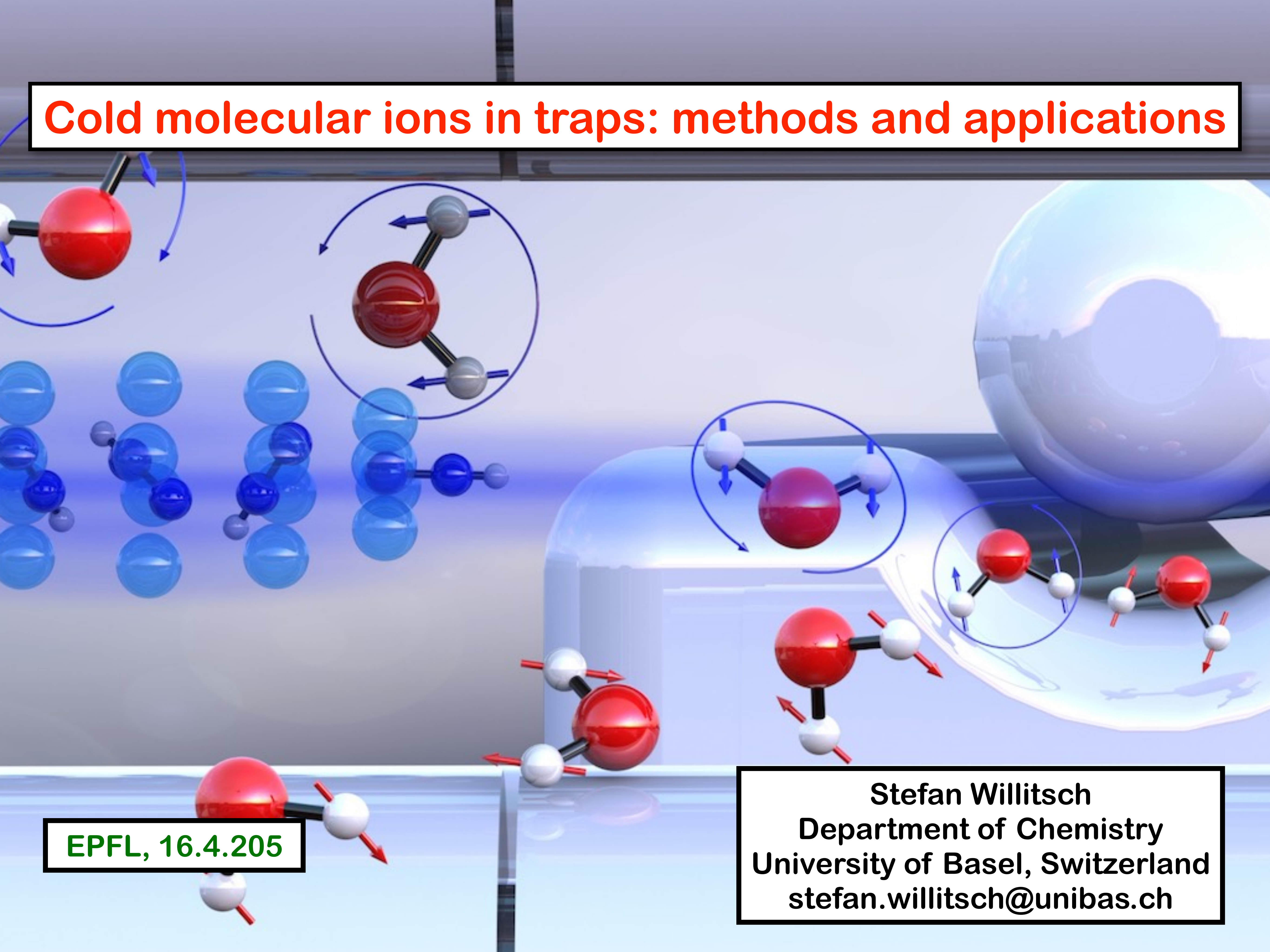
Cold molecular ions in traps: methods and applications



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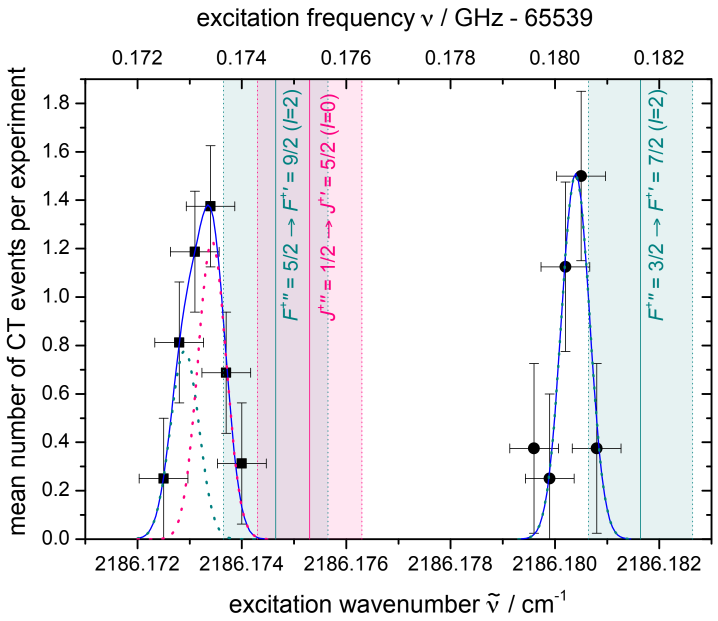
EPFL, 16.4.205

Applications of cold molecular ions in physics and chemistry

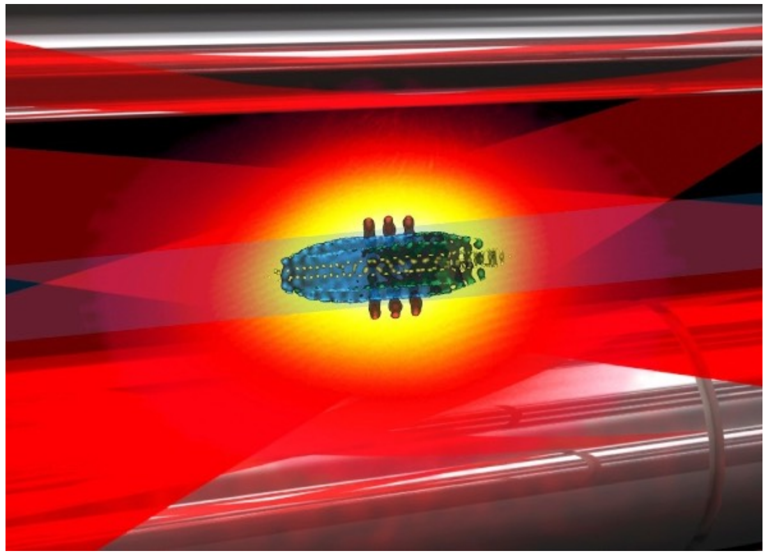
Quantum control over single trapped particles

- Quantum logic and quantum technologies
- Precision spectroscopy



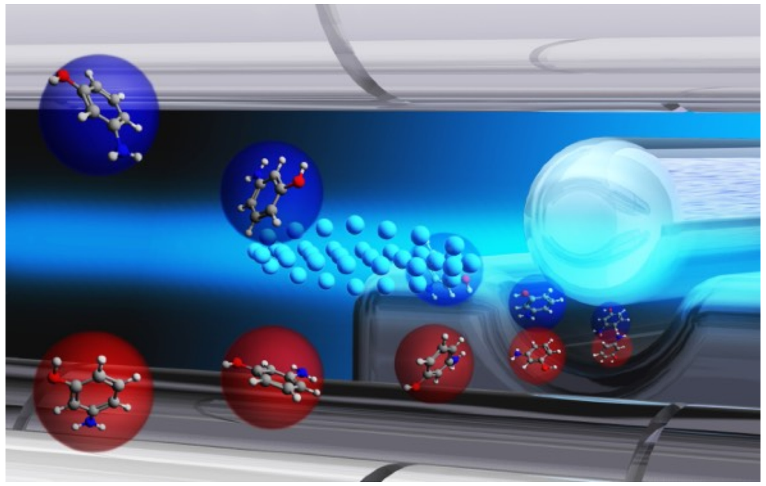
Ion-neutral interactions, collisions and chemical reactions in a new physical regime

- Study “exotic” chemical processes
- Explore quantum character of collisions
- Probe fine details of intermolecular interactions



New methods for studying and controlling chemical reactions

- Accurate quantum-state AND collision-energy control
- Controlled chemistry of large molecules



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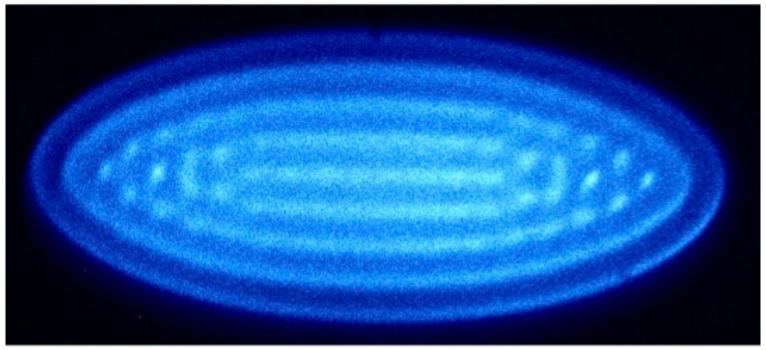
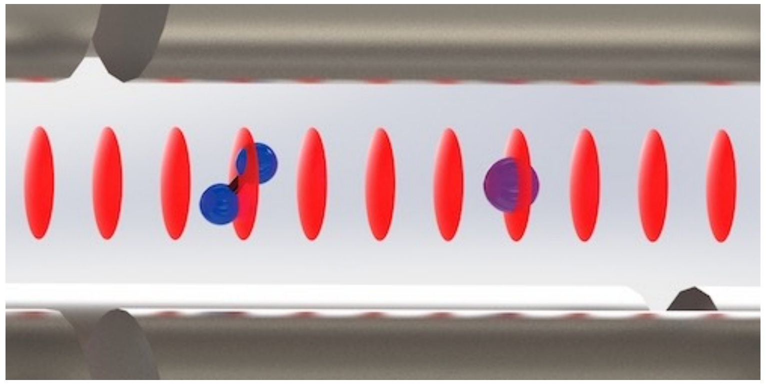
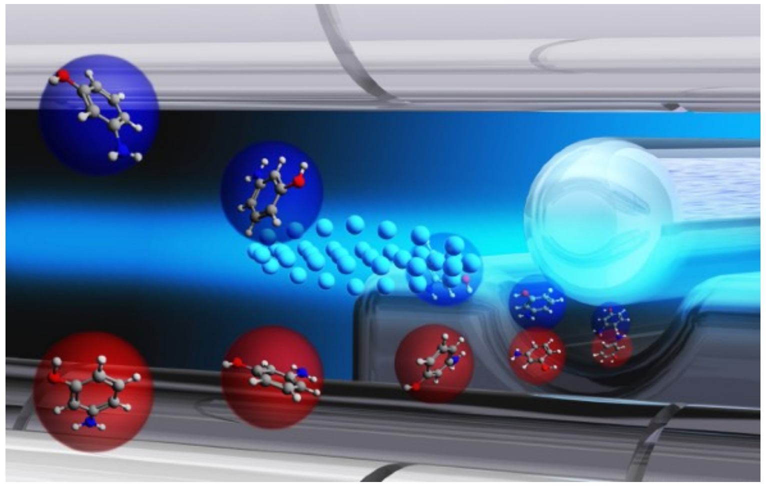
1. Cooling and trapping of molecular ions: basic techniques
2. Internal-state preparation of cold molecular ions
3. Applications:
   1. Molecular-ion quantum technologies and quantum-logic spectroscopy
   2. Unravelling the details of chemical reaction mechanisms with controlled molecules







Recommended books on cold ions

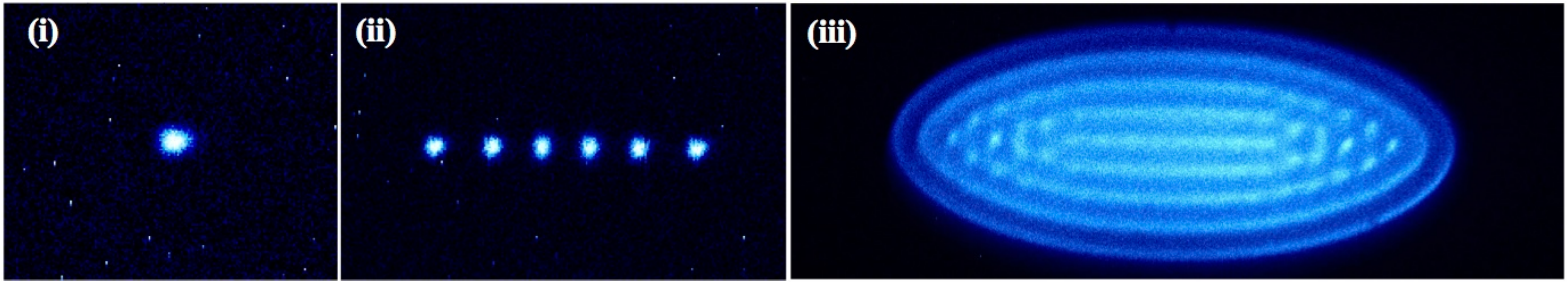
- A. Osterwalder, O. Dulieu (ed.), Cold Chemistry, RSC Publishing, 2018
- F. G. Major et al., Charged Particle Traps Vol. I+II, Springer, 2005 + 2007
- M. Knoop et al. (ed.), Ion Traps For Tomorrow's Applications, Proc. Int. School Phys. E. Fermi Vol. 189, IOS Press, 2015
- M. Knoop et al. (ed.), Trapped Charged Particles, World Scientific, 2016 R.V. Krems et al. (ed.), Cold Molecules, CRC Press 2009

Recommended review articles

- M. Sinhal and S. Willitsch, "Molecular-ion quantum technologies" in "Photonic Quantum Technologies: Science and applications", ed. M. Benyoucef, Wiley-VCH 2023 (arXiv:2204.08814)
- M. Deiß, S. Willitsch and J. H. Denschlag, "Cold trapped molecular ions and hybrid platforms for ions and neutral particles", Nat. Phys. 20 (2024), 713 (arXiv:2311.12640)
- S. Willitsch, "Chemistry with Controlled Ions", Adv. Chem. Phys. 162 (2017), 307

1. Cooling and trapping of molecular ions: basic techniques

Cold ions in traps: ion Coulomb crystals



Fluorescence images of laser-cooled Ca$^+$ ions in an ion trap

Properties of Coulomb-crystallized ions:

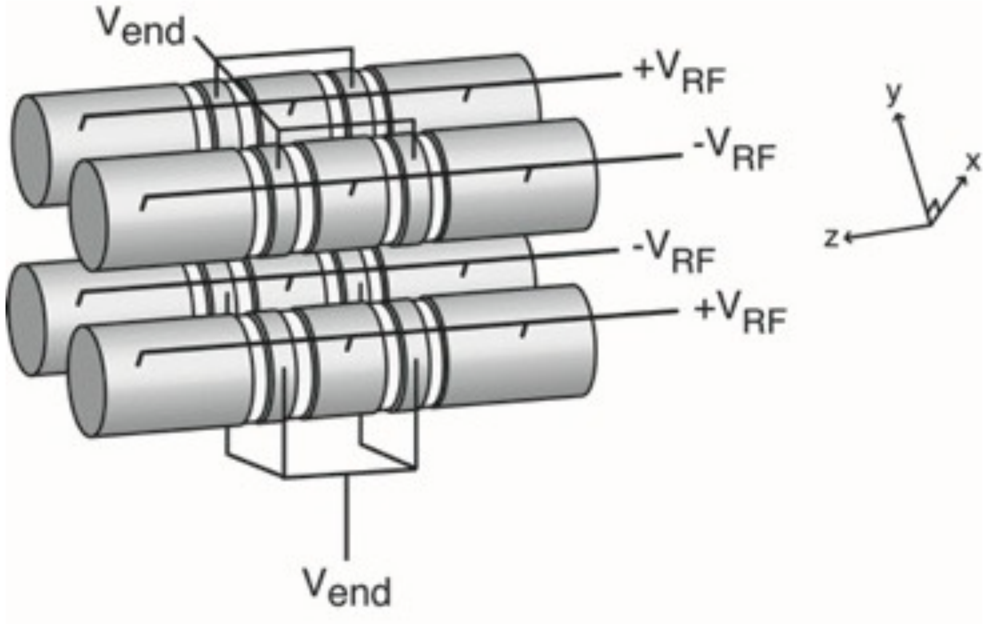
- Cold (μK-mK)
- Long trapping times (> hrs)
- Ordered structures of single, localized particles:
  observe, address and manipulate single ions on the quantum level

Lit.:
- D. Leibfried et al., Rev. Mod. Phys. 75 (2003), 281
- H. Häffner et al., Phys. Rep. 469 (2008), 155
- S. Willitsch, Int. Rev. Phys. Chem. 30 (2012), 175

