Sympathetic cooling of complex molecular ions to milli-Kelvin temperatures

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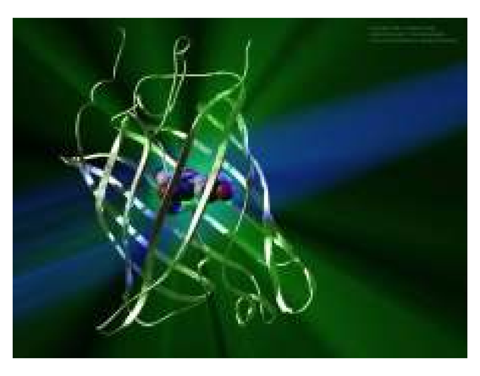
EC Network Ultracold Molecules

Motivation and goals

Sympathetic cooling of complex molecules

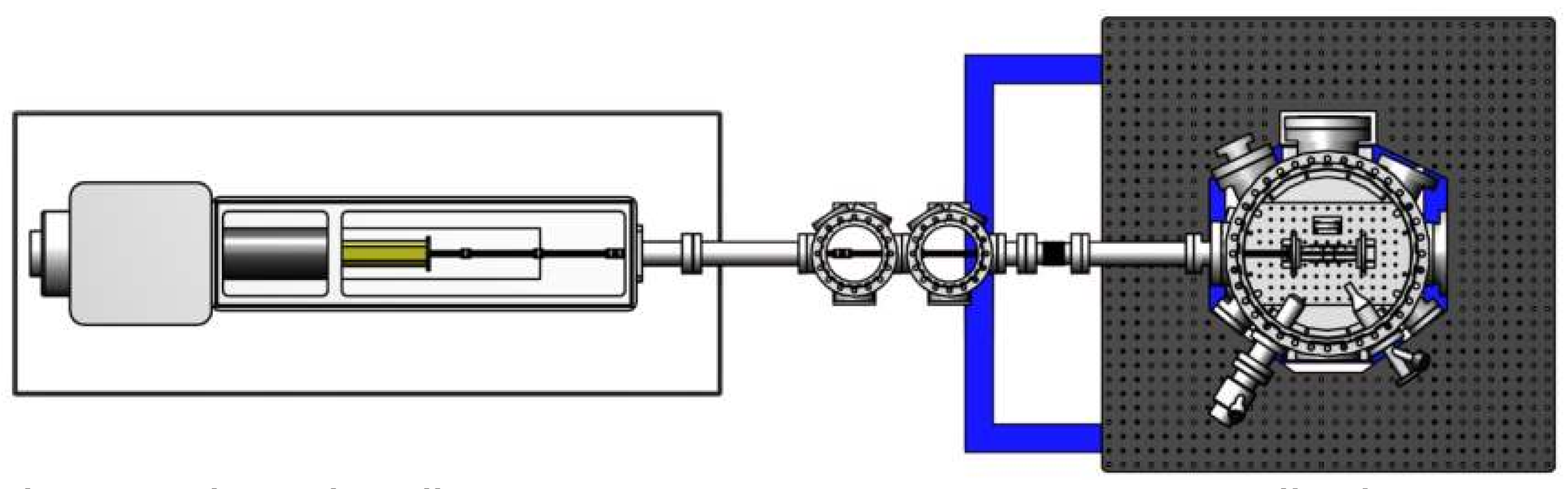
- ⇨ mass range up to 30 000 amu
- ⇨ interesting for chemistry and biology
- ⇨ general method for preparation, storage and cooling independent of:
  - magnetic and electrical moments
  - energy level structure
  - size of the molecule

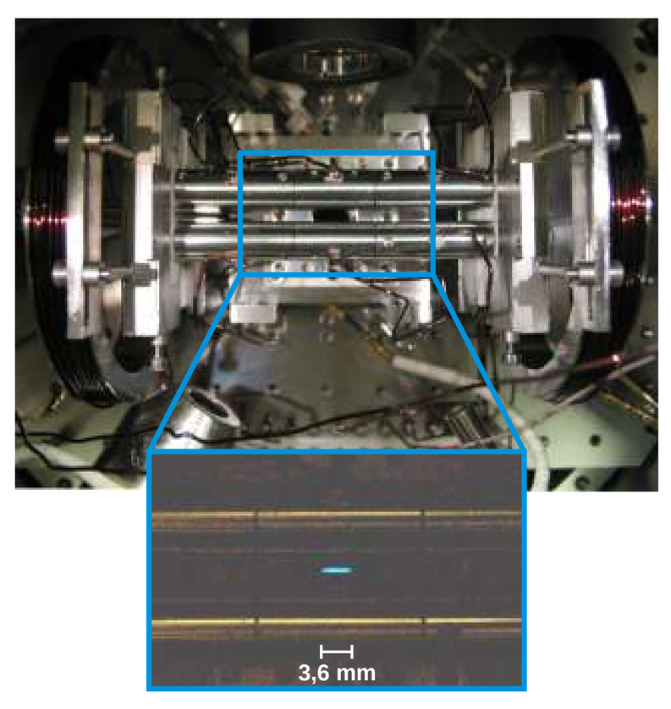


Applications

- ⇨ High resolution spectroscopy of ultracold molecules
- ⇨ Chemistry at ultracold temperatures
  - Charge transfer
  - Chemical reactions with single particle sensitivity
- ⇨ Cold collisions (e.g. with cold atoms)
- ⇨ Study of slow internal processes
- ⇨ Cooling of inner degrees of freedom
  - Anti-Stokes Raman cooling
  - "Molecular thermometer"
- ⇨ Generation of spectroscopically relevant diatomic heteronuclear molecules (e.g. ArH^+)
- ⇨ Parity violation in molecules

