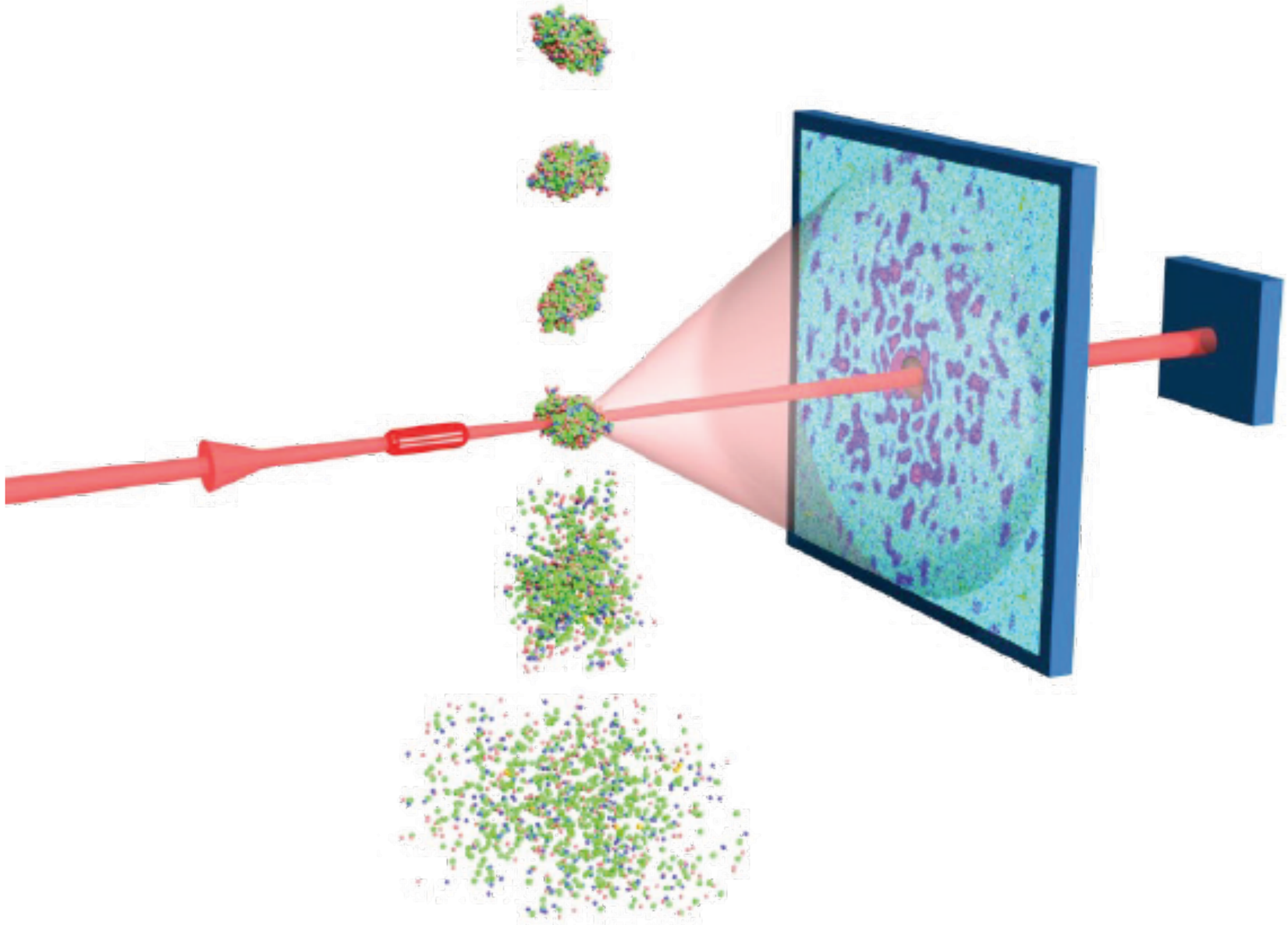




- With atomic resolution in real time

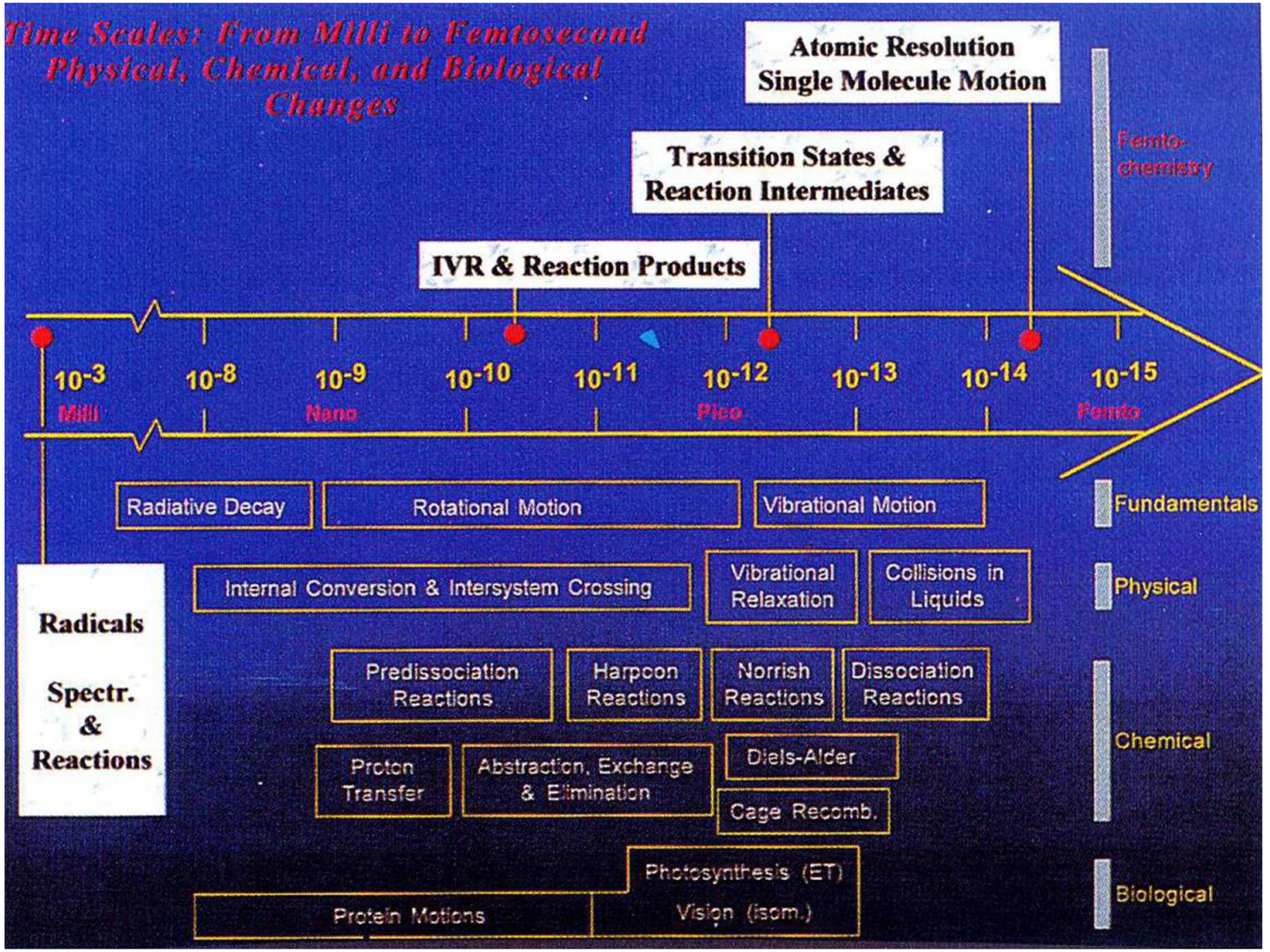


Watching chemistry with atomic spatial (100 pm) and temporal (10 fs) resolution



Barty, Küpper, Chapman, *Ann. Rev. Phys. Chem.* **64**, 415–435 (2013)

Recording the molecular movie - timescales



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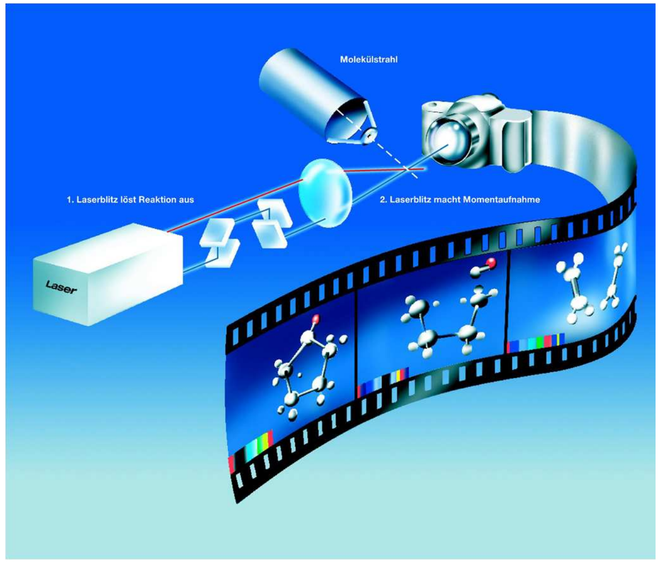

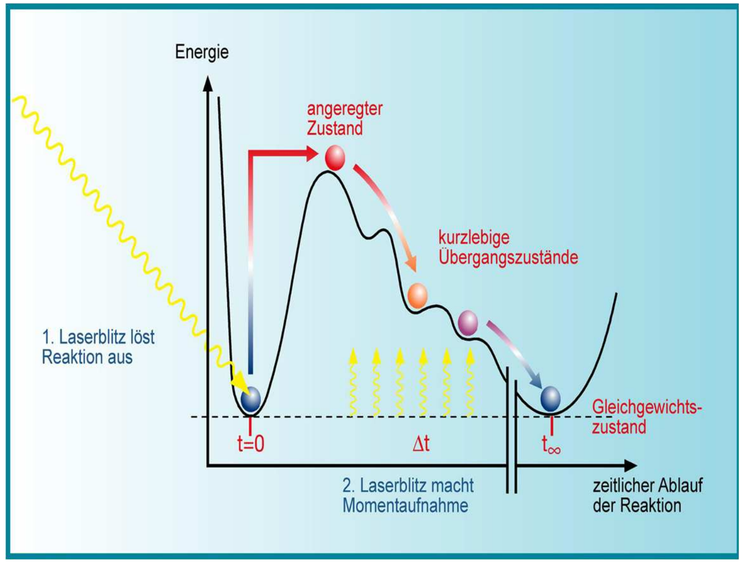

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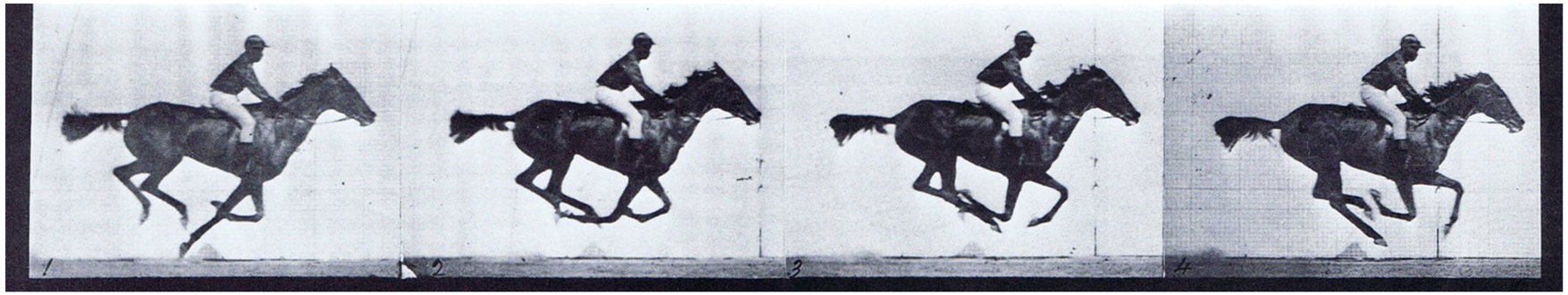
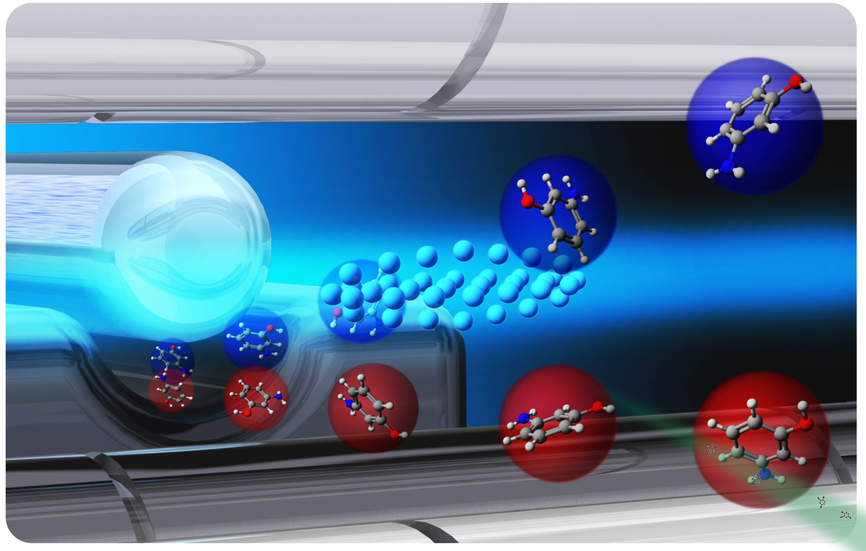
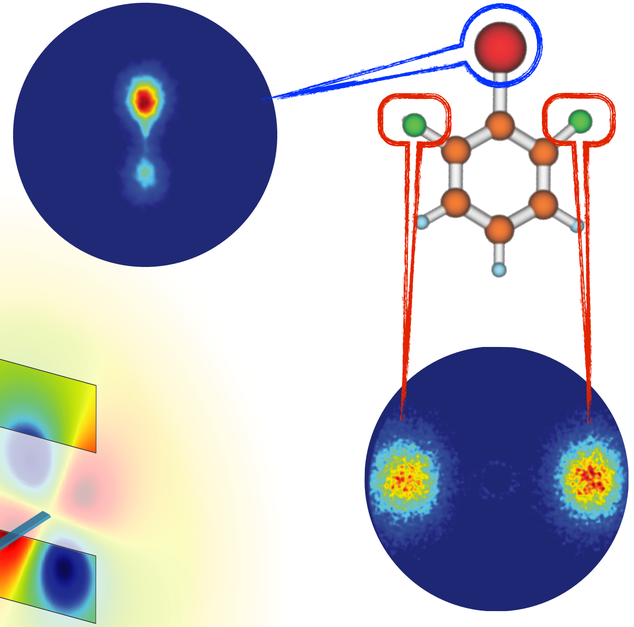
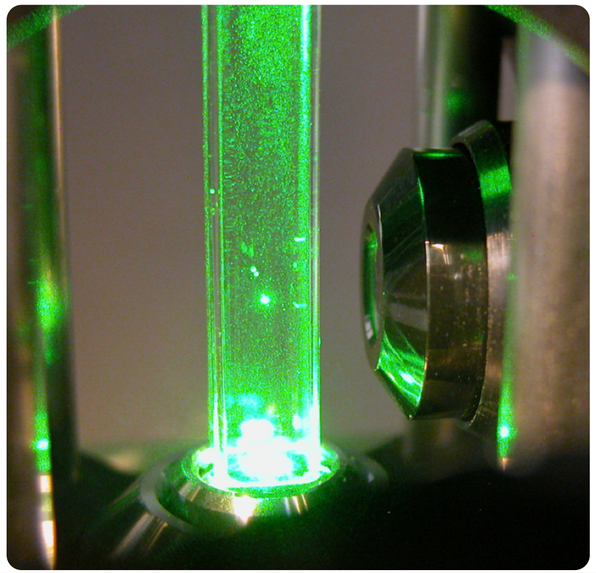
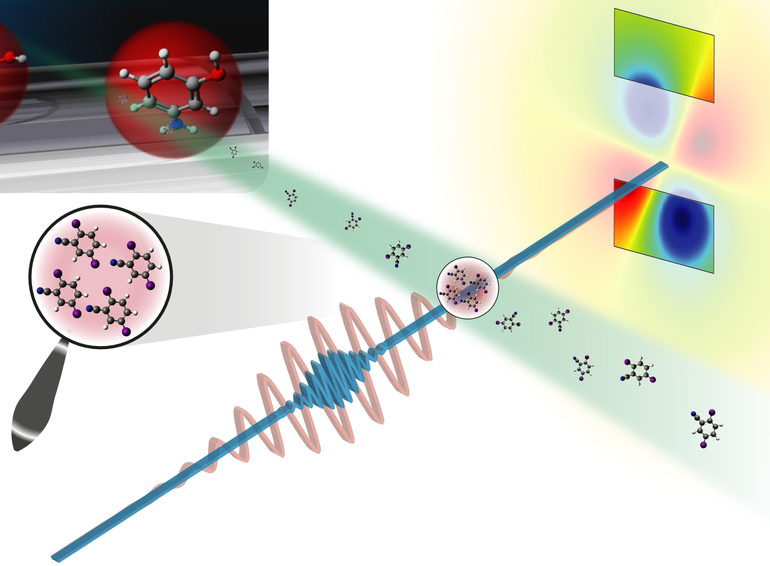


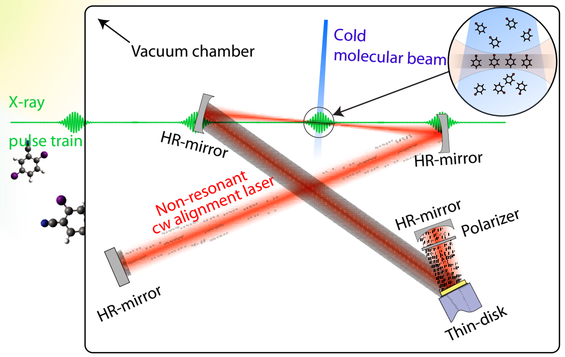
Controlled Molecule Imaging
Toward a microscopic understanding of molecules at work

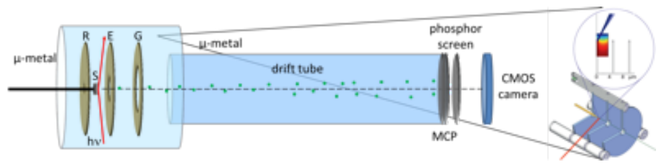








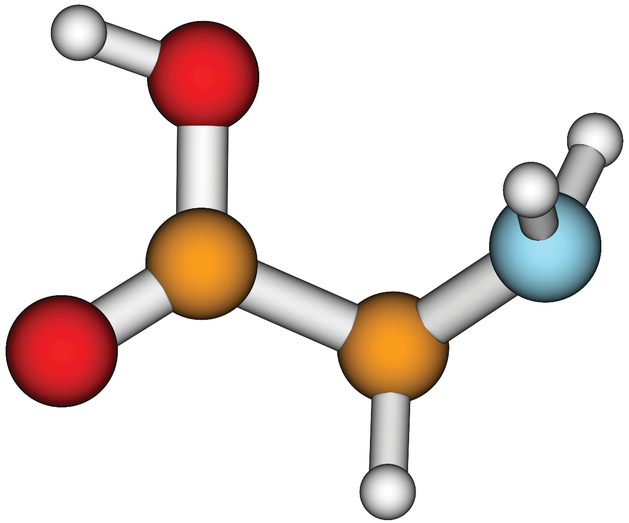




CoMotion

We are looking for motivated colleagues – please see https://www.controlled-molecule-imaging.org/careers

Physics and Chemistry of *complex* molecules
Structural isomers – conformers – of Glycine



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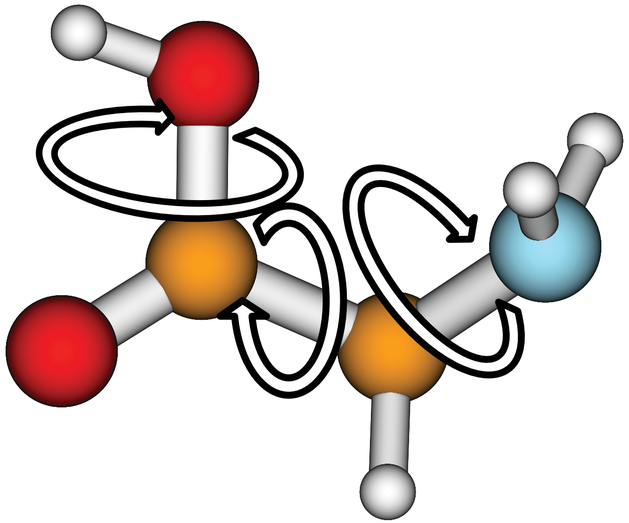

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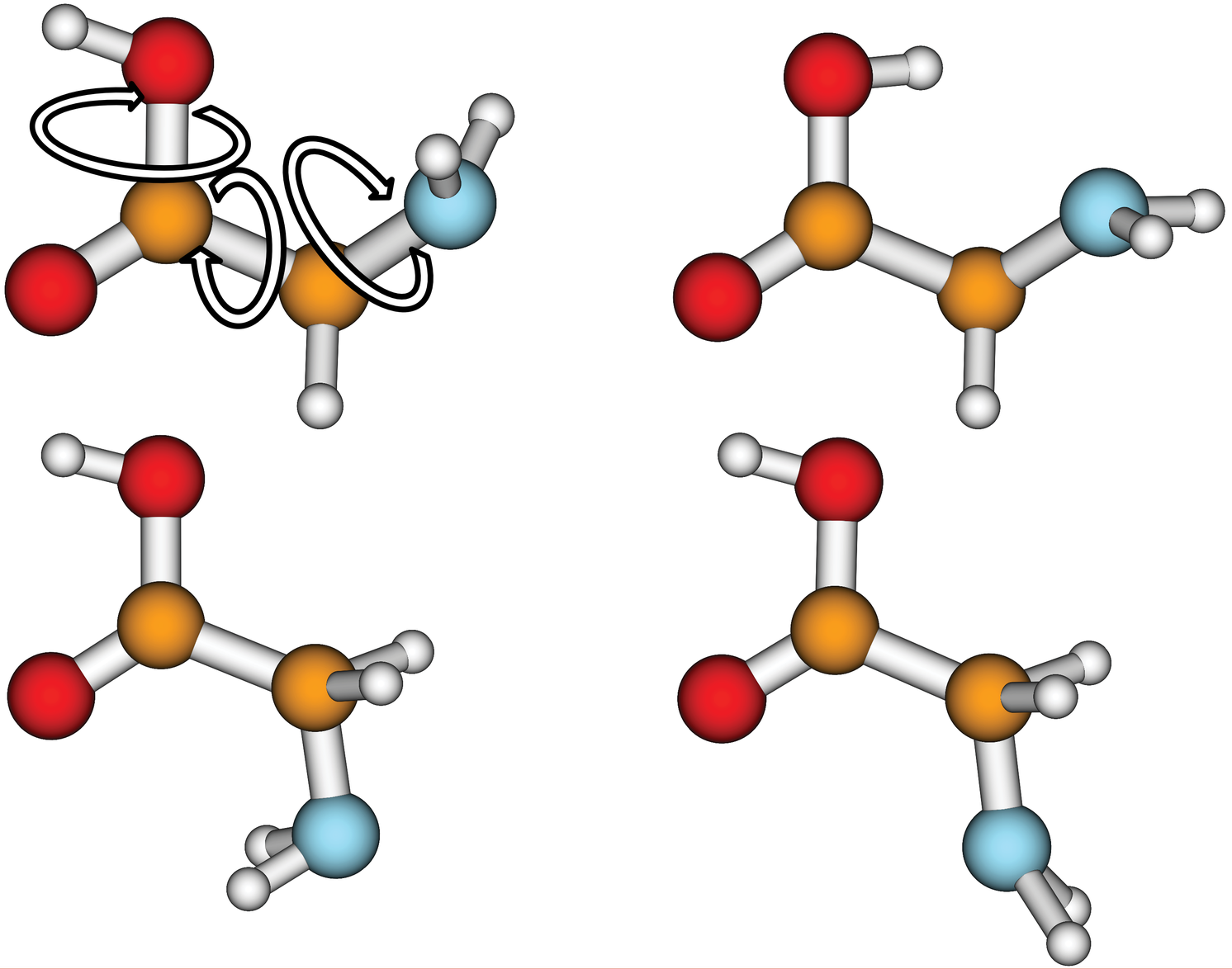
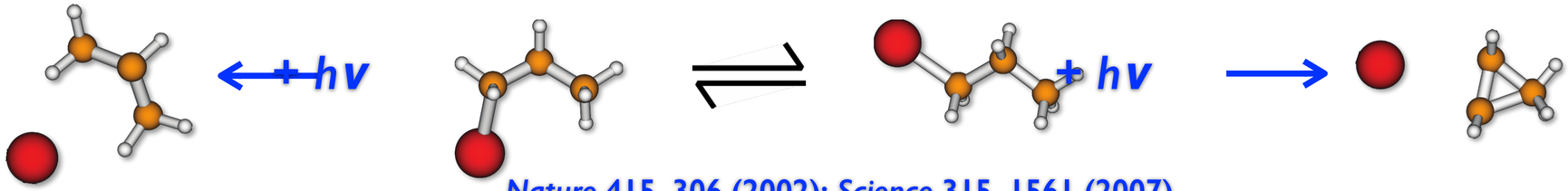


Physics and Chemistry of complex molecules
Unraveling the structure-function relationship

"Structure determines function"

Photodissociation of iodopropane



Nature 415, 306 (2002); *Science* 315, 1561 (2007)

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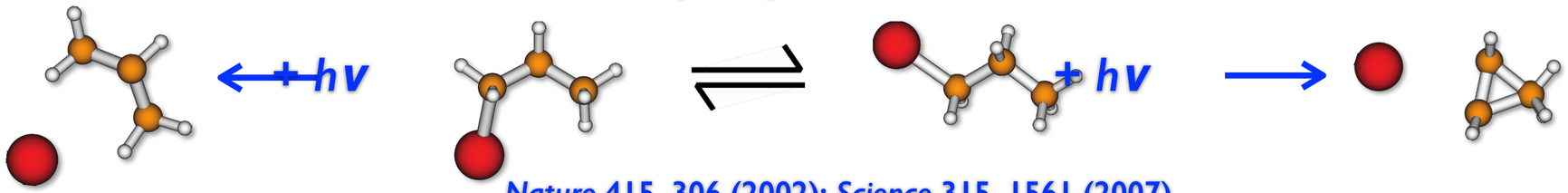

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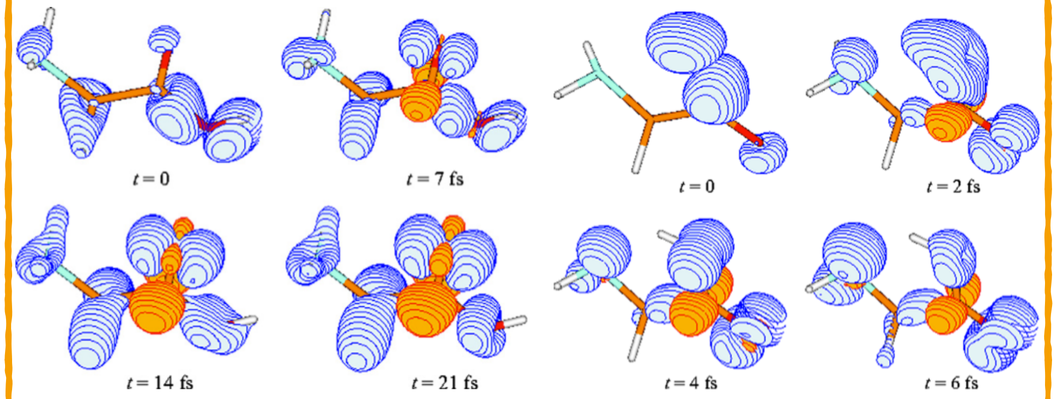
Ultrafast charge (electron hole)

Glycine I – 21 Glycine II –



Kuleff, Cederbaum, *Chem. Phys.* 338, 321 (2007)

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"Structure determines function"

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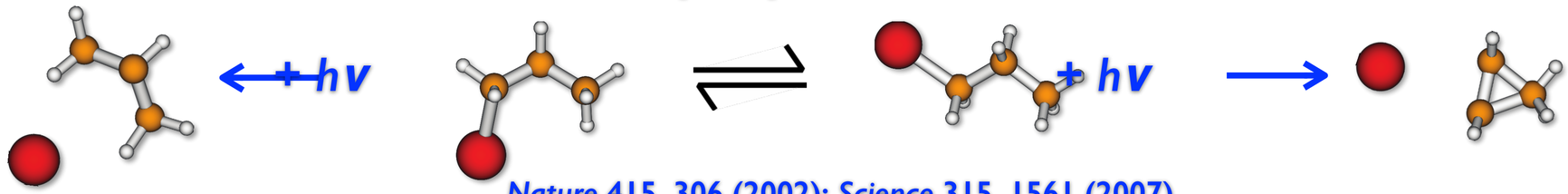
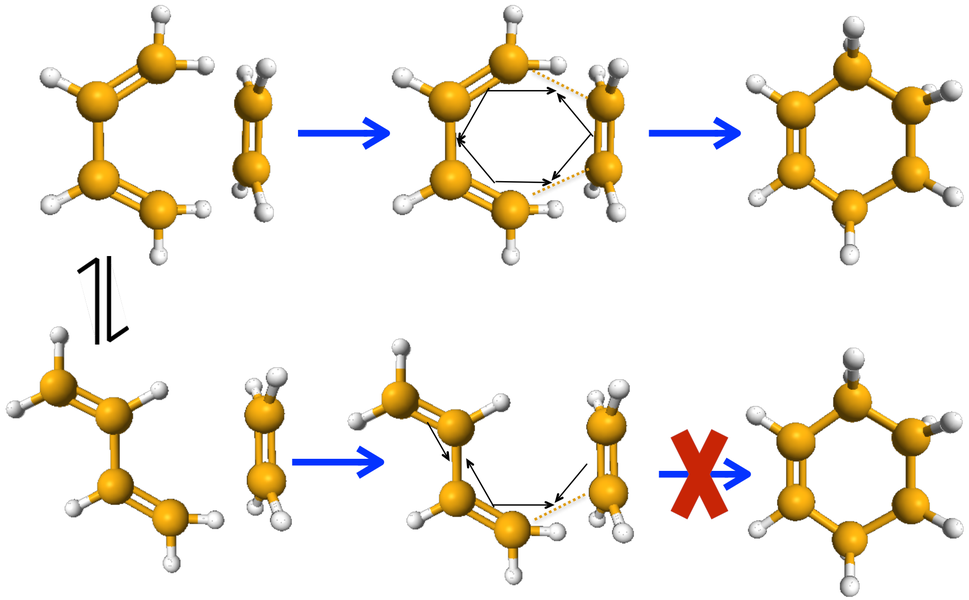