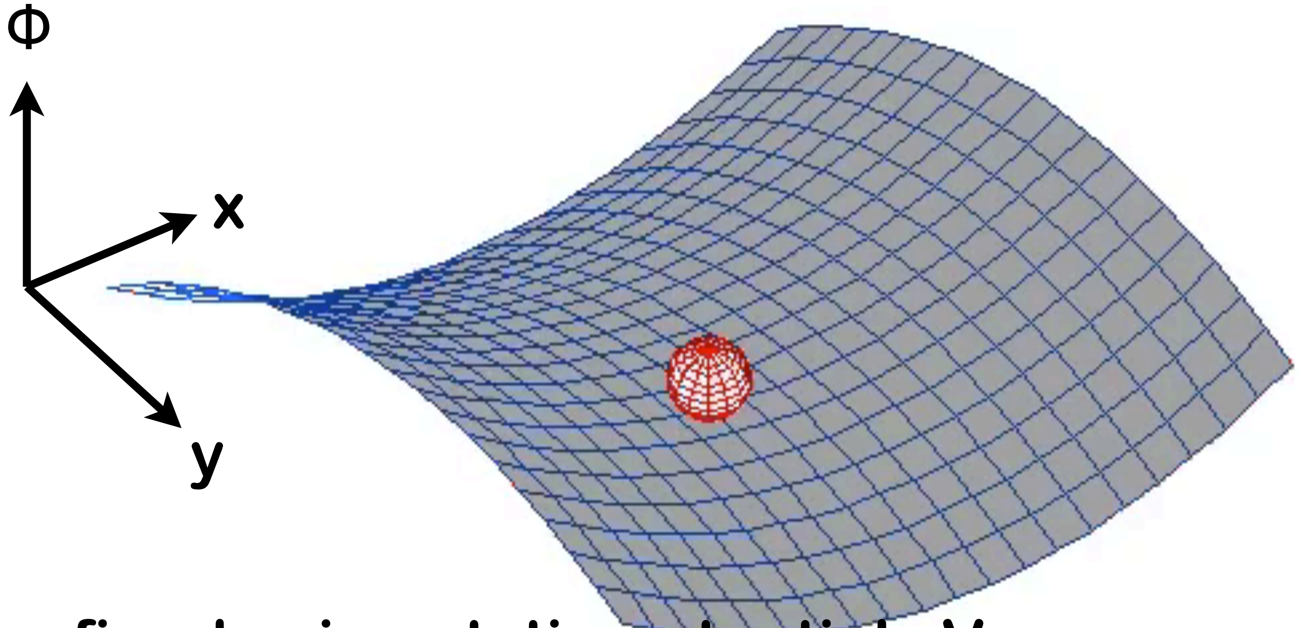
RF ion trapping

- Trapping = confine particles in a suitable potential minimum. For the trapping of ions electric potentials Φ are an obvious choice.
- The Laplace equation $\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Phi=0$

  forbids the formation of a potential minimum with static electric fields in 3D space.
- Solution: radiofrequency ion traps
  Trap ions dynamically in the x,y plane using time-varying voltages V_{RF} applied to the electrodes: $V_{RF}=V_{RF,0}\cos\left(\Omega_{RF}t\right)$



- Linear Paul trap: four electrodes arranged in a quadrupolar configuration
- The RF fields create a rotating potential saddle point which dynamically confines the ions.

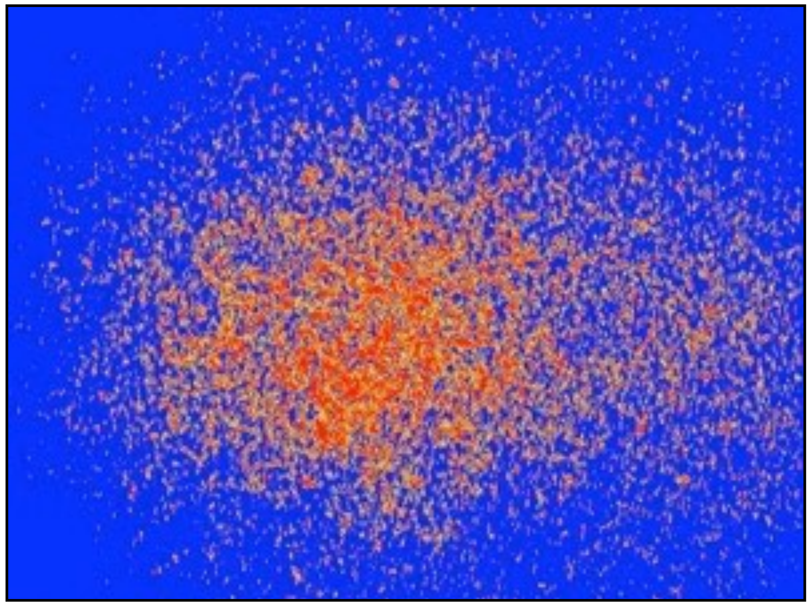


- Along the trap axis (=z axis) the ions are confined using static potentials V_{end} applied to the “endcap electrodes”.

Coulomb crystals

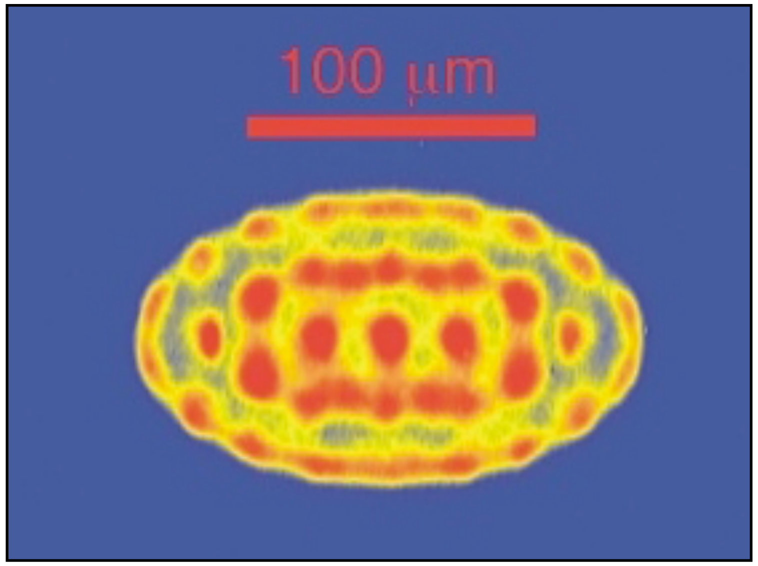
- Ion Coulomb crystals = ordered structures of strongly localised cations in ion traps at very low temperatures T << 1 K.
- Termed in analogy to “Wigner crystals” (ordered structures of electrons in solids) originally predicted by E. Wigner (1934).
- The term “crystal” is actually a misnomer (no translational symmetry !)

Warm Ca^+ ion cloud in ion trap



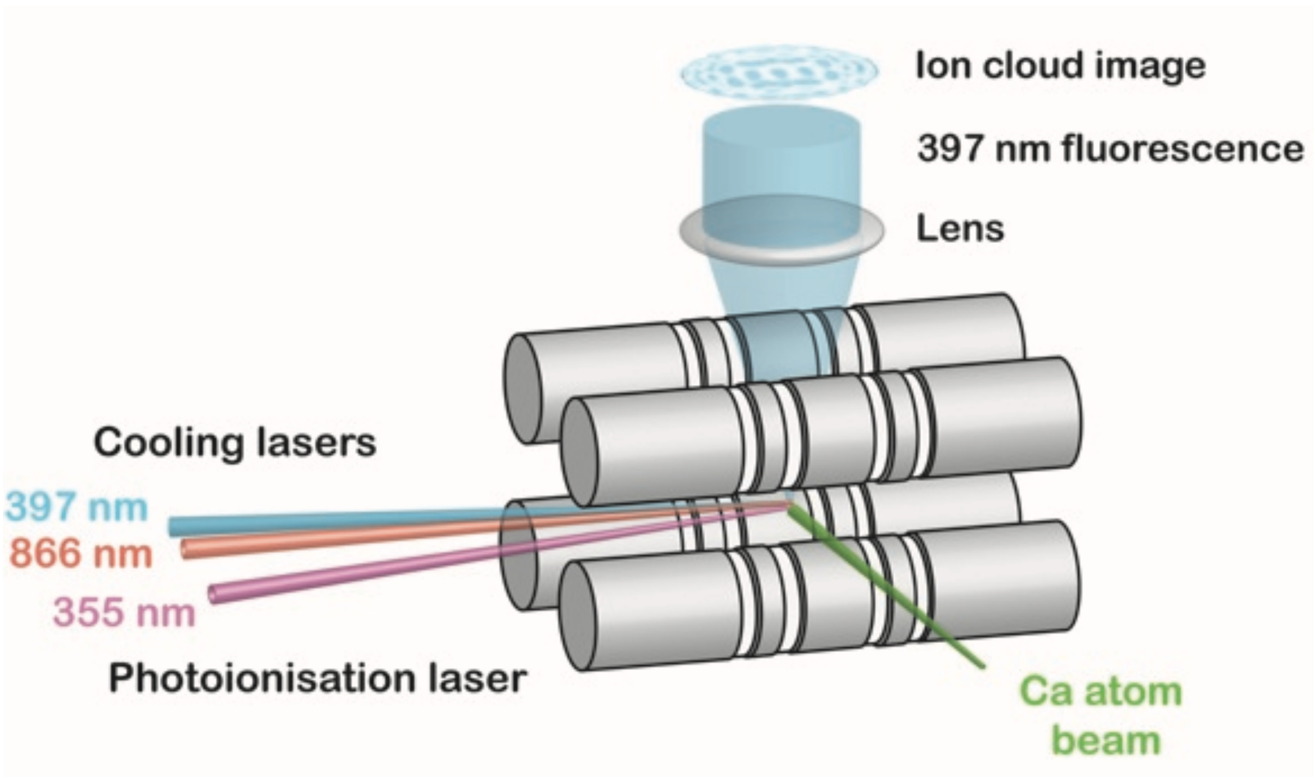
Laser cooling

“Coulomb crystal” at translational temperatures $T \approx 10$ mK

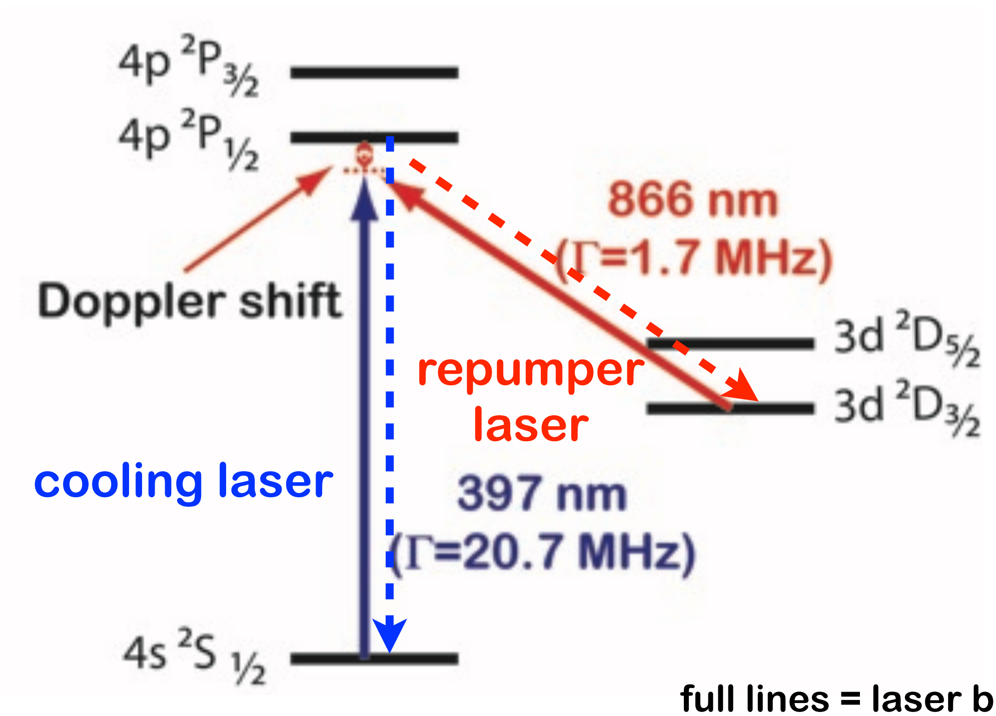


Laser cooling of trapped ions

- Typical ions used for laser cooling in traps are alkaline earth ions (Be^+, Mg^+, Ca^+, Ba^+) often produced directly inside the trap by photoionisation of their neutral atoms.



Example: laser cooling of $^{40}Ca^+$

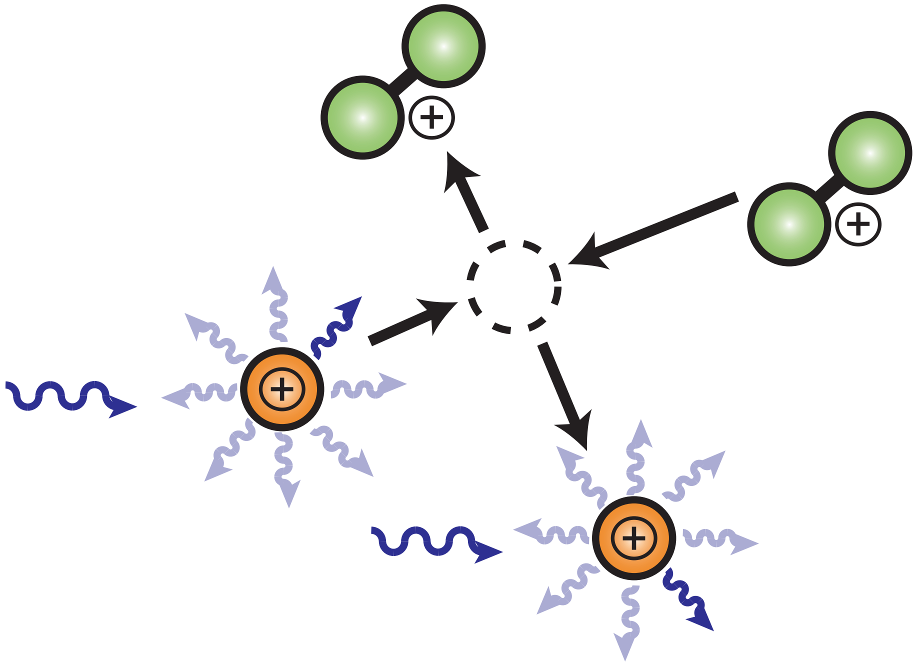


full lines = laser beams
dashed lines = spontaneous emission

Sympathetic cooling of molecular ions

Principle:

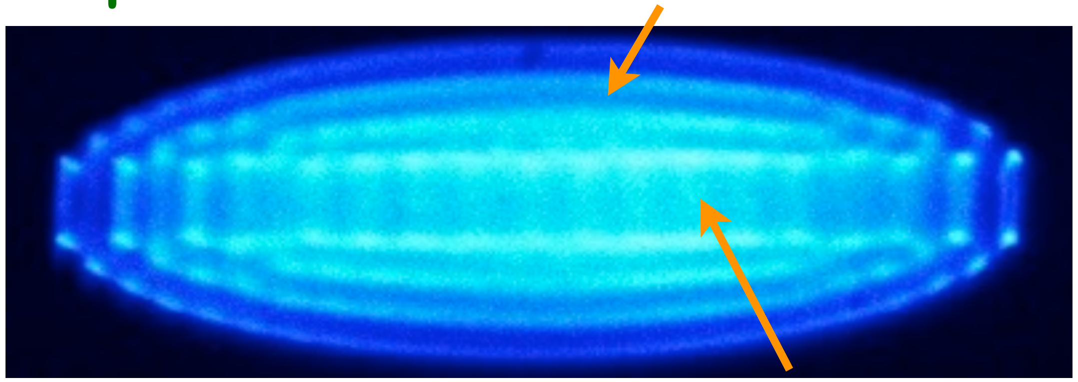
- Molecular ions are simultaneously trapped with laser-cooled atomic ions
- The molecular ions exchange kinetic energy in Coulomb-collisions with the atomic ions
- The energy is removed by laser cooling on the atomic ions



T. Baba & I. Waki , Jpn. J. Appl. Phys. 35 (1996), L1134
K. Molhave & M. Drewsen, Phys. Rev. A 62 (2000), 011401
S. Willitsch et al., Int. Rev. Phys. Chem. 31 (2012), 175

Molecular (or bi-component) Coulomb crystals:

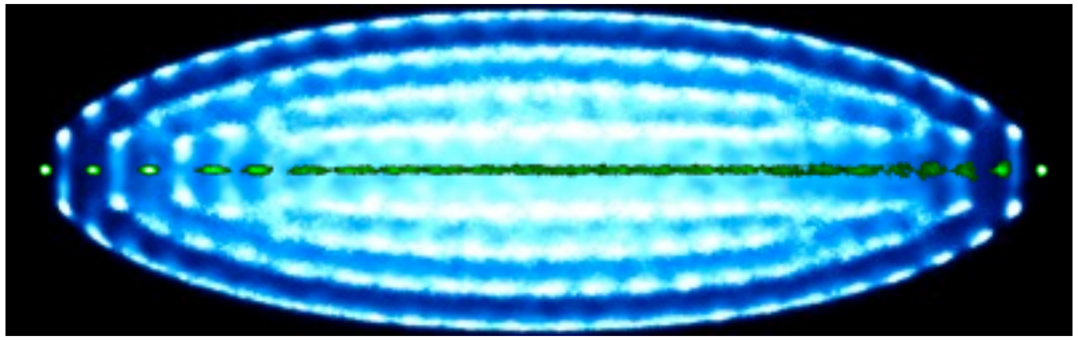
Experiment:



Laser-cooled Ca^+ ions

Sympathetically-cooled N_2^+ ions

Simulation:

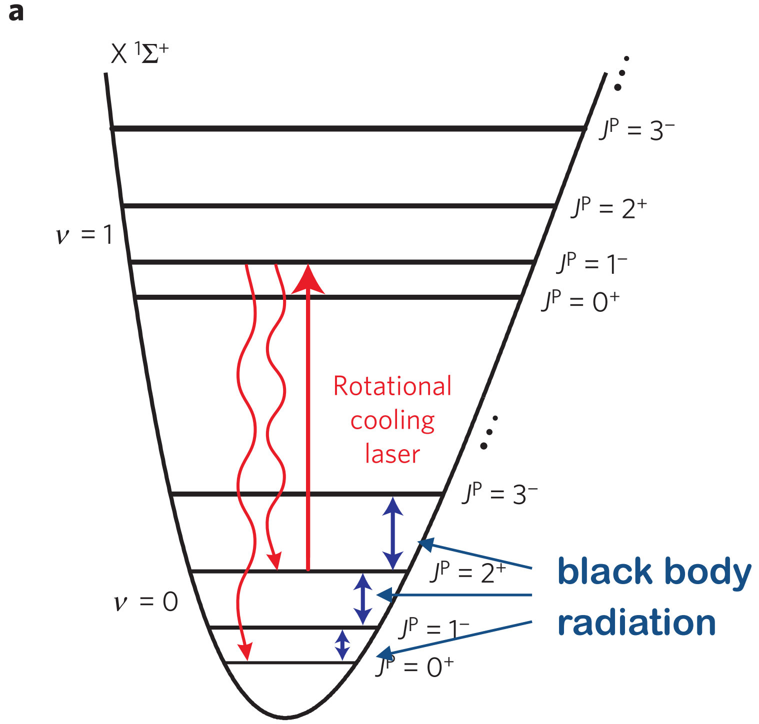


2. Internal state preparation of cold molecular ions

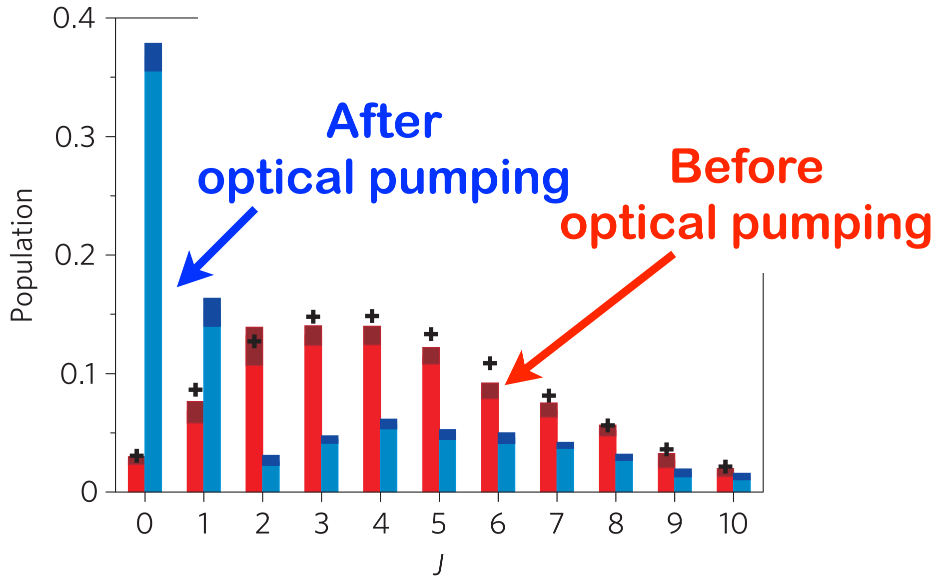
Rotational laser cooling

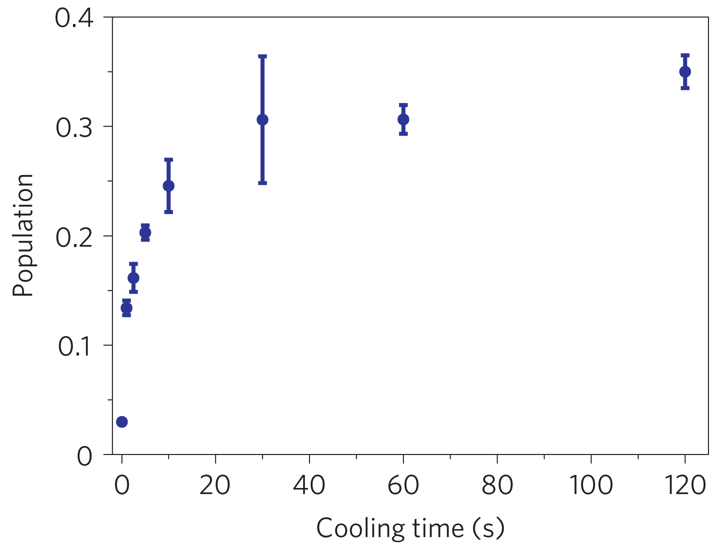
Staanum et al., Nature Phys. 6 (2010), 271
see also: Schneider et al., Nature Phys. 6 (2010), 275

- **Principle:** sympathetically cool the translational motion of molecular ions and then use optical pumping by laser fields to accumulate the population in a specific rotational-vibrational level
- **Example: MgH$^+$.** Use an IR laser to pump on the v=0,J=2 → v=1, J=1 transition. The v=1, J=1 level can only fluoresce down to the v=0, J=0 and J=2 levels (selection rules !).
- Transitions between rotational levels in the v=0 state induced by blackbody radiation constantly redistribute the population.
- In combination with the optical pumping, an accumulation of the population in the v=0, J=0 level results.



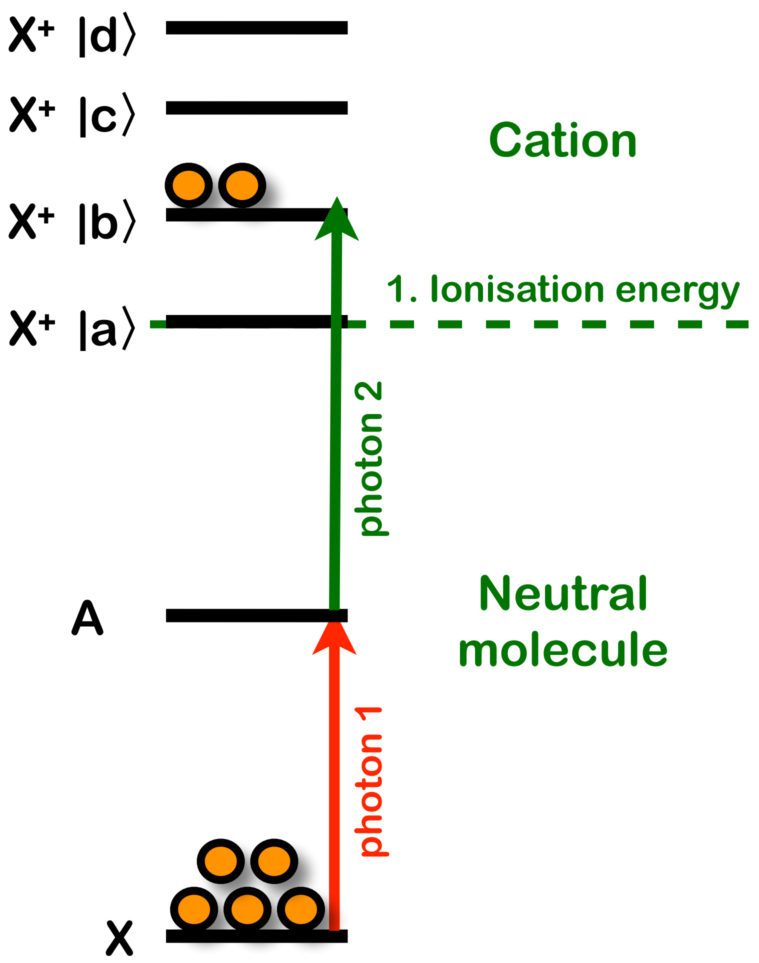
Ro-vibrational energy level scheme of MgH$^+$





Sympathetic cooling of state-prepared molecular ions

- **Principle:** Prepare the molecular ions right from the beginning in a specific rotational-vibrational state by threshold photoionization of their neutral precursor moelcules (i.e., photoionization just above a given ionization energy) and then sympathetically cool their translational motion.

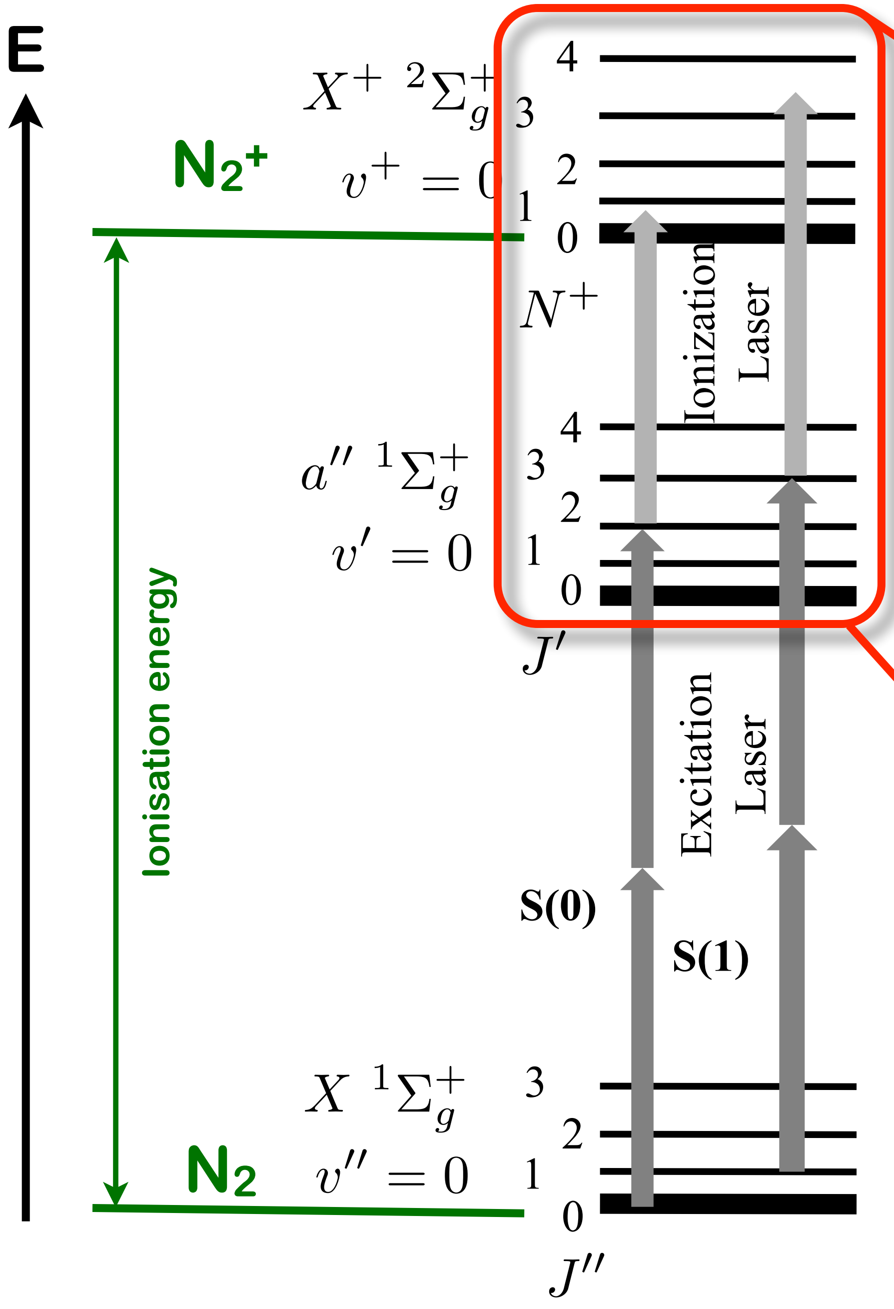


Threshold photoionization of molecules

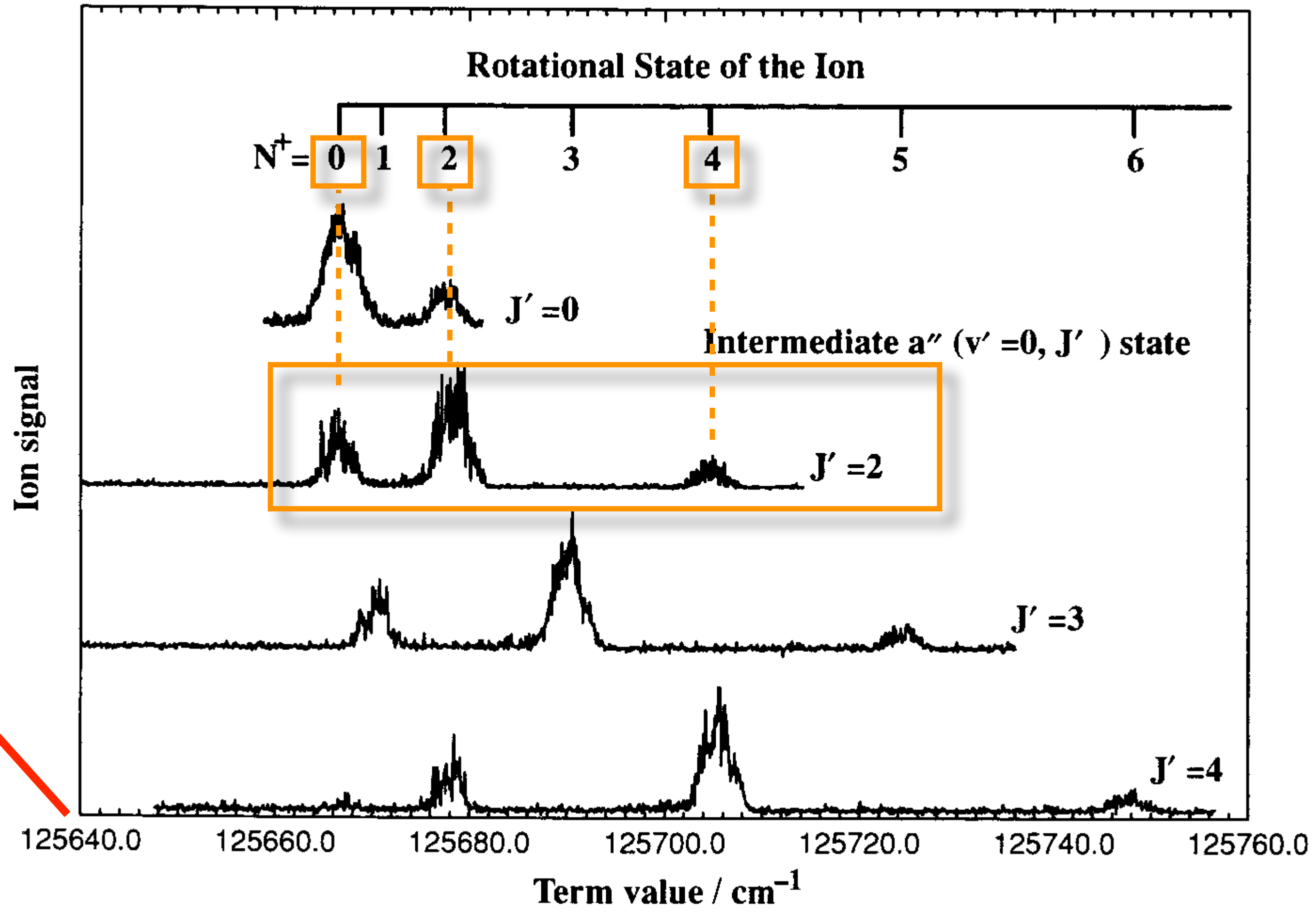
X. Tong, A. H. Winney and S. Willitsch, Phys. Rev. Lett. 105 (2010), 143001

Example: threshold photoionization of N_2:

- [2+1']-photon resonance-enhanced threshold-photoionisation scheme for N_2

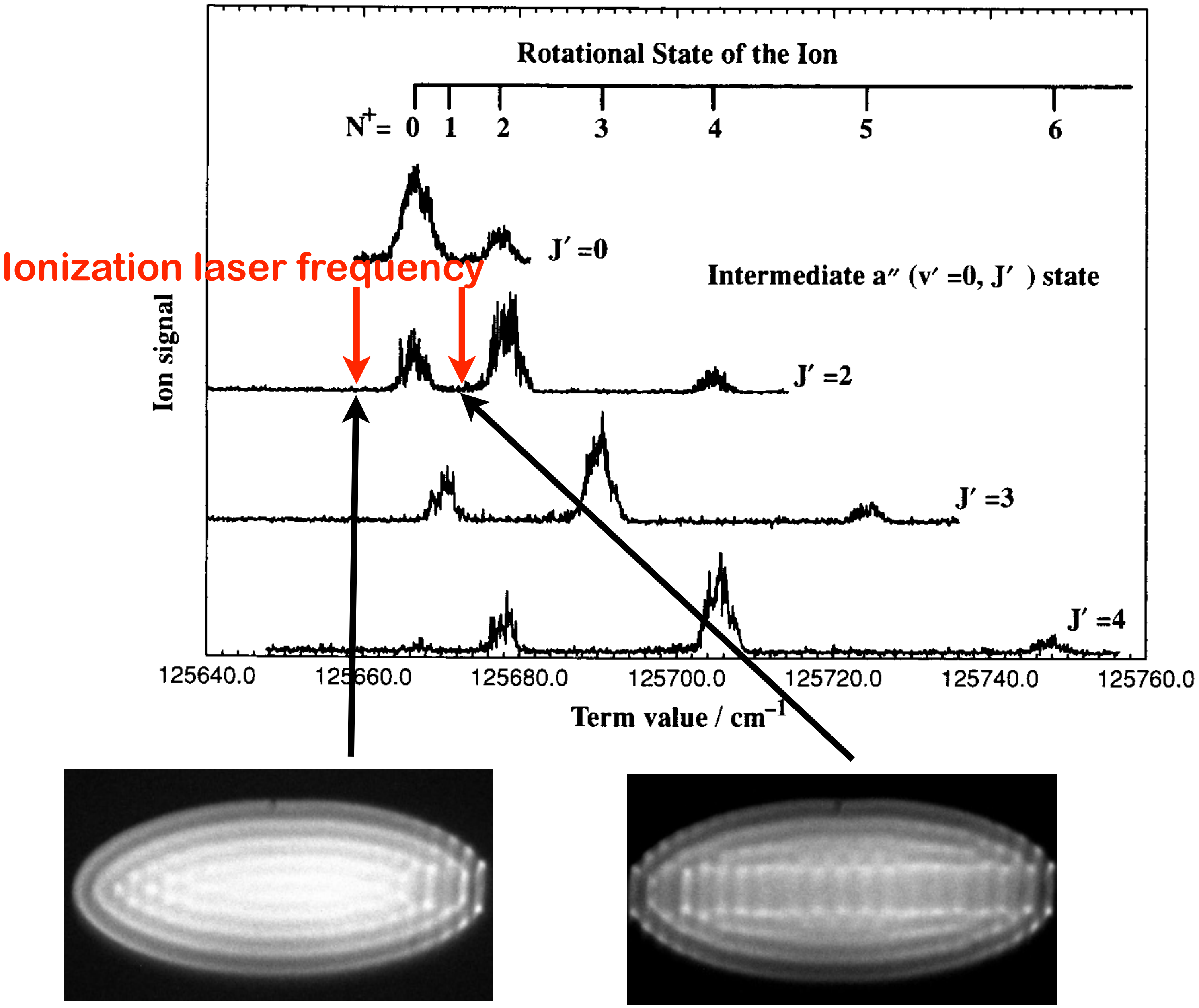


- Rotationally resolved photoelectron spectrum of N_2 showing the cationic rotational levels N^+ produced by threshold photoionisation out of well-defined intermediate rotational levels J'



S.R. Mackenzie et al., Mol. Phys. 86 (1995), 1283

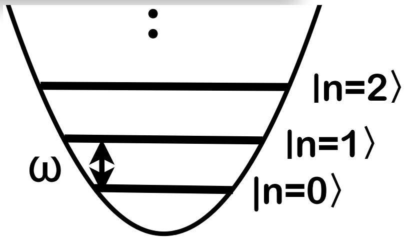
- [2+1'] resonance-enhanced threshold photoionisation via the a" $^1\Sigma^+_g$, J'=2 intermediate state of N_2:



Ionization laser frequency

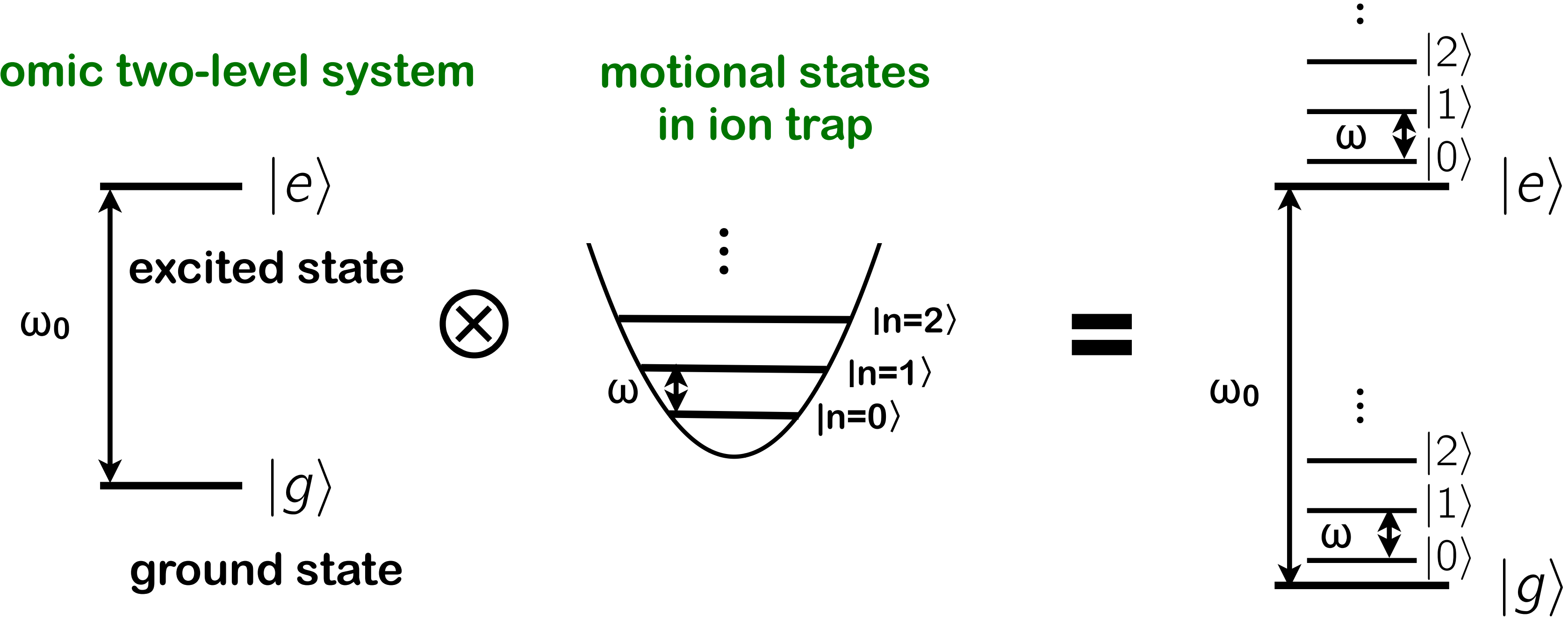
3. Applications: 1. Molecular-ion quantum technologies and quantum-logic spectroscopy

Resolved sideband cooling of ions into the quantum regime

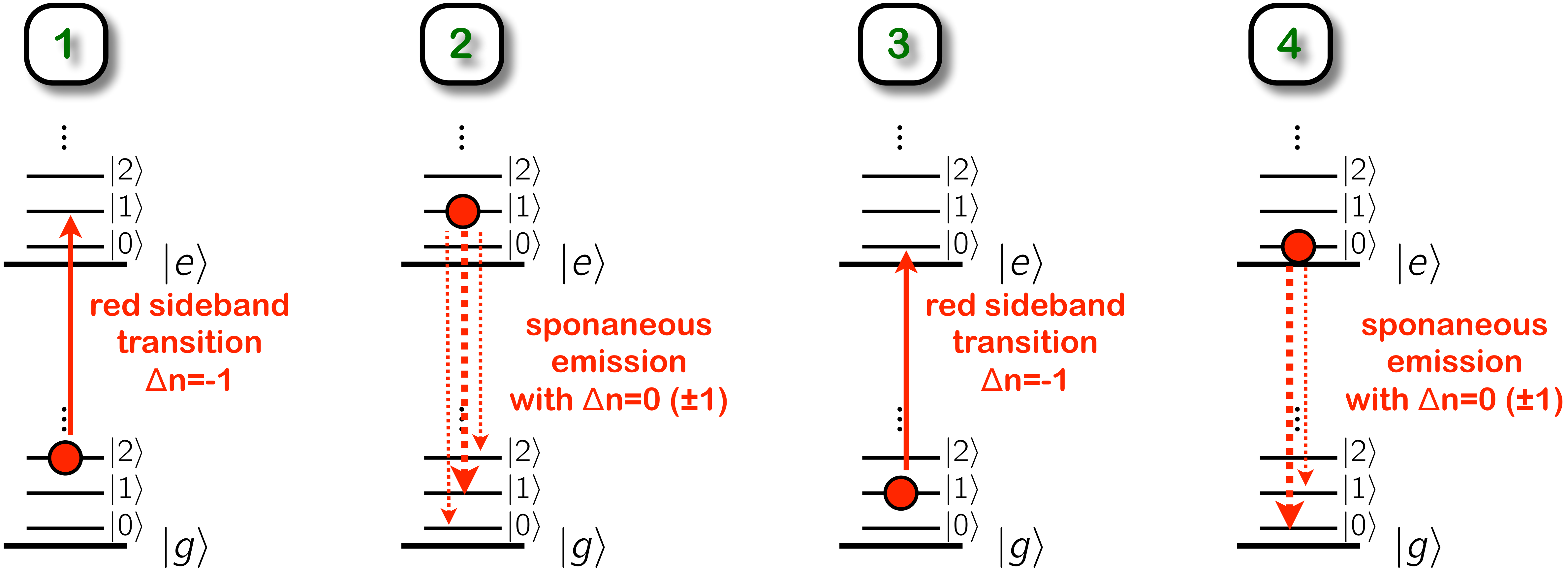


- The motion of an ion in the harmonic pseudopotential of the ion trap corresponds to a QM harmonic oscillator problem:
  - Motional states = the harmonic oscillator eigenstates $|n\rangle$, n = 0,1,2,..
  - Motional states form a ladder of equidistant energy levels $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$

- Resolved sideband cooling: cooling to the motional ground state by addressing the individual motional states



Simple resolved sideband cooling scheme:



1: red sideband transition Δn=-1

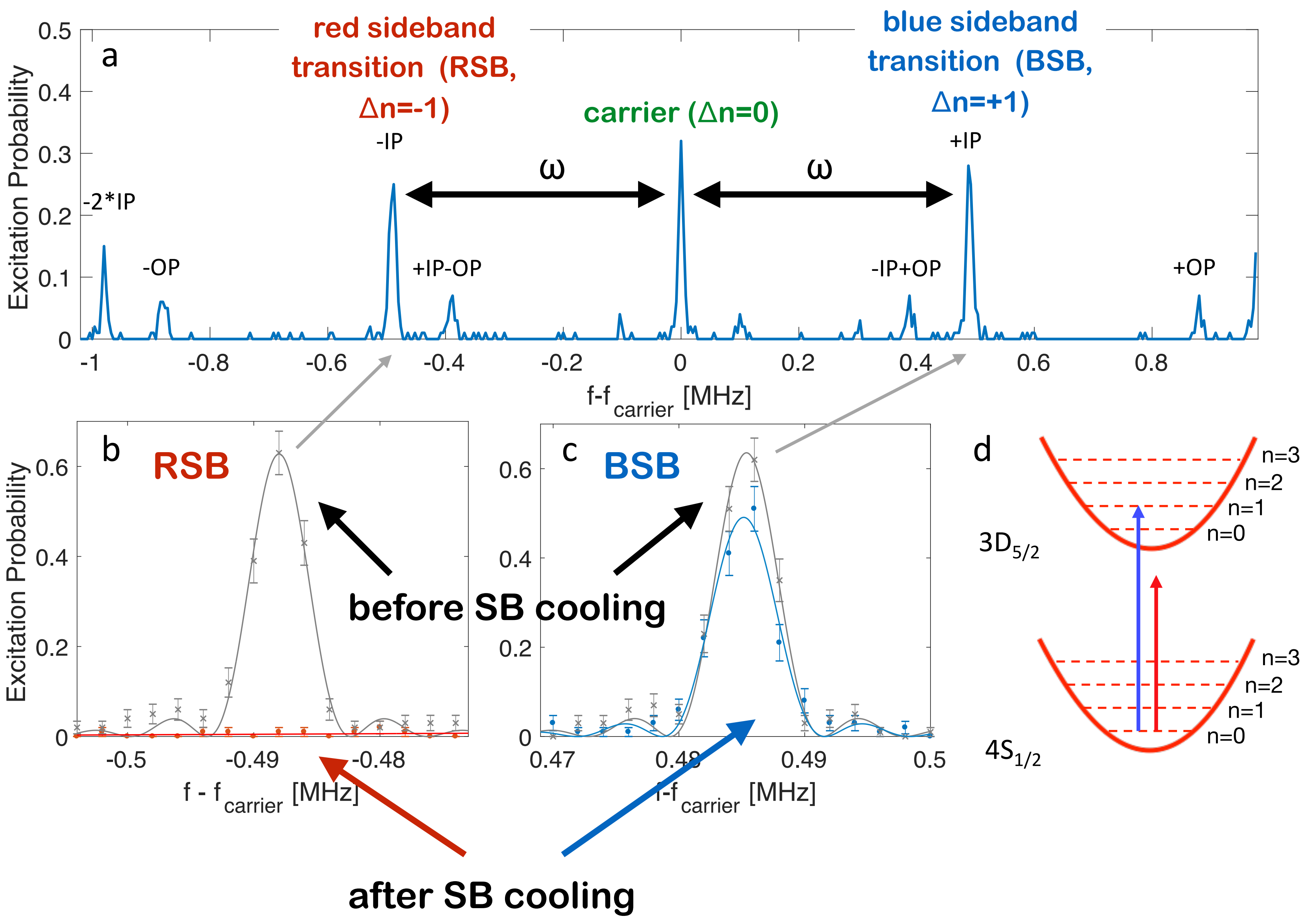
2: sponaneous emission with Δn=0 (±1)

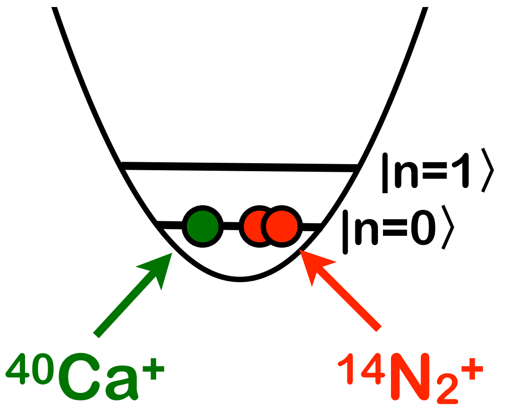
3: red sideband transition Δn=-1

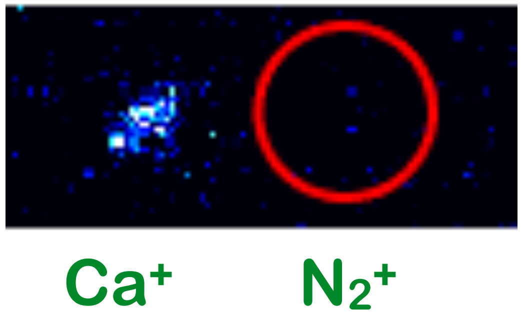
4: sponaneous emission with Δn=0 (±1)