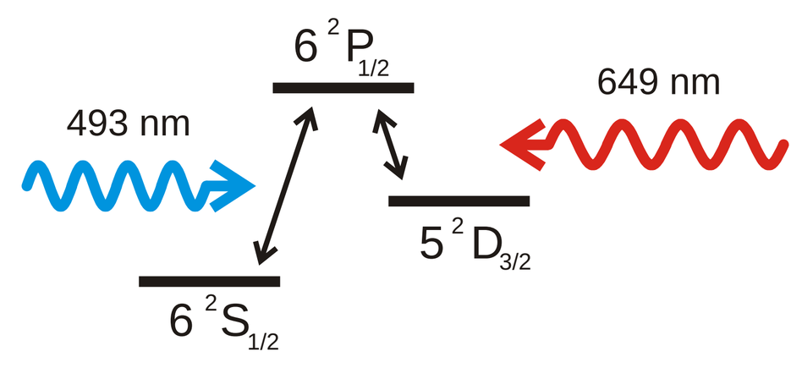
Experimental setup



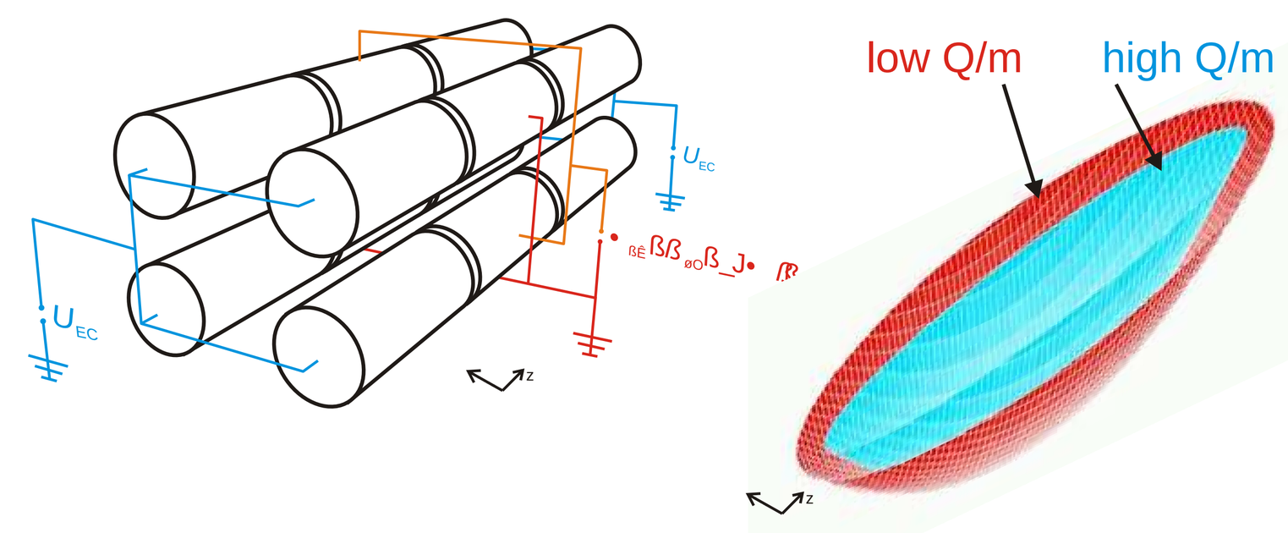


- ⇨ **ESI source for molecular ions covering a wide mass range**
- ⇨ **Molecular ion transfer with octopole ion guide (2 m long)**
- ⇨ **Storage in a linear RF trap (linear Paul trap)**
- ⇨ **Sympathetic (indirect) cooling of the molecular ions by (directly) laser cooled atomic ions**

Laser cooling transitions of $^{138}Ba^+$



Trap configuration and potential



Advantages of the linear RF trap

- storage of large numbers of ions
- vanishing micromotion on trap-axis
- large interaction volume
- good optical access

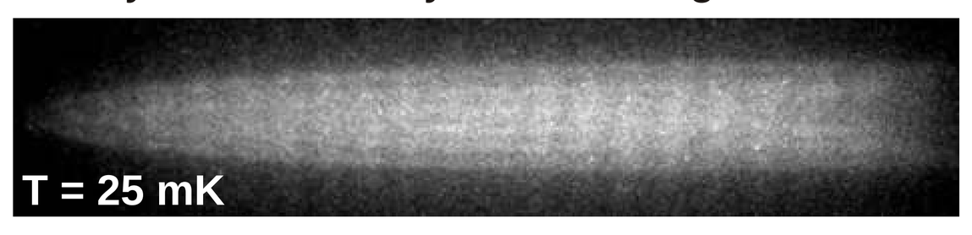
Sympathetic cooling of singly-protonated Alexa Flour 350

1. Loading of $AF350^+$ ions:

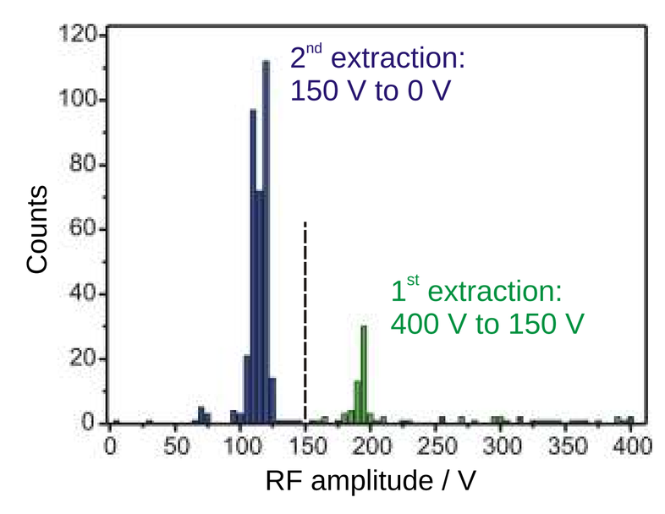
1.1 Injection of He buffer gas (1 10^{-4} mbar)
1.2 Loading of $AF350^+$ ions (6 s)
1.3 Removal of the buffer gas

2. Loading and crystallization of Ba^+ ions:

Ba crystal heated by surrounding AF350+ ions

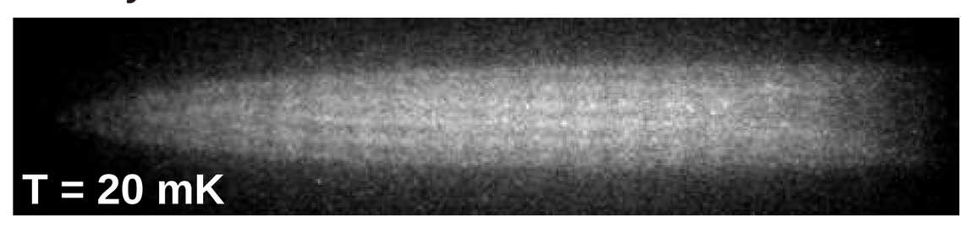


3. Removal of the $AF350^+$ ions:



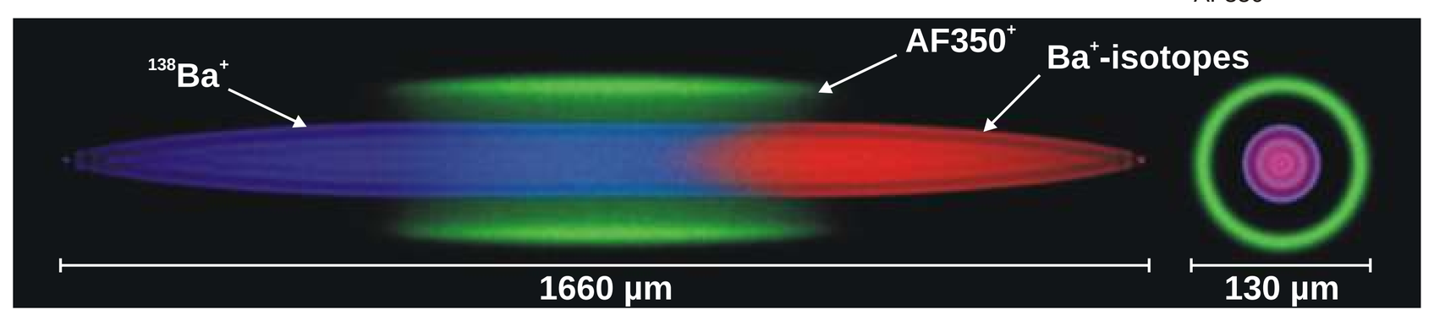
4. After the removal of the $AF350^+$ ions:

Ba crystal cools down



5. Simulation:

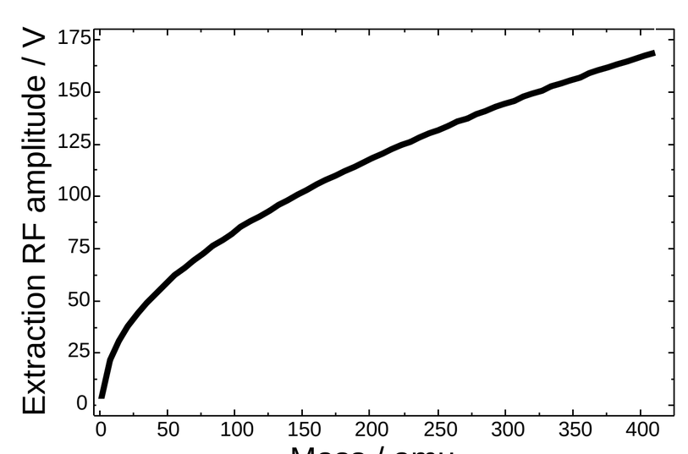
830 $^{138}Ba^+$ ions
420 Ba^+ isotopes
200 $AF350^+$ ions
T_{AF350} = 120 mK

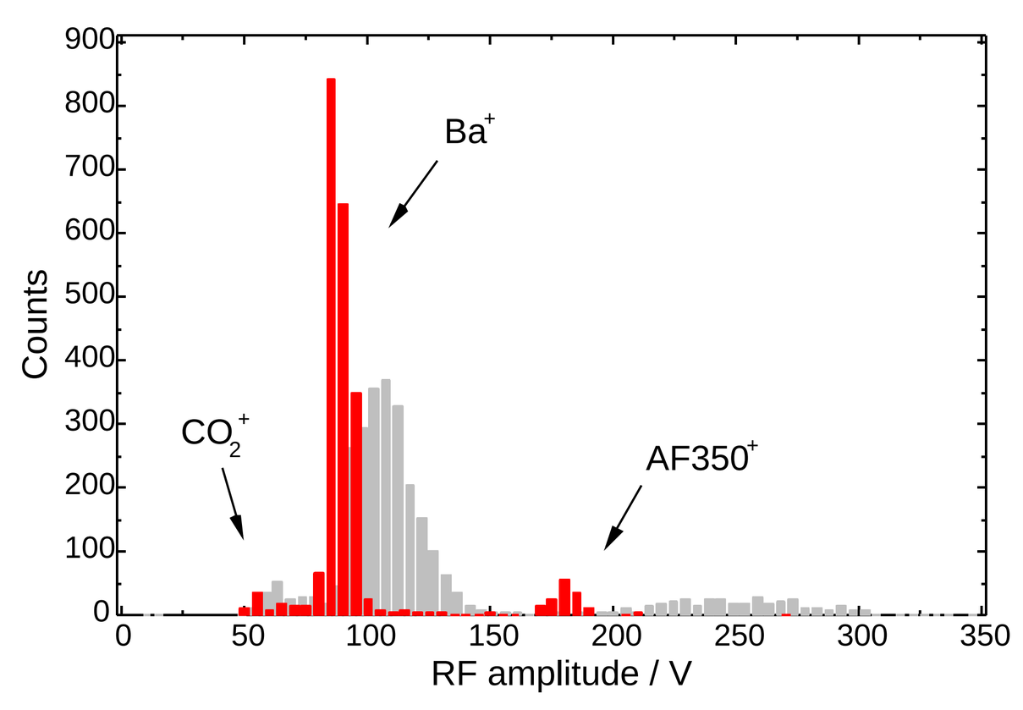


Ion extraction spectra

Ion extraction spectra by lowering of RF trap voltage:

lowering of trap potential depth
heavy and hot ions escape first



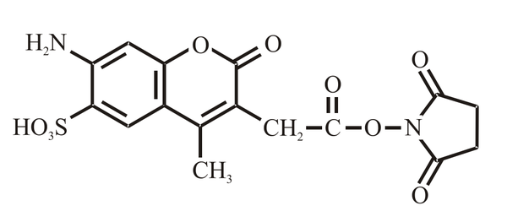


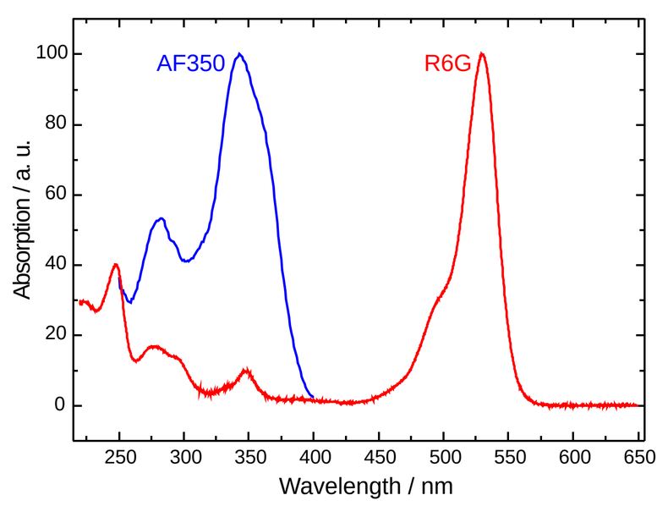
- ⇨ **Ion extraction spectra provide information about ion temperatures**
- ⇨ **Narrowed peaks as evidence of sympathetic cooling**