Nature 415, 306 (2002); *Science* 315, 1561 (2007)

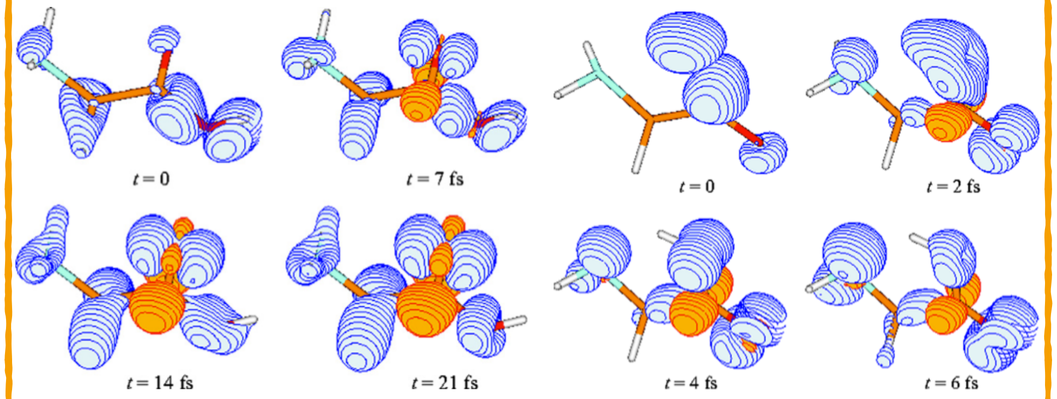
Bimolecular reaction – Diels-Alder cycloaddition



Angew. Chem. Int. Ed. 19, 779

Ultrafast charge (electron hole)

Glycine I – 21 Glycine II –

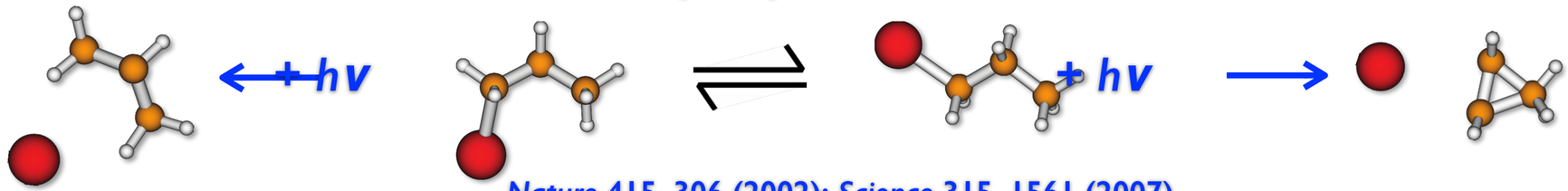


Kuleff, Cederbaum, *Chem. Phys.* 338, 321 (2007)

Physics and Chemistry of complex molecules
Unraveling the structure-function relationship

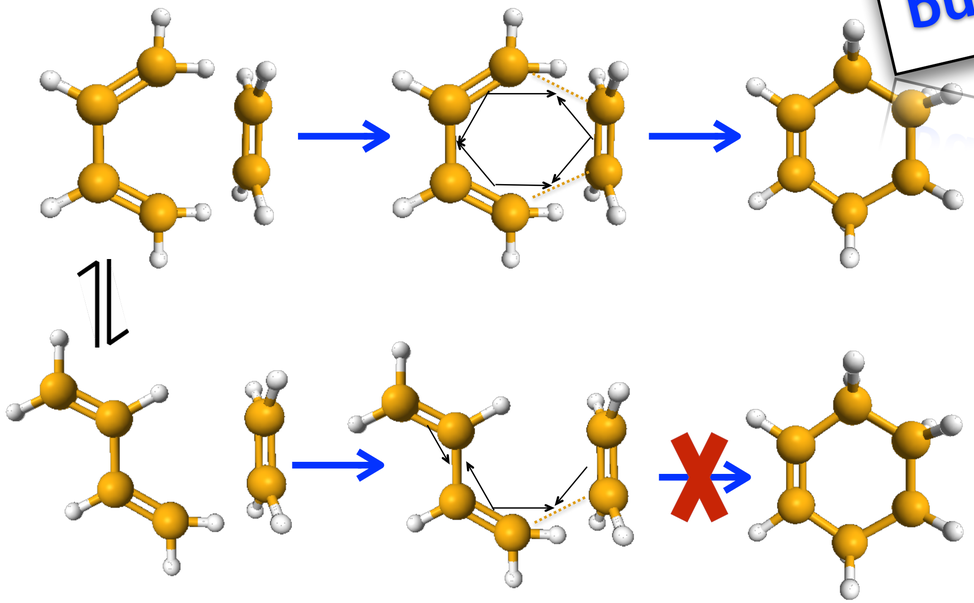
"Structure determines function"

Photodissociation of iodopropane



Nature 415, 306 (2002); *Science* 315, 1561 (2007)

Bimolecular reaction – Diels-Alder cycload



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but how?

Ultrafast charge (electron hole)

Glycine I – 21

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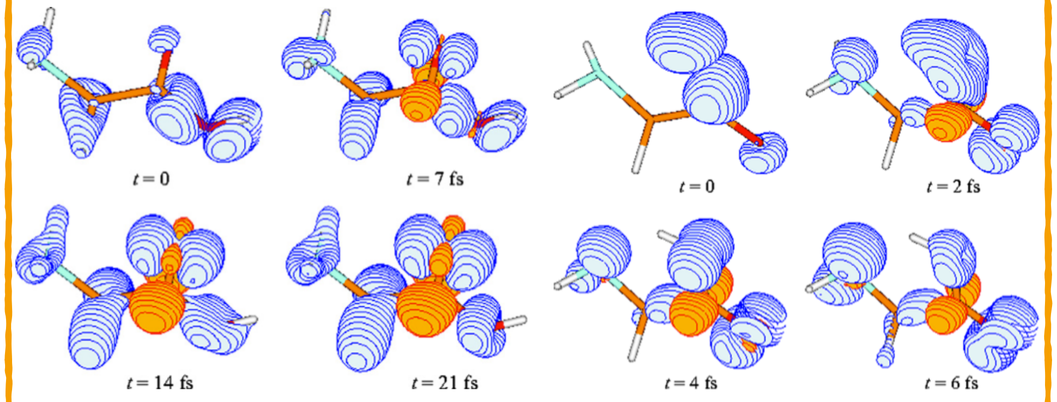
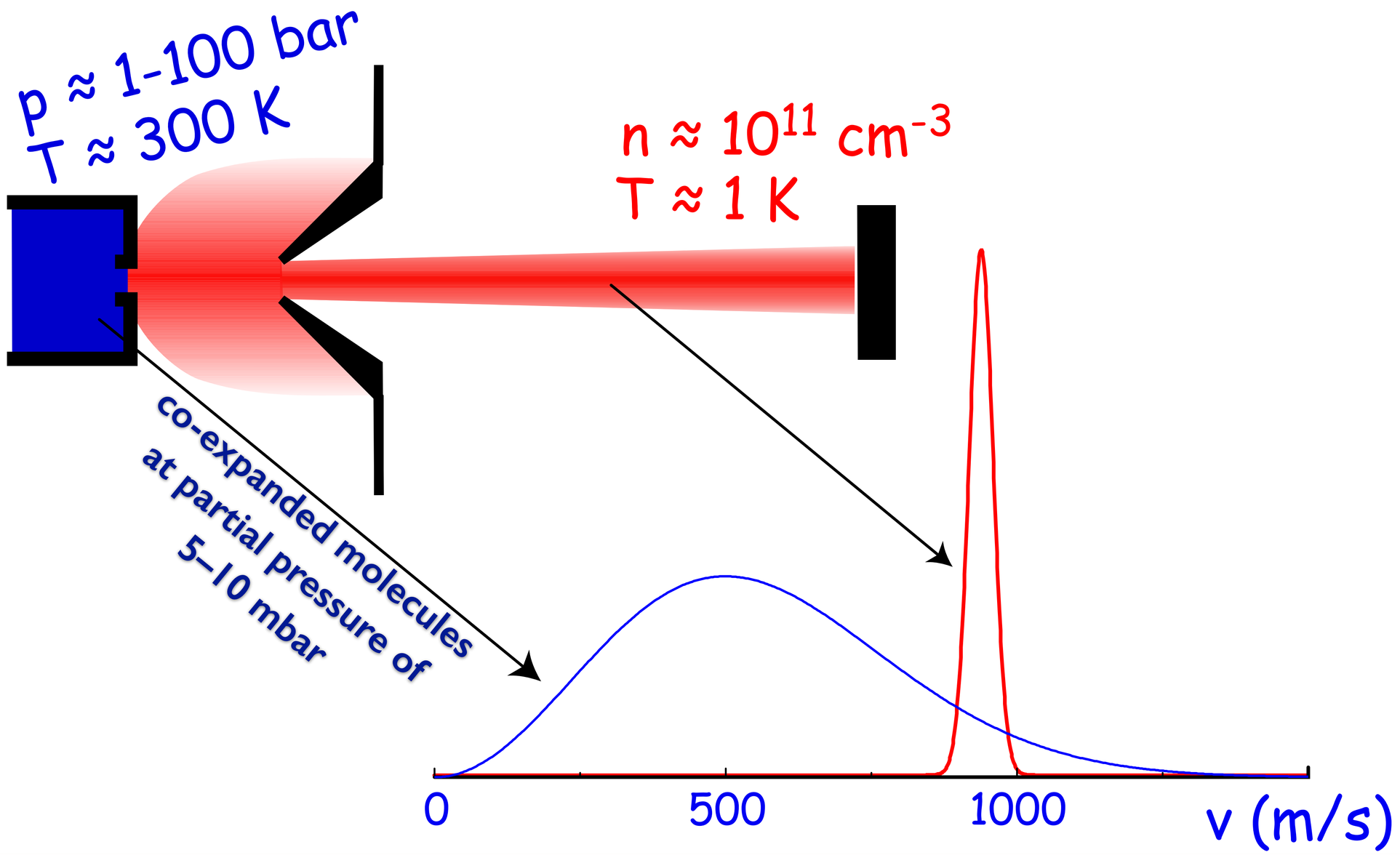
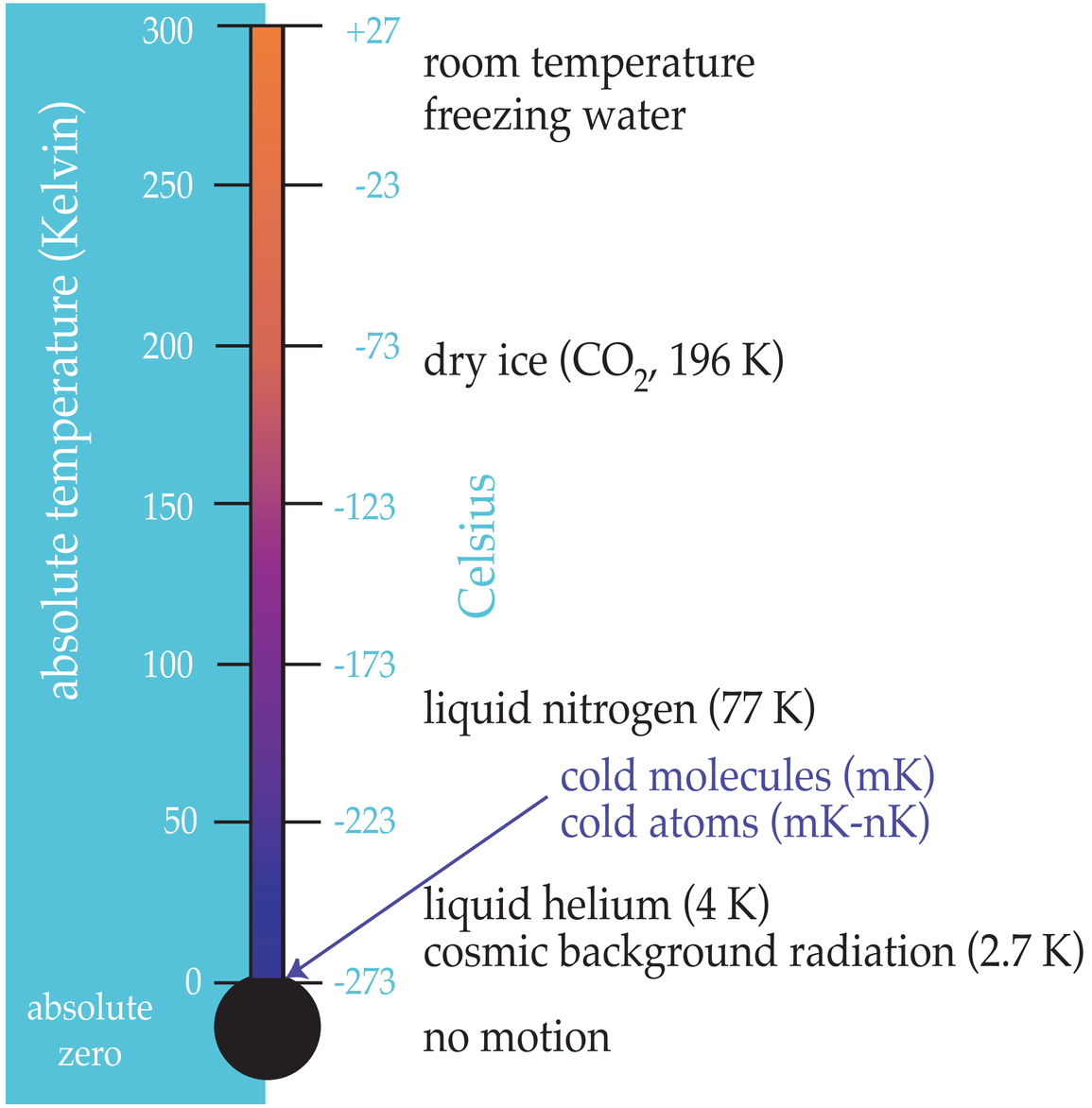


Kuleff, Cederbaum, *Chem. Phys.* 338, 321 (2007)

Manipulating the motion of neutral molecules
Production of controlled/cold molecular samples

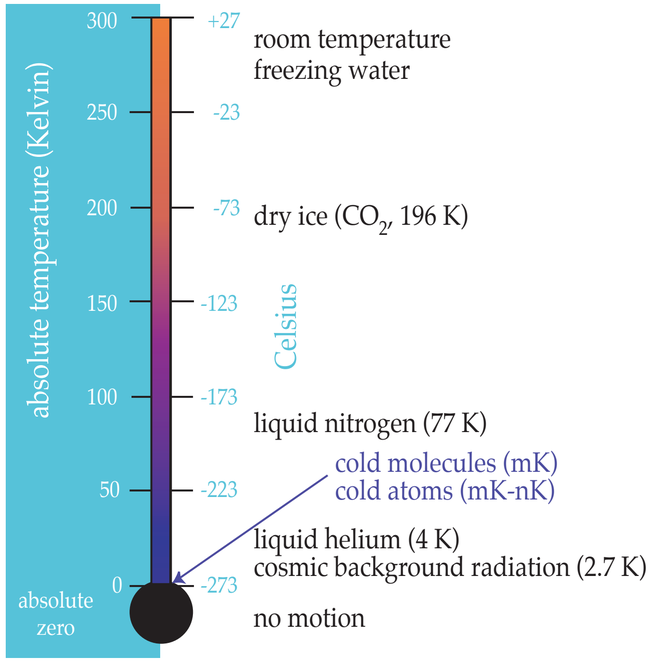


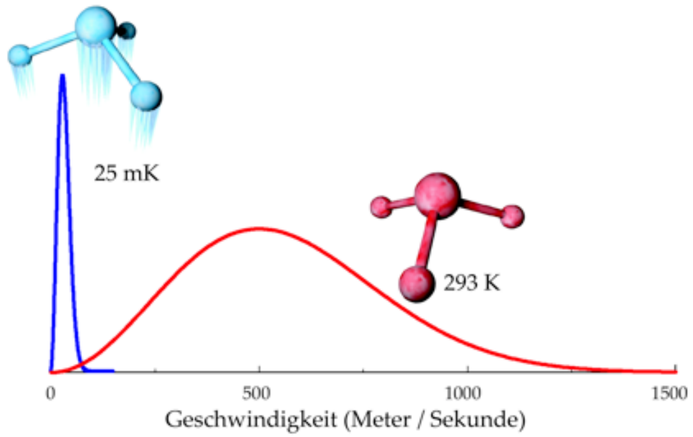
Cold and Controlled Molecules – when are molecules cold?



Cold and Controlled Molecules – when are molecules cold?

Cold matter is slow – fairly controlled – matter





- The temperature characterizes the velocity distribution of atoms/molecules.
  Under normal conditions (T=300 K; p=1 bar): v=500 m/s.
- A velocity distribution with a width of 5 m/s, corresponds to T=30 mK.
- Cold Molecules are slow molecules,
  “kinematically challenged”

When are molecules cold?

Internal degrees of freedom

- Molecules have various internal degrees of freedom: electronic, vibrational, rotational, nuclear spin, ...
- All these degrees of freedom are quantized!
- Orientation of molecules in external fields is also quantized!

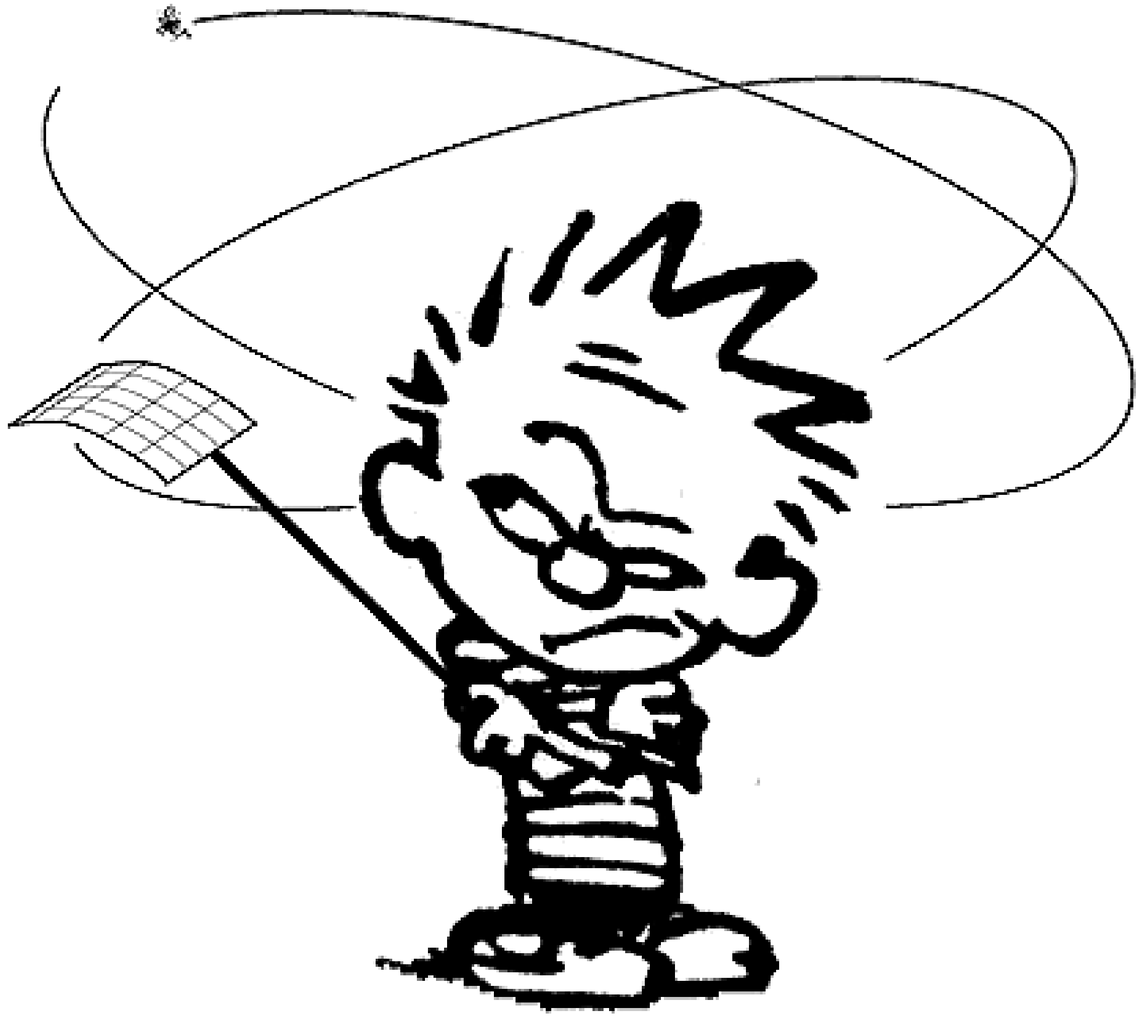
Definition: Cold Molecules

Cold Molecules are *translationally* and *internally* cold:

- They have a small momentum spread (“they move slowly”)
- They are in a few, or even a single (rotational, vibrational, . . .) quantum-state(s), preferably (but not necessarily) in the absolute ground-state.

Additionally, the molecules shall be oriented in space.

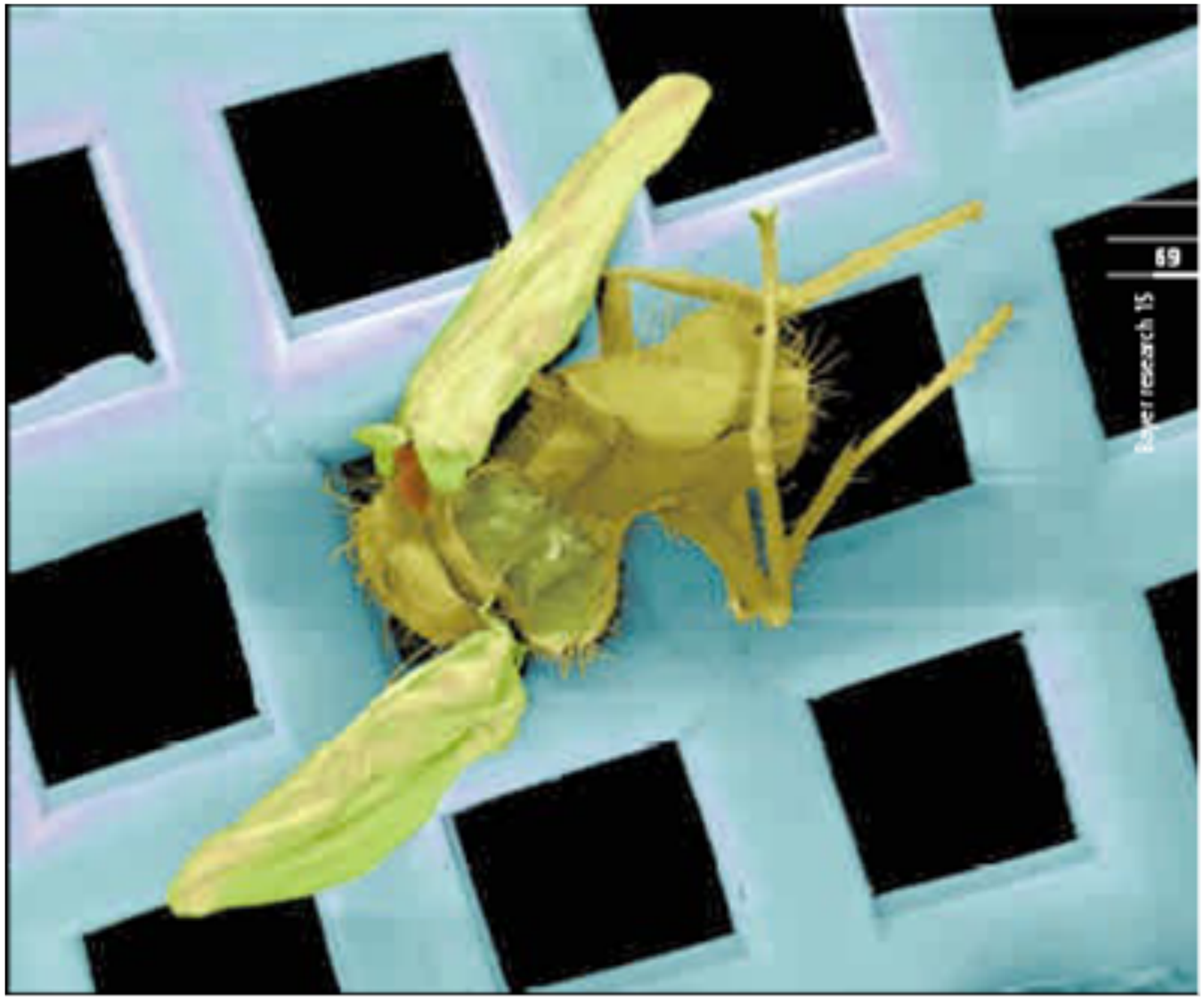
Studying cold/slow matter



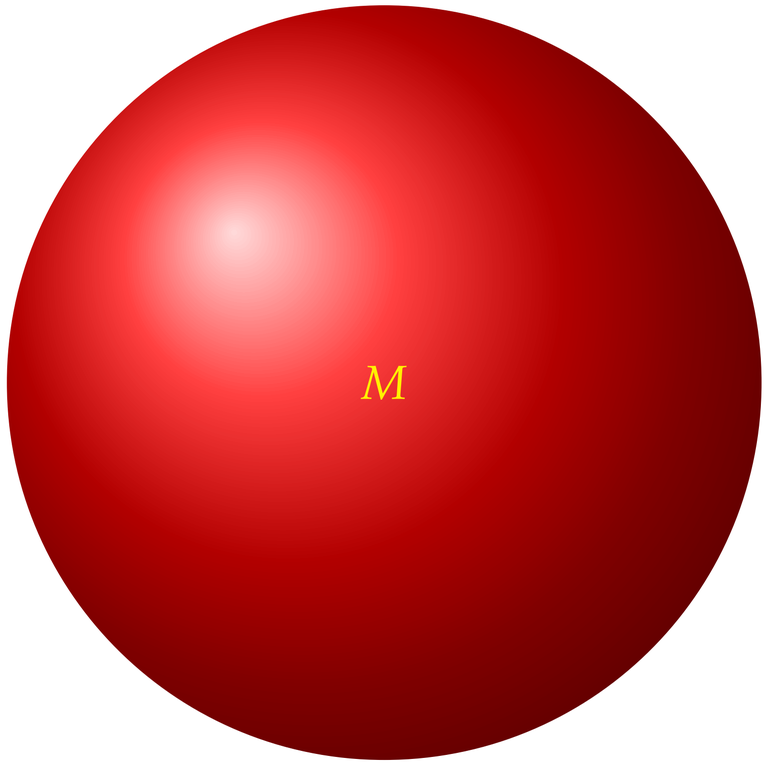
Studying cold/slow matter

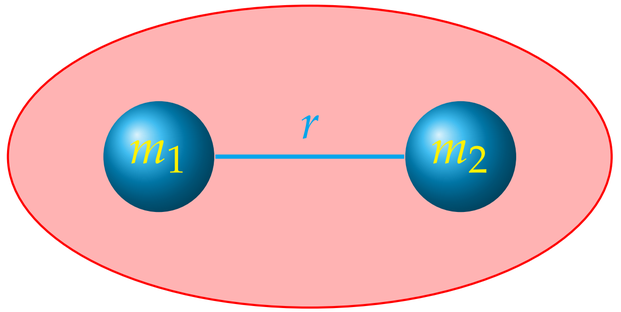
Cold matter behaves differently

Matter handled in this way
- can be studied in greater detail
- might behave differently
  - Shock-freezing can prevent that.



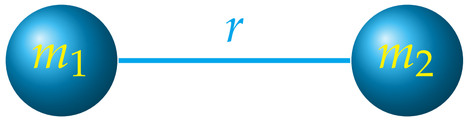
Diatomic molecules





Molecule
A set of atoms

- Example: diatomic molecule:
  - Dumb-bell model: two point masses (m_1, m_2) separated by r.