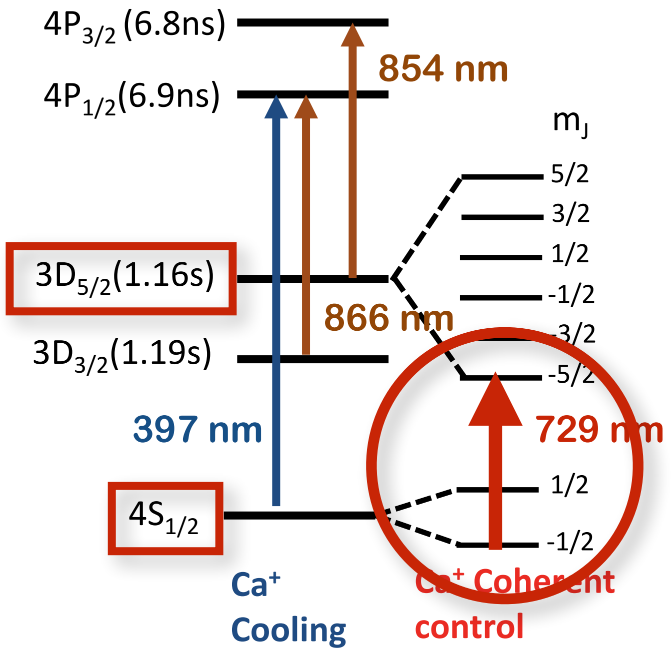
Lit.: D. Leibfried et al., Rev. Mod. Phys. 75 (2003), 281
H. Häffner et al., Phys. Rep. 469 (2008), 155

Example: Resolved-sideband cooling and spectroscopy of the Ca^+ 4p $^2S_{1/2} \rightarrow$ 3d $^2D_{5/2}$ transition at 729 nm in a Ca^+ - N_2^+ two-ion crystal







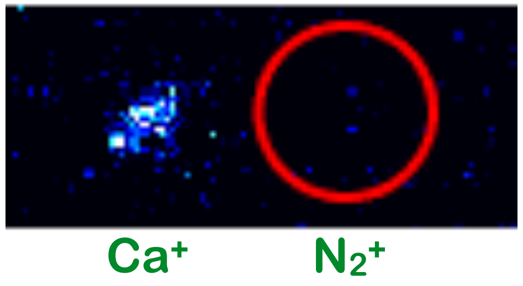


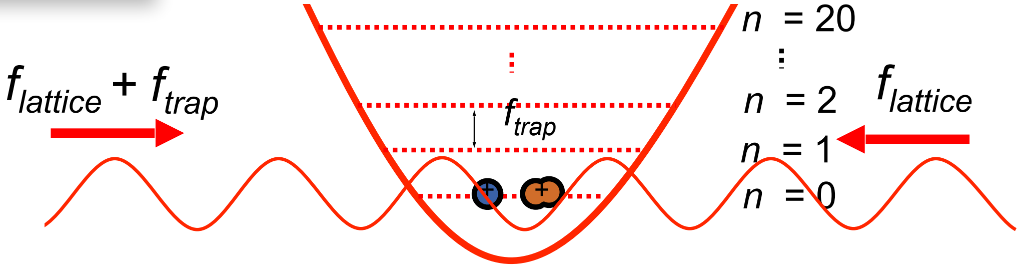
Ca^+ spectroscopy

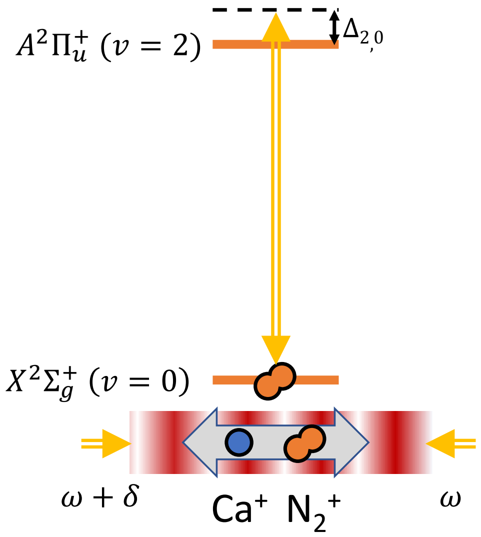
Quantum-non-demolition state detection of single molecular ions by coherent motional excitation of a two-ion crystal

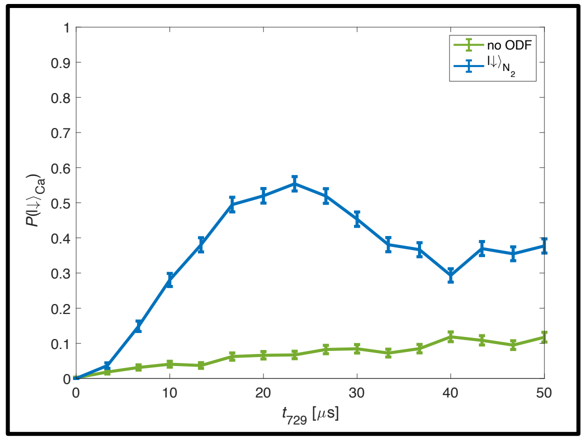
Non-destructive state-detection and spectroscopy of a single molecule

- **Step 1: Preparation of a Ca^+ - N_2^+ two-ion string**
- **Step 2: Sympathetic cooling of the molecule to the QM ground state of the trap**
- **Step 3: Application of an 1D optical lattice near-resonant with a spectroscopic transition in the molecule to generate an optical dipole force (ODF)**
- **Step 4: Modulation of the optical lattice at the frequency of vibration of the ions in the trap to excite their motion**
- **Step 5: Detection of the motional excitation of the ions by sideband Rabi spectroscopy on Ca^+**





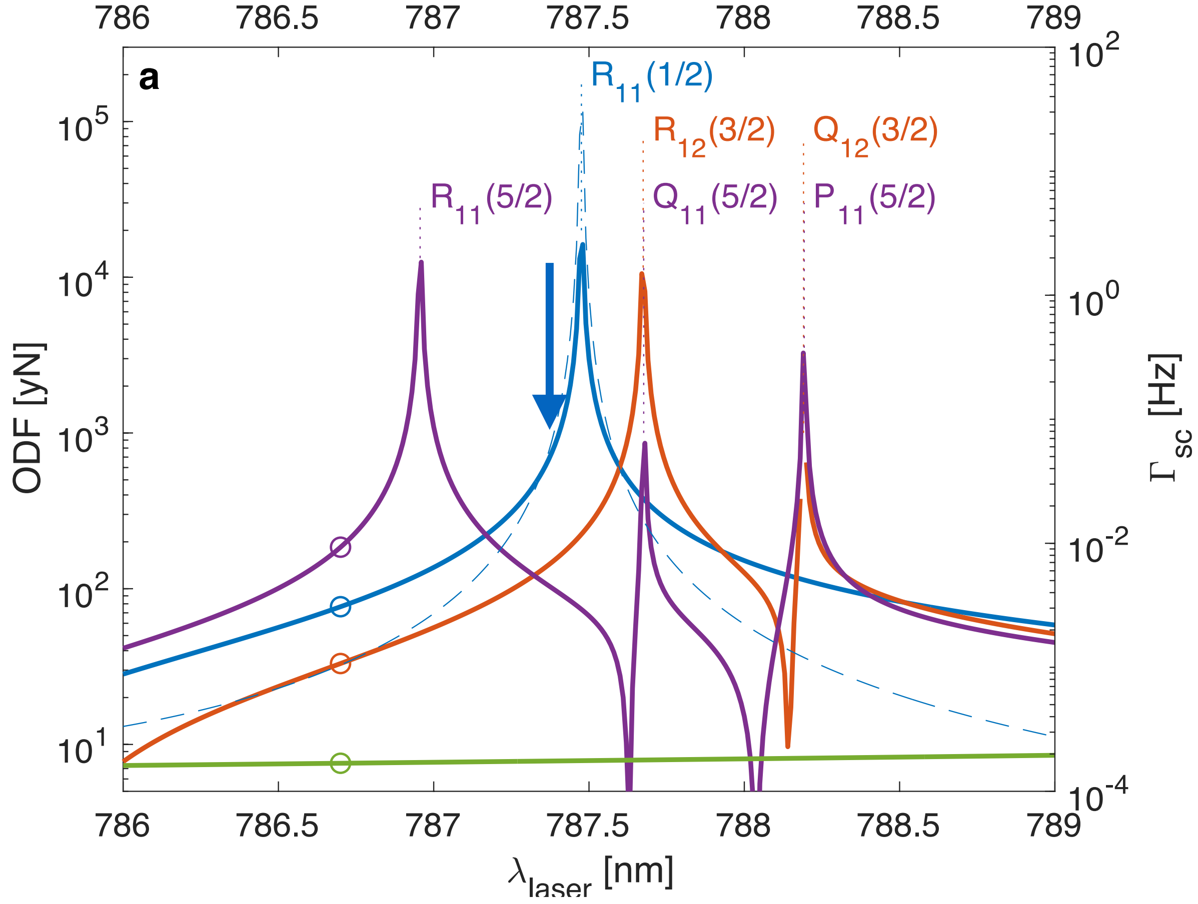




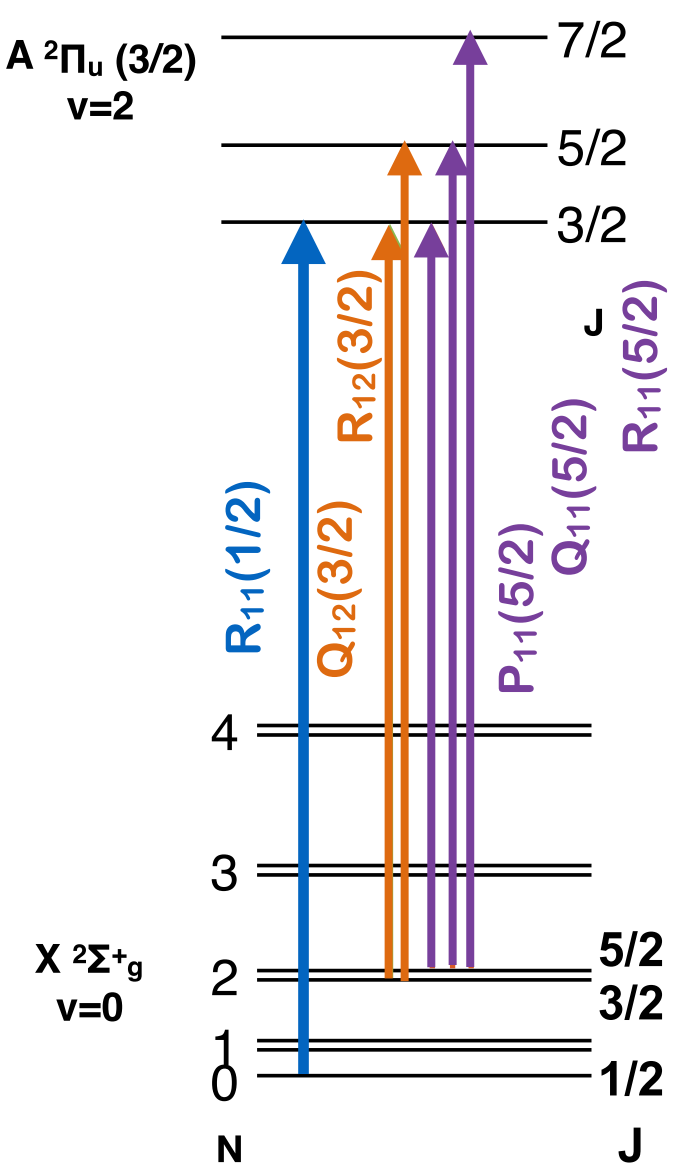
M. Sinhal et al., Science 367 (2020), 1213

Step 3: ODF for N_2^+ in different spin-rotational states

- ODF as a function of lattice-laser wavelength

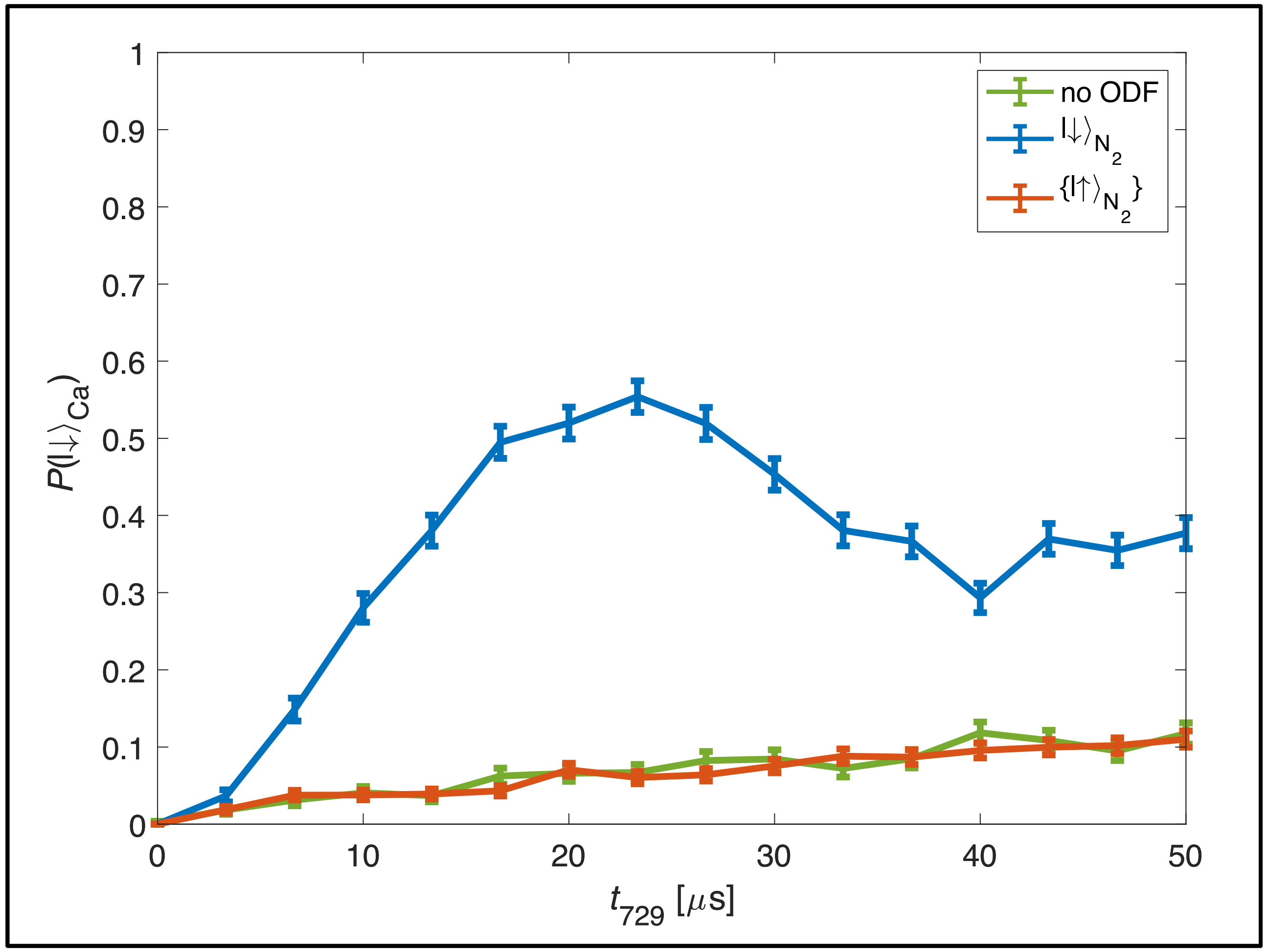


- Excerpt of energy-level structure of N_2^+ with spectroscopic transitions giving rise to strong ODFs

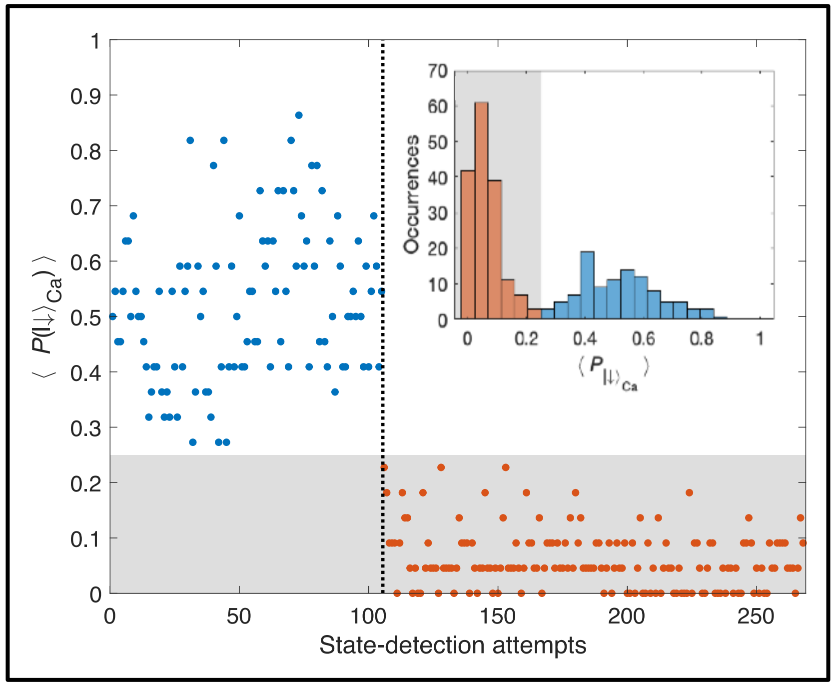


M. Sinhal et al., Science 367 (2020), 1213

Steps 4 and 5: Rabi flops on the Ca^+ $^2S_{1/2} \leftarrow {}^2D_{5/2}$ sideband transition after CME of N_2^+ in $N^+=0$

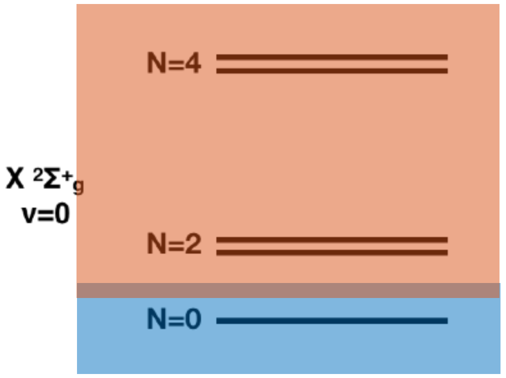


Fidelity of finding the molecule in the correct state (blue) or not (red)



99.1(9)%

99.4(6)%

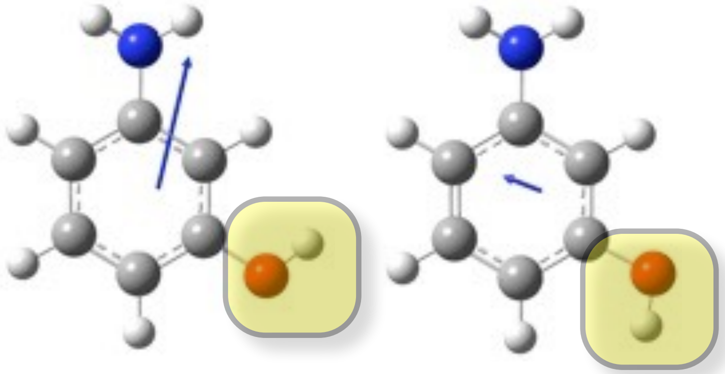


M. Sinhal et al., Science 367 (2020), 1213

3. Applications: 2. Unravelling the details of chemical reaction mechanisms with controlled molecules

How does chemical reactivity depend on the shape of a molecule (i.e., its conformation) ?