Photo fragmentation of dye molecules

Alexa Fluor 350

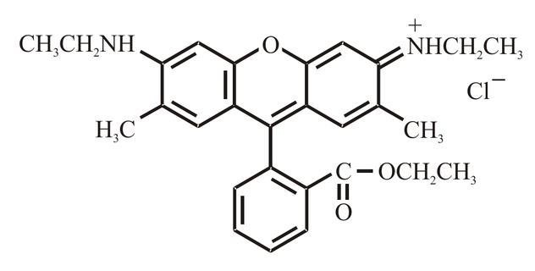
m = 410 amu

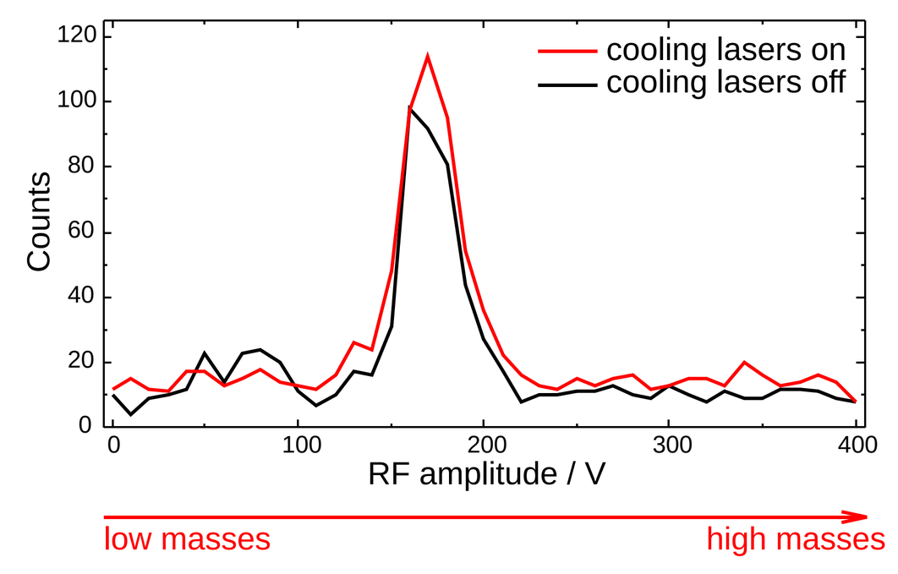


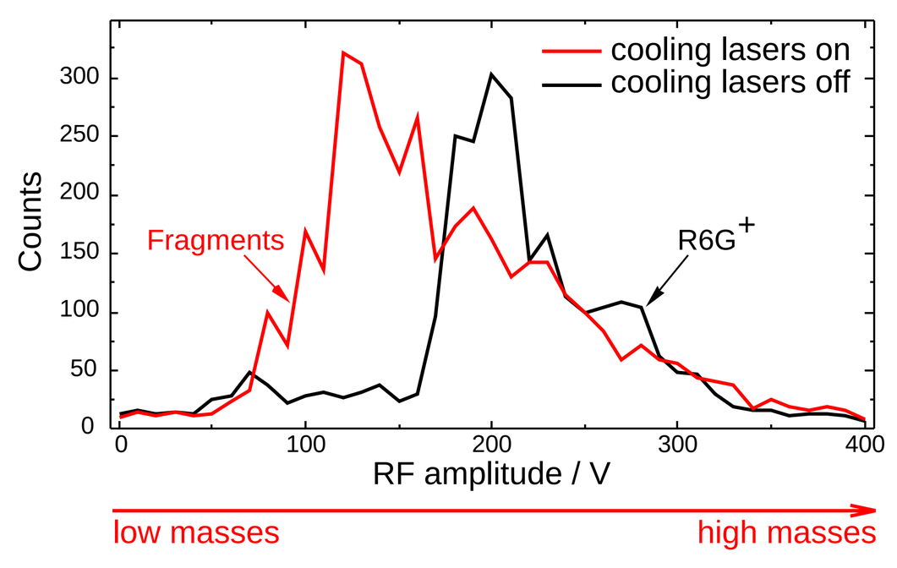


Rhodamine 6G

m = 479 amu



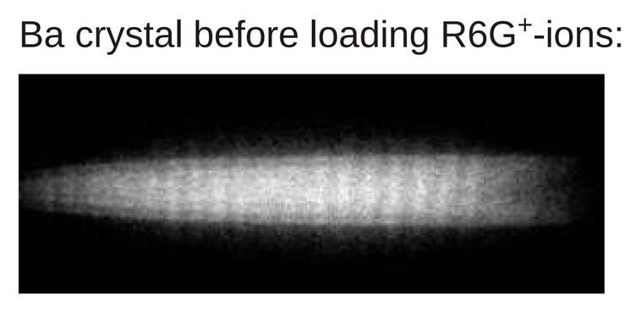




- ⇨ **Cooling laser light (493 nm <=> 2.5 eV) can cause photo fragmentation of trapped molecular ions**
- ⇨ **Mass selective ion extractions show photo fragmentation of Rhodamine 6G and 101**
- ⇨ **Alexa Flour 350 shows no fragmentation**

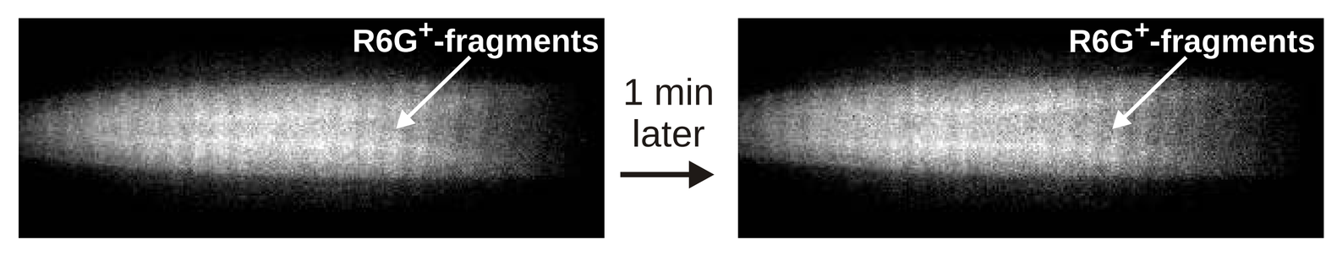
Real time observation of photo fragmentation

Ba crystal before loading $R6G^+$-ions:

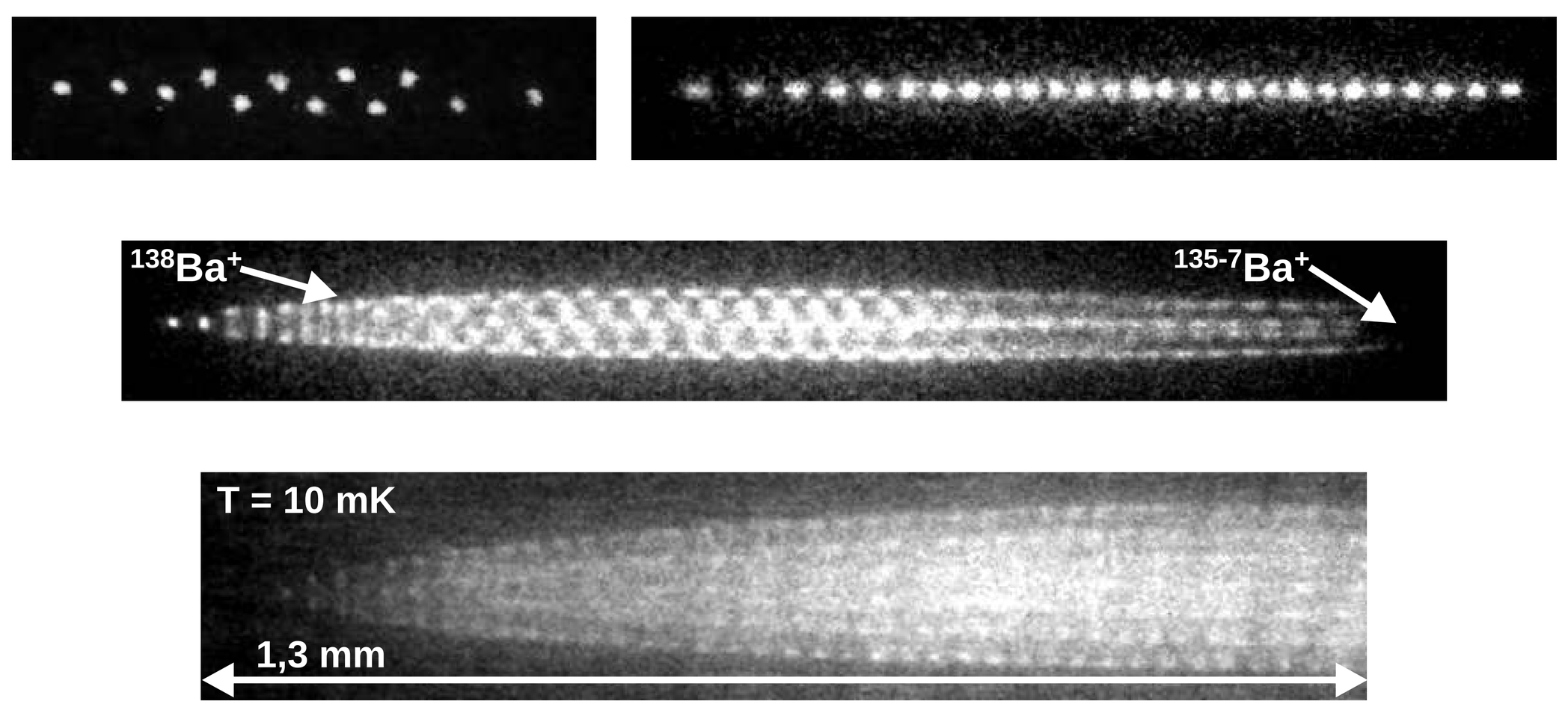


- ⇨ Fragments lighter than Barium accumulate in the center of the Barium crystal
- ⇨ Process of photo fragmentation can be observed in real time with a CCD camera

Ba crystal after loading $R6G^+$-ions:



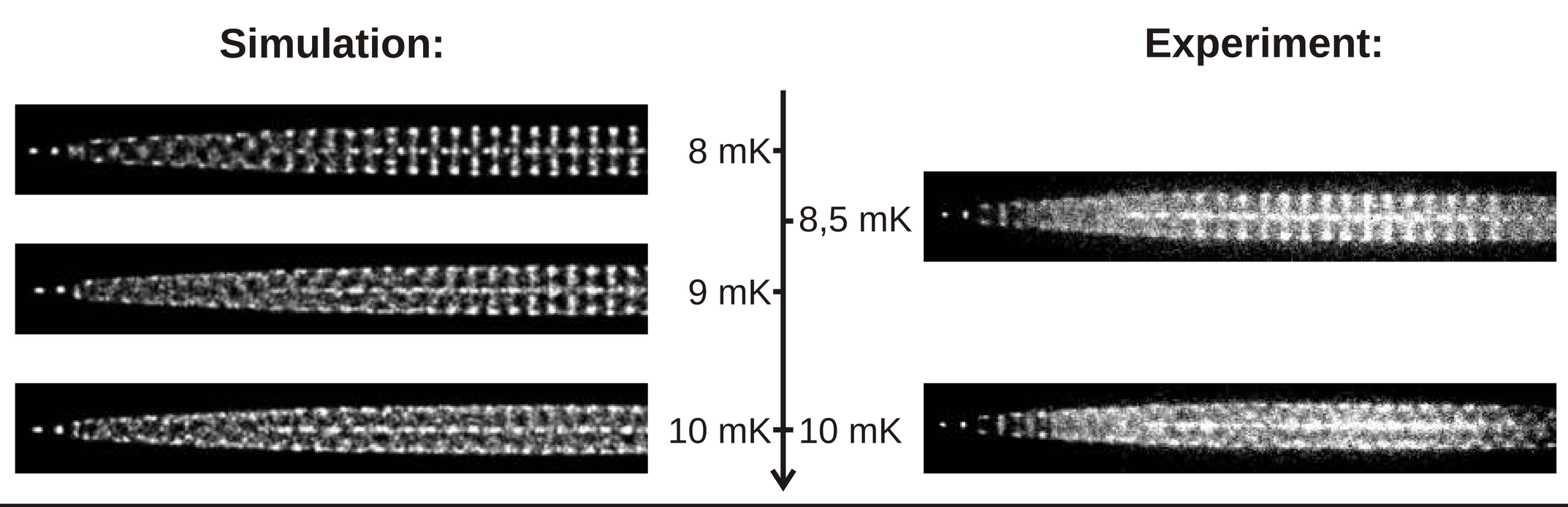
Barium Coulomb crystals



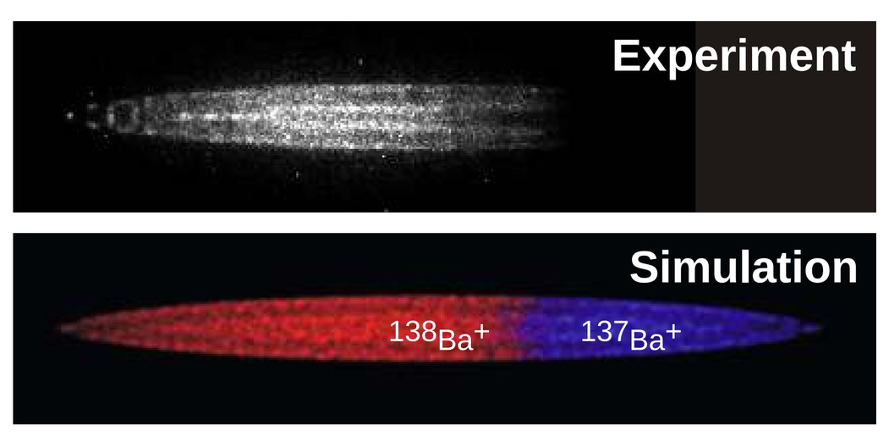
- ⇨ **Reliable production of Ba^+ Coulomb crystals**
- ⇨ **Various sizes and shapes**
- ⇨ **Long storage times (several hours)**
- ⇨ **Negligible trap losses**

Molecular Dynamics simulations

Determination of temperature



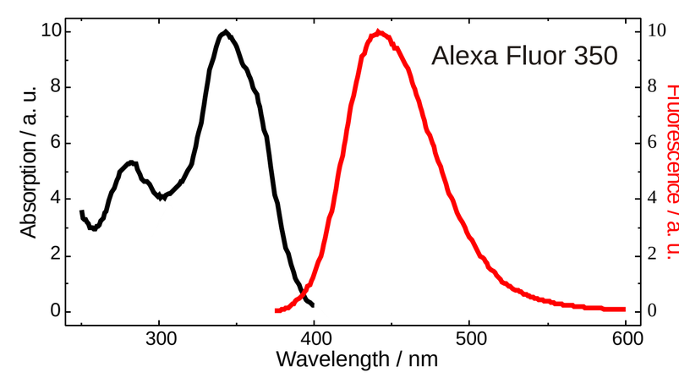
Barium crystal structure



- ⇨ **Prediction of crystal structures**
- ⇨ **Explanation of isotope separation for Barium**
- ⇨ **Estimate of ion numbers**
- ⇨ **Upper limit for translational temperature**

Current work / Next steps

- ⇨ **Molecular dynamics simulations**
  - Simulation of rf-heating in time-varying electric fields
  - Simulation of heating and cooling rates in large (up to 1000 ions) multi-species Coulomb crystals
- ⇨ **Fluorescence excitation and detection of sympathetically cooled $AF350^+$ ions**
  - Using UV lasers (266 and 313 nm)