- Semi-rigid nuclear frame immersed in the charge cloud of the molecular electrons.
- homo-nuclear — all atoms identical
  hetero-nuclear — different atoms present

Molecule
A set of atoms

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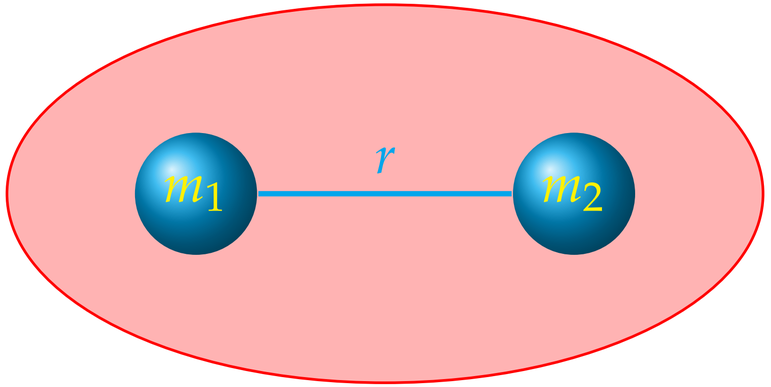

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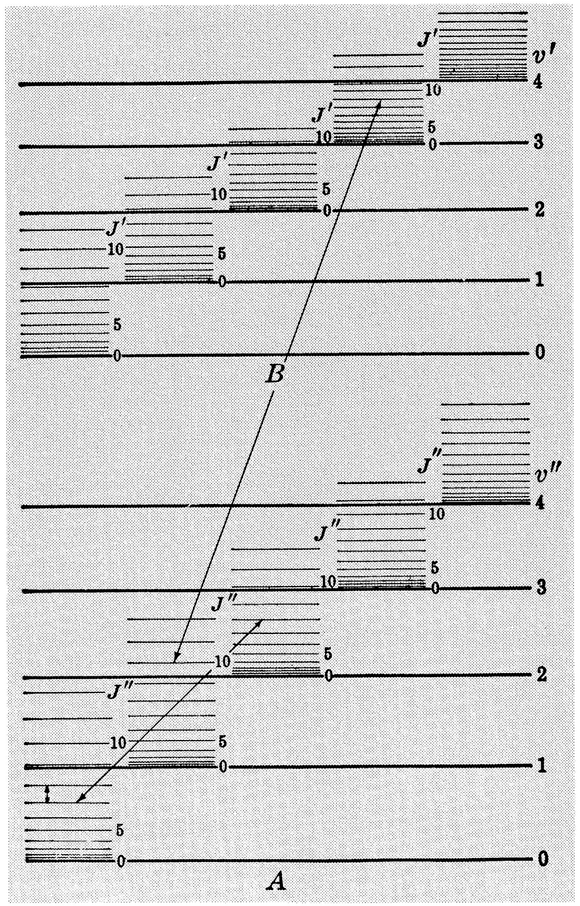
Energy scale

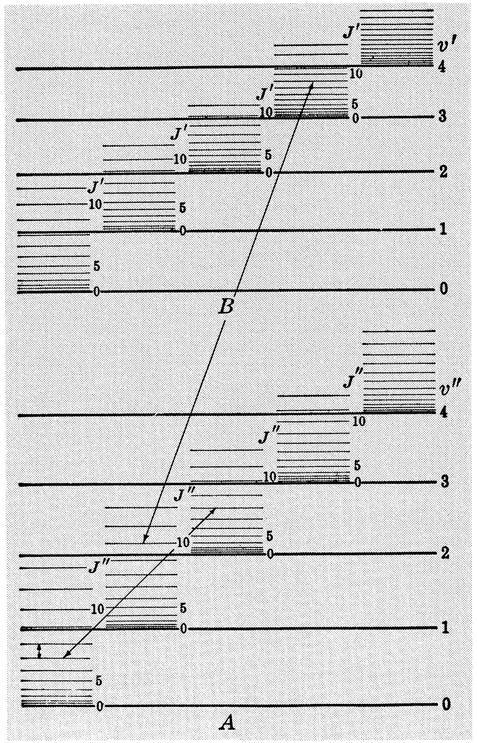


- Energy-scale of electronic states: 10000–50000 cm^{-1}
- Energy-scale of vibrational states: 100–4000 cm^{-1}
- Energy-scale of rotational states: 1–20 cm^{-1}
  (for larger molecules down to 1 GHz or less)
- Molecules *perform* all motions at the same time.
- Within one rotational period molecules typically vibrate 10-100 times.

$$1\,\mathrm{eV} = 8065.5\,\mathrm{cm}^{-1} = 241.799\,\mathrm{THz} = 96.5\,\mathrm{kJ/mol} \qquad (1)$$

See also the OH term scheme.

Born-Oppenheimer approximation



- Separation of electronic and nuclear motion:
  - Energy-scale of electronic states: 10000–50000 cm^{-1}
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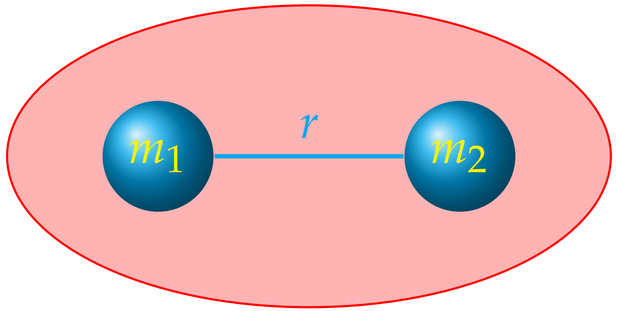


- Seen from the electrons, the nuclear frame is rigid in space.
- The slowly moving nuclei see a smeared out electronic charge cloud (whose effect on the nuclei depends on the internuclear separation).
  Or: the electrons adjust, essentially instantaneously, to the changing position of the nuclei.

Born-Oppenheimer approximation
Separation of electronic and nuclear motion

Definition: Born-Oppenheimer approximation

Electrons are lighter and faster than the nuclei. For the electrons the nuclei seem to be fixed in space, and the nuclei move in an effective distribution of electrons (electron cloud).

- The molecular wavefunction can be written as a product of a *nuclear* wavefunction and an *electronic* wavefunction, where the nuclear coordinates $\vec{R}_j$ are parameters:

$$\Psi\left(\vec{r}_i, \vec{R}_j\right) = \Psi_{\mathrm{e}}\left(\vec{r}_i; \vec{R}_j\right) \cdot \Psi_{\mathrm{n}}\left(\vec{R}_j\right) \tag{2}$$

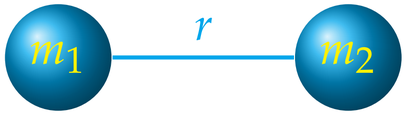
- The eigenvalues of the electronic wave equation serve as an *effective potential* for the nuclear motion in the vicinity of the field configuration $\vec{R}_j$.
- Electrons move as if the nuclei were fixed in their instantaneous positions and follow the nuclear motion adiabatically.
- Electrons do not make transitions to other states, the electronic states are only deformed by the nuclear displacements.
- The electronic isotope shift is zero within the Born-Oppenheimer approximation.

Separation of rotational and vibrational motion

- Separation of translation: $3N-3$ coordinates in the center of mass frame. This separation is trivial in the absence of external fields.
- Separation of rotation: $3N-6$ ($3N-5$ for linear molecules) vibrational coordinates. But molecules are *not* rigid bodies, rotation and vibration are coupled! There are many ways to attach a "molecular frame", a set of axes that rotate with the molecule, to a non-rigid body
- The separated nuclear wavefunction reads in the end:

$$\Psi_{\mathrm{n}}\left(\vec{R}_j\right) = \Psi_{\mathrm{t}}\left(X_{\mathrm{cm}}, Y_{\mathrm{cm}}, Z_{\mathrm{cm}}\right) \cdot \Psi_{\mathrm{r}}\left(\alpha, \beta, \gamma\right) \cdot \Psi_{\mathrm{v}}\left(Q_1, \ldots, Q_{3N-6}\right) \cdot \qquad (3)$$

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 $J(J+1)$

Term values

In molecular spectroscopy term values are used for convenience:

$$F(J) = \frac{E_r}{hc} = BJ(J+1) \tag{12}$$

with the rotational constant

$$B = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu r^2} \tag{13}$$

Here we use cm^{-1}, often also Hz (MHz) are used.

Typical rotational constants of diatomic molecules are $20\,\mathrm{cm}^{-1}$ for hydrides (HF, OH, CH, ...) to less than $1\,\mathrm{cm}^{-1}$ for heavier small molecules; they become very small (e.g., $< 10^{-6}$ cm^{-1}) for large polyatomic molecules.

	B_e (cm^{-1})	r_e $(10^{-12}$ m)
H_2	60.8	74.16
N_2	2.010	109.4
O_2	1.446	120.7
Li_2	0.673	267.3
NO	1.705	115.1
HCl	10.59	127.4

$1\,\mathrm{cm}^{-1} \mathrel{\hat{=}} 2.99 \cdot 10^{10}\,\mathrm{s}^{-1} \mathrel{\hat{=}} 1.23992 \cdot 10^{-4}\,\mathrm{eV}$

Rigid rotor
Wavefunctions and probability distributions

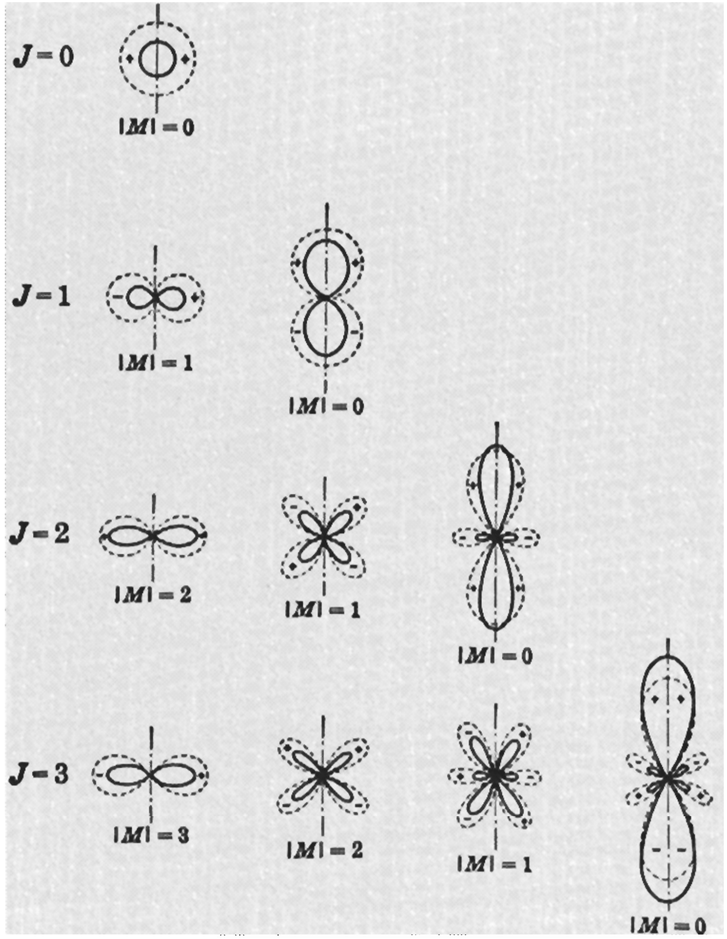
Hydrogen atom

Coulomb potential

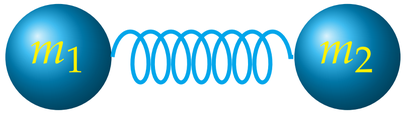
Diatomic rigid rotor

Fixed distance

$$\Psi_{rot}(r) = Y_{JM}(\vartheta, \varphi)$$



Harmonic oscillator



- Potential energy of harmonic oscillator:

$$V = \frac{1}{2}k(r - r_e)^2 \tag{15}$$

- Classical vibration frequency:

$$2\pi\nu_{\text{osc}} = \sqrt{\frac{k}{\mu}} \tag{16}$$

- Quantum-mechanical vibration energy:

$$E_{\text{vib}} = h\nu_{\text{osc}}(v + \frac{1}{2}) \tag{17}$$

  - energy levels are equidistant
  - ground state has finite (non-zero) energy

Harmonic oscillator

- Term values in practically used units (cm^{-1}):

$$G(v) = \frac{E_{\mathrm{vib}}}{hc} = \omega_e (v + \frac{1}{2}) \tag{18}$$

with

$$\omega_e = \frac{\nu_{\mathrm{osc}}}{c} \tag{19}$$

- Example frequencies:

H_2	$4401\,\mathrm{cm}^{-1}$
HF	$4138\,\mathrm{cm}^{-1}$
OH	$3738\,\mathrm{cm}^{-1}$
HCl	$2991\,\mathrm{cm}^{-1}$
NaCl	$366\,\mathrm{cm}^{-1}$

Harmonic oscillator

- Schroedinger equation:

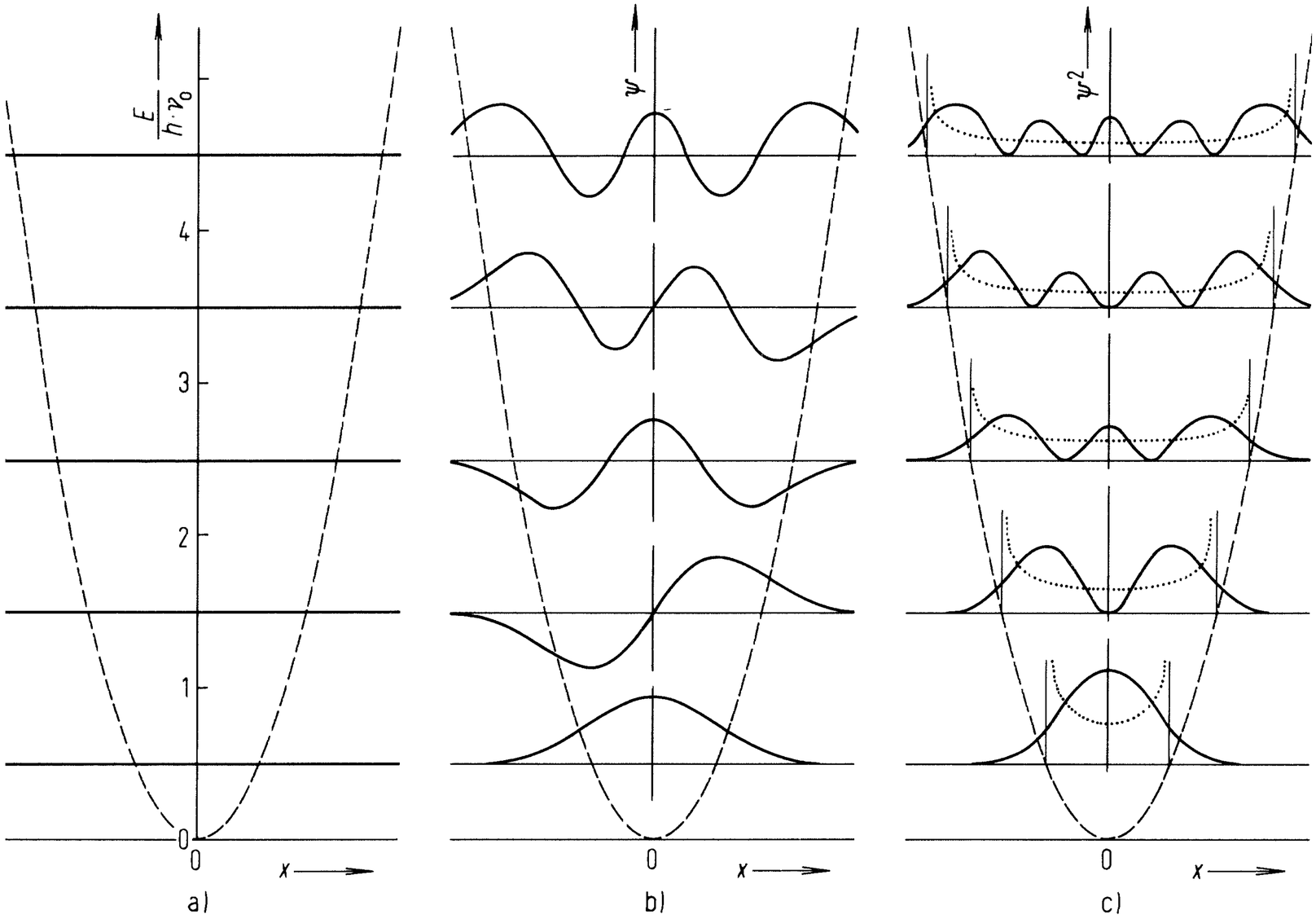
$$\left[-\frac{\hbar^2\Delta}{2\mu}+\frac{k}{2}(r-r_e)^2\right]\Psi_{vib}(r-r_e)=E_{vib}\Psi_{vib}(r-r_e) \tag{20}$$

- Wavefunctions of the harmonic oscillator are the Hermite polynomials

v	E_v	Ψ
0	$\frac{1}{2}\hbar\omega_e$	$A_0\cdot e^{-\frac{\alpha}{2}(r-r_e)^2}$
1	$\frac{3}{2}\hbar\omega_e$	$A_1\cdot 2(r-r_e)\cdot e^{-\frac{\alpha}{2}(r-r_e)^2}$
2	$\frac{5}{2}\hbar\omega_e$	$A_2\cdot(1-2\alpha(r-r_e)^2)\cdot e^{-\frac{\alpha}{2}(r-r_e)^2}$

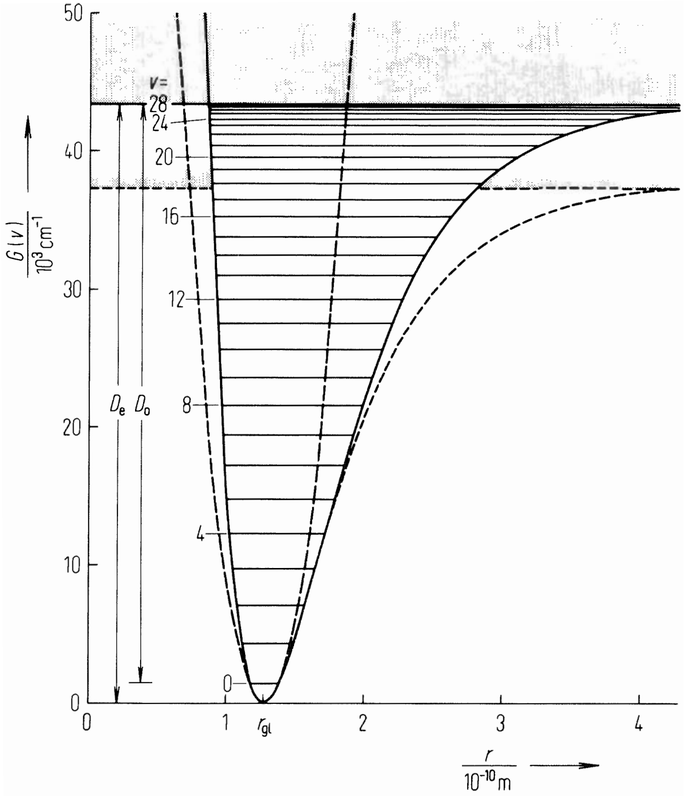
mit $\alpha=\frac{1}{\hbar}\sqrt{\mu\cdot k}$

Harmonic oscillator wavefunctions



Morse oscillator

A more realistic potential must resemble the bond-breaking at large distance!



$$V = D_e \left(1 - e^{-\beta(r-r_e)}\right)^2 \quad (21)$$

- vibrational level spacing decreases
- finite number of vibrational levels (Compare Coulomb potential with an infinite number of bound states.)
- For small $r - r_e$:

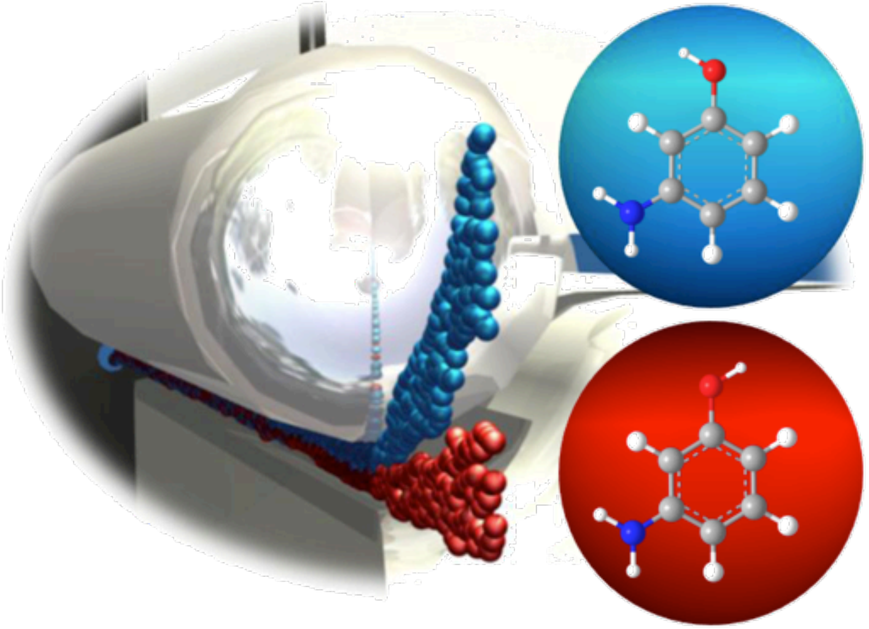
$$V = D_e \left(1 - (1 - \beta(r - r_e))\right)^2 \quad (22)$$

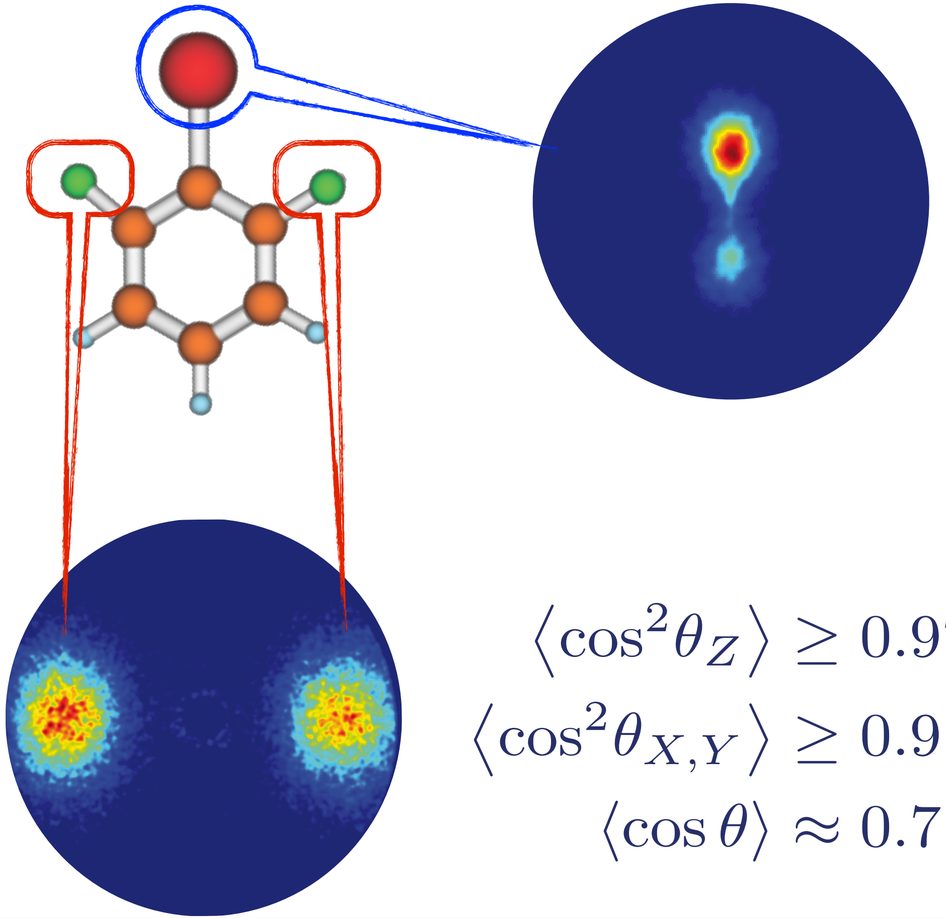
- term values

$$G(v) = \omega_e(v + \frac{1}{2}) + \text{correction term} \quad (23)$$

$$= \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 \quad (24)$$

Molecules in fields
Manipulation of translational and rotational motion

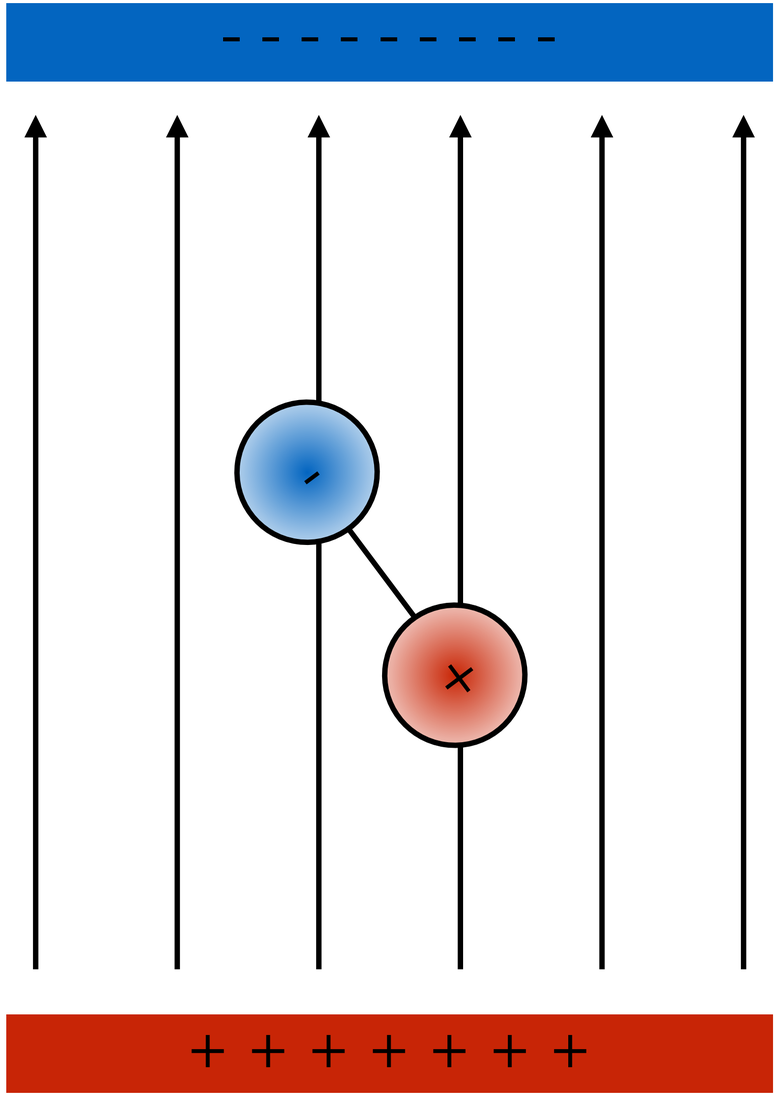




$$\langle \cos^2\theta_Z \rangle \geq 0.975$$
$$\langle \cos^2\theta_{X,Y} \rangle \geq 0.9$$
$$\langle \cos\theta \rangle \approx 0.7$$

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)

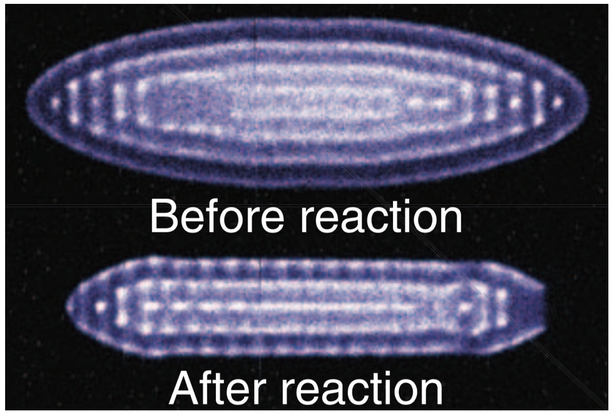
How to control particles, molecules …?