Example: 3-Aminophenol (3AP)
2 conformers: cis / trans

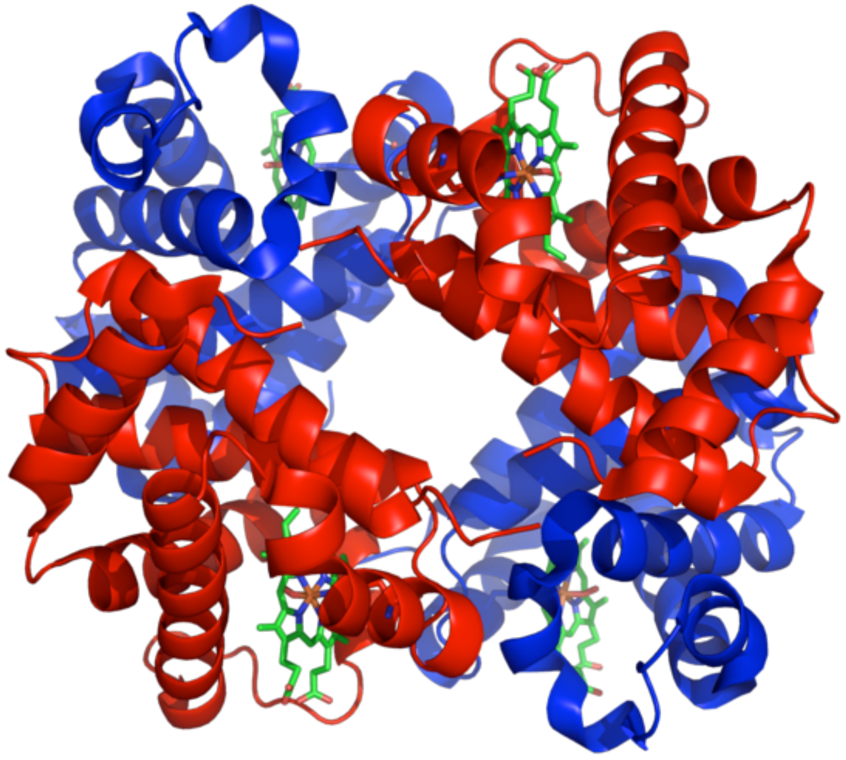


cis-3AP
μ=2.33 D

trans-3AP
μ=0.77 D

Conformations: why bother ?

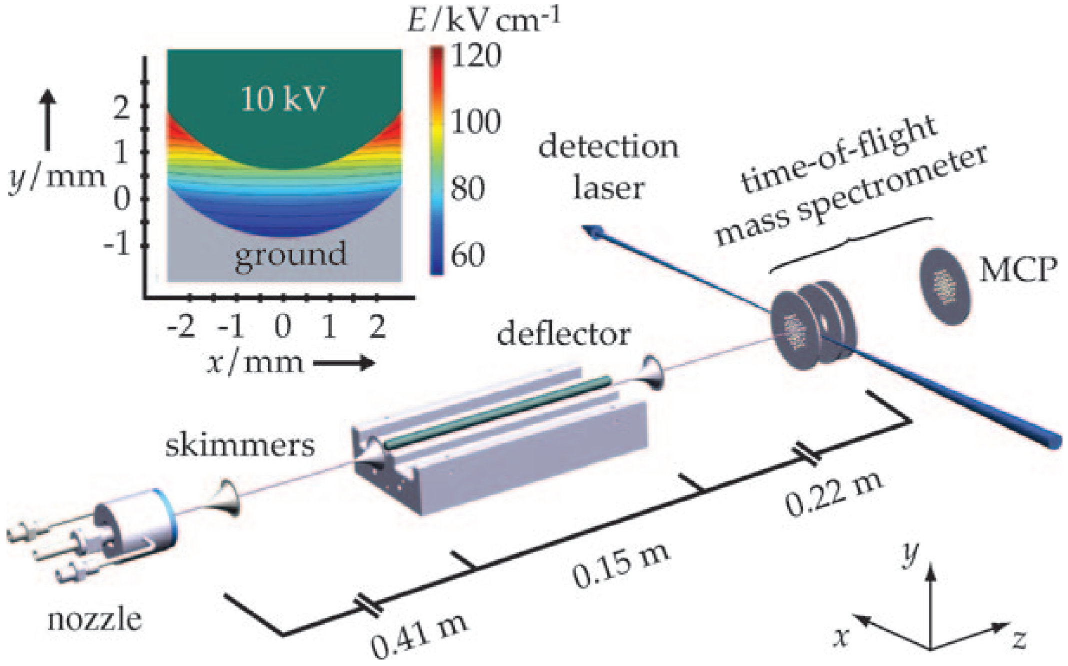
- Conformers are the dominant form of structural isomers of complex molecules, e.g., proteins such as hemoglobin.
- The chemical reactivity of complex molecules often depends on their conformation ("steric effects")
- Conformers often easily interconvert between one another under ambient conditions: single conformers are difficult to isolate and study !



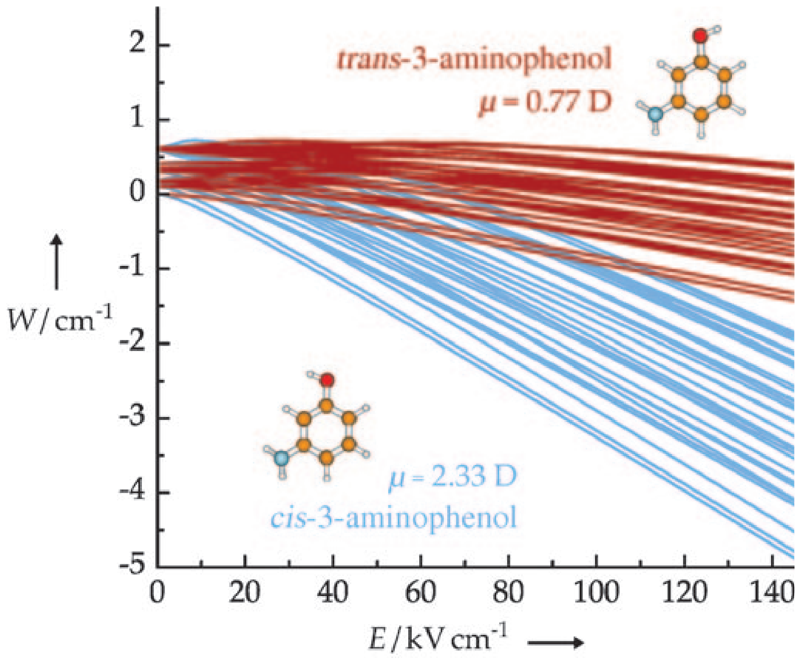
hemoglobin

Electrostatic separation of molecular conformations in a molecular beam:

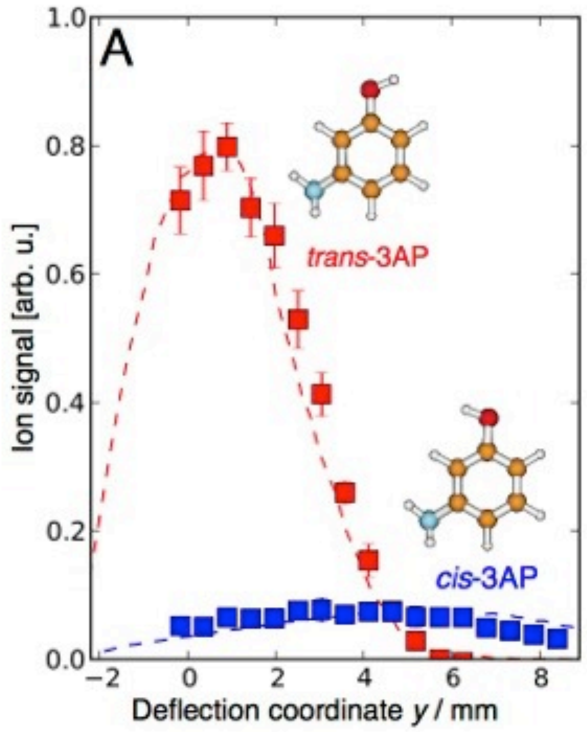
F. Filsinger, J. Küpper, G. Meijer, et al., Angew. Chemie Int. Ed. 48 (2009), 6900



Experimental setup



Stark energies W of the lowest rotational states of cis/trans-3-aminophenol as a function of the electric field strength E

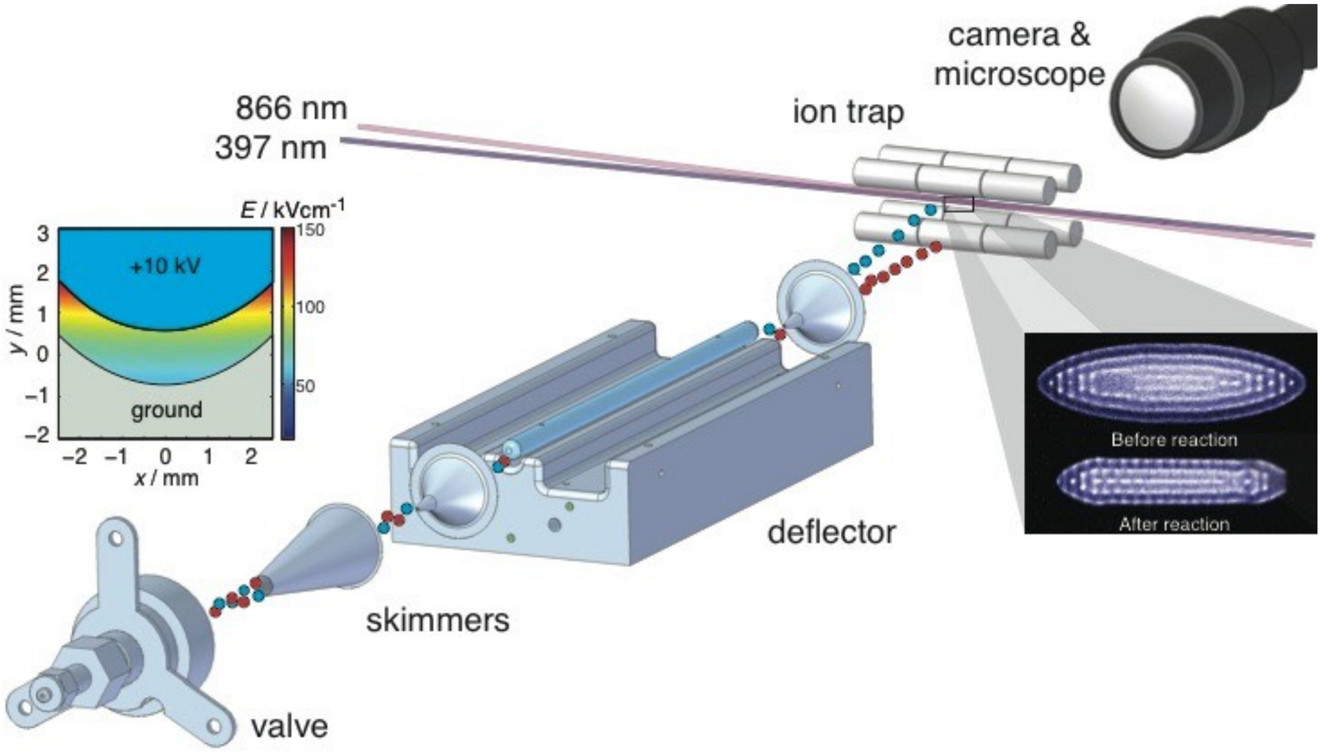


"Deflection profiles" of cis-/trans-3-aminophenol (3AP)

Cold molecular ions in traps: methods and applications

Chemical reactions of selected molecular conformations:

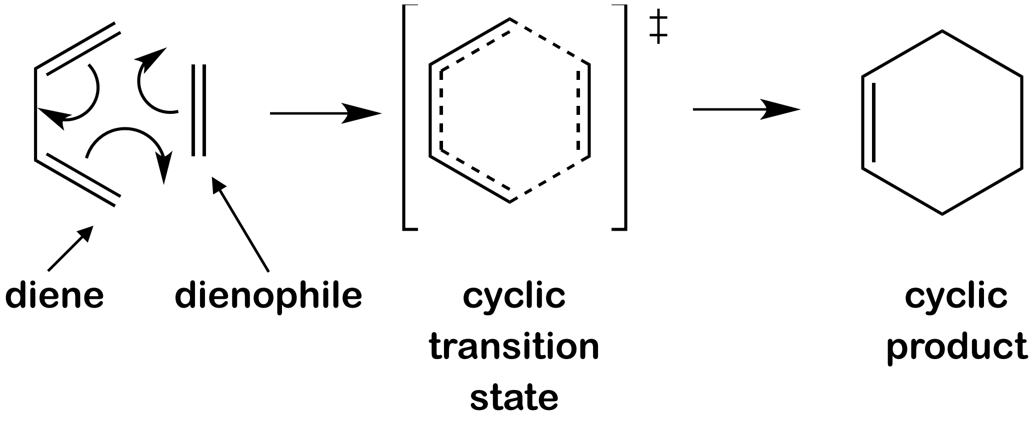
- Spatially separate specific molecular conformations from a molecular beam
- Direct the conformationally selected components of the beam at a stationary reaction target consisting of a Coulomb crystal of cold ions
- Measure conformation-specific reaction rates to probe conformation-specific chemical reactivities



Y.-P. Chang, K. Dlugolecki, J. Küpper, D. Rösch, D. Wild and SW, Science 342 (2013), 98

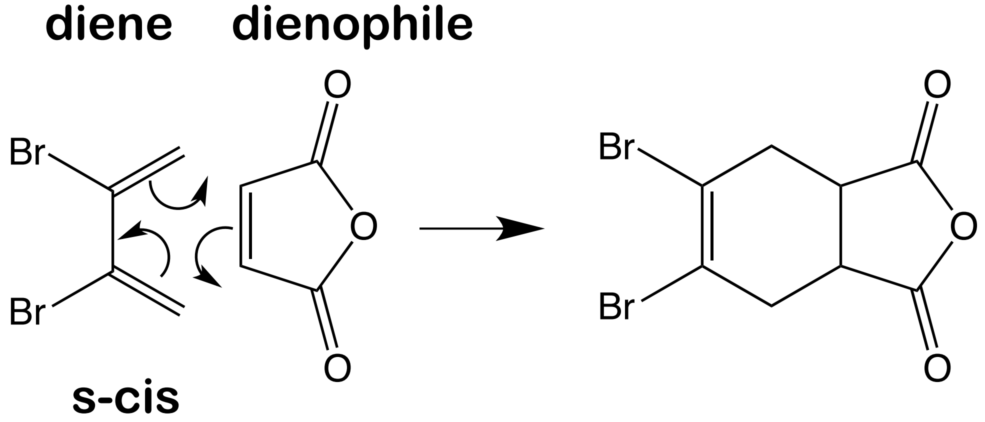
Example I: Mechanism of Diels-Alder reactions