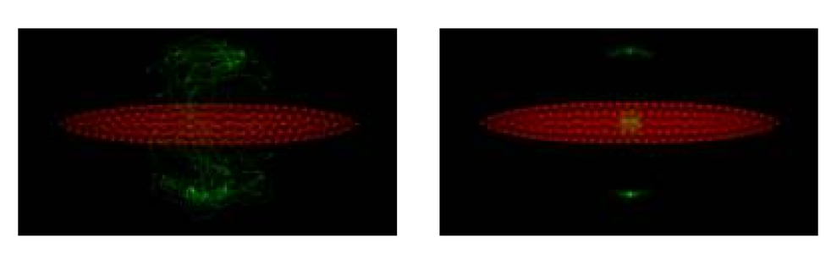
Fluorescence of AF350 in solution excited by 266 nm light

- ⇨ **Spectroscopy of ultracold complex molecules**
- ⇨ **Exploring high mass range of cooling and trapping**
  - e. g. $DsRed^{n+}$ or GFP^{n+}

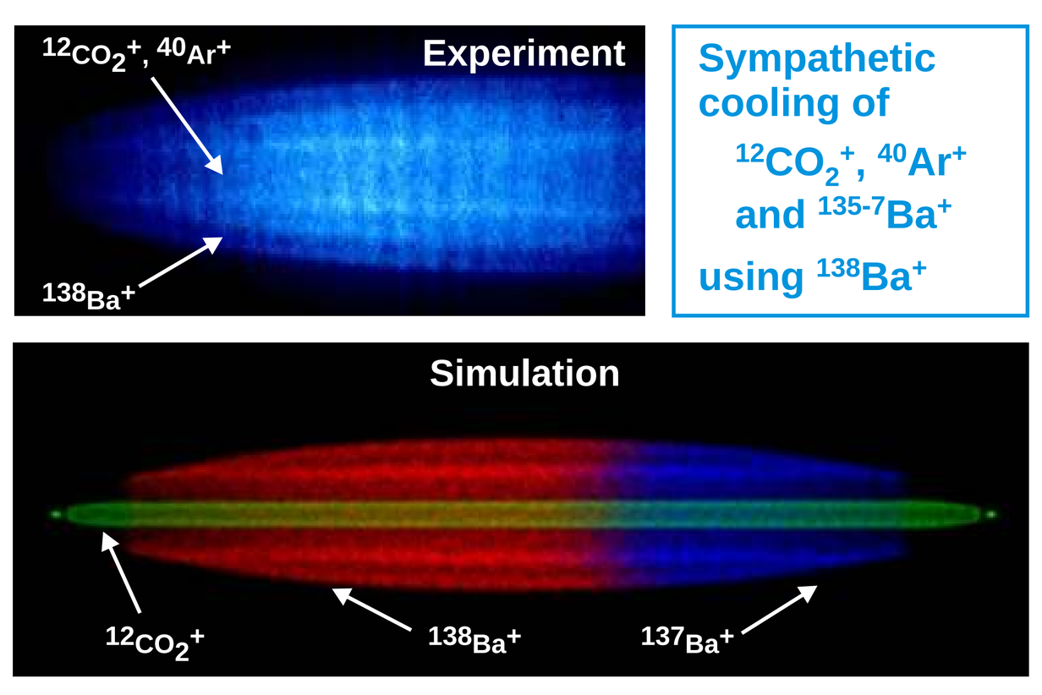
Simulation of sympathetic cooling of proteins:

500 $^{138}Ba^+$ and 4 complex molecules (mass 20.000, charge 20)

towards lower temperature

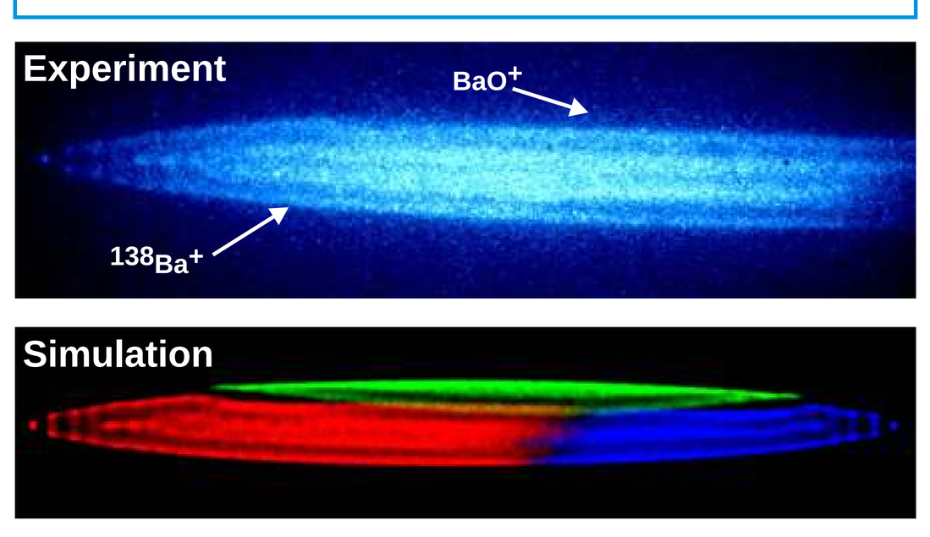


Sympathetic cooling of other molecular ions

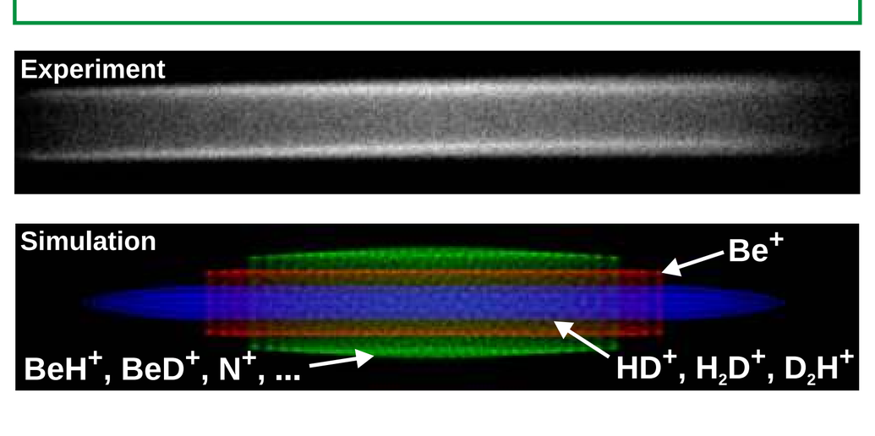


Sympathetic cooling of $^{12}CO_2^+$, $^{40}Ar^+$ and $^{135-7}Ba^+$ using $^{138}Ba^+$

Sympathetic cooling of impurity ions



Sympathetic cooling of various ions using $^9Be^+$



- ⇨ **Simple atomic and molecular ions embedded in Coulomb crystals:**
  - **Ba^+:** O_2^+, Ar^+, CO_2^+, Kr^+, BaO^+
  - **Be^+:** p^+, H_2^+, HD^+, H_3^+, He^+, Ne^+, ArH^+ ...
- ⇨ **Complex molecular ions embedded:**
  - $C_4F_8^+$, Rhodamine 6G and 101, MRFA, Alexa Fluor 350 and their fragments
- ⇨ **Largest mass ratio between laser cooled and sympathically cooled ion species: 20.2**