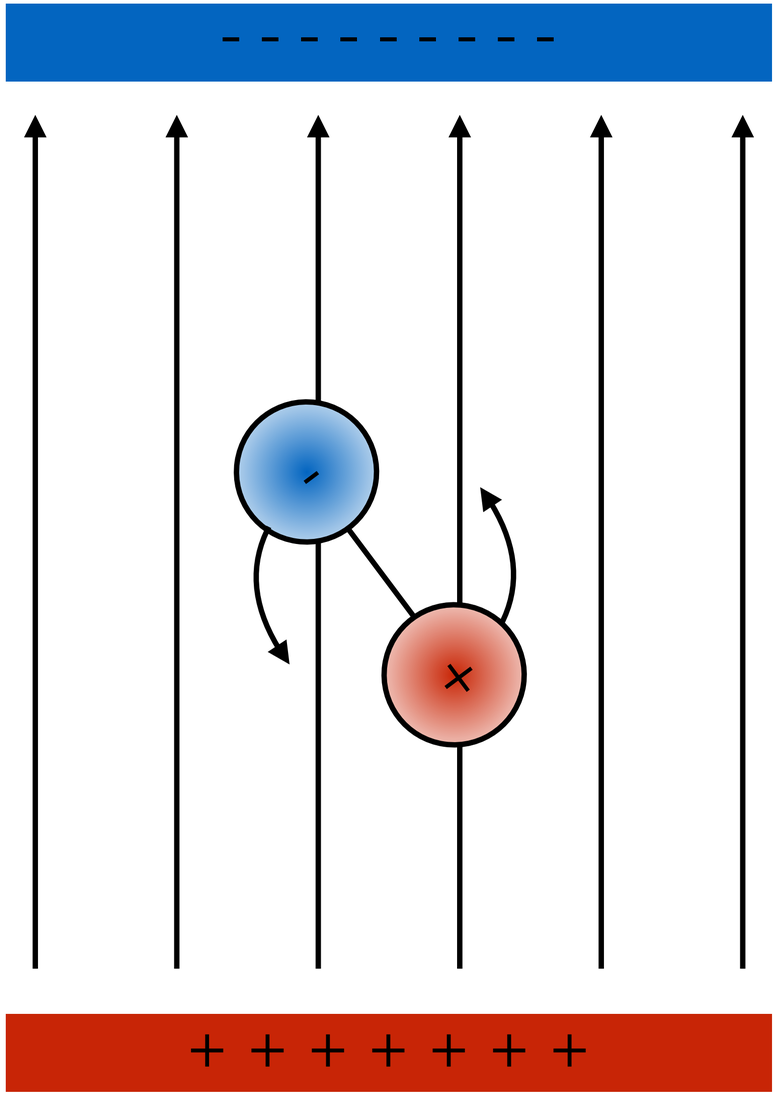
Taylor expansion of the energy:

$$U = q\phi - \vec{\mu} \cdot \vec{E} - \frac{1}{2}\vec{E}\hat{\alpha}\vec{E} - \ldots$$

A “handle” on charged particles



Charge distribution in an external electric field



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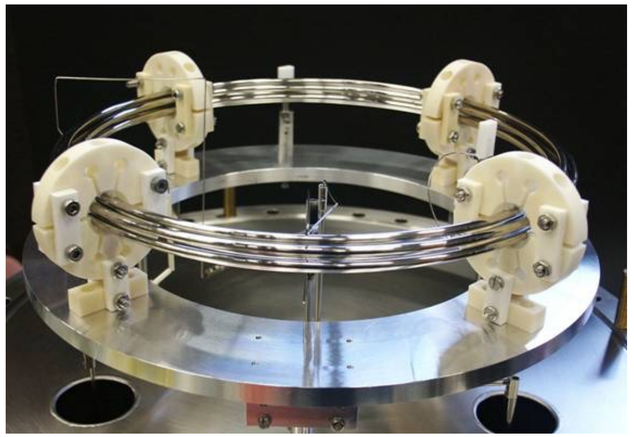
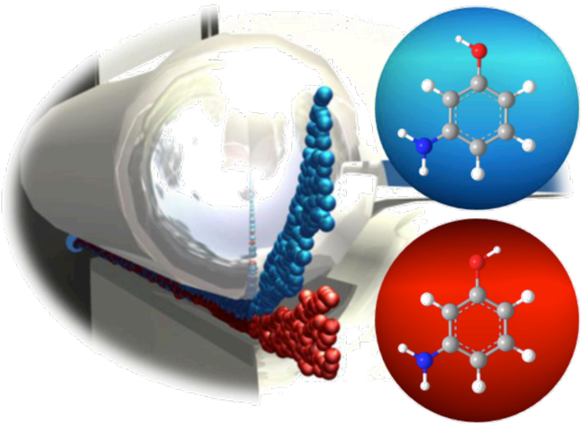
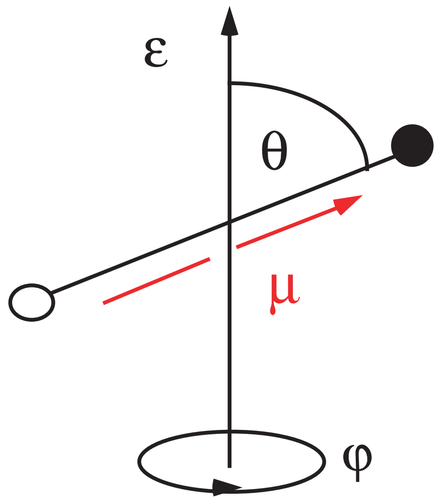
A “handle” on neutral particles

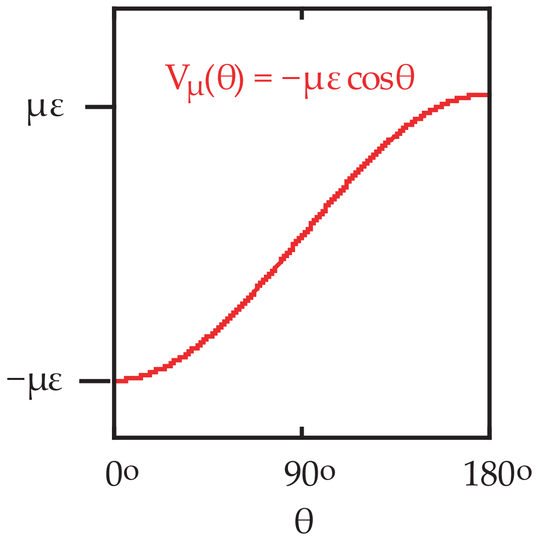




Heiner, Carty, Meijer, and Bethlem, *Nature Physics* **3**, 115 (2007)
Chang, Horke, Trippel, and Küpper. *Int. Rev. Phys. Chem.* **34**, 557 (2015)

Molecules in fields
Pendular states and the effective dipole moment





- 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.

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

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

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

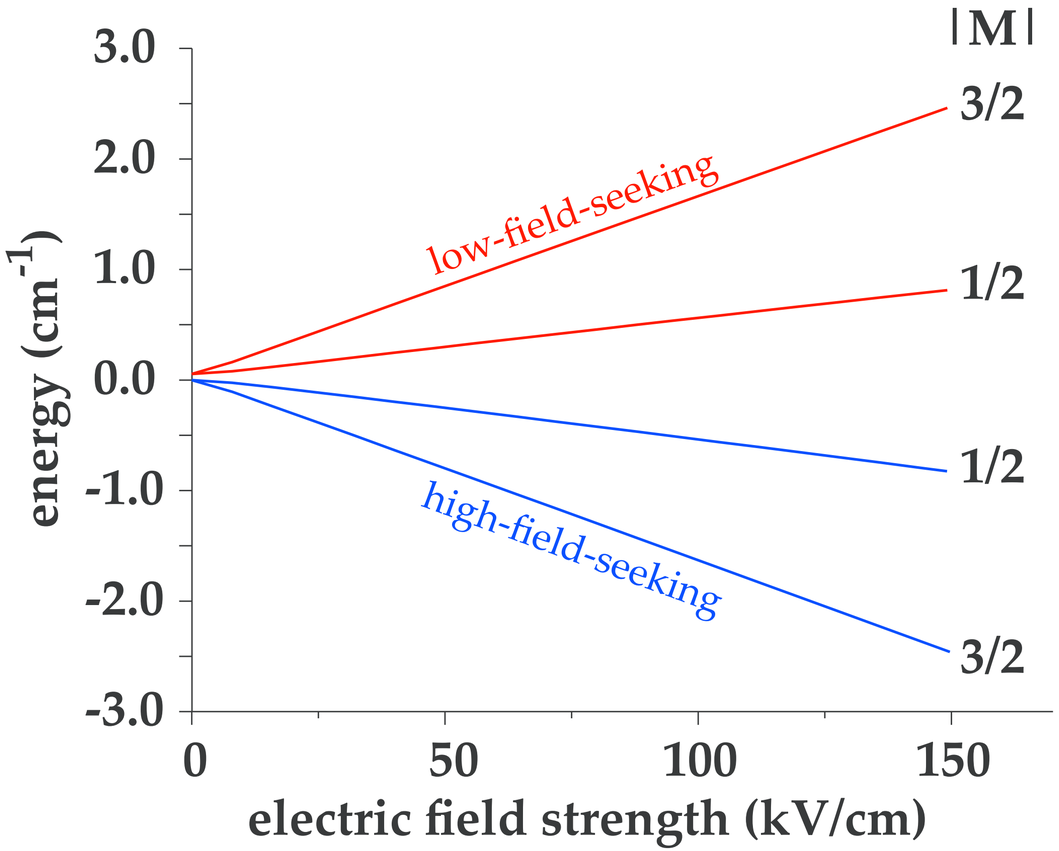
$$\langle JM|\cos\theta|JM\rangle = 0 \tag{53}$$

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

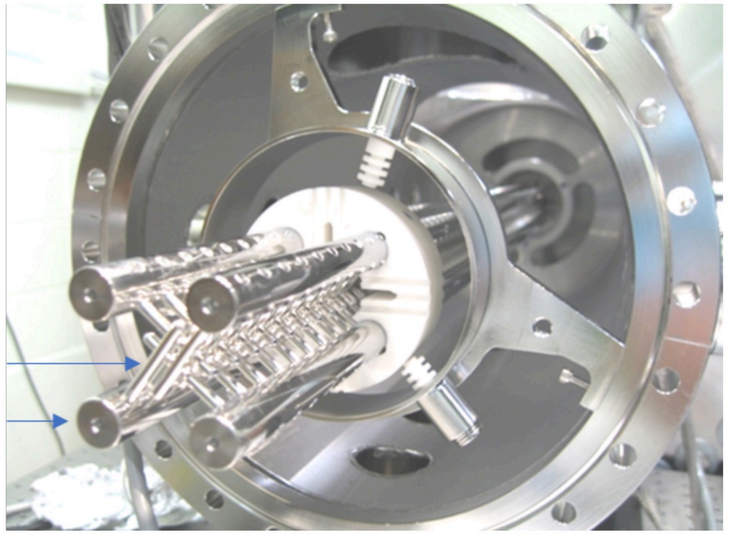
Stark curve of OH (simple example)

Energy Eigenvalues of two coupled states

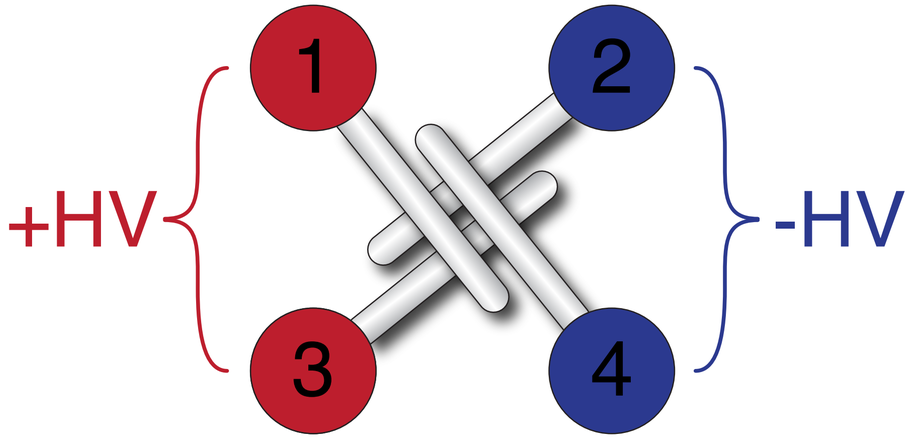
$$\begin{pmatrix} W_1 & \mu E \\ \mu E & W_2 \end{pmatrix} \rightarrow W_{\pm} = \frac{W_1 + W_2}{2} \pm \sqrt{\left(\frac{W_1 - W_2}{2}\right)^2 + (\mu E)^2}$$

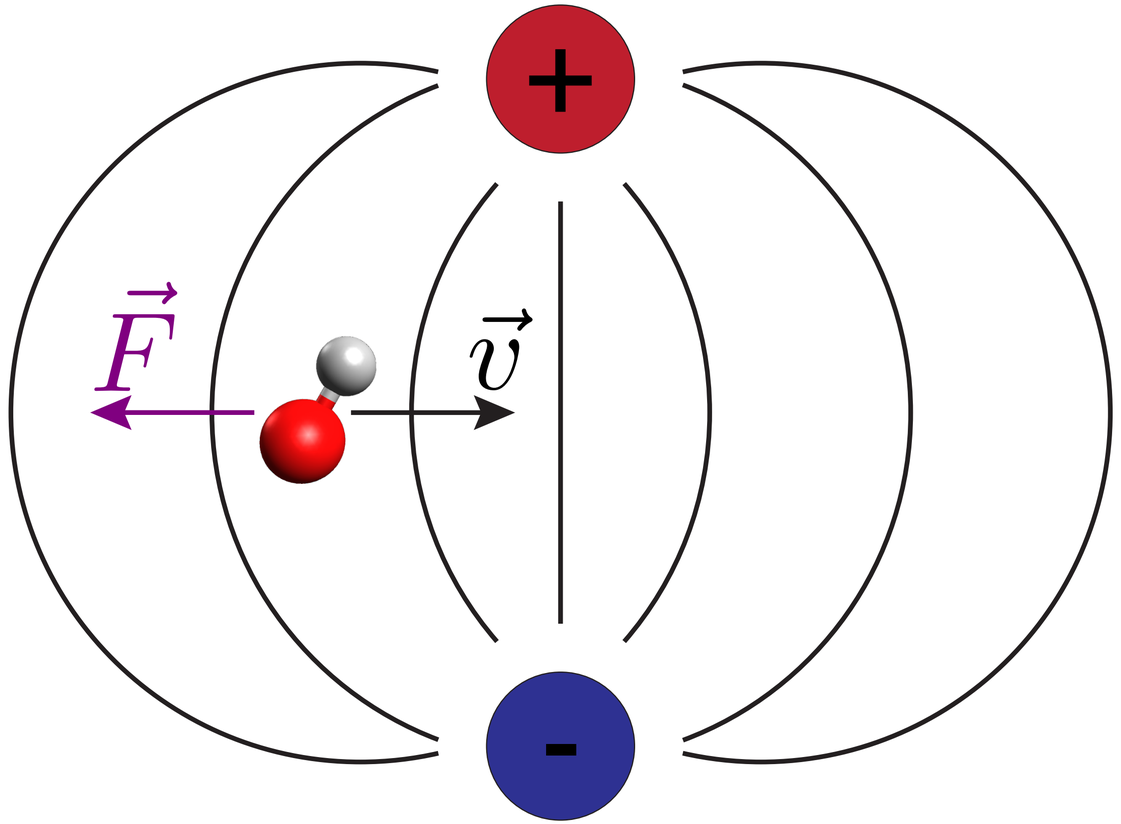


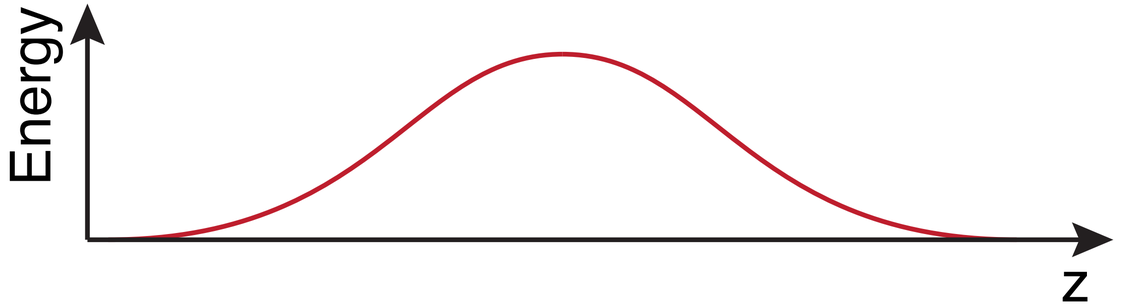
Deceleration of OH radicals



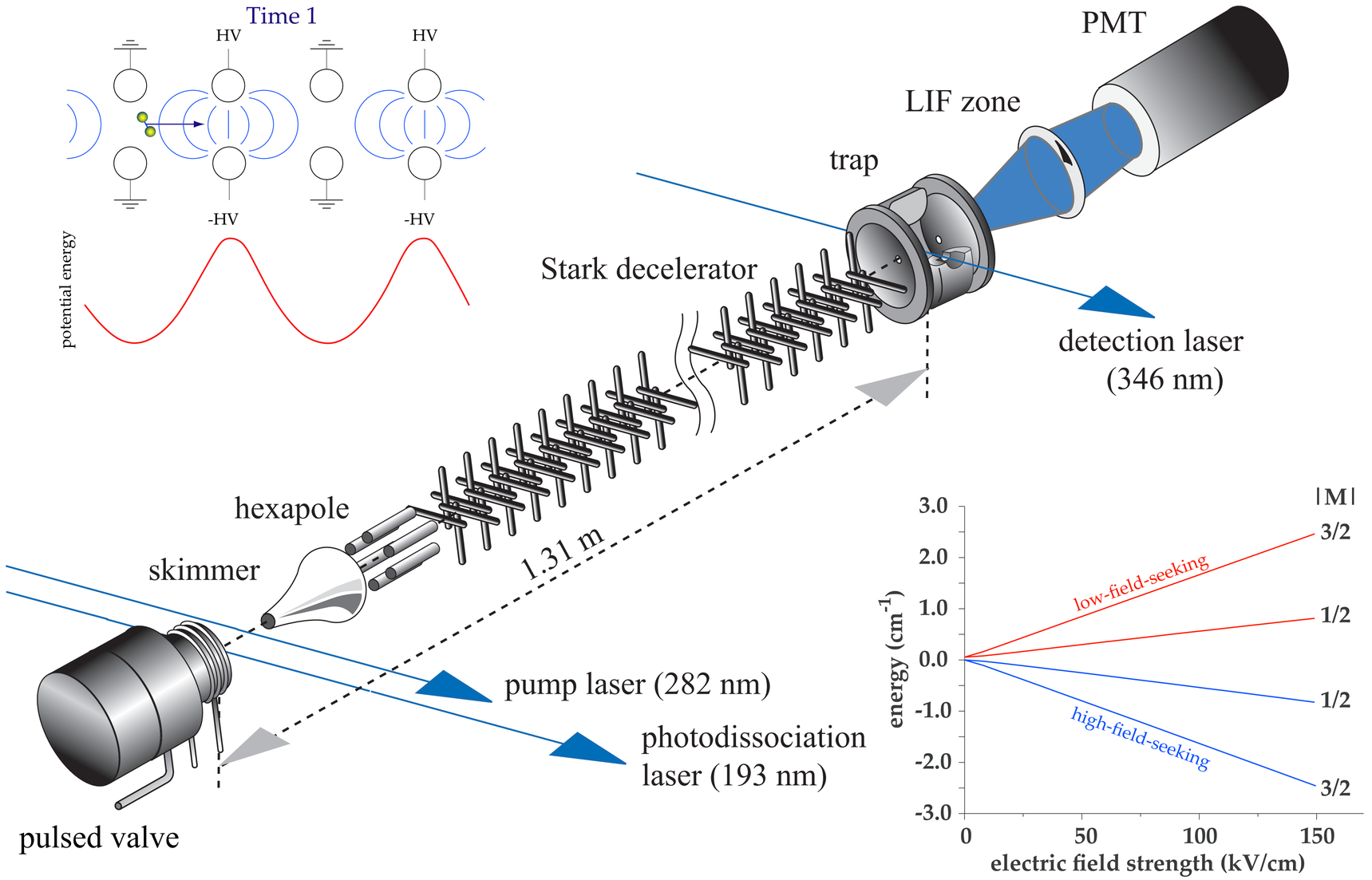
(a) Pin decelerator







Experimental setup of the Stark decelerator



Meerakker, Smeets, Vanhaecke, Jongma, Meijer, *Phys. Rev. Lett.* **94**, 023004 (2005)

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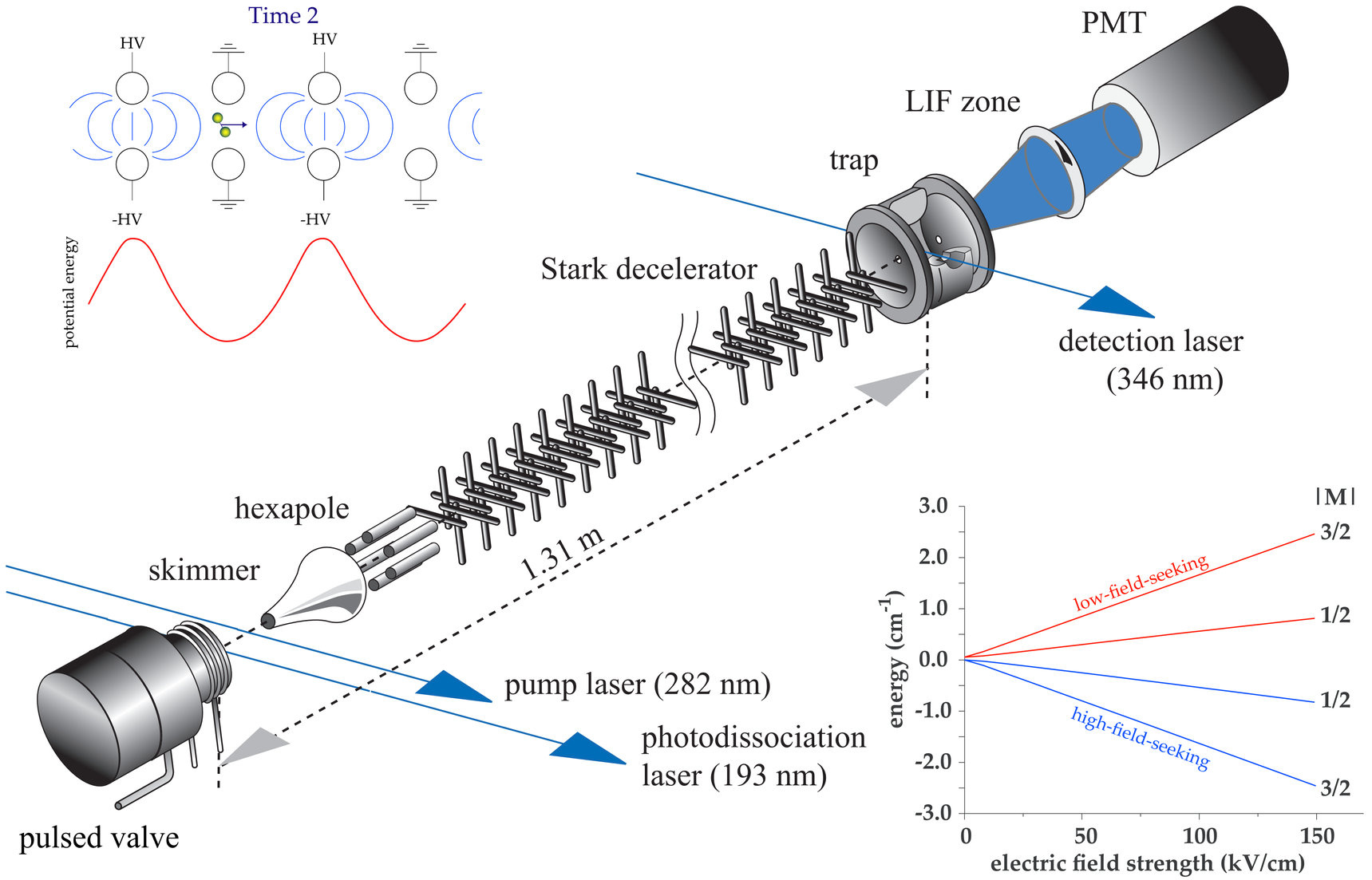
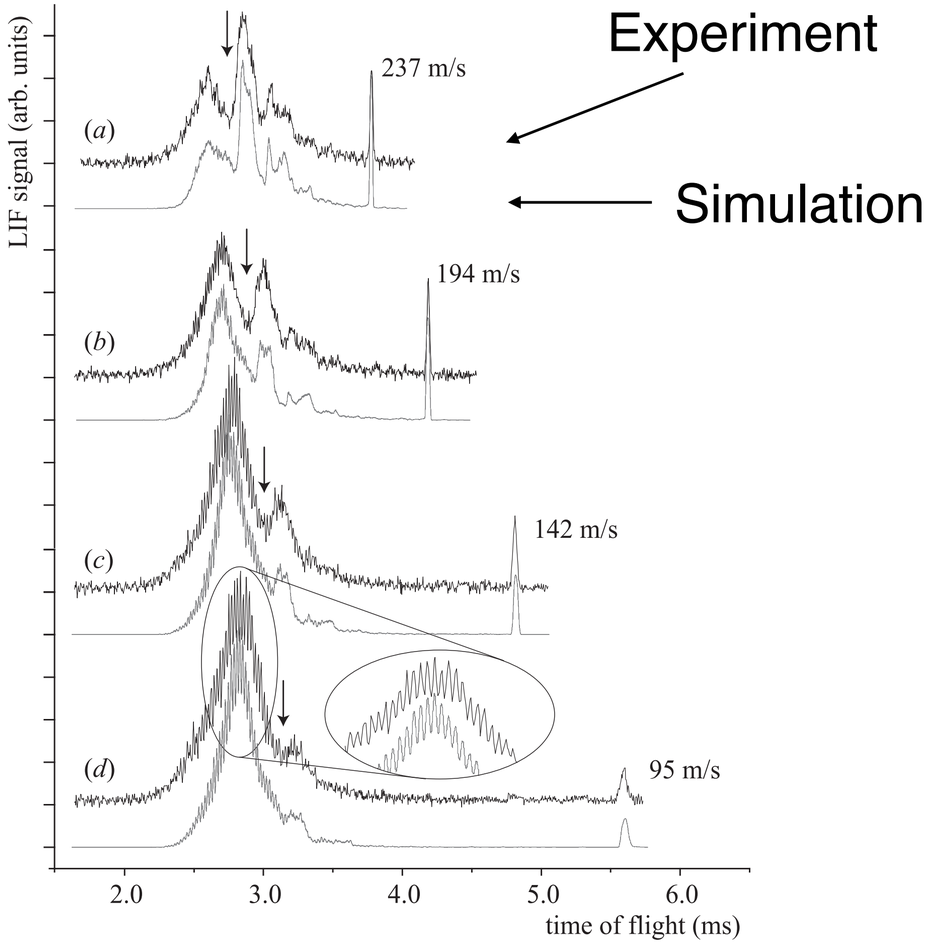
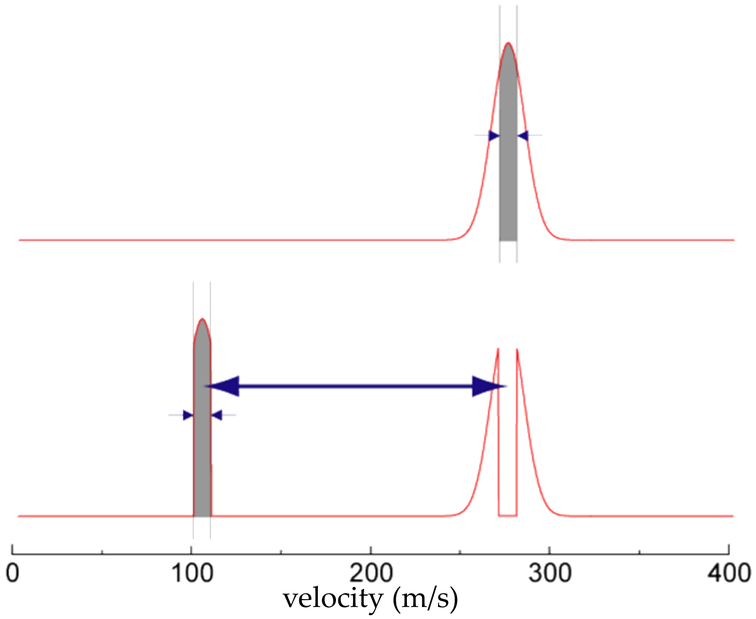


Meerakker, Smeets, Vanhaecke, Jongma, Meijer, *Phys. Rev. Lett.* **94**, 023004 (2005)

Decelerating OH



Selection and deceleration



Meerakker, Smeets, Vanhaecke, Jongma, Meijer, *Phys. Rev. Lett.* **94**, 023004 (2005)

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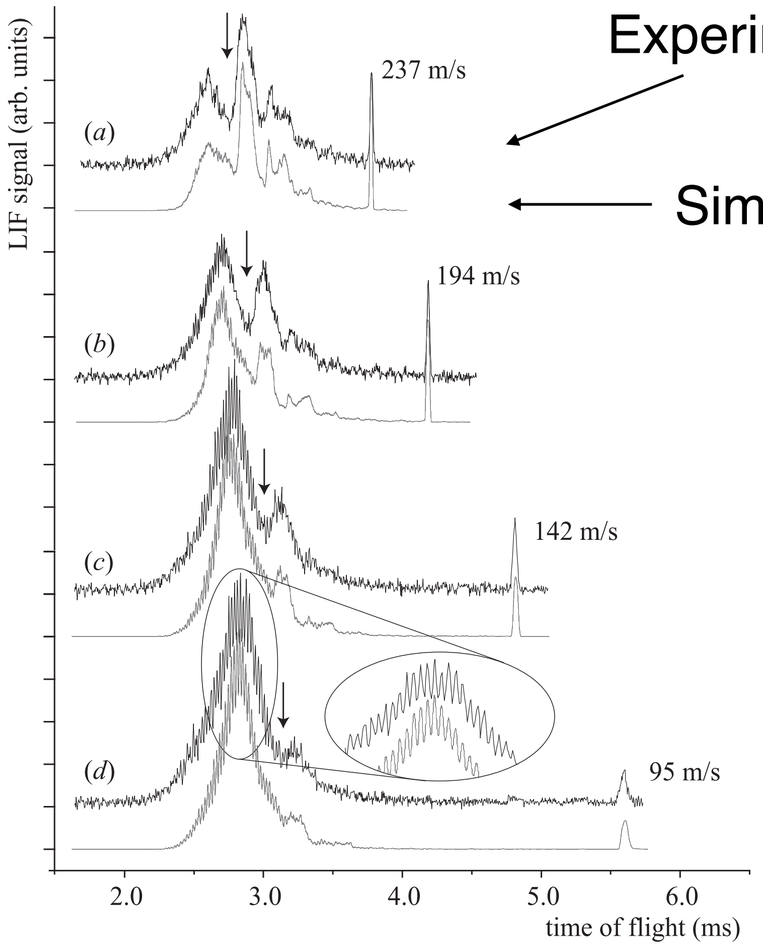
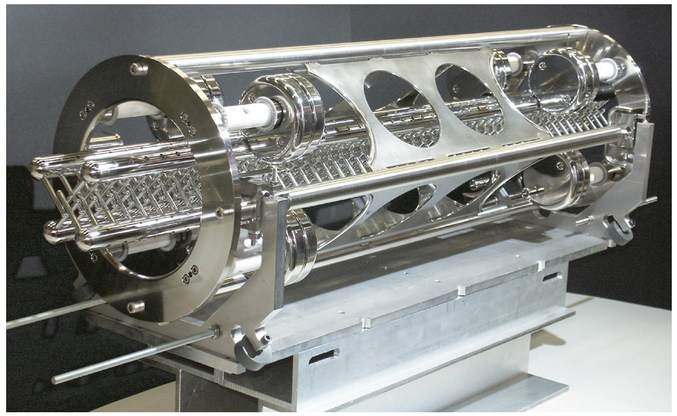
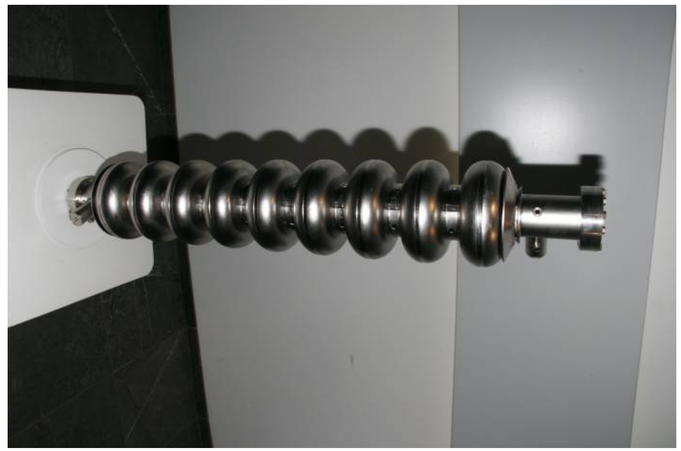