The Diels-Alder reaction:



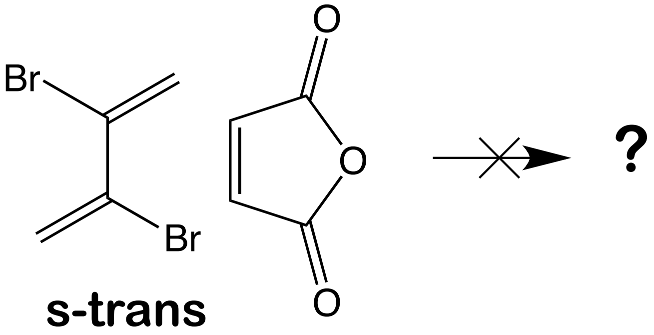
O. Diels and K. Alder, Justus Liebigs Ann. Chem. 460 (1928), 98

Activated Diels-Alder reactions:

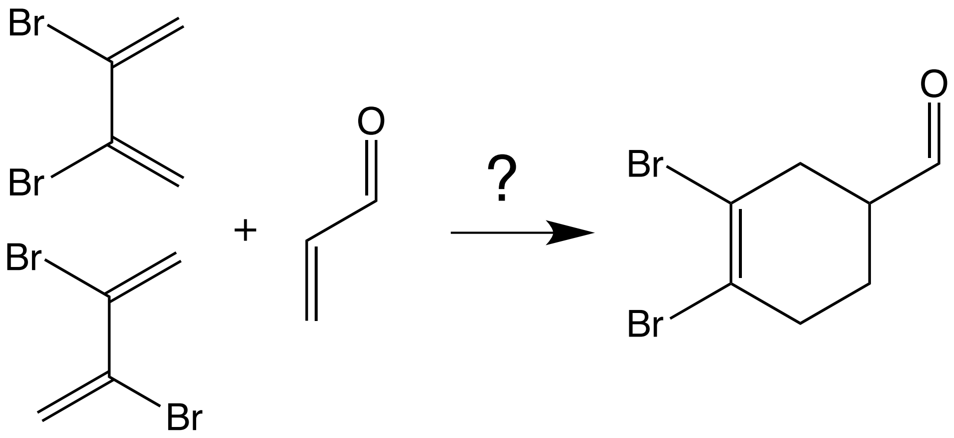


Open questions:

- Conformational selectivity

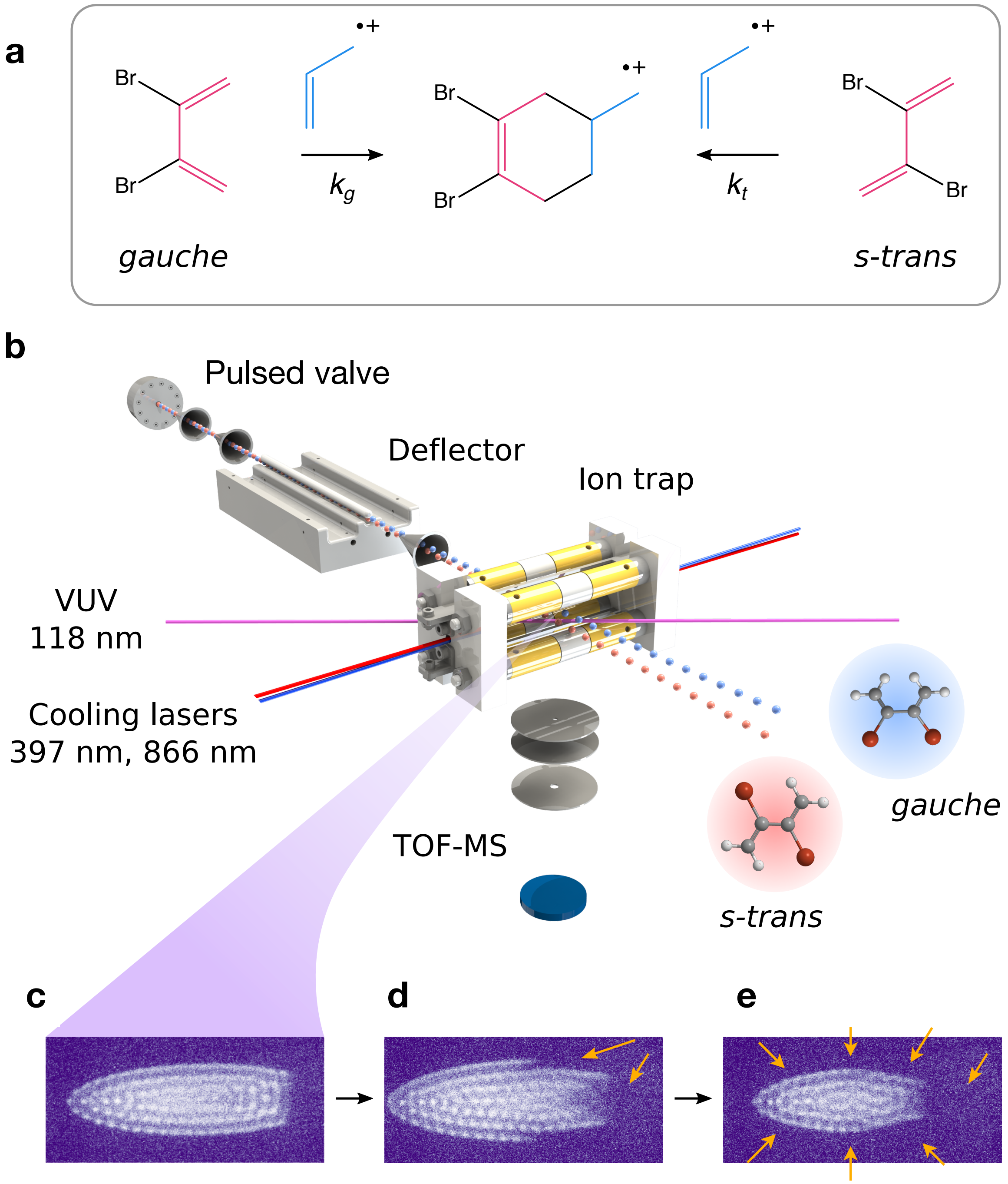


- Mechanism in asymmetric systems: concerted or stepwise, synchronicity



- Polar cycloadditions: effect of charge

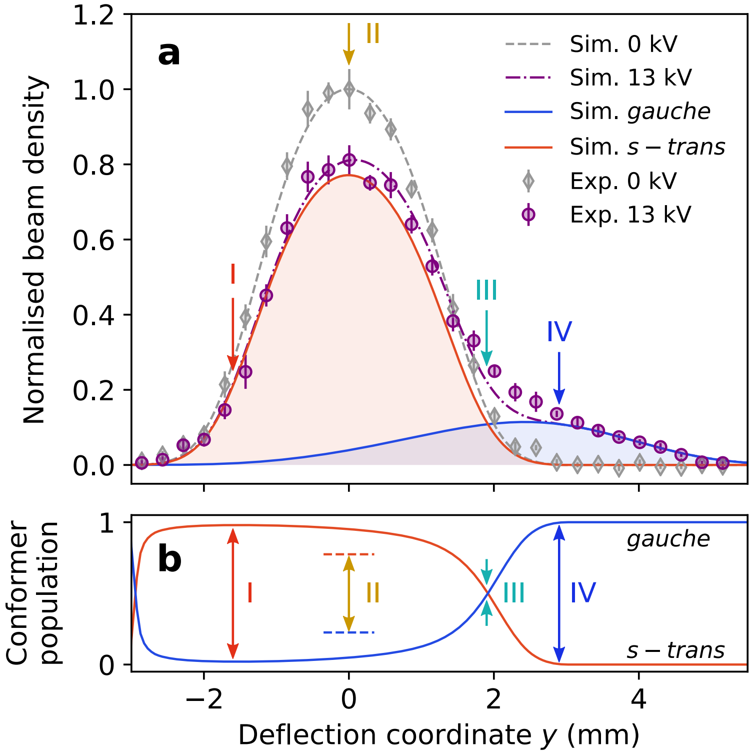
Conformer-specific polar cycloaddition of 2,3-dibromobutatdiene with propene ions



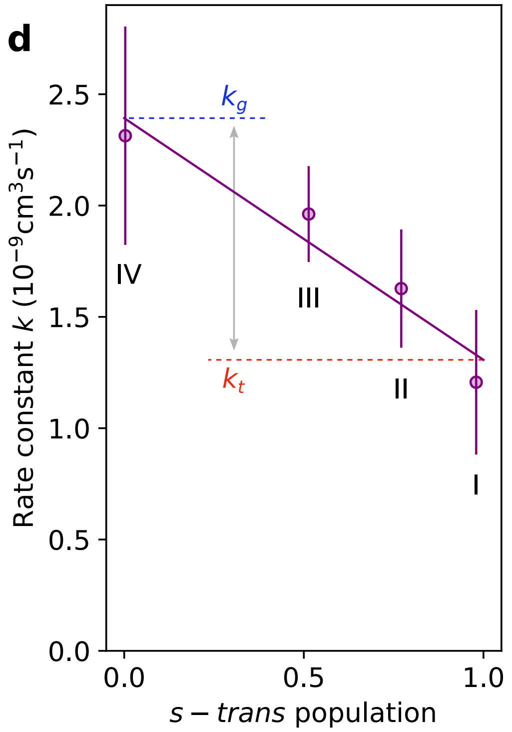
Ca^+ Coulomb crystal → $C_3H_6^+$ loaded → after reaction

A. Kilaj et al., Nat. Commun. 12 (2021), 6047

Reaction rates of s-trans- and gauche-DBB: both conformers react



Deflection profiles of 2,3-dibromobutadiene (DBB)

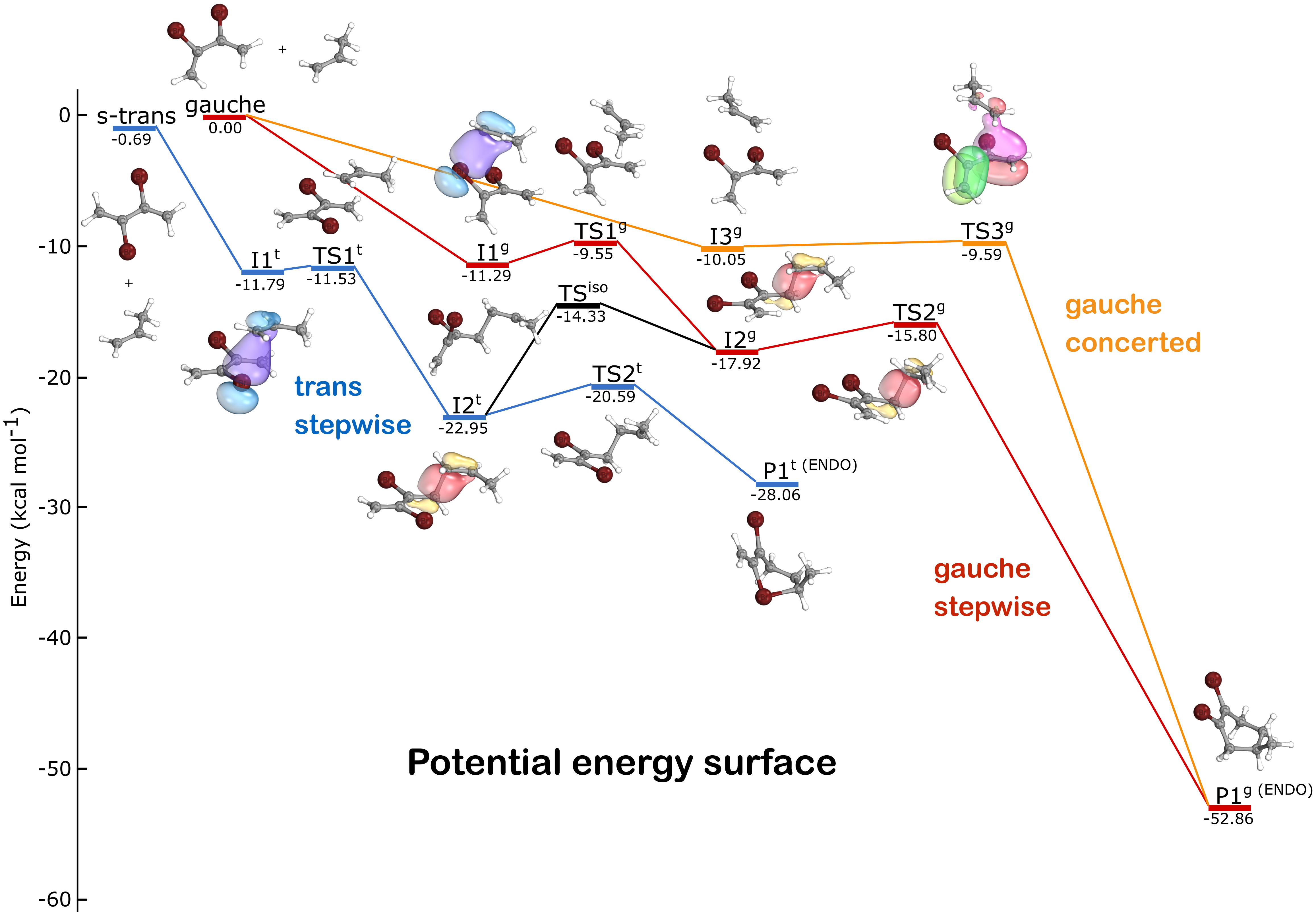


Bimolecular rate constants as a function of the relative conformer population

- **Both conformers react fast (capture limited) !**
- **gauche-DBB reacts 60% faster than trans-DBB**

A. Kilaj et al., Nat. Commun. 12 (2021), 6047

Rationalisation: simultaneous competition of concerted and stepwise reaction mechanisms involving both conformers

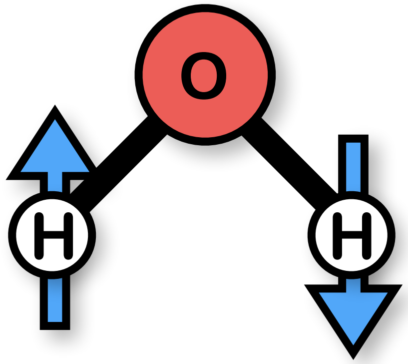


Potential energy surface

Example II: Different reactivities of ortho- and para-water

A. Kilaj, H. Gao, D. Rösch, U. Rivero, J. Küpper and SW, Nat. Commun. 9 (2018), 2096

- Like H_2 (see Sec. 2.1.3), water H_2O consists of two nuclear spin isomers ortho (o, I=1) and para (p, I=0)
- The interconversion between the two isomers is in principle forbidden in isolated molecules, by dipole radiation and by dipole collisions
- Interconversion rates between the two isomers are still disputed in the literature
- Because of the generalised Pauli principle, they are associated with different rotational wavefunctions (like in H_2, Sec. 2.1.3)
- Is there a difference in their chemical reactivity ?

