Studying chemistry using trapped ions

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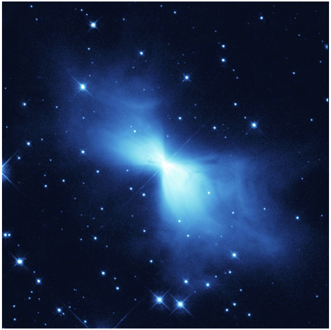
Why do we bother to study them

- Astrochemical motivation:
  - Temperature in pre-stellar cores as low as 10 K. Even 1 K in runaway nebulae.
  - Ionising radiation → Generation of hydrocarbons by ion-molecule reactions.
  - Complex molecules → loss of kinetic energy by radiation

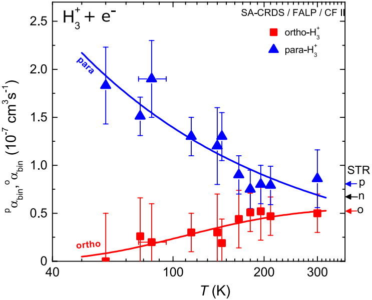


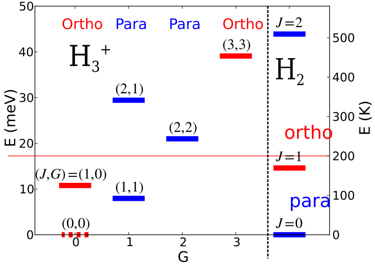
Boomerang nebula taken by Hubble Space Telescope

Cold chemistry – trihydrogen cation-electron recombination

Influence of rotational and nuclear spin states – Pathway from chemical kinetics to chemical dynamics

rate coefficient $\dot{n}_A = -k n_A n_B$





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Hejduk et al., J. Chem. Phys 143 (4), 2015

- Efficient capture of electron at low temperatures
- Thermal averaging at high temperatures
- ortho-H_3^+: Internal dynamics suppresses the recombination at low temperatures

Cold chemistry – trihydrogen cation-electron recombination

Influence of rotational and nuclear spin states – Pathway from chemical kinetics to chemical dynamics

rate coefficient $\dot{n}_{\mathrm{A}} = -k n_{\mathrm{A}} n_{\mathrm{B}}$

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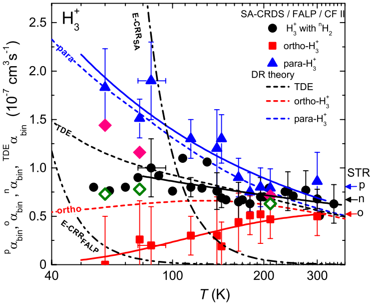

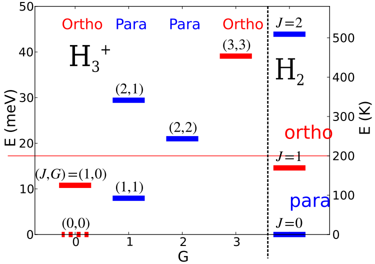

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Hejduk et al., J. Chem. Phys 143 (4), 2015

- High densities: many processes involved
  - $H_3^+ + e \rightarrow$ neutral products
  - $H_3^+ + e + He \rightarrow$ neutral products $+$ He
  - $H_3^+ + e + e \rightarrow$ neutral products $+$ e
- Separation not always easy.

Cold chemistry - enhanced sensitivity using traps

Influence of rotational and nuclear spin states

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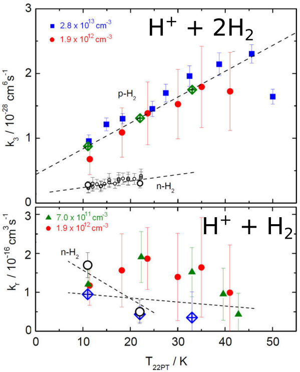
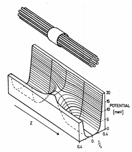
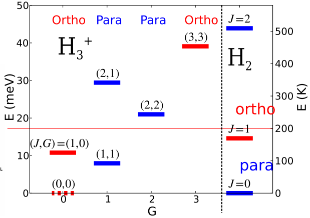
$$\mathrm{H}^+ + \text{para/ortho-}\mathrm{H}_2 \rightarrow \mathrm{H}_3^+$$