Stark decelerator: 0.01 eV/m



RF accelerator: 0.1 GeV/m



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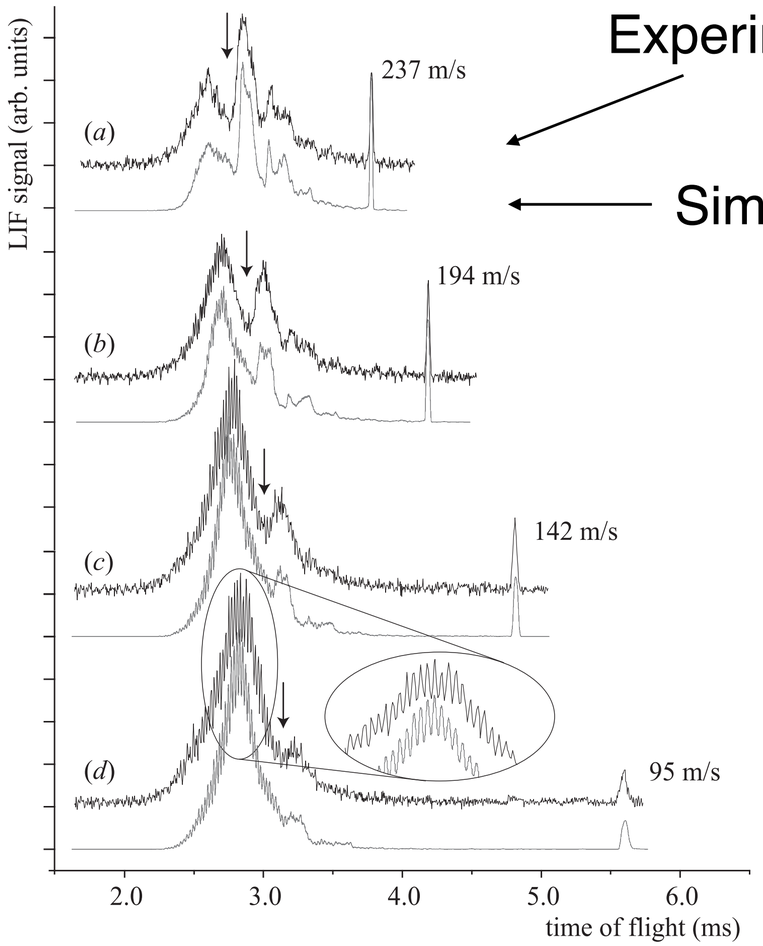
Decelerating OH



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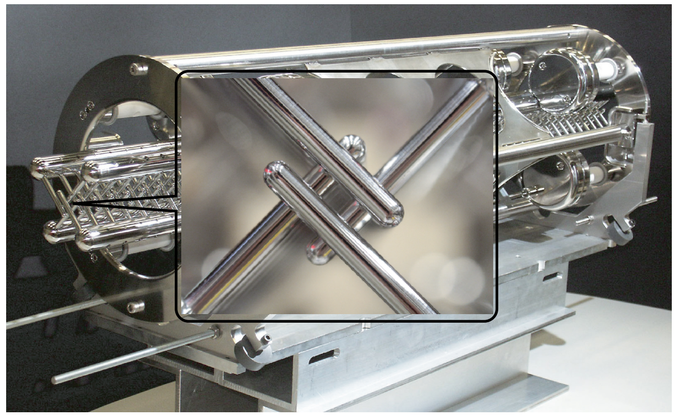

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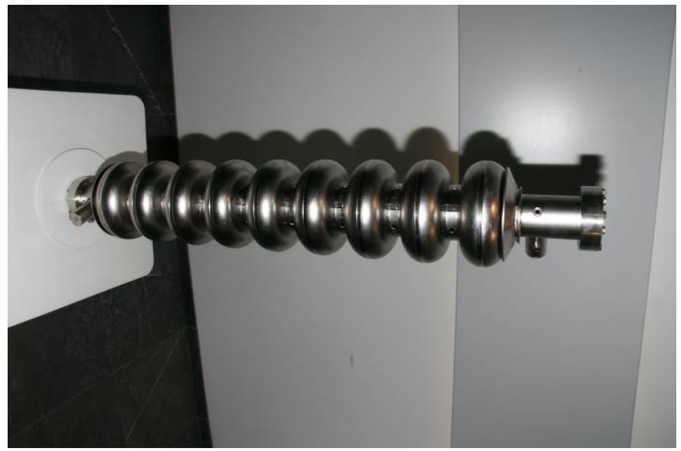
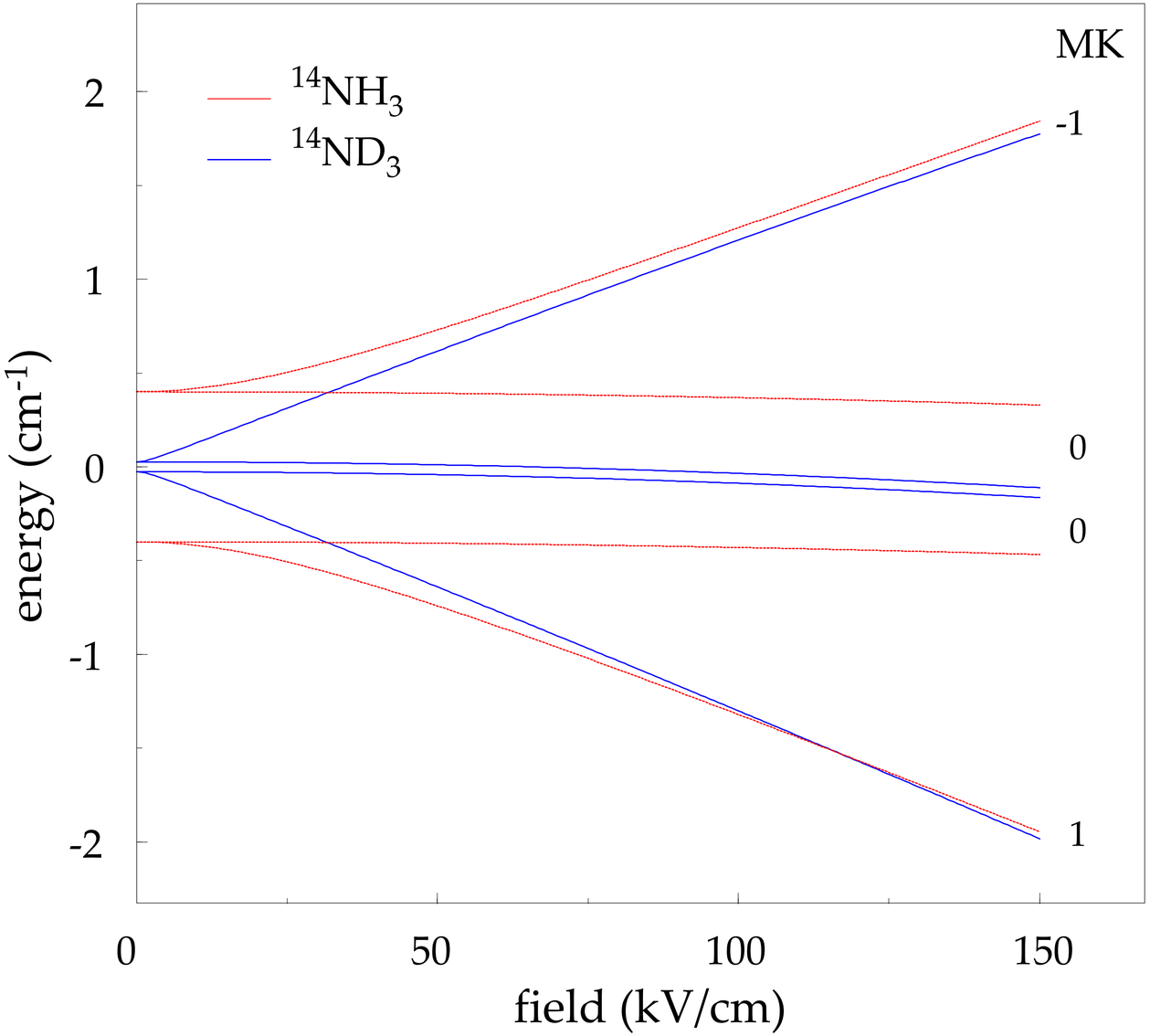


Meerakker, Smeets, Vanhaecke, Jongma, Meijer, *Phys. Rev. Lett.* **94**, 023004 (2005)

Stark curves of NH_3 and ND_3



Ammonia Maser

PHYSICAL REVIEW VOLUME 99, NUMBER 4 AUGUST 15, 1955

The Maser—New Type of Microwave Amplifier, Frequency Standard, and Spectrometer*†

J. P. Gordon,‡ H. J. Zeiger,§ and C. H. Townes
Columbia University, New York, New York

(Received May 4, 1955)

A type of device is described which can be used as a microwave amplifier, spectrometer, or oscillator. Experimental results are given. When operated as a spectrometer, the device has good sensitivity, and, by eliminating the usual Doppler broadening, a resolution of 7 kc/sec has been achieved. Operated as an oscillator, the device produced a frequency stable to at least 4 parts in 10^{12} in times of the order of a second, and stable over periods of an hour or more to at least a part in 10^{10}. The device is examined theoretically, and results are given for the expected sensitivity of the spectrometer, the stability and purity of the oscillation, and the noise figure of the amplifier. Under certain conditions a noise figure approaching the theoretical limit of unity, along with reasonably high gain, should be attainable.

INTRODUCTION

A TYPE of device is described below can be used as a microwave spectrometer, a microwave amplifier, or as an oscillator. As a spectrometer, it has good sensitivity and very high resolution since it can virtually eliminate the Doppler effect. As an amplifier of microwaves, it should have a narrow band width, a very low noise figure and the general properties of a feedback amplifier which can produce sustained oscillations. Power output of the amplifier or oscillator is small, but sufficiently large for many purposes.

The device utilizes a molecular beam in which molecules in the excited state of a microwave transition are selected. Interaction between these excited molecules and a microwave field produces additional radiation and hence amplification by stimulated emission. We call an apparatus utilizing this technique a "maser," which is an acronym for "microwave amplification by stimulated emission of radiation."

Some results obtained with this device have already been briefly reported.[1] An independent proposal for a system of this general type has also been published.[2] We shall here examine in some detail the general behavior and characteristics of the maser and compare experimental results with theoretical expectations. Particular attention is given to its operation with ammonia molecules. The preceding paper,[3] which will hereafter be referred to as (I), discusses an investigation of the hyperfine structure of the microwave spectrum of $N^{14}H_3$ with this apparatus. Certain of its properties which are necessary for an understanding of the relative intensities of the hyperfine structure components are also discussed there.

BRIEF DESCRIPTION OF OPERATION

A molecular beam of ammonia is produced by allowing ammonia molecules to diffuse out a directional source consisting of many fine tubes. The beam then transverses a region in which a highly nonuniform electrostatic field forms a selective lens, focusing those molecules which are in upper inversion states while defocusing those in lower inversion states. The upper inversion state molecules emerge from the focusing field and enter a resonant cavity in which downward transitions to the lower inversion states are induced. A simplified block diagram of this apparatus is given in Fig. 1. The source, focuser, and resonant cavity are all enclosed in a vacuum chamber.

For operation of the maser as a spectrometer, power of varying frequency is introduced into the cavity from an external source. The molecular resonances are then observed as sharp increases in the power level in the cavity when the external oscillator frequency passes the molecular resonance frequencies.

At the frequencies of the molecular transitions, the beam amplifies the power input to the cavity. Thus the maser may be used as a narrow-band amplifier. Since the molecules are uncharged, the usual shot noise existing in an electronic amplifier is missing, and essentially no noise in addition to fundamental thermal noise is present in the amplifier.

If the number of molecules in the beam is increased beyond a certain critical value the maser oscillates. At the critical beam strength a high microwave energy density can be maintained in the cavity by the beam alone since the power emitted from the beam compensates for the power lost to the cavity walls and coupled wave guides. This oscillation is shown both experimentally and theoretically to be extremely monochromatic.

* Work supported jointly by the Signal Corps, the Office of Naval Research, and the Air Research and Development Command.
† Submitted by J. P. Gordon in partial fulfillment of the requirements of the degree of Doctor of Philosophy at Columbia University.
‡ Now at the Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.
§ Carbide and Carbon Postdoctoral Fellow in Physics, now at Project Lincoln, Massachusetts Institute of Technology, Cambridge, Massachusetts.
[1] Gordon, Zeiger, and Townes, Phys. Rev. **95**, 282 (1954).
[2] N. G. Bassov and A. M. Prokhorov, J. Exptl. Theoret. Phys. (U.S.S.R.) **27**, 431 (1954). Also N. G. Bassov and A. M. Prokhorov, Proc. Acad. of Sciences (U.S.S.R.) **101**, 47 (1945).
[3] J. P. Gordon, preceding paper [Phys. Rev. **99**, 1253 (1955)].

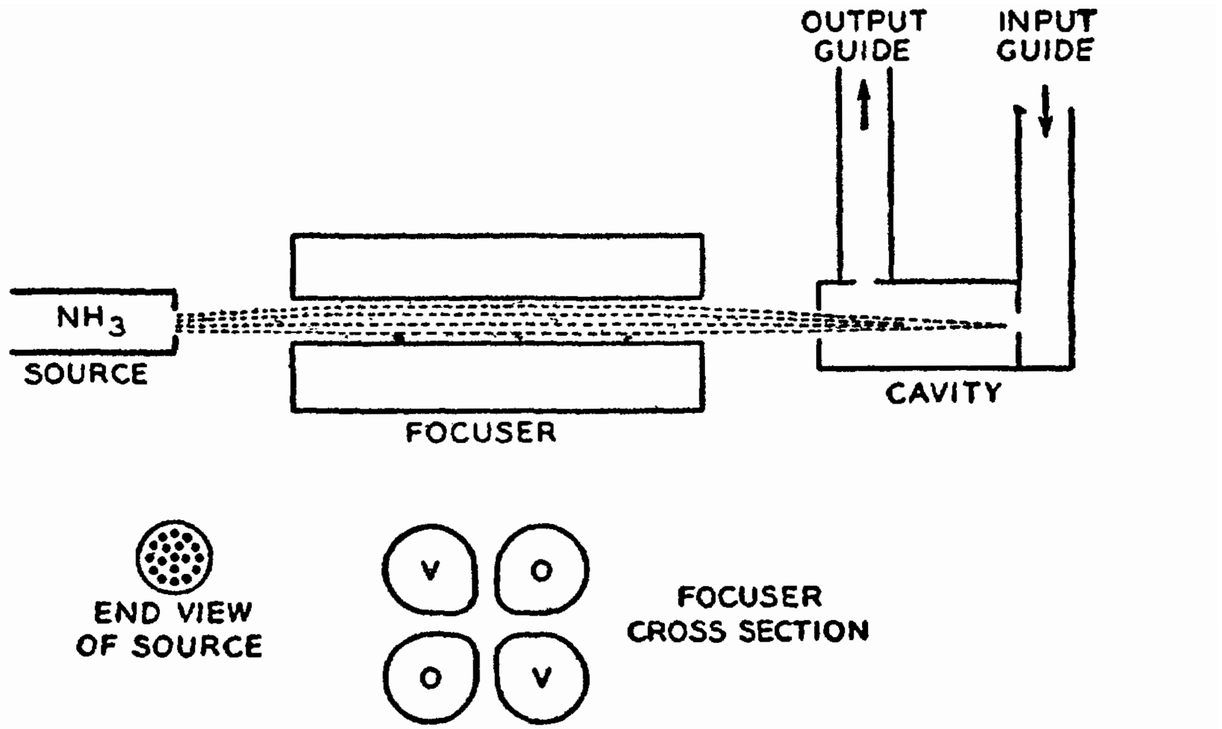


FIG. 1. Simplified diagram of the essential parts of the maser.

Gordon, Zeiger, and Townes, *Phys. Rev.* **99**, 1264 (1955)

Nobel prize in physics 1964

"for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle"

Charles Hard Townes

1/2 of the prize

USA

Massachusetts Institute of Technology (MIT)
Cambridge, MA, USA

b. 1915

Nicolay Gennadiyevich Basov

1/4 of the prize

USSR

P.N. Lebedev Physical Institute
Moscow, USSR

b. 1922
d. 2001

Aleksandr Mikhailovich Prokhorov

1/4 of the prize

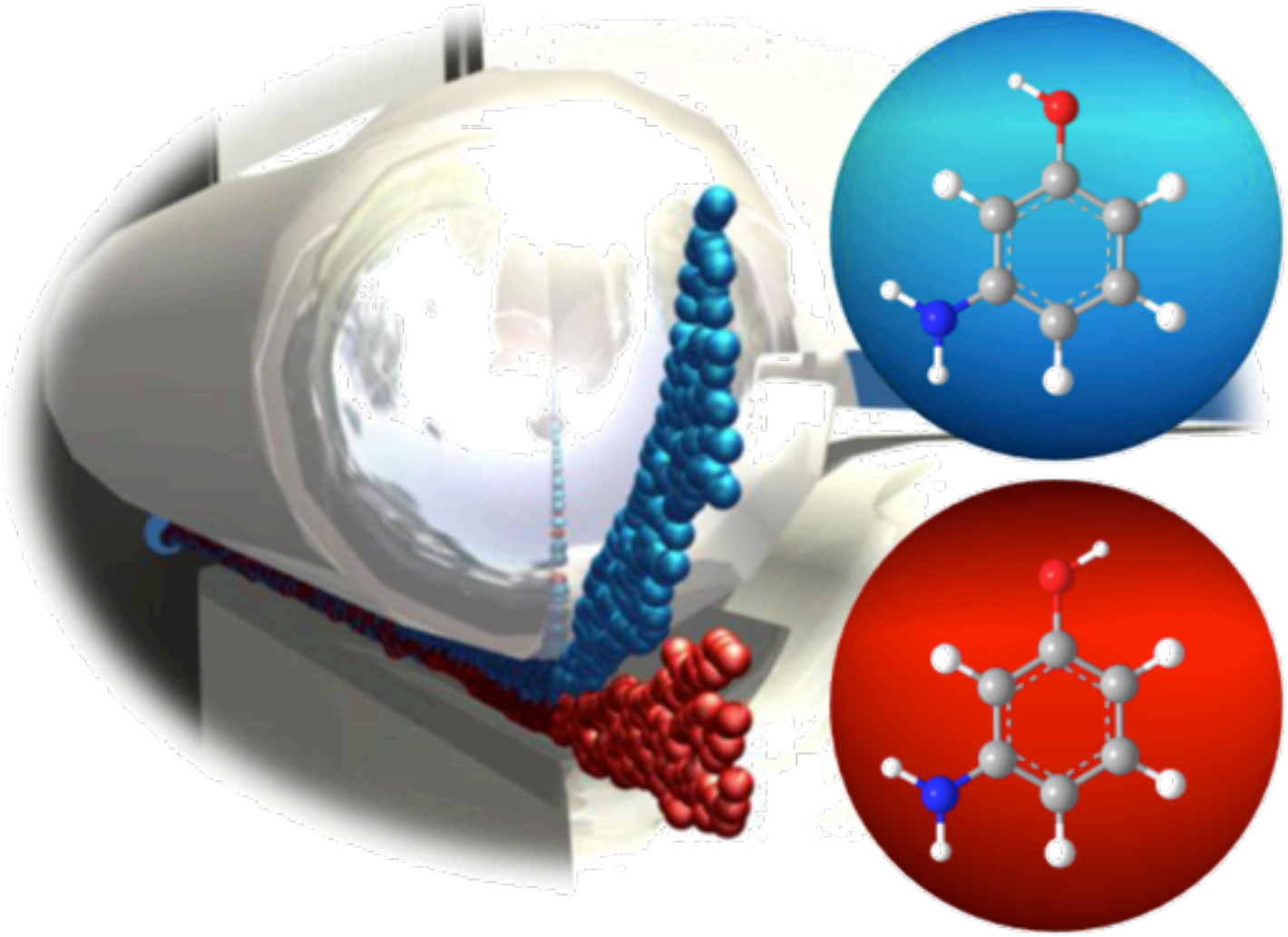
USSR

P.N. Lebedev Physical Institute
Moscow, USSR

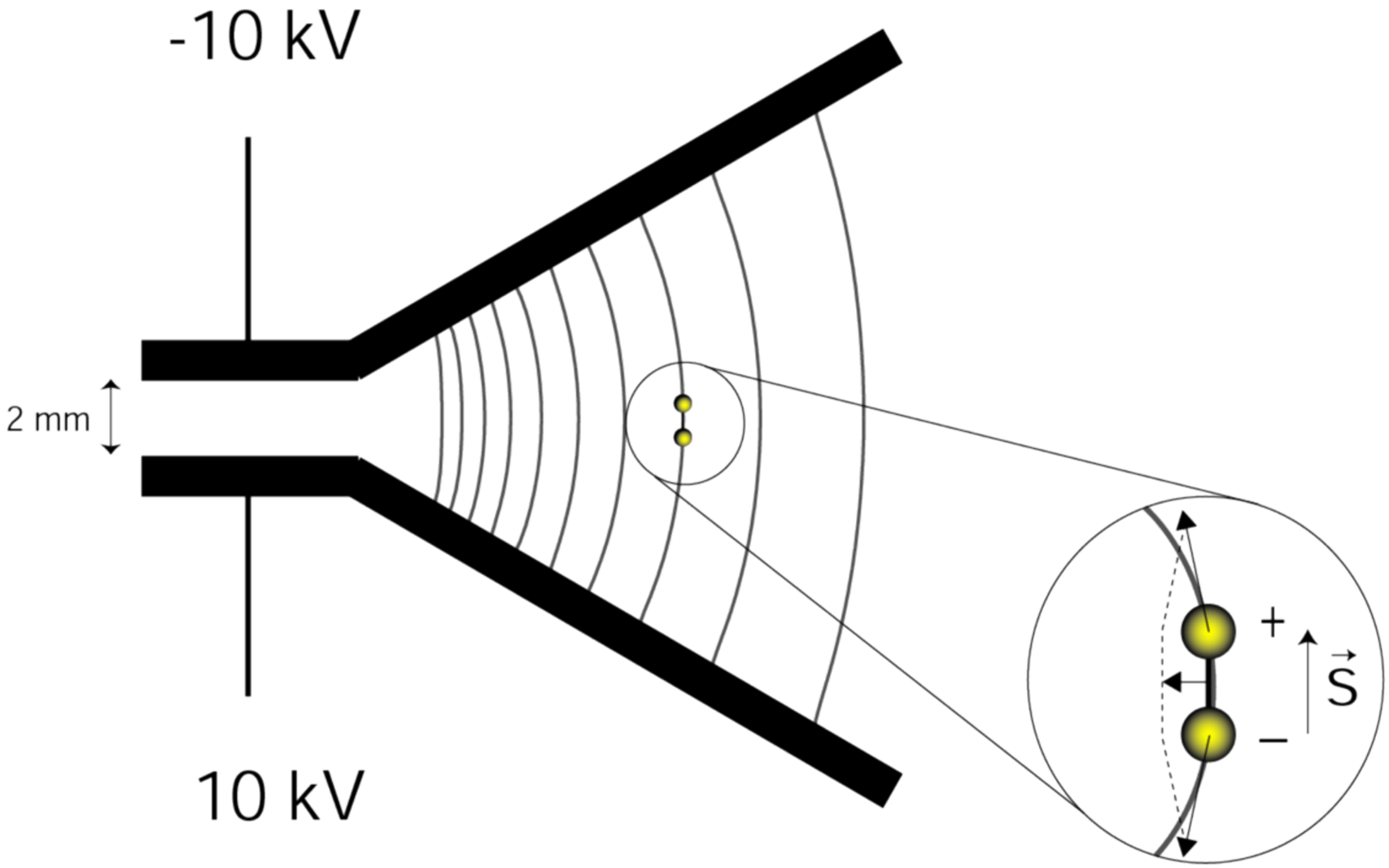
b. 1916
d. 2002

https://www.nobelprize.org/prizes/physics/1964/summary/

The electric deflector

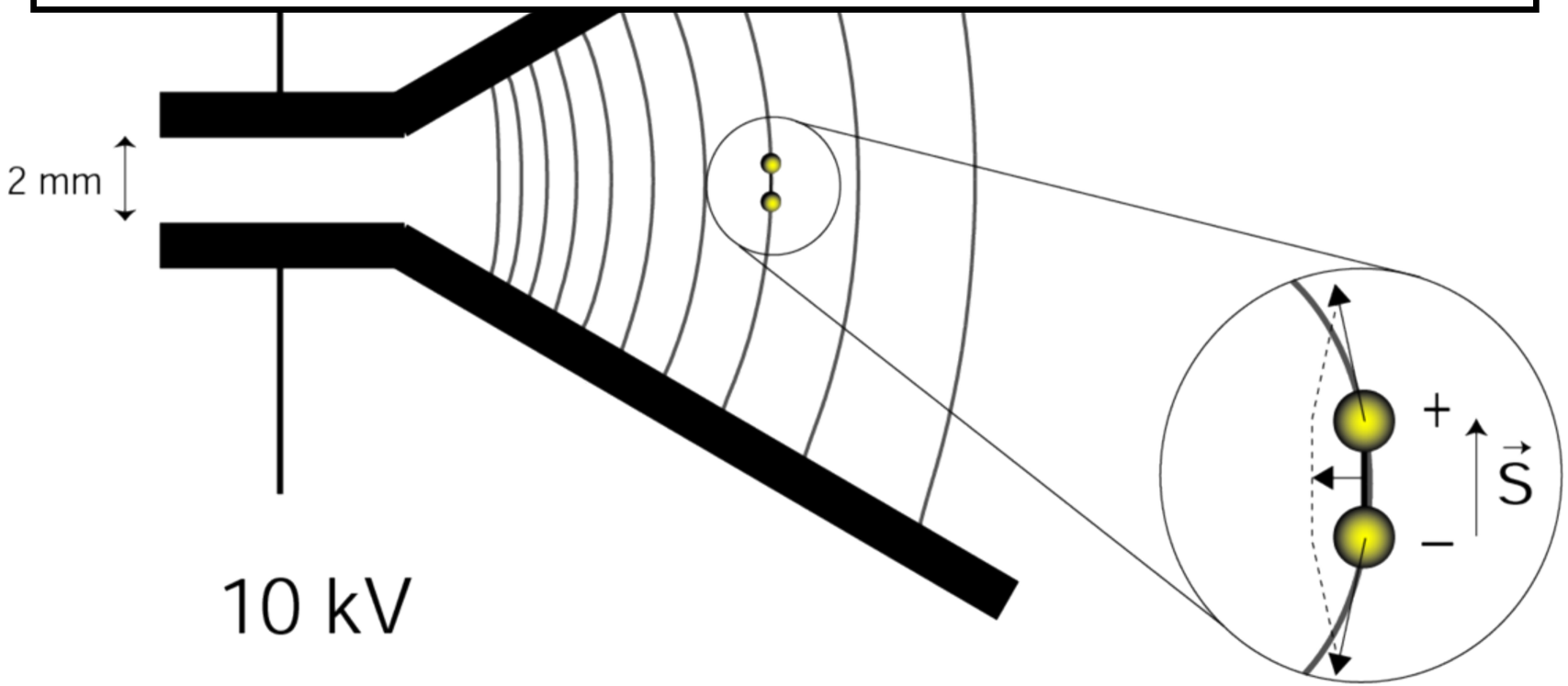


Interactions of molecules with electric fields



Interactions of molecules with electric fields

In "quantum-mechanical" reality, the Stark effect (the laboratory-fixed dipole moment) depends on the exact quantum state,