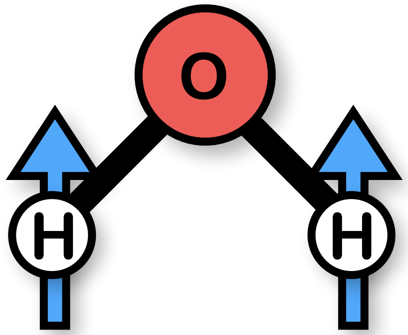


para (I=0)

K_aK_c = ee or oo

ground state:

$J_{K_aK_c}=0_{00}$



ortho (I=1)

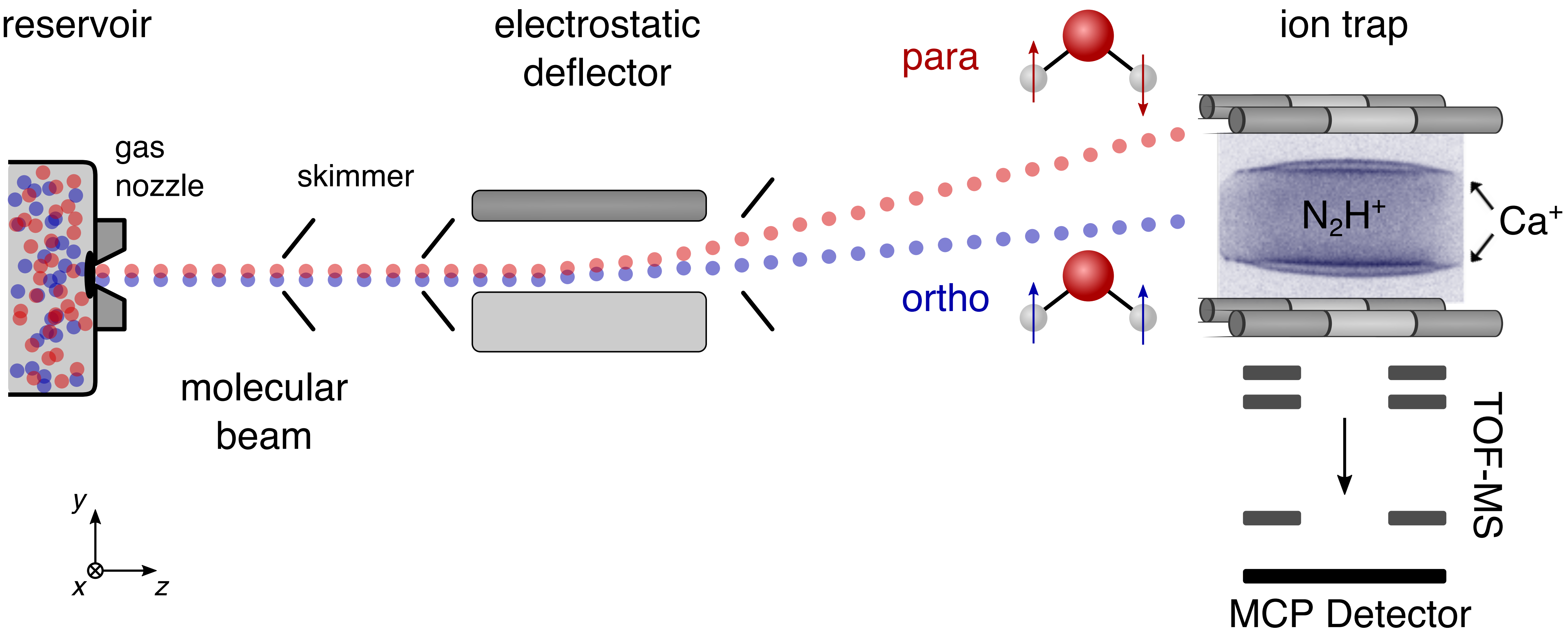
K_aK_c = eo or oe

ground state:

$J_{K_aK_c}=1_{01}$

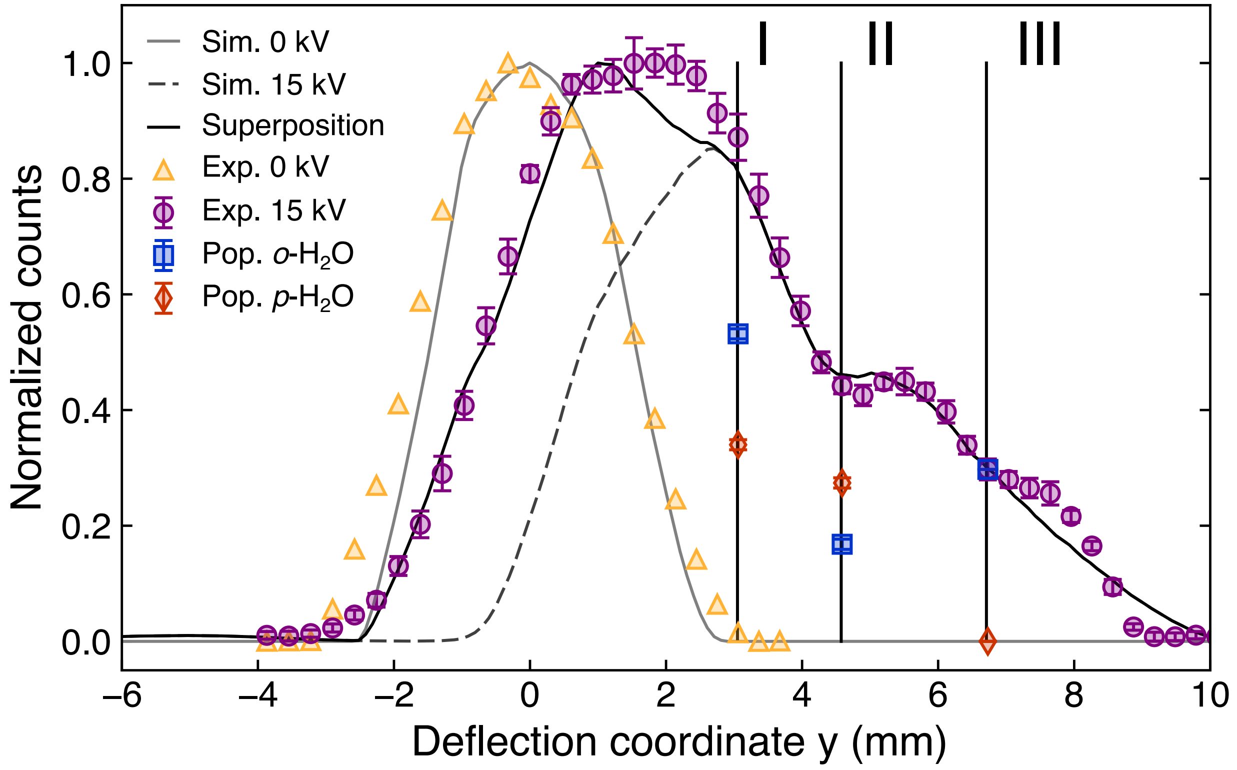
Cold molecular ions in traps: methods and applications

Target reaction: $H_2O + N_2H^+ \rightarrow H_3O^+ + N_2$

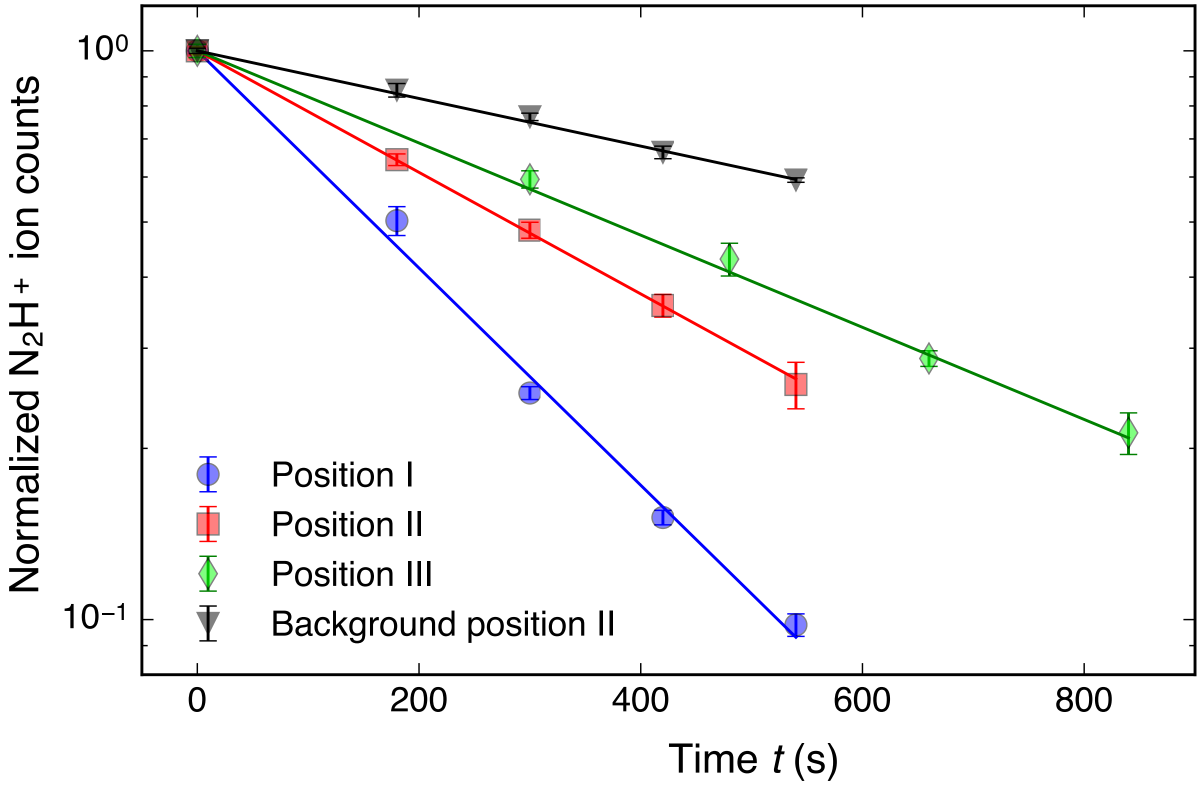


Reaction rate measurements

Deflection profile



Pseudo-first-order reaction rates at positions I, II and III



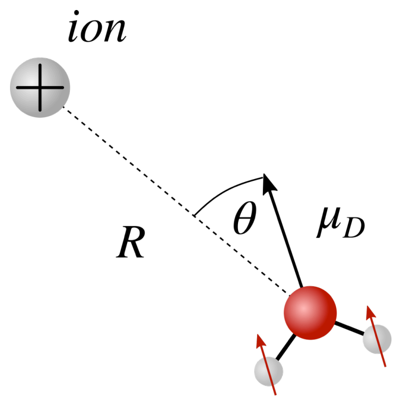
Second-order rate constants:

- k(para) = $6.0(10) \times 10^{-9}$ cm^3 s^{-1}
- k(ortho) = $4.8(9) \times 10^{-9}$ cm^3 s^{-1}
- relative difference: 23(9) %
  (as inferred from pseudo-first order rate const.)

Rationalisation of results: adiabatic capture theory

D.C. Clary, J. Chem. Soc. Faraday Trans. II 83 (1987), 139; T. Stoecklin et al., J. Chem. Soc. Far. Trans. 88 (1992), 901

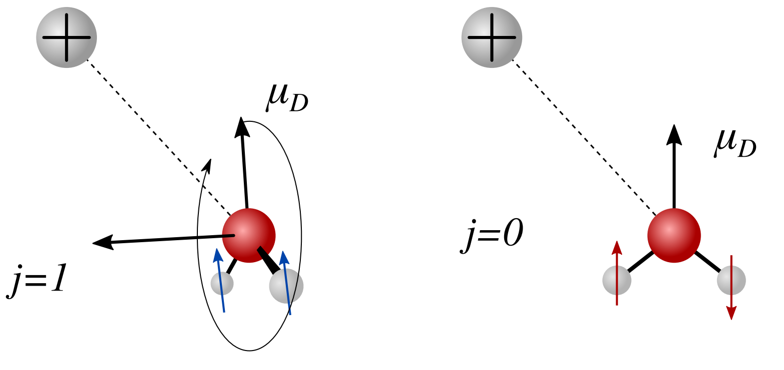
- **Long-range interaction potential:**



$$V(R,\beta) = -\frac{\alpha q^2}{2R^4} - \frac{q\mu_D \cos\beta}{R^2}$$

charge-induced dipole

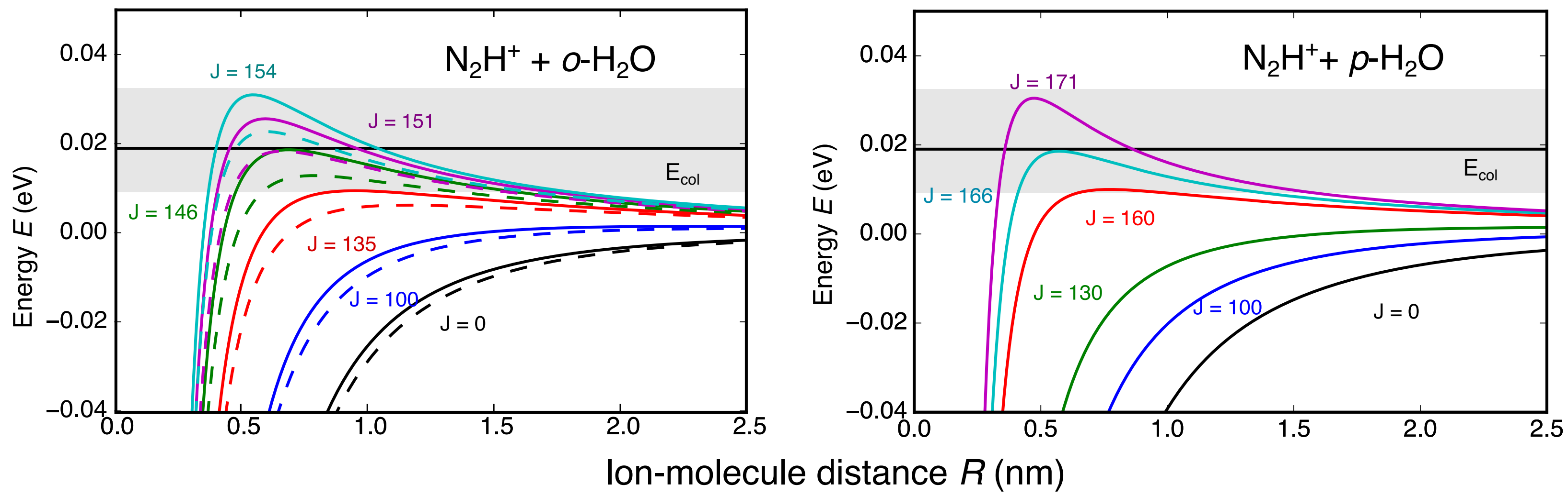
charge-permanent dipole



ortho-water

para-water

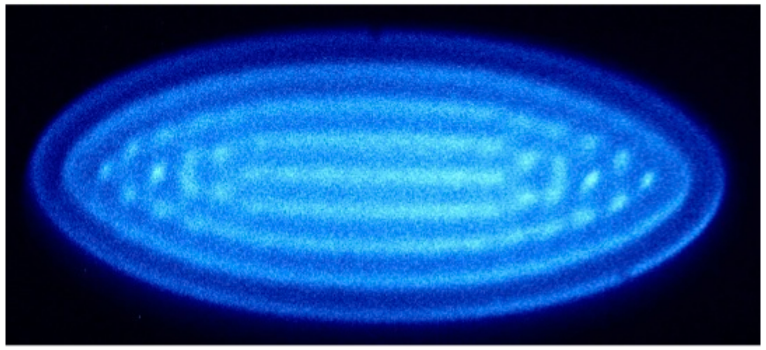
- **Centrifugally corrected rotationally adiabatic potentials for H_2O ($J_{K_aK_c}$) + N_2H^+**

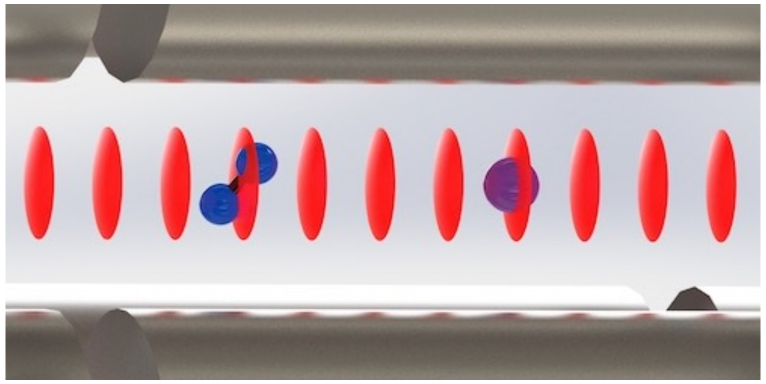


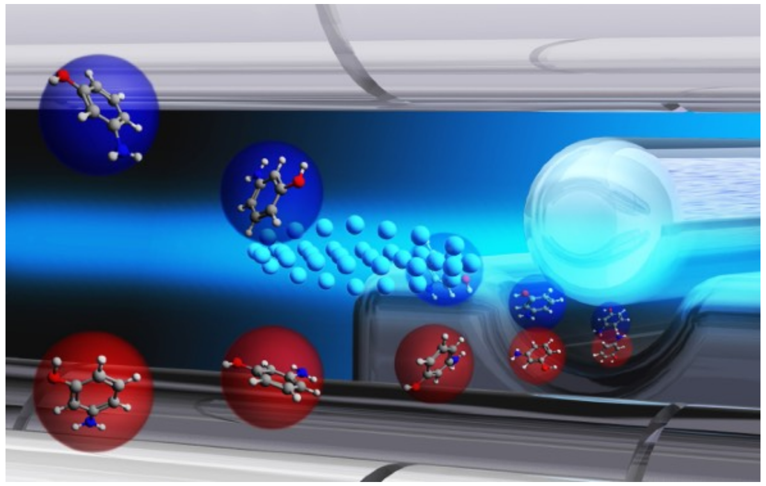
- **Relative difference of rate constant according to adiabatic capture theory: 24(5) % (expt.: 23(9) %)**

- **Conclusion: The difference is due to different rotational averaging of ion-dipole long-range interactions for the two nuclear-spin isomers.**

Summary







1. Cold molecular ions represent a versatile and powerful platform for performing highly controlled experiments on the single-particle level
2. Applications range from molecular quantum technologies over precision spectroscopy to accurate studies of chemical reaction mechanisms

Acknowledgements

Universität Basel SNI Swiss Nanoscience Institute Eine Initiative der Universität Basel und des Kantons Aargau Basel Quantum Center Swiss National Science Foundation COMOMET metrology with cold molecules