Rovibrational spectroscopy of ultracold HD^+

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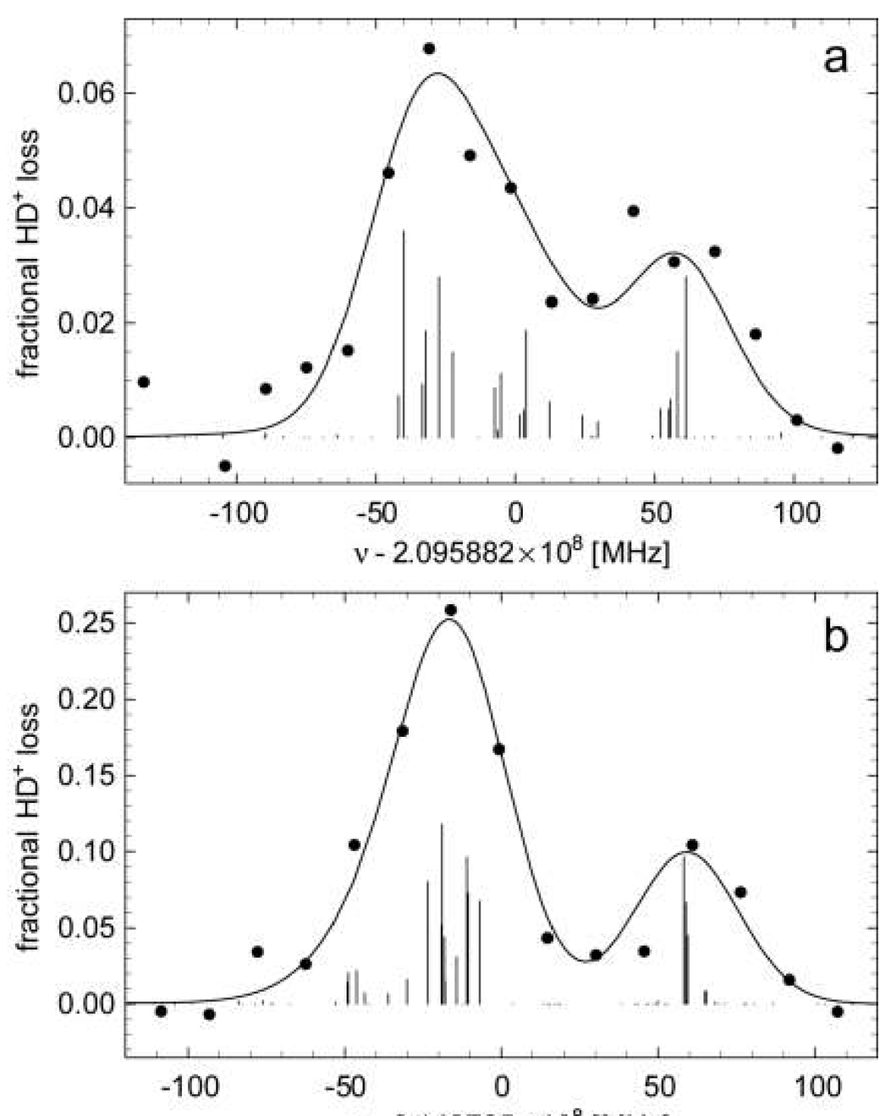
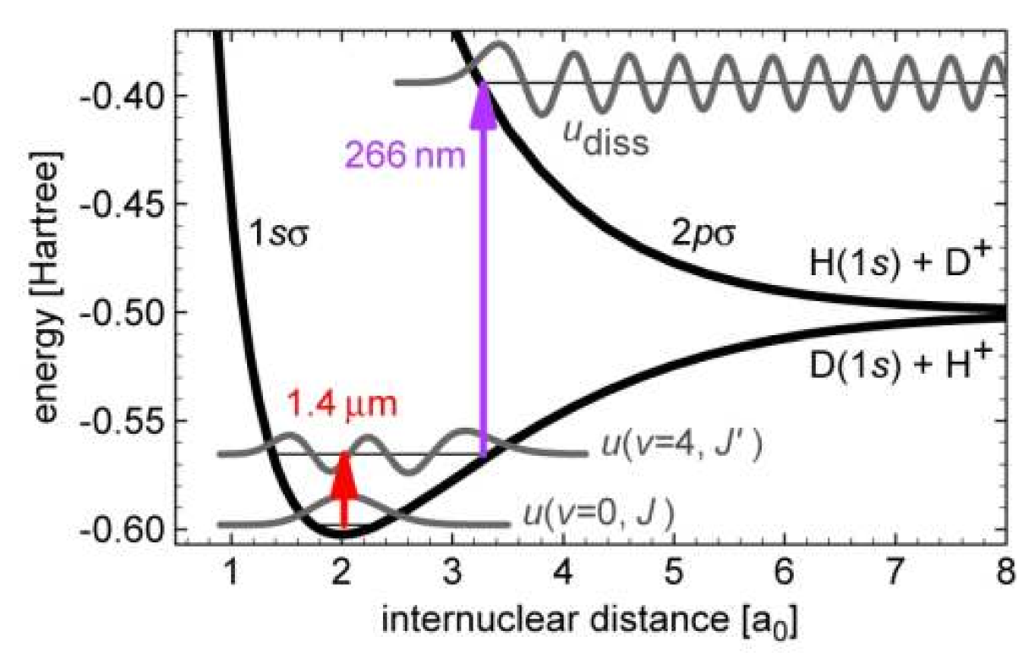