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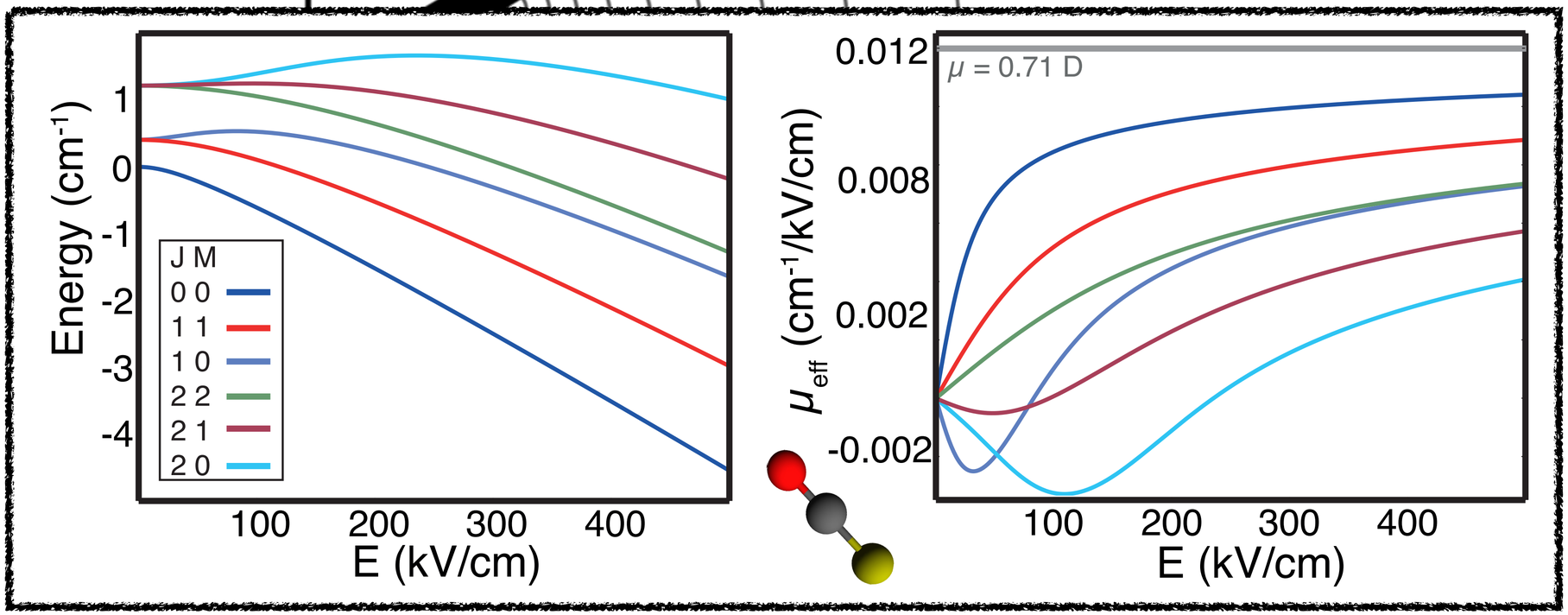
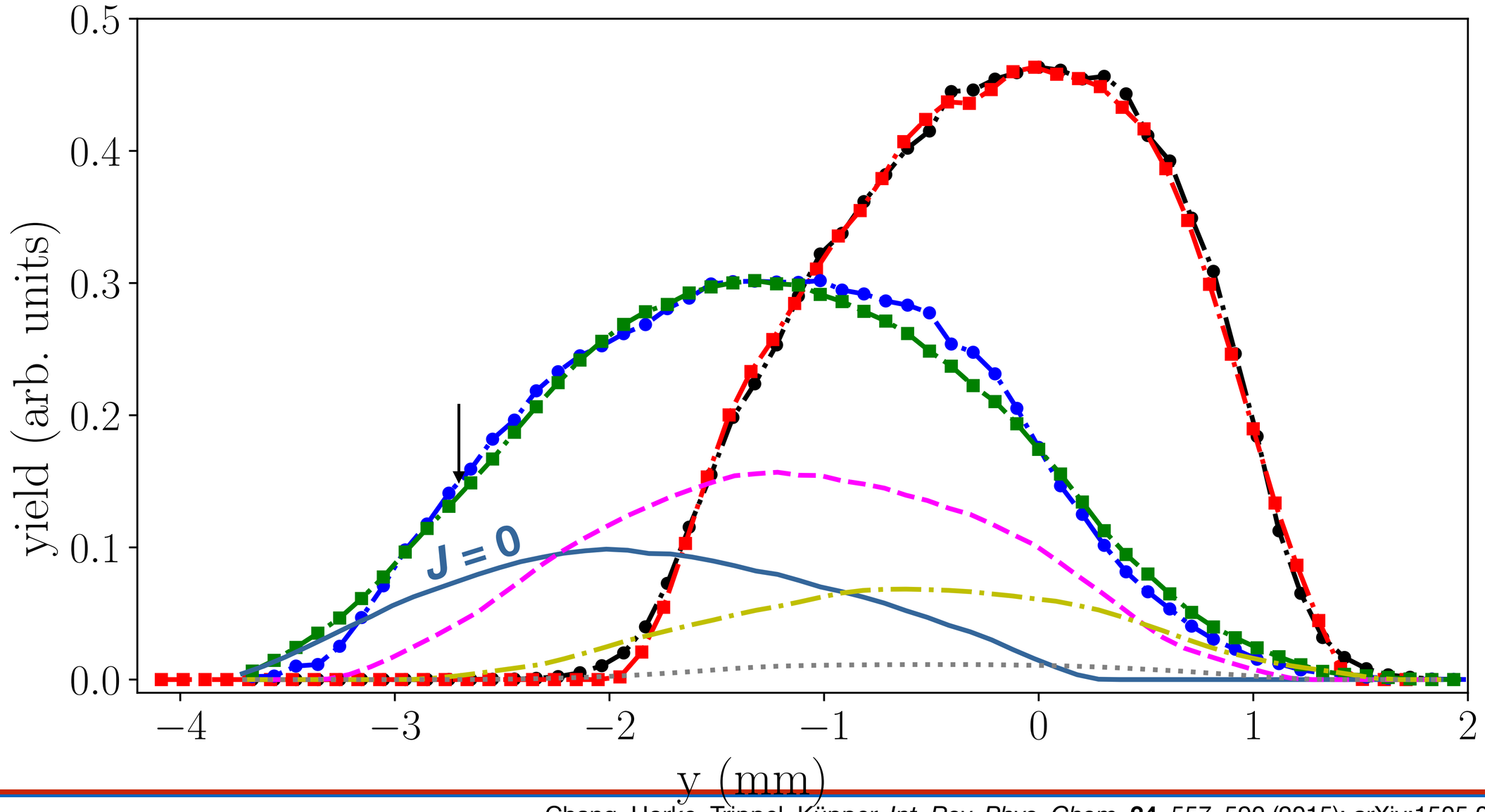
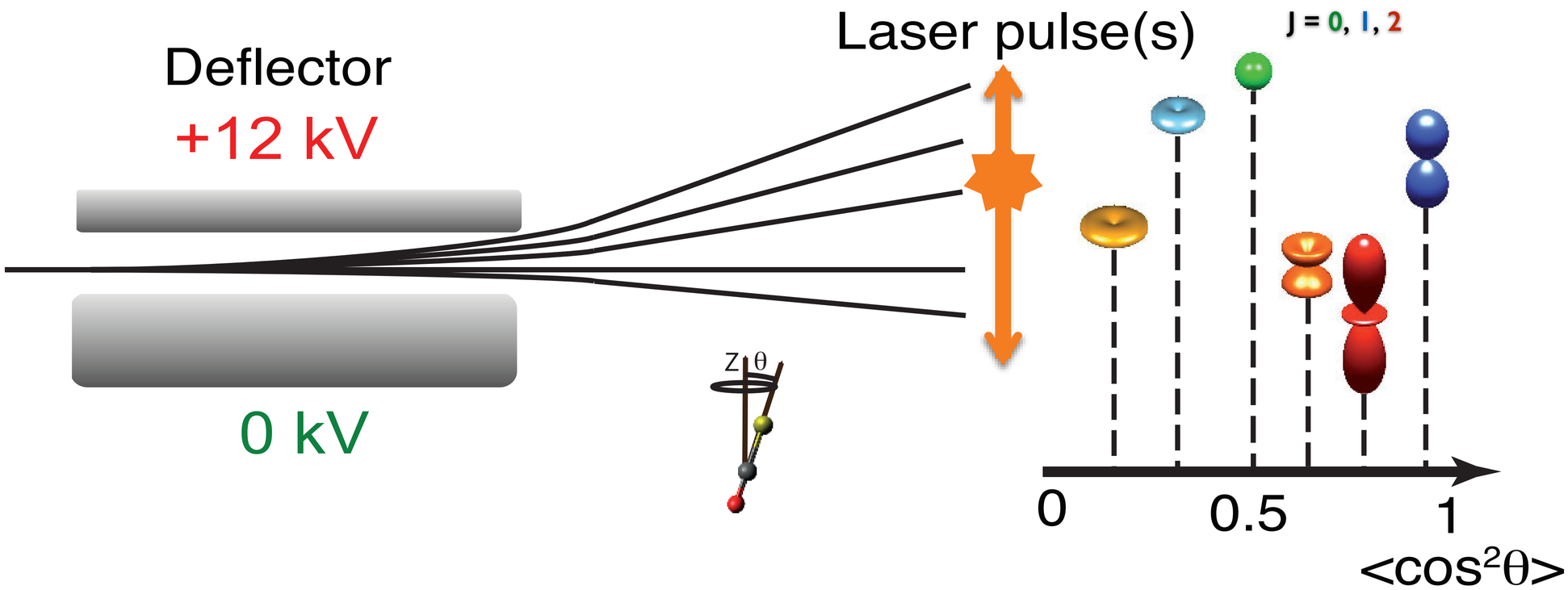


Ground-state samples of OCS

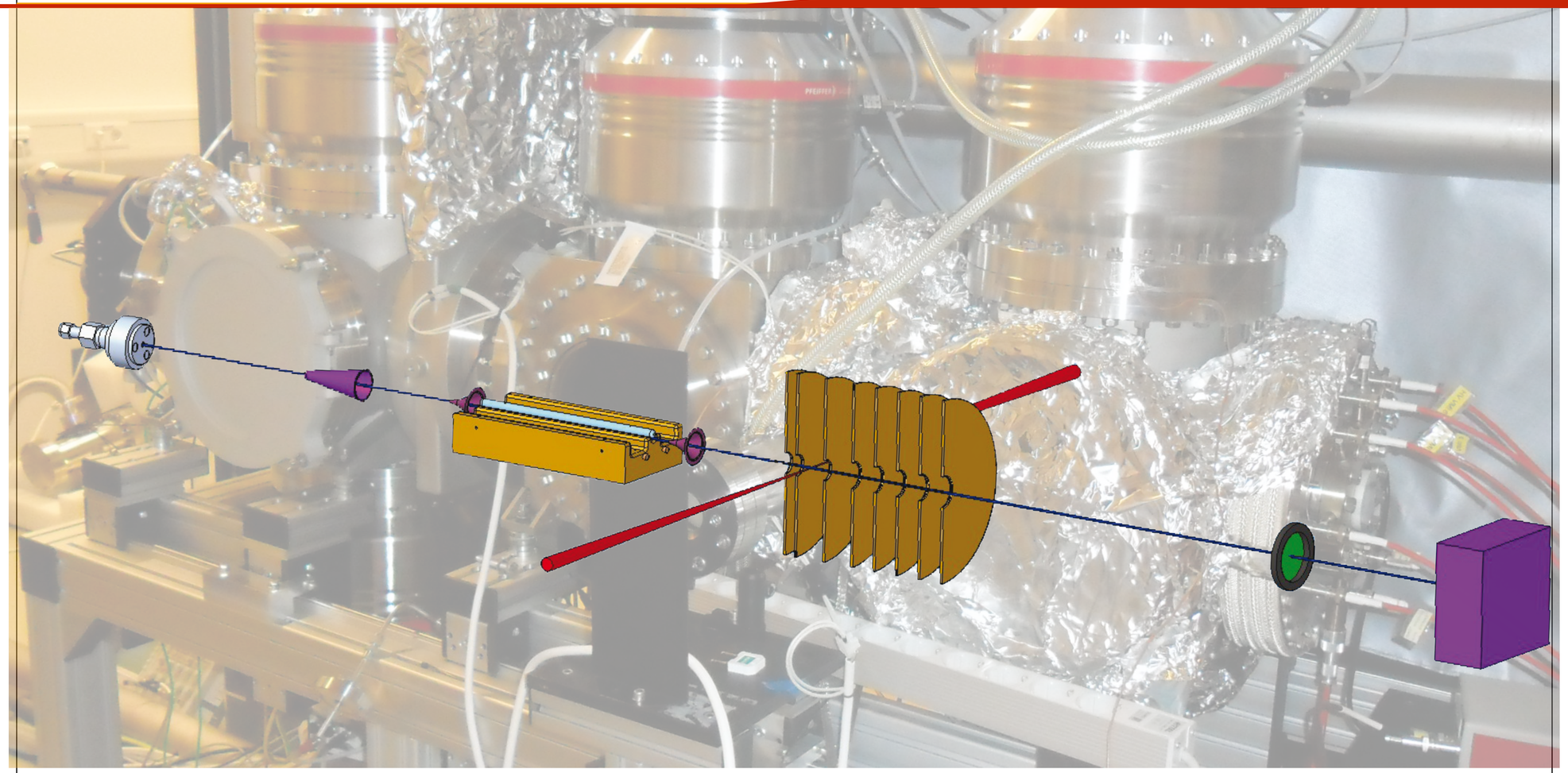


Chang, Horke, Trippel, Küpper, *Int. Rev. Phys. Chem.* **34**, 557–590 (2015); arXiv:1505.05632 [physics]
Karamatskos, *et int.* (13 authors) Rouzée, Küpper, *Nat. Comm.* DOI: 10.1038/s41467-019-11122-y. (2019); arXiv:1802.06622 [physics]

Dispersion of molecules by an electric field



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



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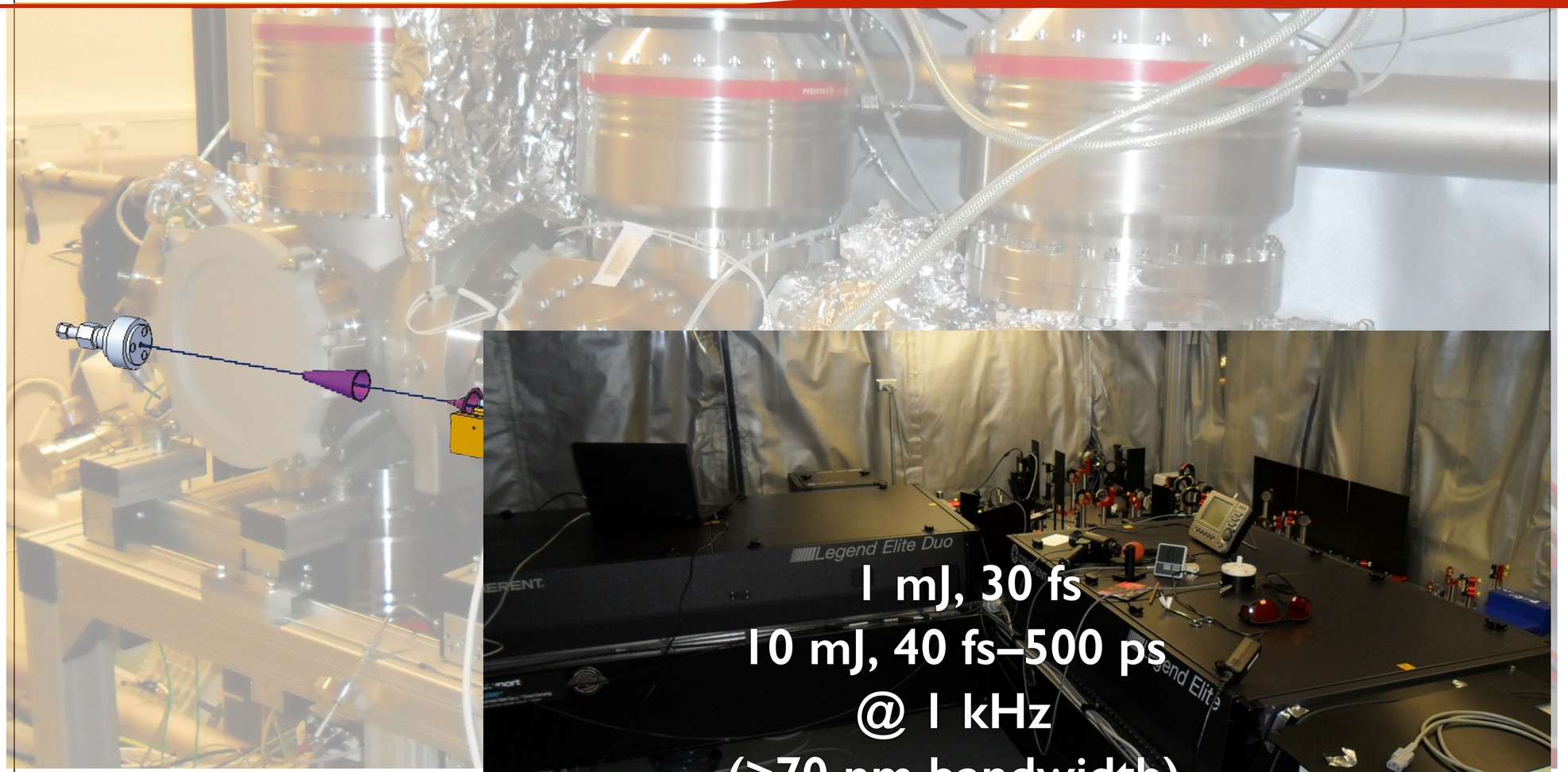


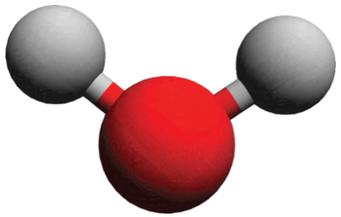
1 mJ, 30 fs

10 mJ, 40 fs–500 ps

@ 1 kHz

(>70 nm bandwidth)

Furhter details: nuclear-spin hyperfine structure
Nuclear-spin isomers of water (H_2O)



$$(12)\Psi = -\Psi$$

$$\Gamma_{\Psi_{\mathrm{tot}}} = \Gamma_{\Psi_{\mathrm{ns}}} \otimes \Gamma_{\Psi_{\mathrm{rve}}}$$

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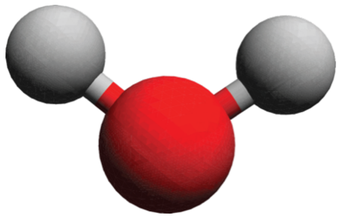

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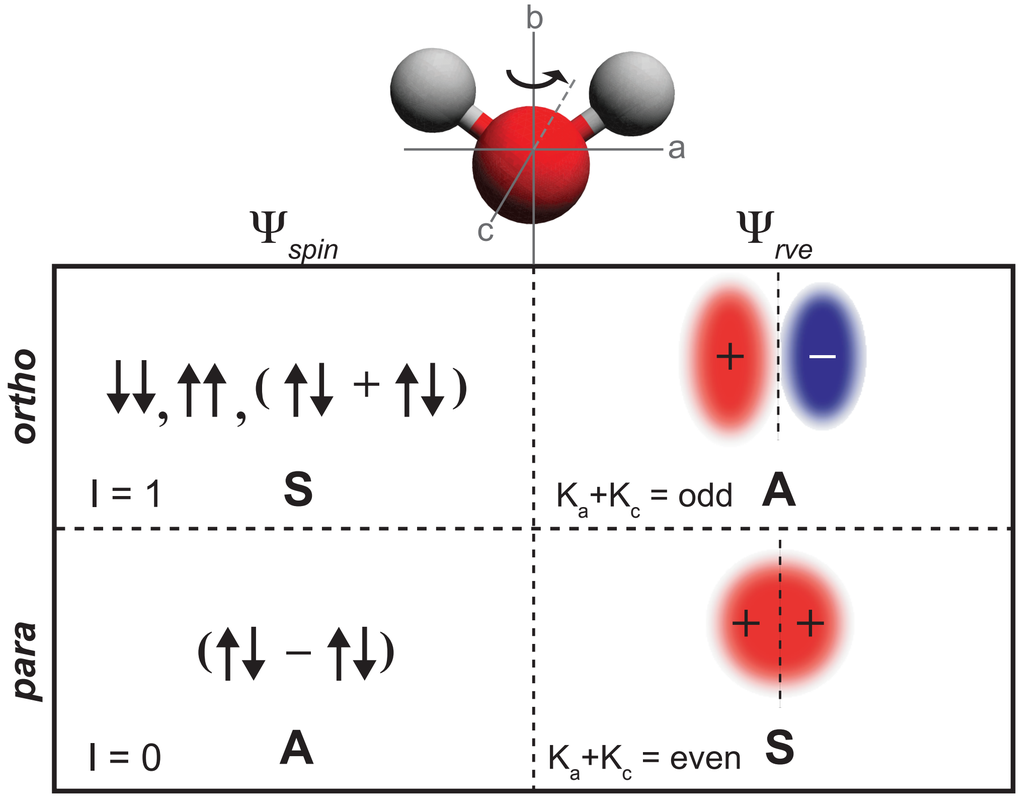

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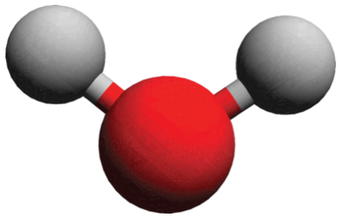

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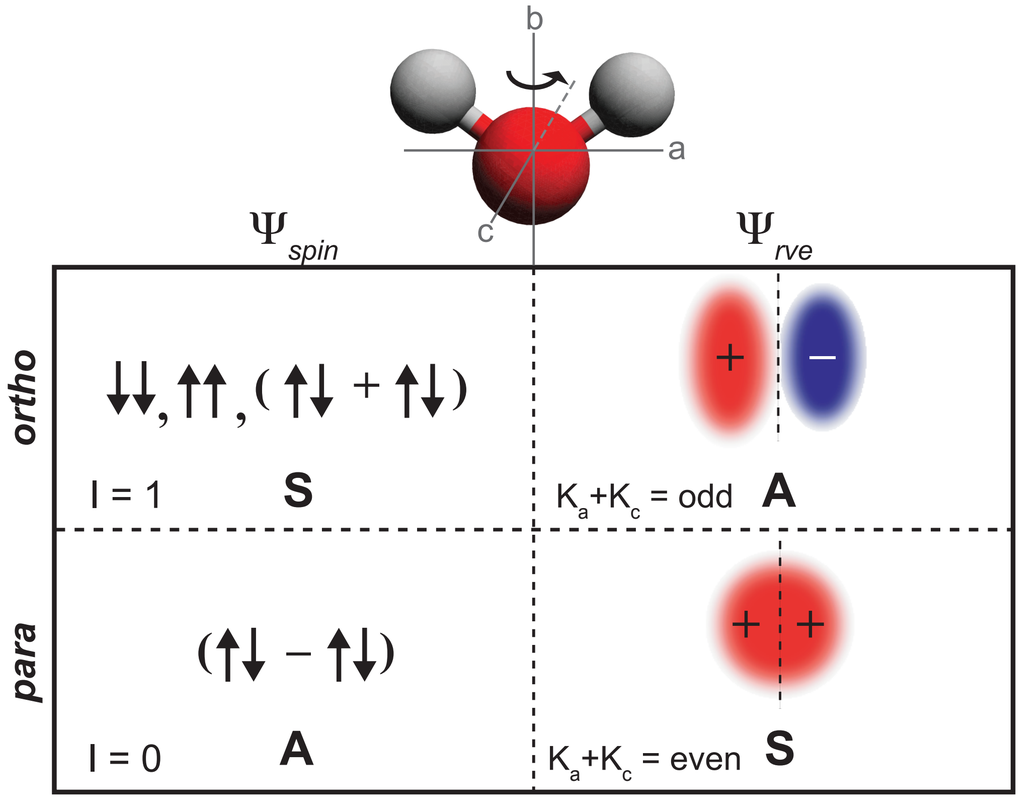

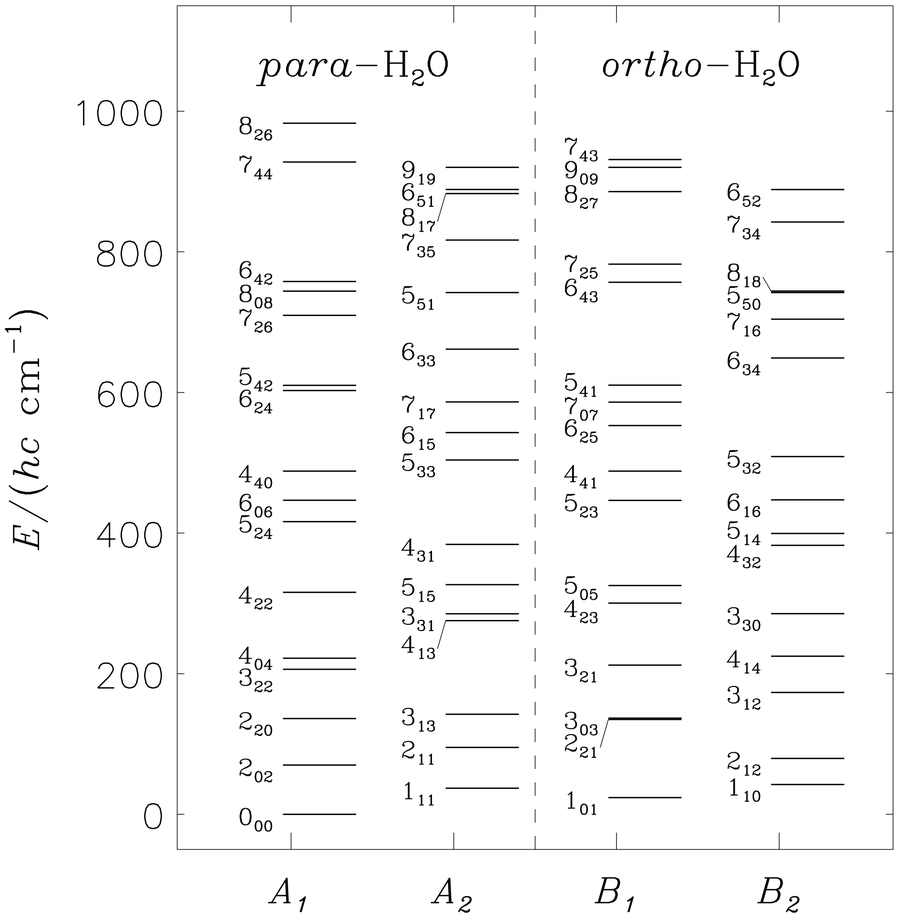

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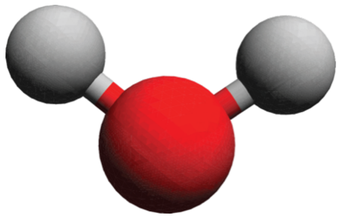
Nuclear-spin isomers of water (H_2O)



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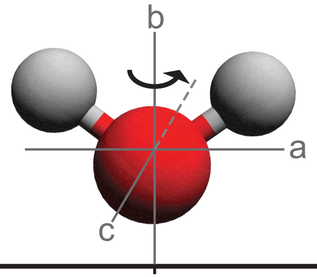

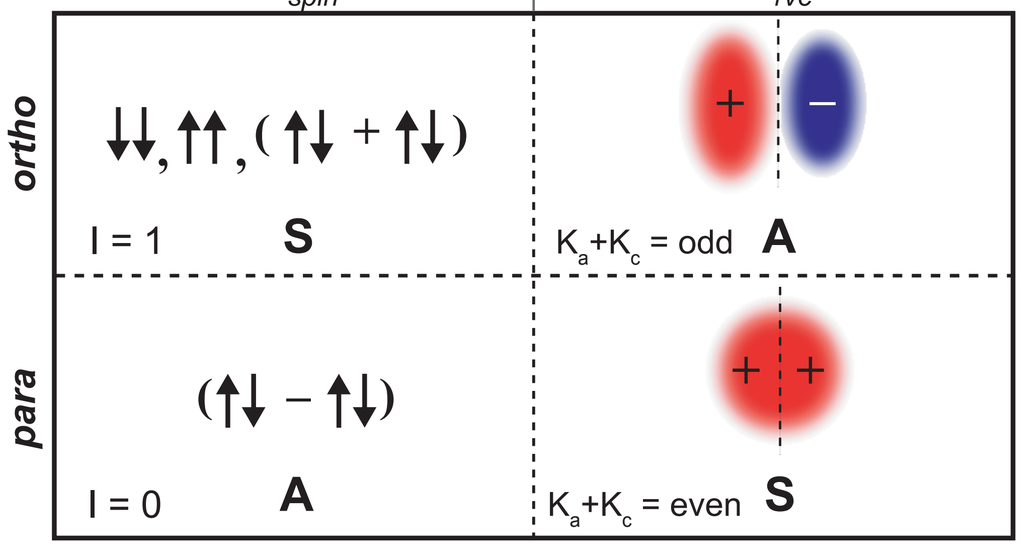

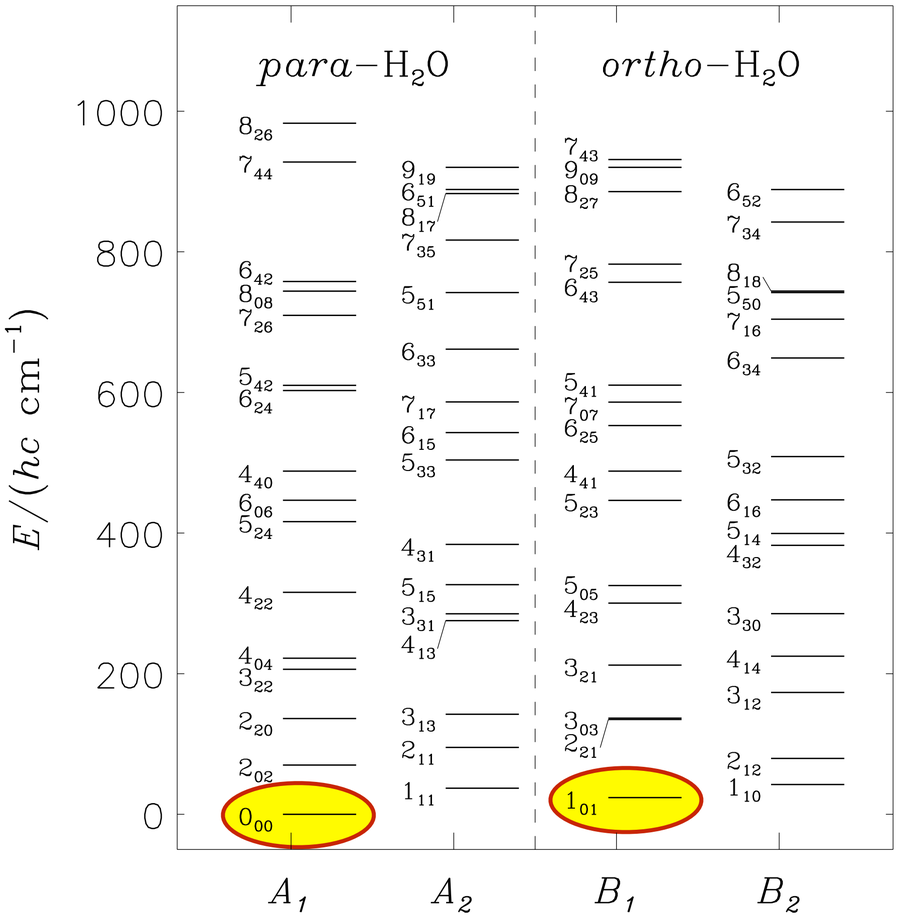

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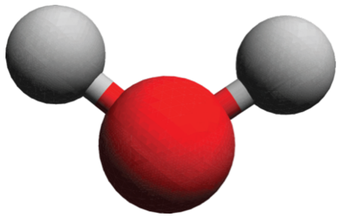