D. Gerlich, et al., J. Phys. Chem. A, 117 (39), 2013





- three body process: para-hydrogen clusters grow faster at higher temperatures?!
- two body process: no significant difference visible because of sensitivity

Chemistry in the ultra-cold regime

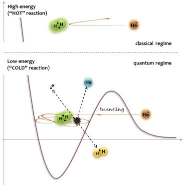
Cold chemistry in traps

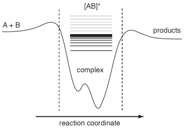
We have

- Reduced thermal averaging. Only few states.
- Low concentrations but enhanced sensitivity

Quantum mechanical effects

- State-selectivity
- Symmetry restrictions





Ultra-cold chemistry

- No thermal averaging. Only specified states.
- Even lower concentrations and higher sensitivity

Quantum mechanical effects

- Tunnelling through (reflection at) centrifugal barrier
- $\Rightarrow$ Resonances
- Stabilisation of intermediates

Ion trap for ultra-cold chemistry

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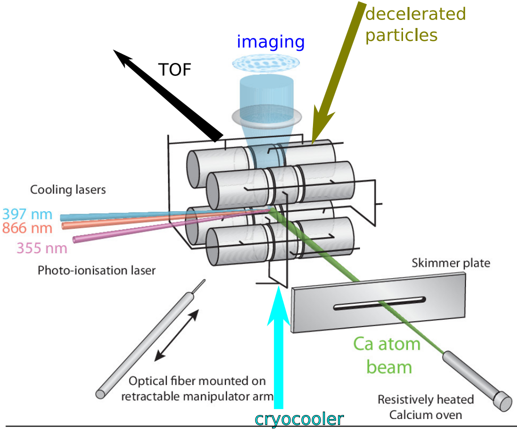
Congestion of beams



Requirements

- Introduction of slow reactants
- Cooling of molecular ions
- Mass analysis

Coulomb crystals

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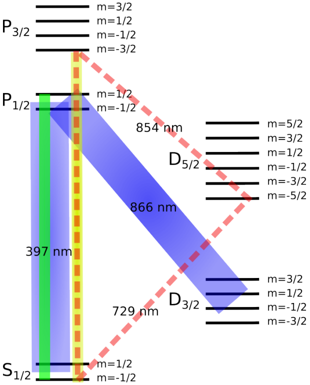
- Plasma coupling parameter
  $\Gamma = \frac{1}{4\pi\epsilon_0}\frac{q^2}{ak_B T} > 160$
- T given by cooling technique:
  - Doppler cooling limit
    $T_D = \frac{\hbar\gamma}{2k_B} = 0.5\,\text{mK}$ for Ca^+
  - Resolved sideband cooling, EIT etc.: to motional ground state of the trapping potential.
- With Doppler cooling $a < \lambda_{dB} \rightarrow$ no correlation
- Made in UHV environment



Wikipedia - Resolved Sideband cooling

Sympathetic cooling

How to decrease kinetic temperature of molecular ions

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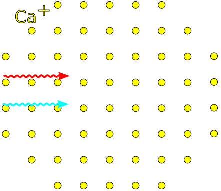
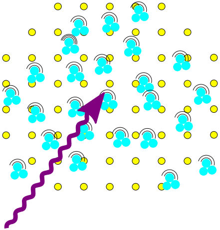
1.



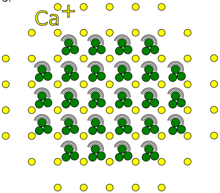
Laser cooling

2.



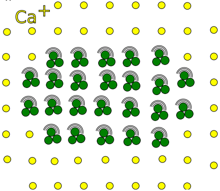
Generation of molecular ions

3.