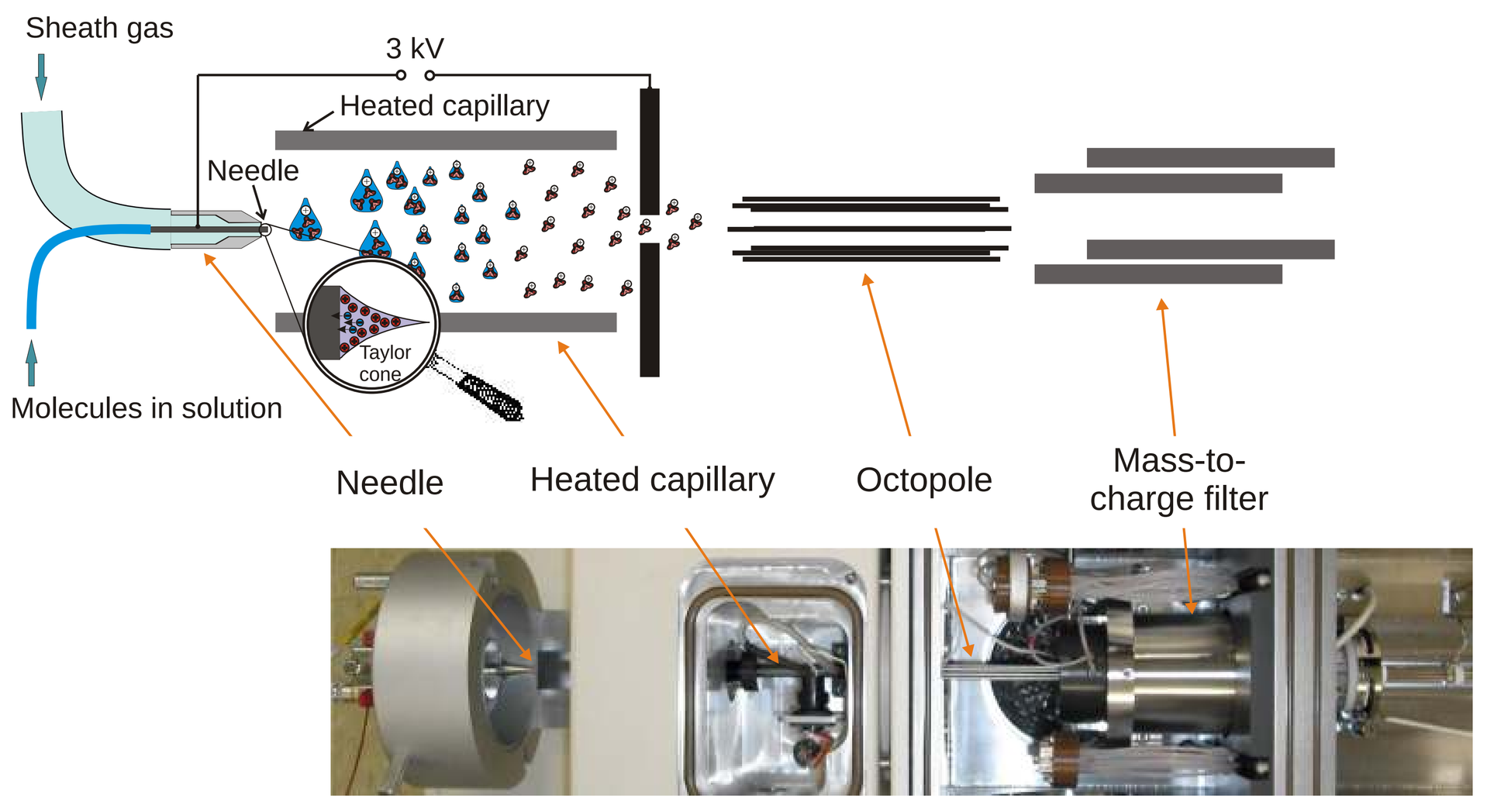


Scheme of REMPD spectroscopy

- ⇨ **Measurement of the HD^+ loss as function of the IR excitation frequency**
- ⇨ **HFS partly resolved**

Electrospray Ionization (ESI)

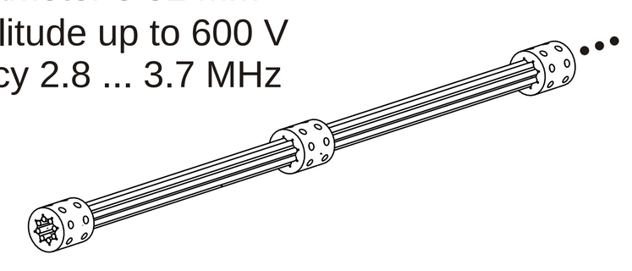
- ⇨ **Electrospray Ionization (ESI) is suitable for transferring complex (large) molecules into the gasphase**
- ⇨ **ESI is a "soft" method for ionization of complex molecules**
- ⇨ß»ŠRÐÆýÅ¶3ò°ƒ[KÜÍÃA¾<,àÜ¼hc^?ë|'³"? À ß‡ƒ~yuVQün ß(úêÛË½**essential for sympathetic cooling and crystallization of heavy molecules**



Ion transfer using RF ion guides

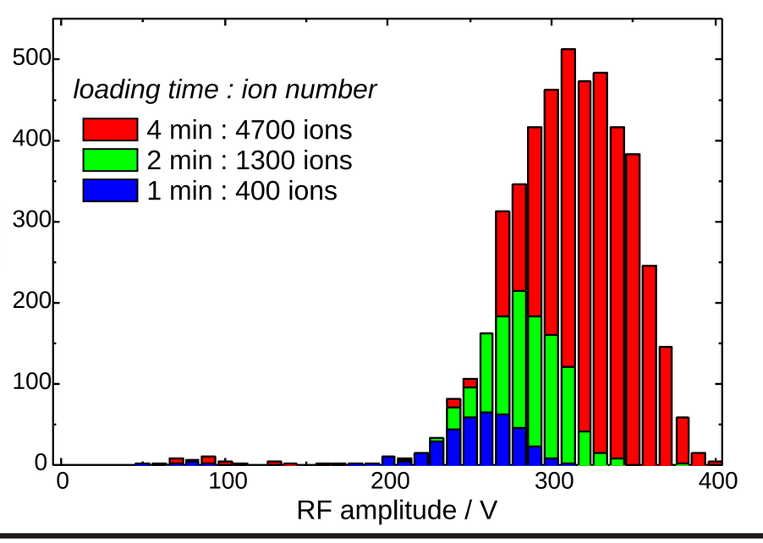
RF octopole

- **Operational parameters:**
  electrodes-diameter 1.6 mm
  inner diameter 5.52 mm
  RF amplitude up to 600 V
  frequency 2.8 ... 3.7 MHz

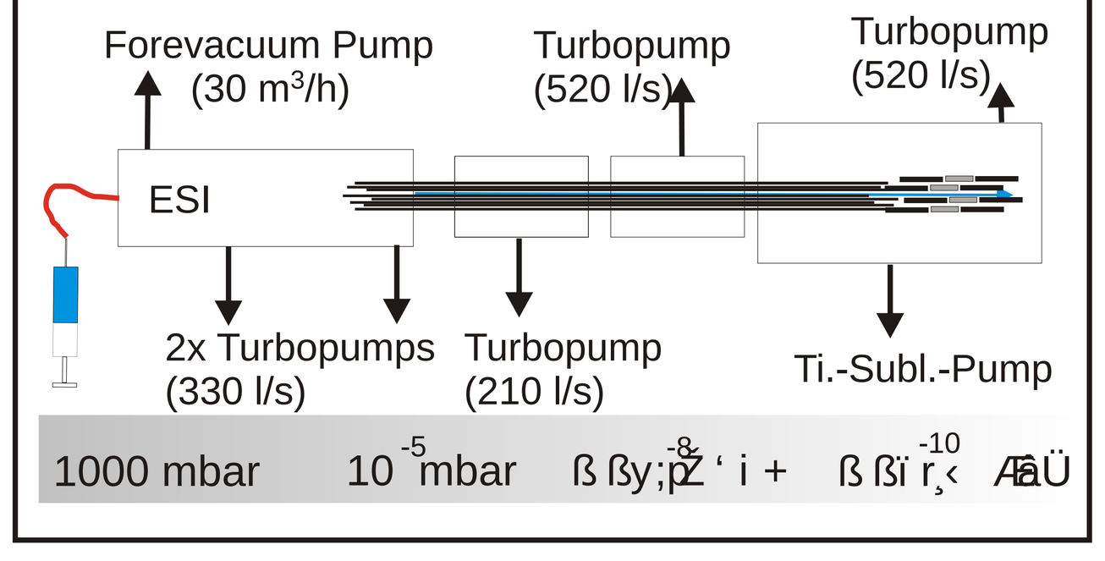


- **Achieved transfer rate:** up to 40 %
- **Ion flux:** up to 100 000 ions/sec

Transfer efficiency



Differential vacuum system



Under investigation:

transfer of further complex molecular ion species

e. g. $DsRed^{n+}$

References

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