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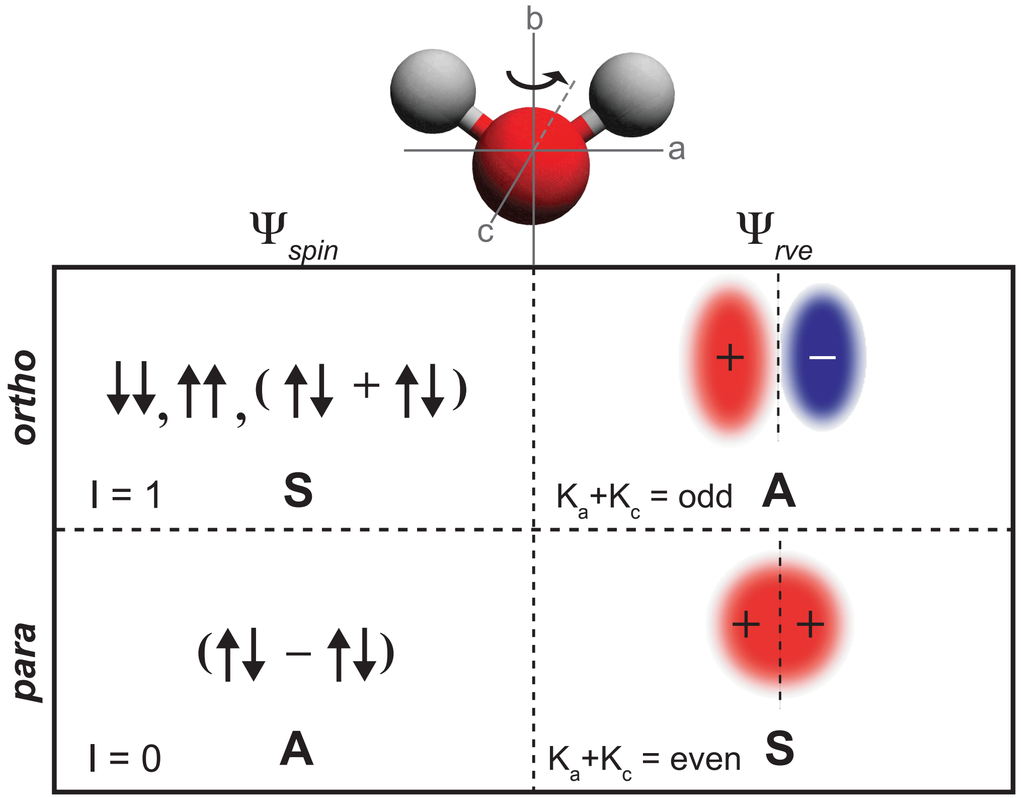
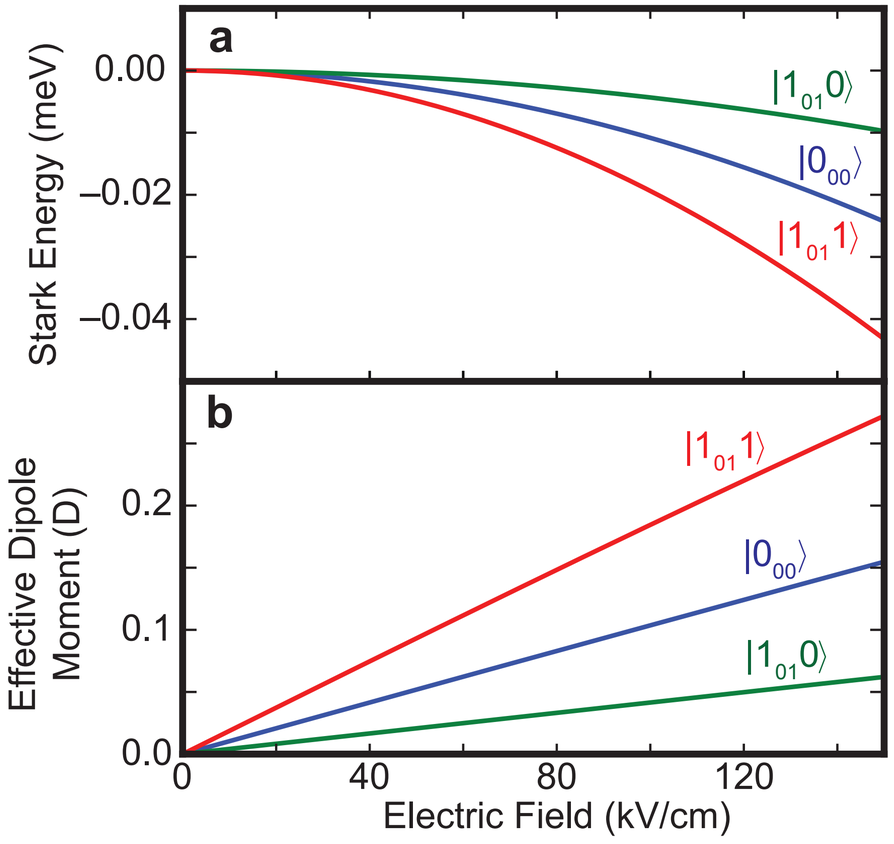
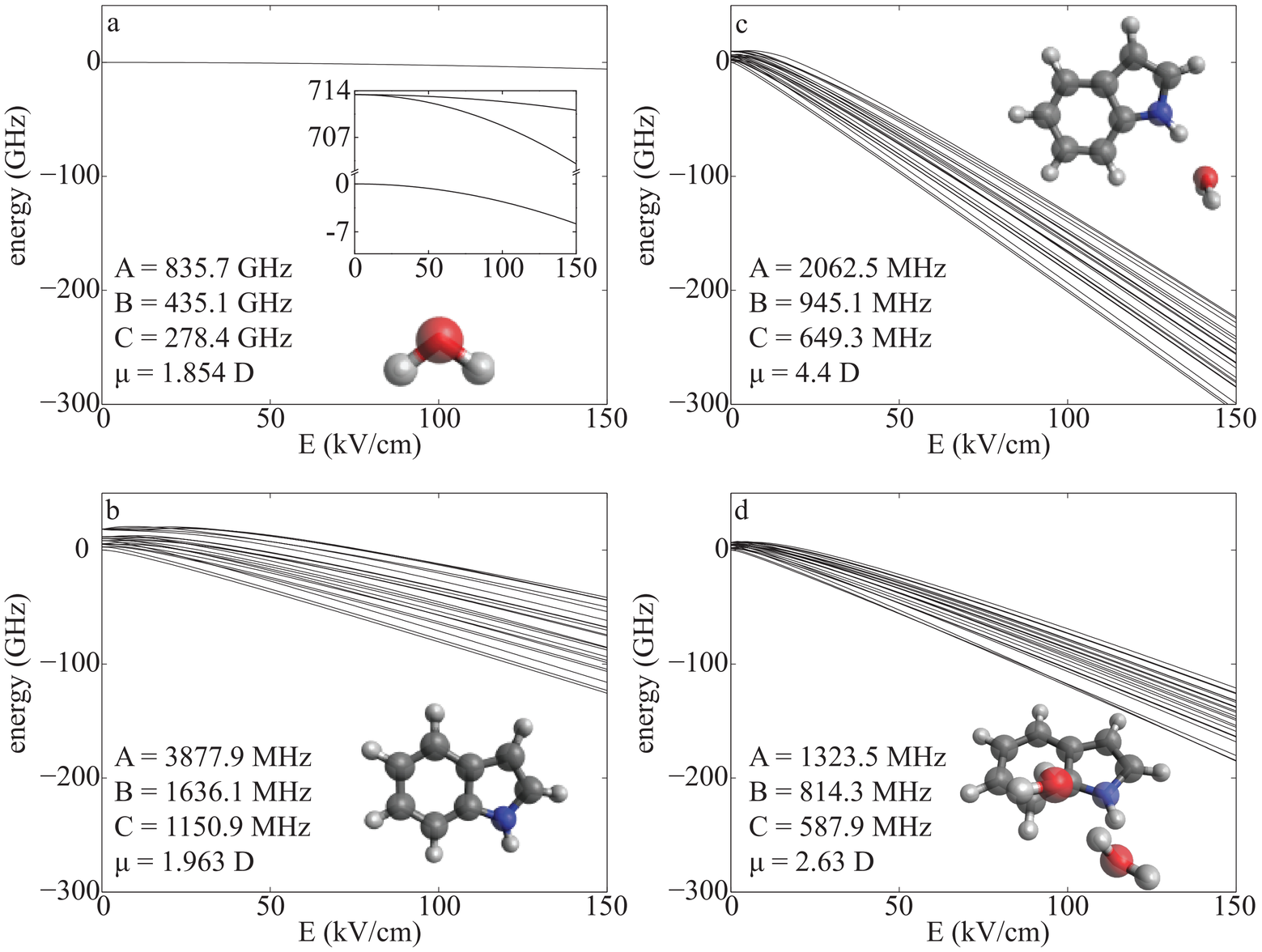




Spatial separation of neutral clusters using the m/μ deflector
pure samples of indole-water (indole-$(H_2O)_1$)



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

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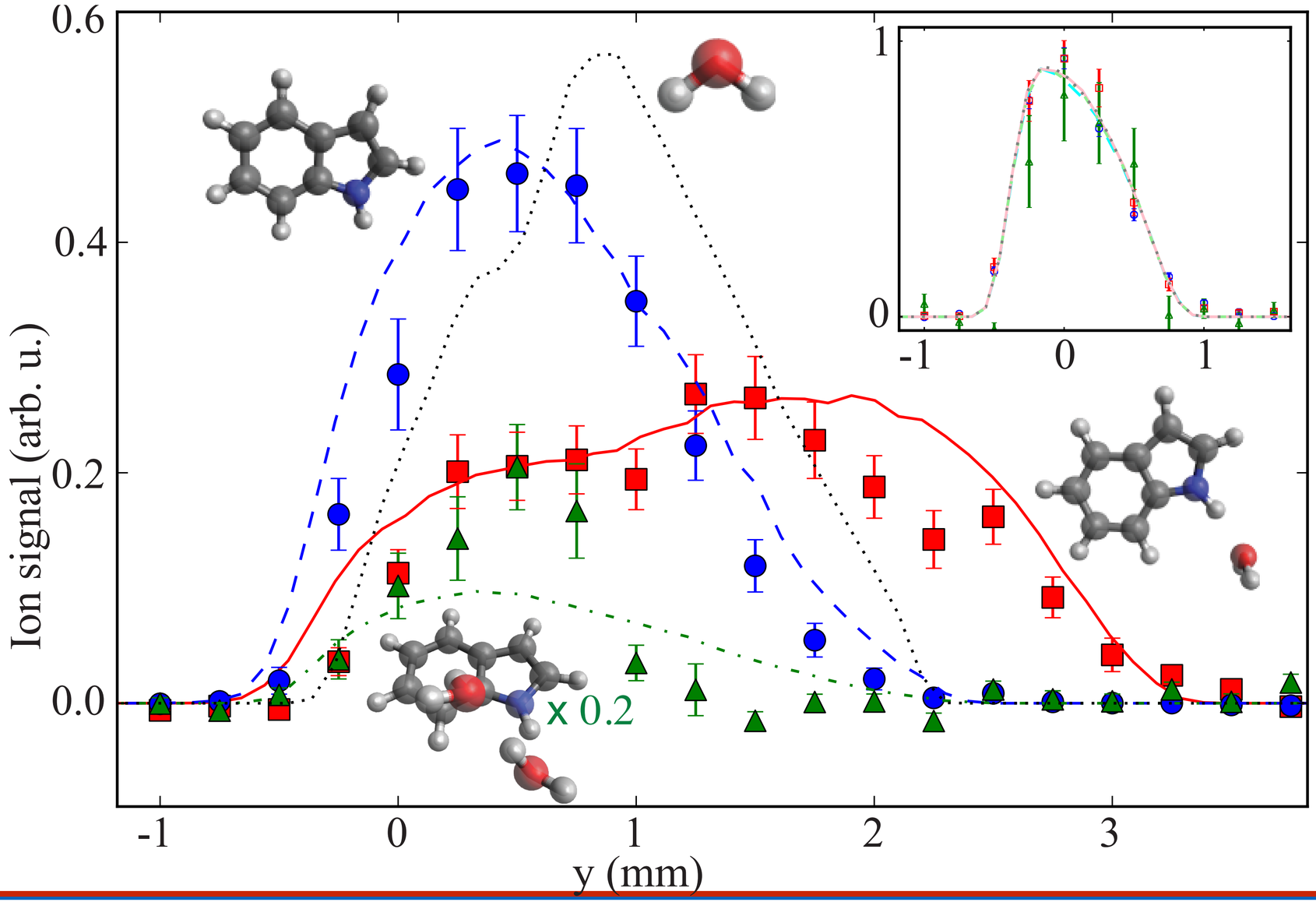
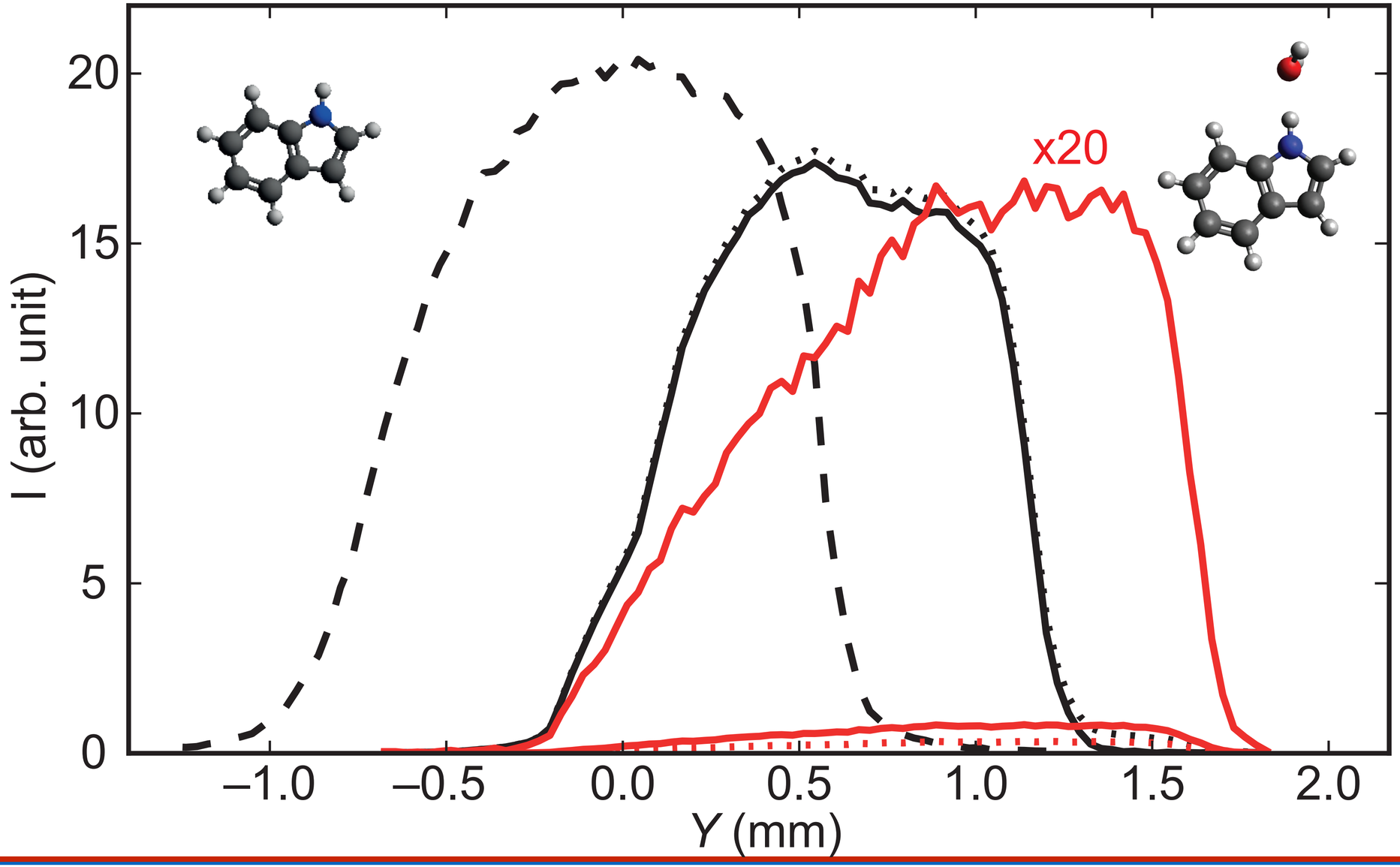


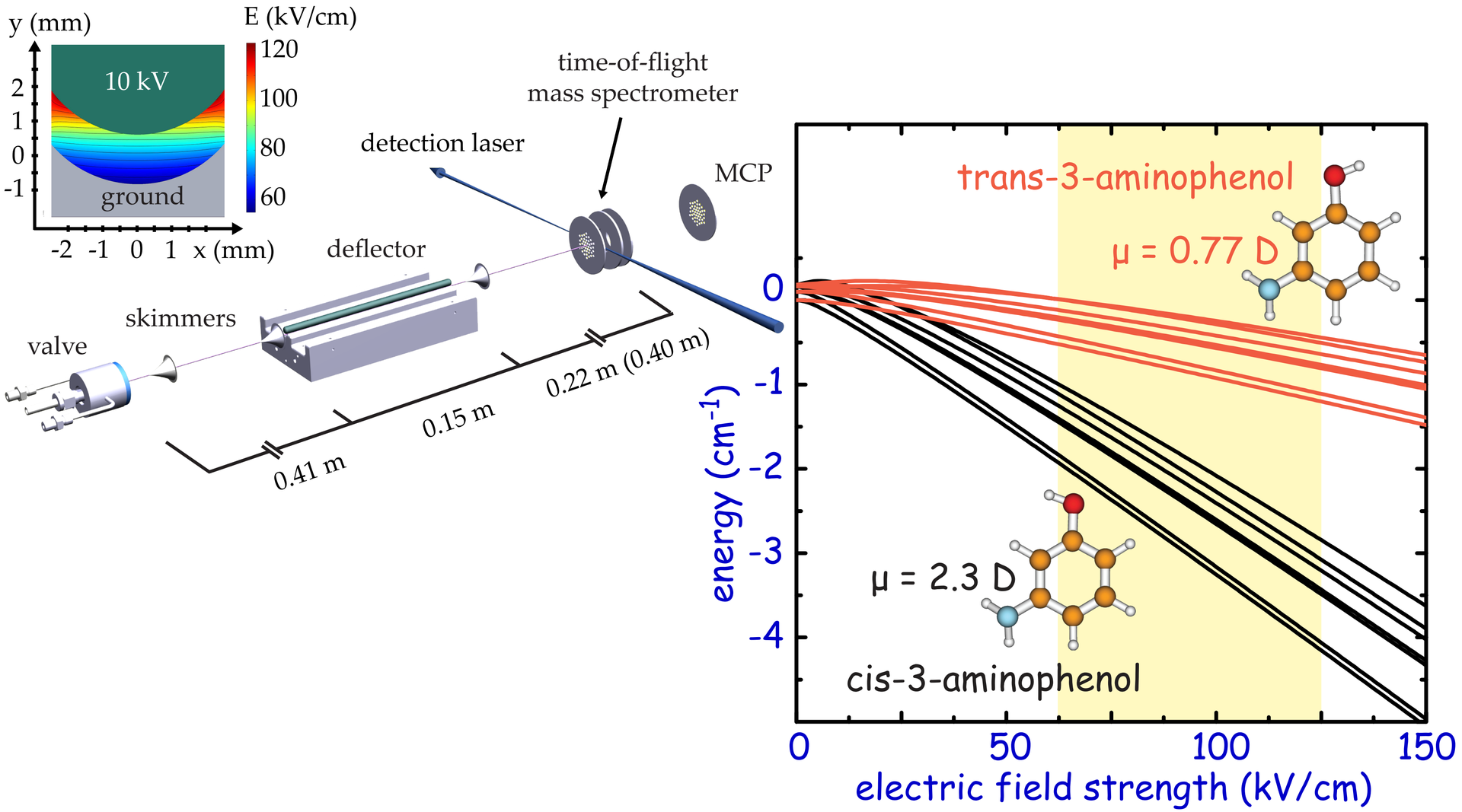
Trippel, Chang, Stern, Mullins, Holmegaard, JK, Phys. Rev. A 86, 033202 (2012)
Chang, Horke, Trippel, JK, Int. Rev. Phys. Chem. 34, 557–590 (2015)

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

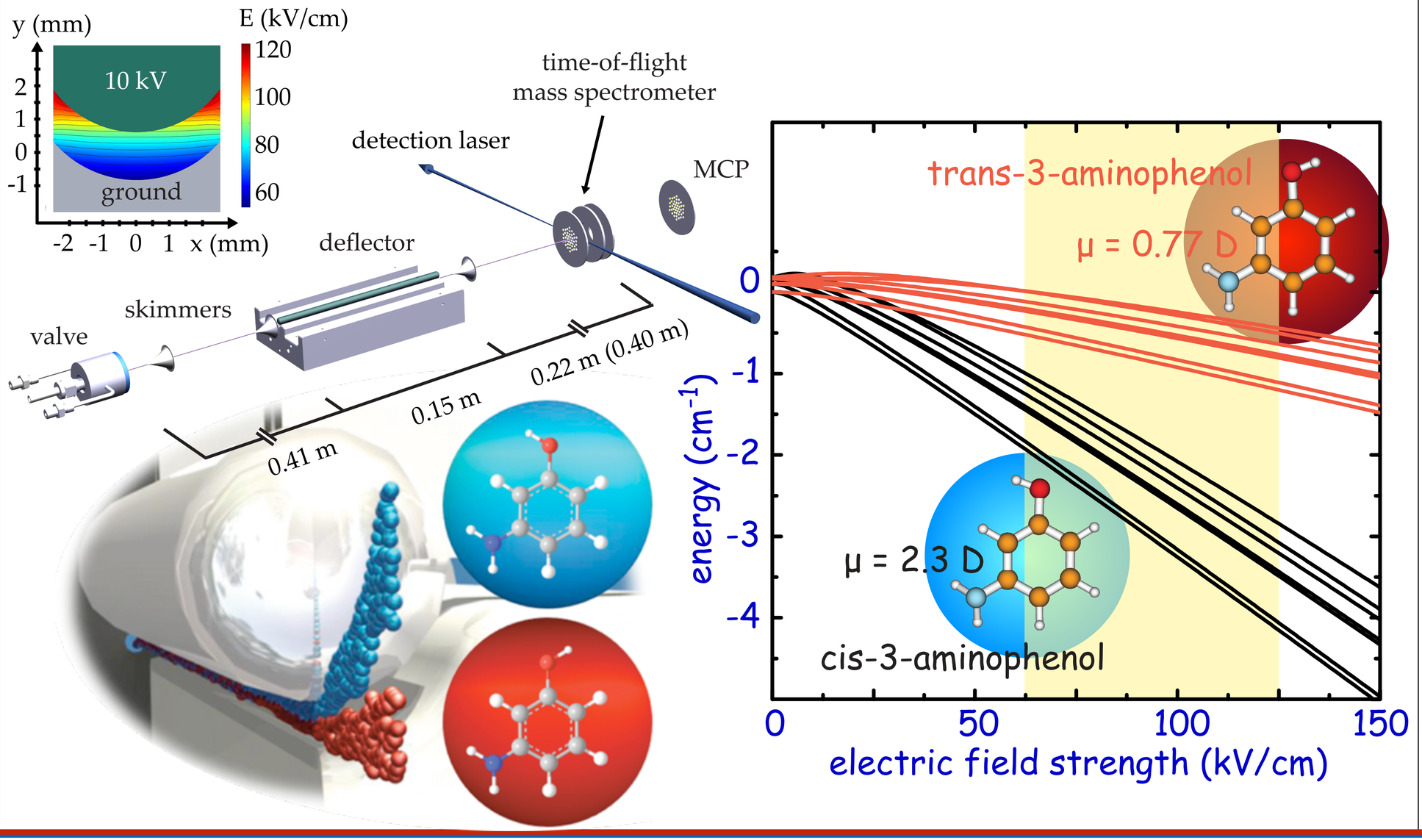
Conformer selection with the m/μ deflector



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)

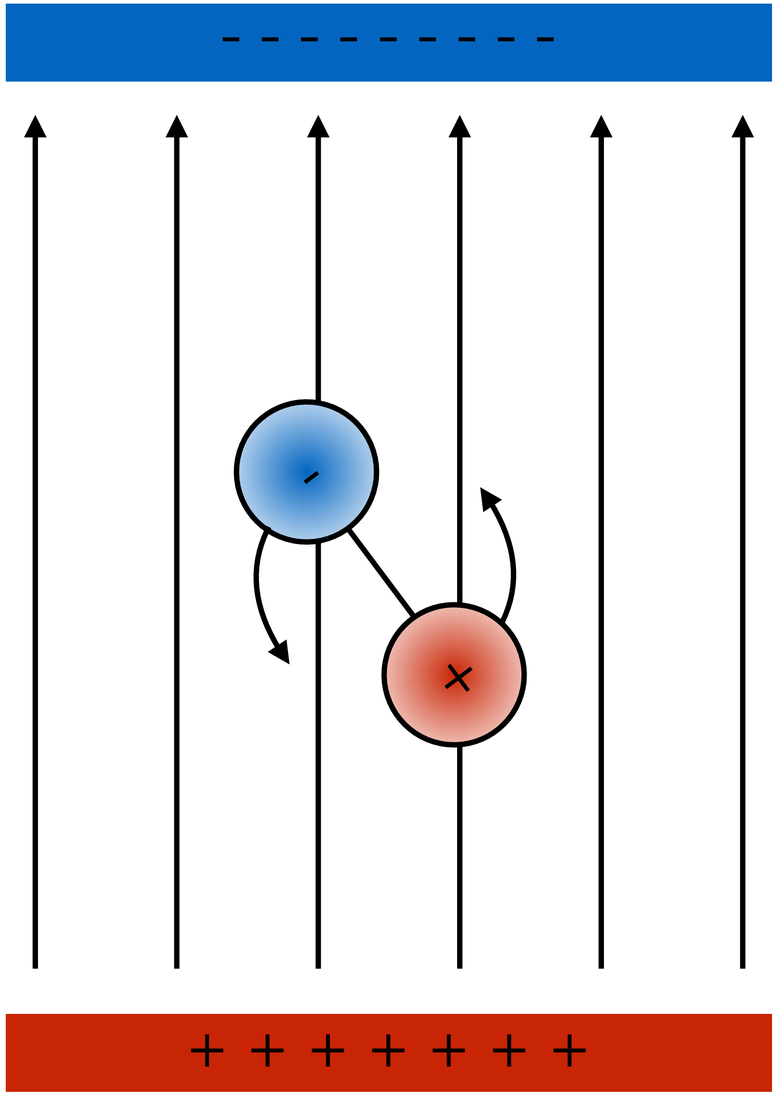
Conformer selection with the m/μ deflector



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)

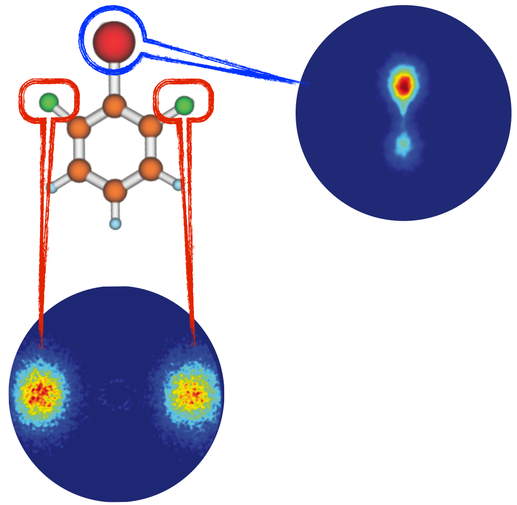
Molecules in fields
Alignment and orientation with electric fields



Taylor expansion of the energy:

$$U = q\phi - \vec{\mu} \cdot \vec{E} - \frac{1}{2}\vec{E}\hat{\alpha}\vec{E} - \ldots$$

A “handle” on neutral particles



Laser-molecule interaction

Hamiltonian:

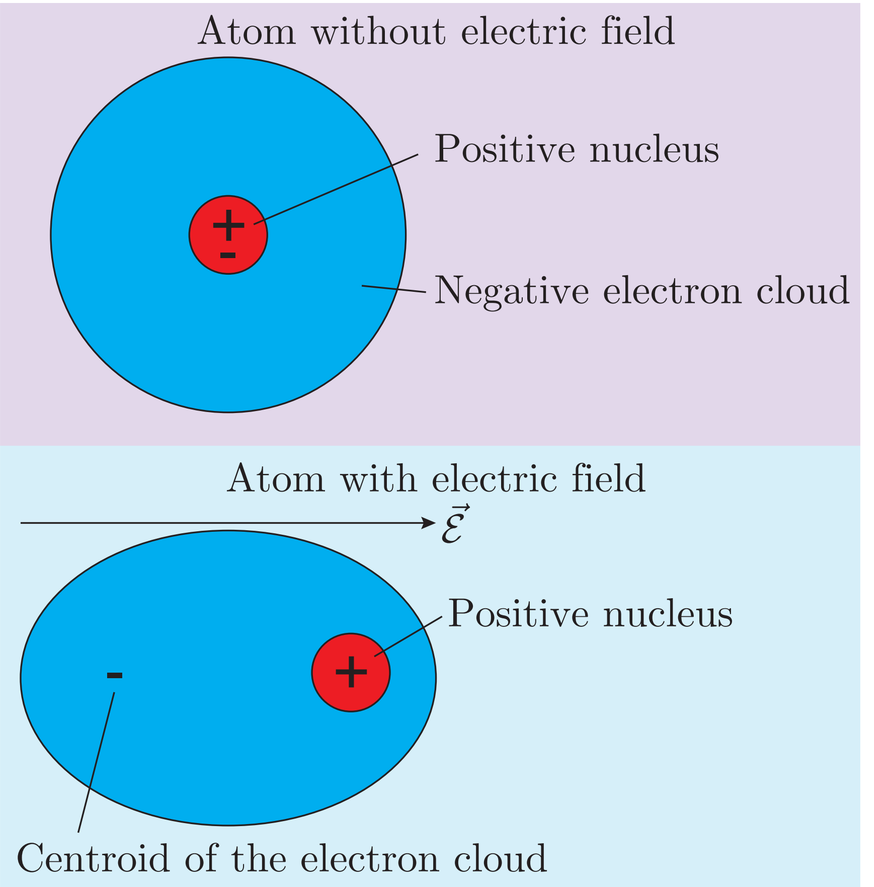
$$H = H_{\text{rot}} + H_{\text{DC}} + H_{\text{ind}}$$

$$H_{\text{DC}} = -\vec{\mu} \cdot \vec{\mathscr{E}} = -\left|\mu\right| \left|\mathscr{E}\right| \cos\theta$$

$$H_{\text{ind}} = -\frac{1}{2} \sum_{\rho,\rho'} \mathscr{E}_{\rho} \alpha_{\rho\rho'} \mathscr{E}_{\rho'}$$

$$\alpha = \begin{bmatrix} \alpha_{XX} & \alpha_{XY} & \alpha_{XZ} \\ \alpha_{YX} & \alpha_{YY} & \alpha_{XZ} \\ \alpha_{ZX} & \alpha_{ZY} & \alpha_{ZZ} \end{bmatrix}$$