Coulomb interaction

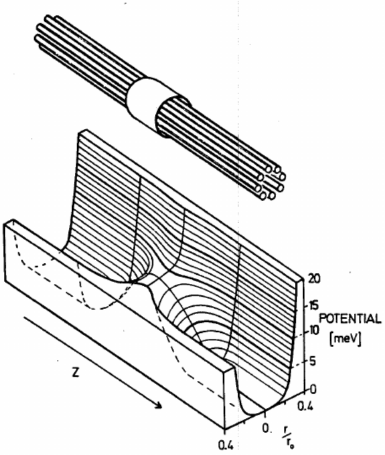
4.



Redistribution

Linear radio-frequency ion traps

- Alternating field $\Phi(r,\varphi) = V_0\cos(\Omega t)\left(\frac{r}{R}\right)^n \cos n\varphi +$ offset
- Effective potential $\frac{n^2}{4}\frac{q^2}{m\Omega^2}\frac{V_0^2}{R^2}\left(\frac{r}{R}\right)^{2n-2}$
- Axial confinement $q\kappa U_0\left[z^2 - \frac{1}{2}r^2\right]$



D. Gerlich, Inhomogeneous RF Fields... (1992)

Practical realisation
$Xe^+ + NH_3/ND_3 \to Xe + NH_3^+/ND_3^+$ charge exchange reaction

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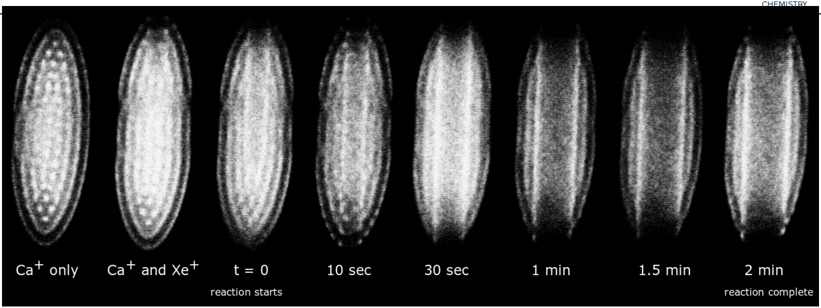

Light masses $\to$ tightly confined $\left(V^* = \frac{q^2}{m\Omega^2}\frac{V_0^2}{R^2}\left(\frac{r}{R}\right)^2\right)$ $\to$ dark core

Ammonia leaked in, $300 k_B$ K

Result

ND_3 reacts 3 times faster than NH_3

Combination of Zeeman deceleration and ion trapping

Our approach

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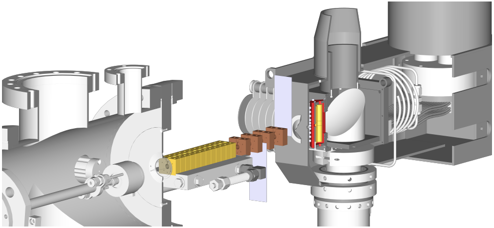


Zeeman decelerator

- relative velocity of reactants $\approx x \times 10\,\mathrm{m/s},\ x \in (0, 30\rangle$

Ion trap

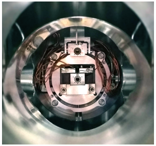
- Kinetic temperature down to several K
- Rovibrational temperatures lower than 10 K

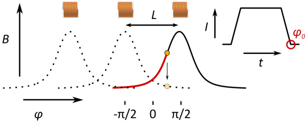
Degeneracy removed only in presence of magnetic field $\rightarrow$ possibility of state selective studies

Zeeman decleration and velocity filtering

Generation of slow neutrals - results

Deceleration:





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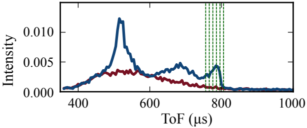
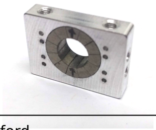
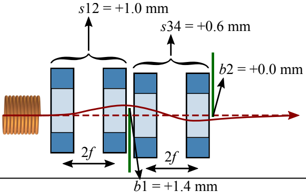