- $\rho, \rho' = X, Y, Z$: space-fixed cartesian coordinates
- $\alpha_{\rho\rho'}$: molecular polarisability tensor (space-fixed coordinates)
- $\mathscr{E}_{\rho}$, $\mathscr{E}_{\rho'}$: space fixed components of the electric field



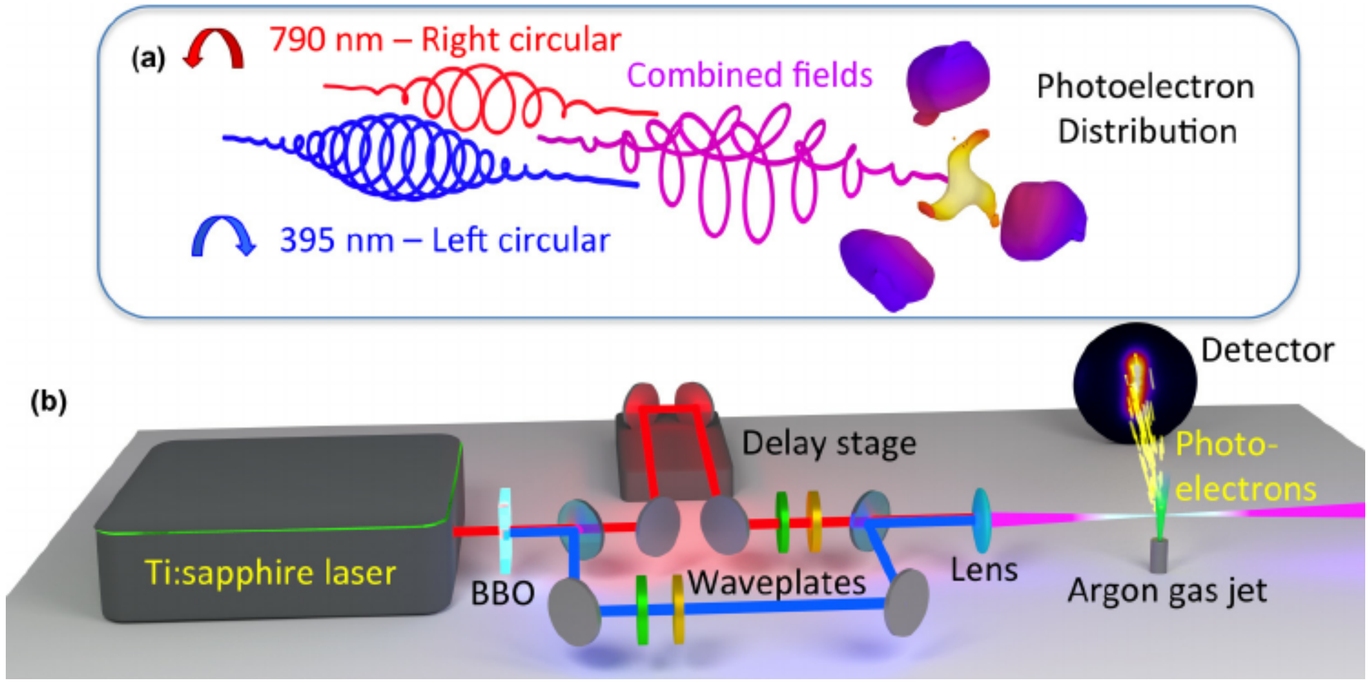
$\Longrightarrow$ the alignment depends on the molecular properties (polarizability) and the properties of the light field, so a knob you can control in the laboratory

The light field

General light field:

$$\vec{\mathscr{E}}(t) = \begin{pmatrix} \mathscr{E}_X \cos(\omega t + \phi_1) \\ \mathscr{E}_Y \cos(\omega t + \phi_2) \\ \mathscr{E}_Y \cos(\omega t + \phi_3) \end{pmatrix}$$

- $\mathscr{E}_\rho$: smooth envelope
- cos terms $\hat{=}$ ”fast oscillation”
- ω can be time-dependent ($\omega = \omega(t)$)



Example: linear molecule

A linear molecule in a linearly polarized field

$\alpha_{ZZ} = \alpha_{\parallel}, \alpha_{XX} = \alpha_{YY} = \alpha_{\perp}$

X, Y, and Z are the body fixed components

Interaction Hamiltonian:

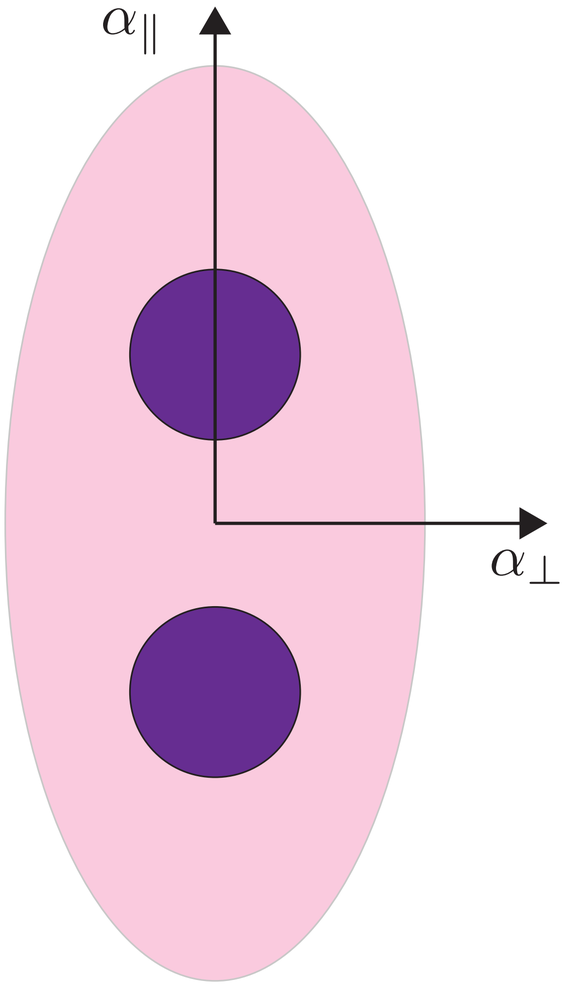
$$H_{\text{ind}} = -\frac{1}{4}\epsilon^2(t)\left(\alpha_{\parallel} - \alpha_{\perp}\right)\cos^2\theta$$
$$= \frac{2\pi I(t)}{c}\Delta\alpha'\cos^2\theta$$

$\Delta\alpha' = \alpha'_{\parallel} - \alpha'_{\perp}$

I: intensity

c: speed of light

$\alpha' = \dfrac{\alpha}{4\pi\epsilon_0}$ (polarizability volume)



Polarizability volume

Hydrogen atom as an example:

Charges are not fixed in distance

Charges react on an external field by a linear increase in distance

$$F = -kx = q\epsilon$$

Induced dipole moment:

$$p = qx = \frac{q^2}{k}\epsilon = \alpha\epsilon$$

Coulomb force:

$$F = \frac{q}{4\pi\epsilon_0 r^2}$$

$$k \approx -\frac{\partial F}{\partial r} \approx \frac{q^2}{2\pi\epsilon_0 r^3}$$

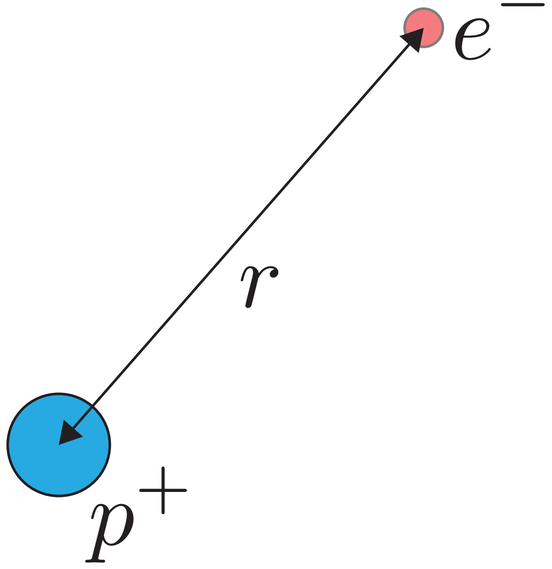
$\alpha = 2\pi\epsilon_0 r^3$

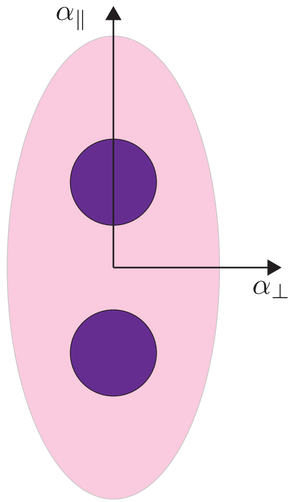
α' is the volume of the molecule or atom

$\alpha' \approx \frac{r^3}{2}$

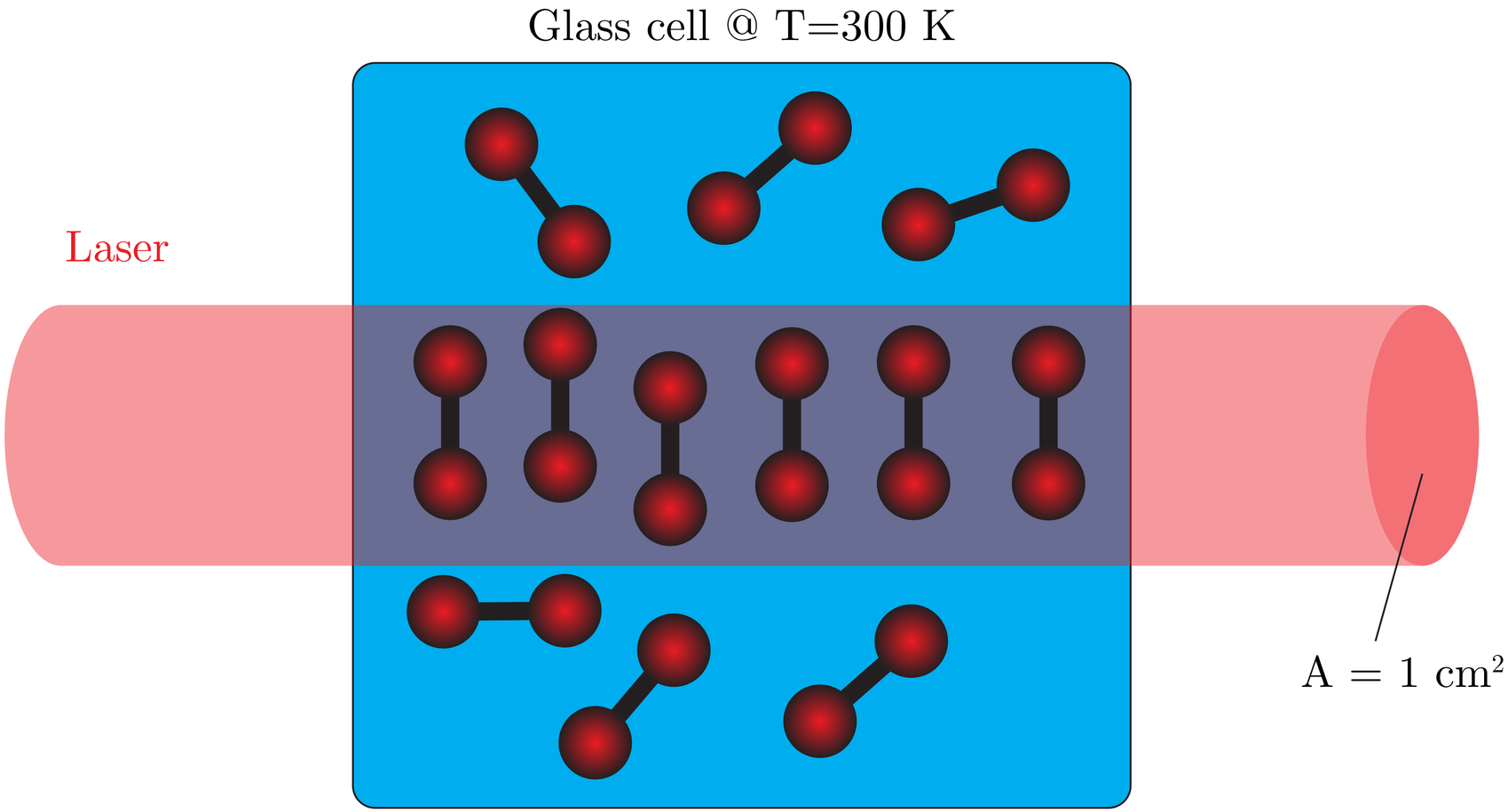
$\alpha' = 0.66\ \text{Å}^3$ for the Hydrogen atom

$\alpha'_{\parallel} > \alpha'_{\perp}$ for linear molecules



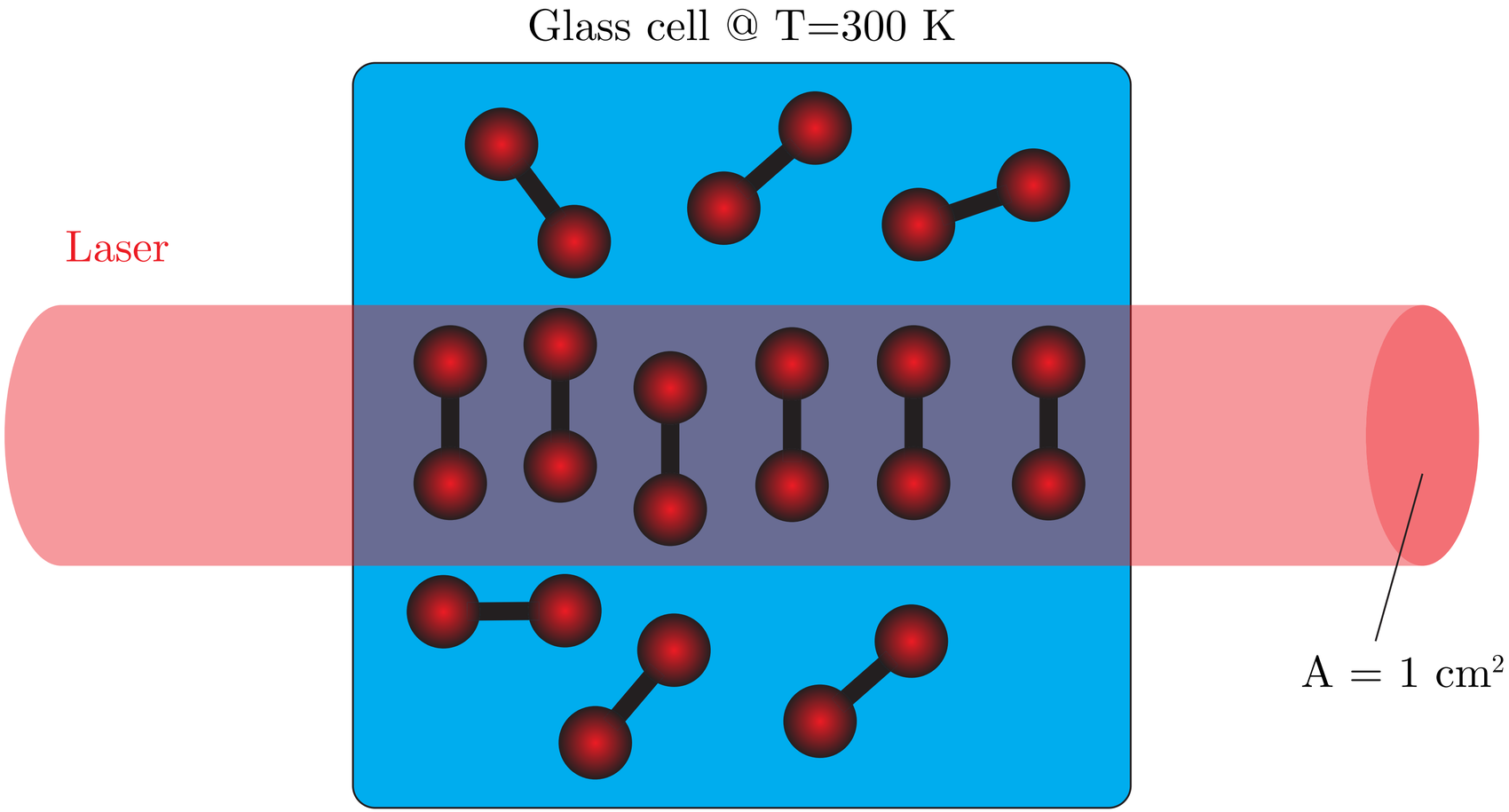


Design of an experiment



https://www.science.org/content/article/paradox-cleaner-air-now-adding-global-warming

Design of an experiment



$$T = 300\ \text{K} = 25\ \text{meV} = 4 \cdot 10^{-21}\ \text{J}$$

$$I = \frac{E}{2\pi\Delta\alpha'}c = \frac{4 \cdot 10^{-21} \cdot 10^{8}}{6 \cdot 10^{-30}} = 2 \cdot 10^{17}\ \text{W/m}^2 = 2 \cdot 10^{13}\ \text{W/cm}^2$$

Design of an experiment

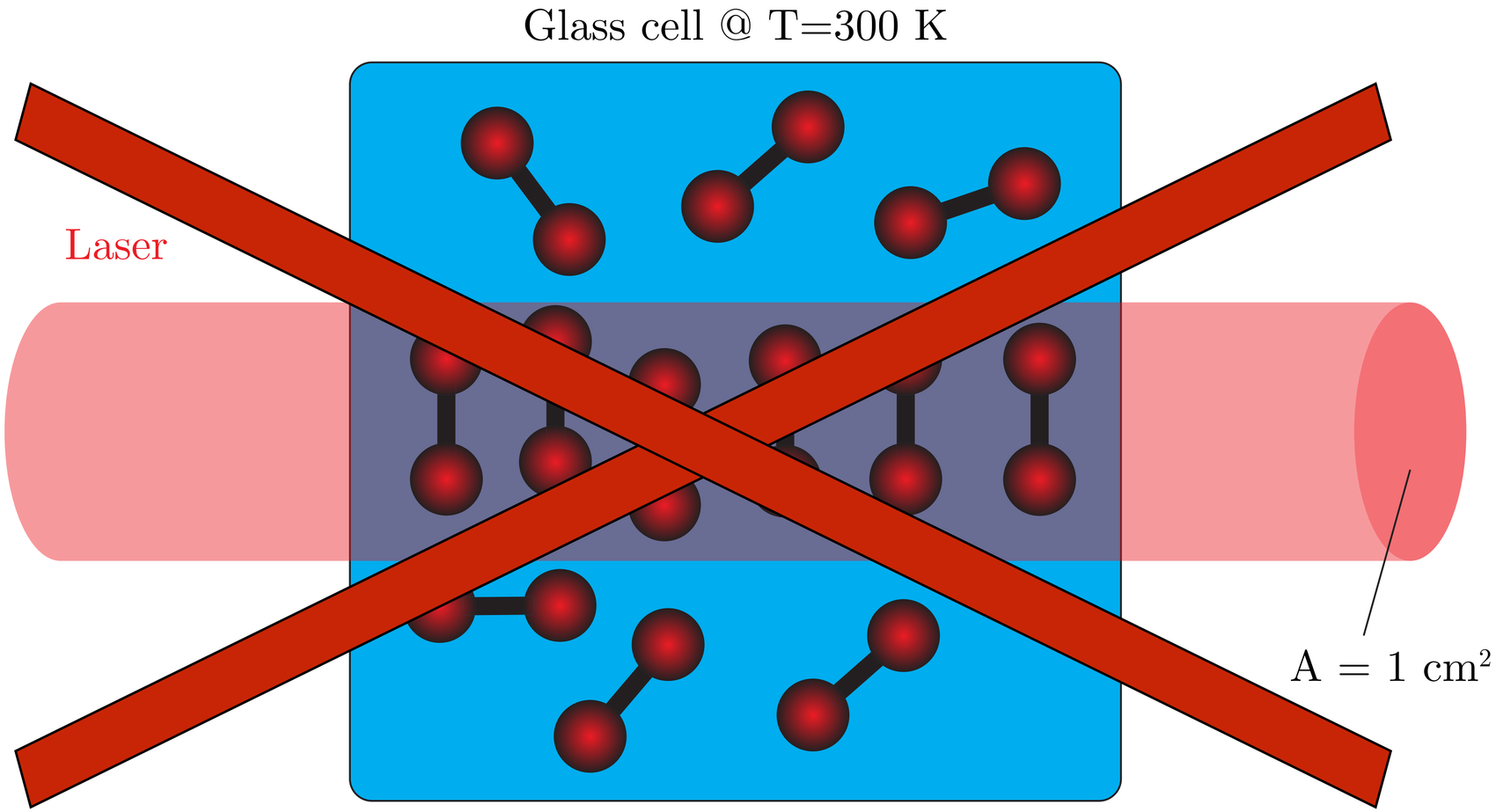
Nuclear power plant: 1 GW

Mean power consumption world wide (2001): 10 TW

$$T = 300\ \mathrm{K}$$
$$= 25\ \mathrm{meV}$$
$$= 4 \cdot 10^{-21}\ \mathrm{J}$$

$$I = \frac{E}{2\pi\Delta\alpha'}c$$
$$= \frac{4 \cdot 10^{-21} \cdot 10^{8}}{6 \cdot 10^{-30}}$$
$$= 2 \cdot 10^{17}\ \mathrm{W/m^2}$$
$$= 2 \cdot 10^{13}\ \mathrm{W/cm^2}$$

Design of an experiment



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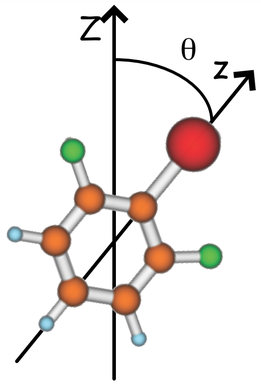
https://www.science.org/content/article/paradox-cleaner-air-now-adding-global-warming

Design of an experiment

- Ionization starts typically at $10^{13}\ \mathrm{W/cm^2}$
- Cool the molecules down to a few K
- typical intensity needed to align small molecules: $10^{12}\ \mathrm{W/cm^2}$
- use pulsed lasers with durations in the order of nanoseconds
- focus the laser down to a few microns
- few mJ/pulse is enough

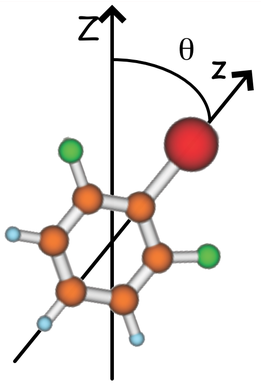
Molecular alignment and orientation
Connecting molecular and laboratory frame



$\langle \cos\theta \rangle$ **orientation**

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

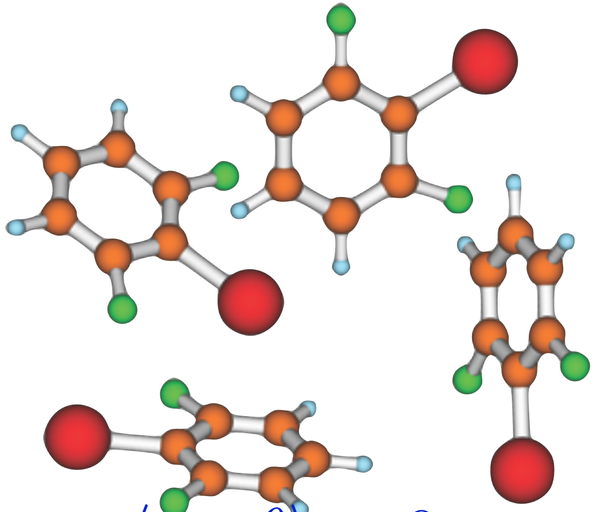
Molecular alignment and orientation
Connecting molecular and laboratory frame



$\langle \cos\theta \rangle$ **orientation**

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

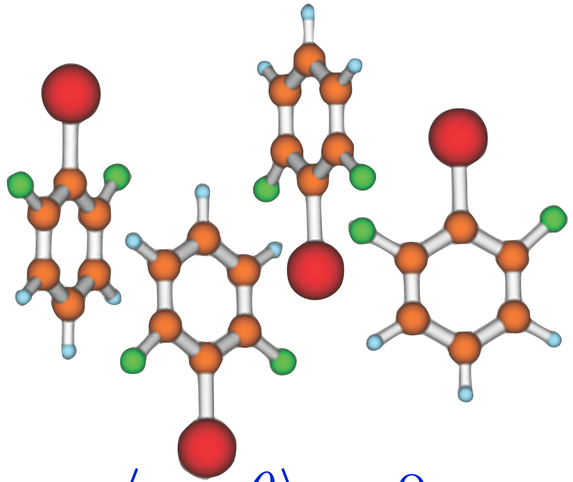
isotropic



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

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

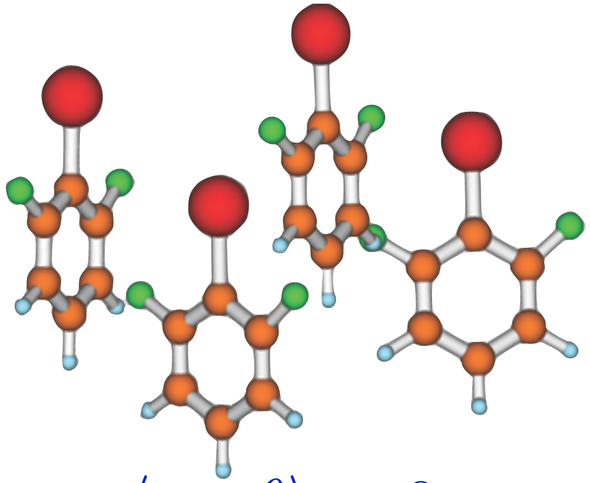
aligned



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

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

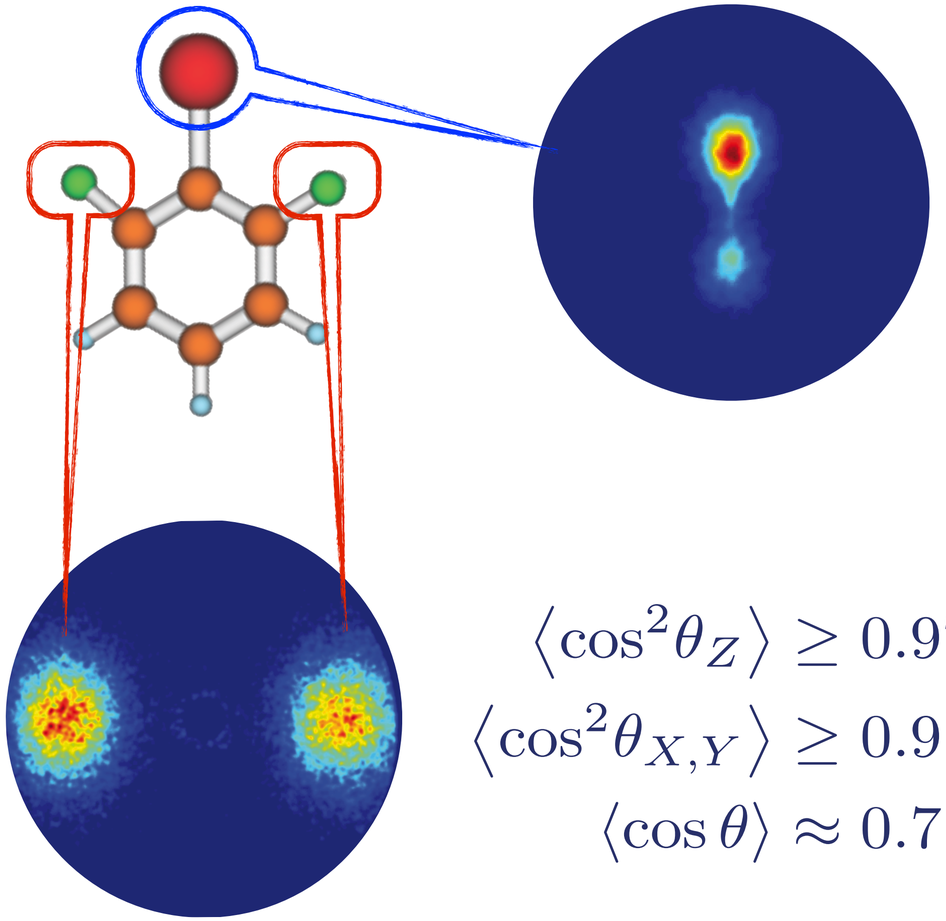
oriented



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

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

Molecular alignment and orientation
Connecting molecular and laboratory frame



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