Velocity filtering:





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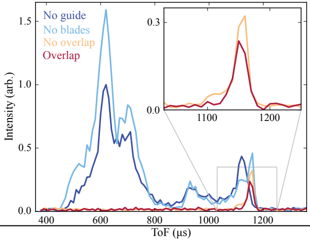
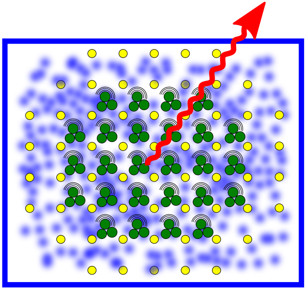


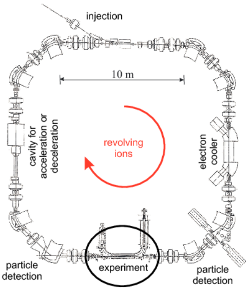
Spontaneous rovibrational cooling can take from ms to ∞ s

- Walls need to be cooled to avoid radiative heating
- Appropriate buffer gas is needed for cooling



10 K

Storage ring



This did not work with H_3^+

Where are the electrons?

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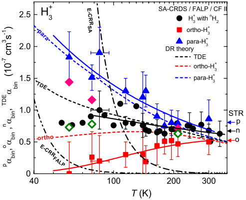
- Cores of white dwarfs and neutron star crusts: nuclear CC with degenerate electron gas
- Surface of helium droplet: Wigner crystal of electrons

Questions

- Can we make CC with electrons in the laboratory?
- Can we crystalise electrons?



In order to

- study many body electron-ion recombinations (e-e-i, e-i-i);
- construct models of solid-state matters;
- construct classical-quantum hybrid systems (S. Kotler et al. Phys. Rev. A 95 (2017) 022327).

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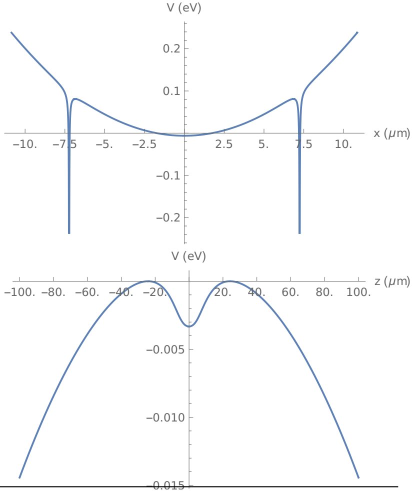
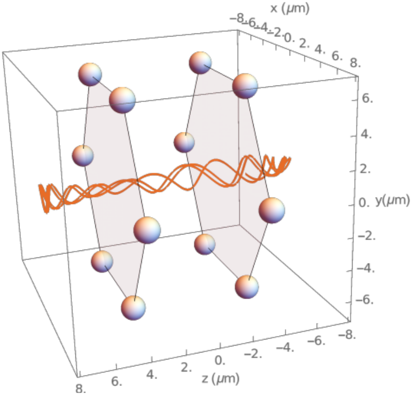
Procedure

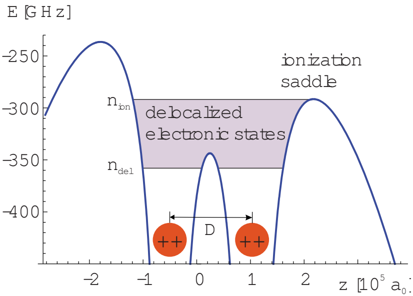
- Laser cooling of multiply charged ions (Th^{3+}, Y^{2+})
- Near-threshold photo-ionisation of trapped ion
- Electron capture in trapping fields
  - Radial direction: Effective potential of the trap
  - Axial direction: Coulomb potential of ions

C. Foot et al., *Int. J. Mass. Spec.* 430 (2018) 117–125



Motion of electron in the Coulomb crystal





I. Lesanovsky, M. Müller and P. Zoller, *Phys. Rev. A* 79(1) (2009) 010701

Thank you for your attention

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