Lecture 7: Gas Phase Experiments

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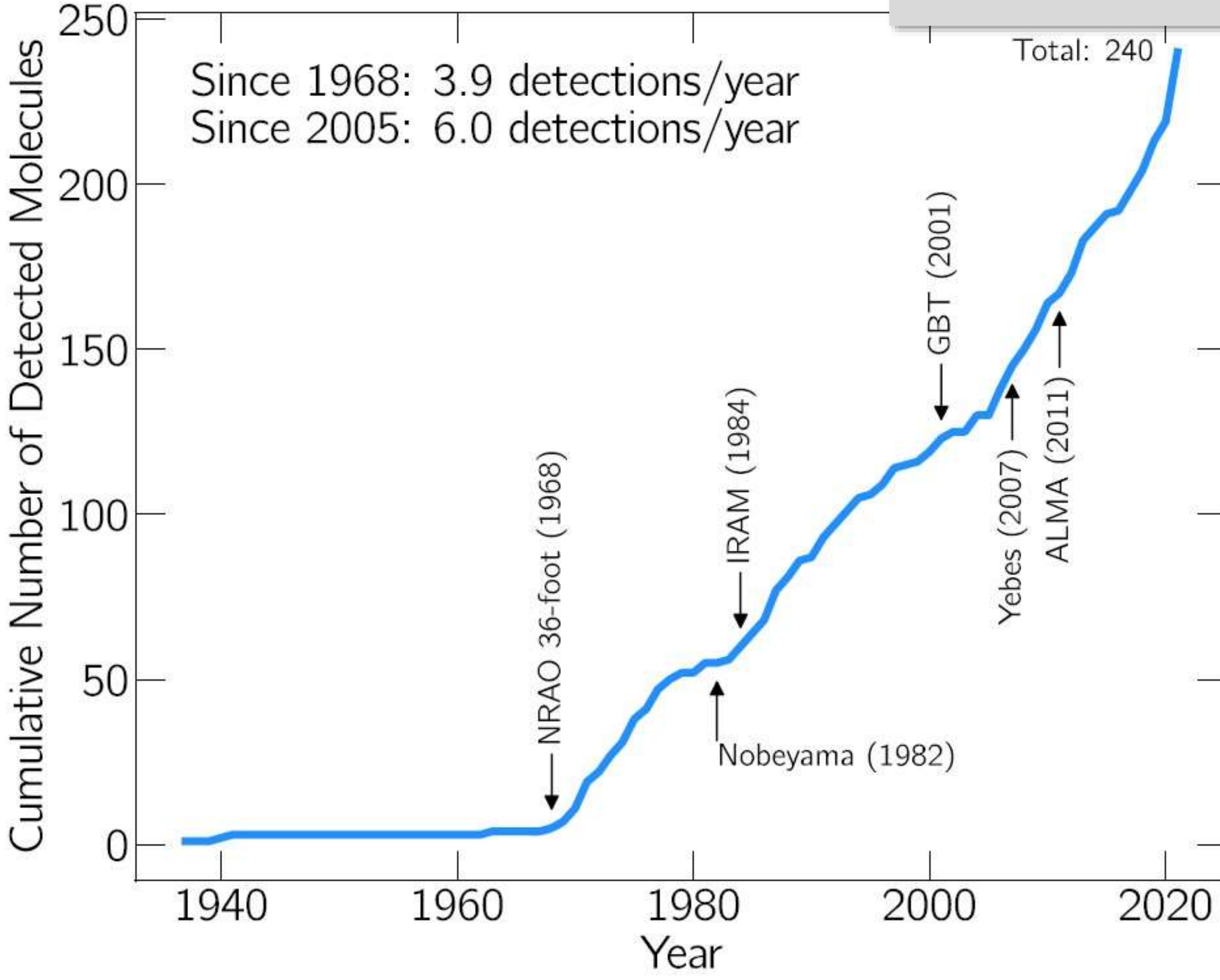
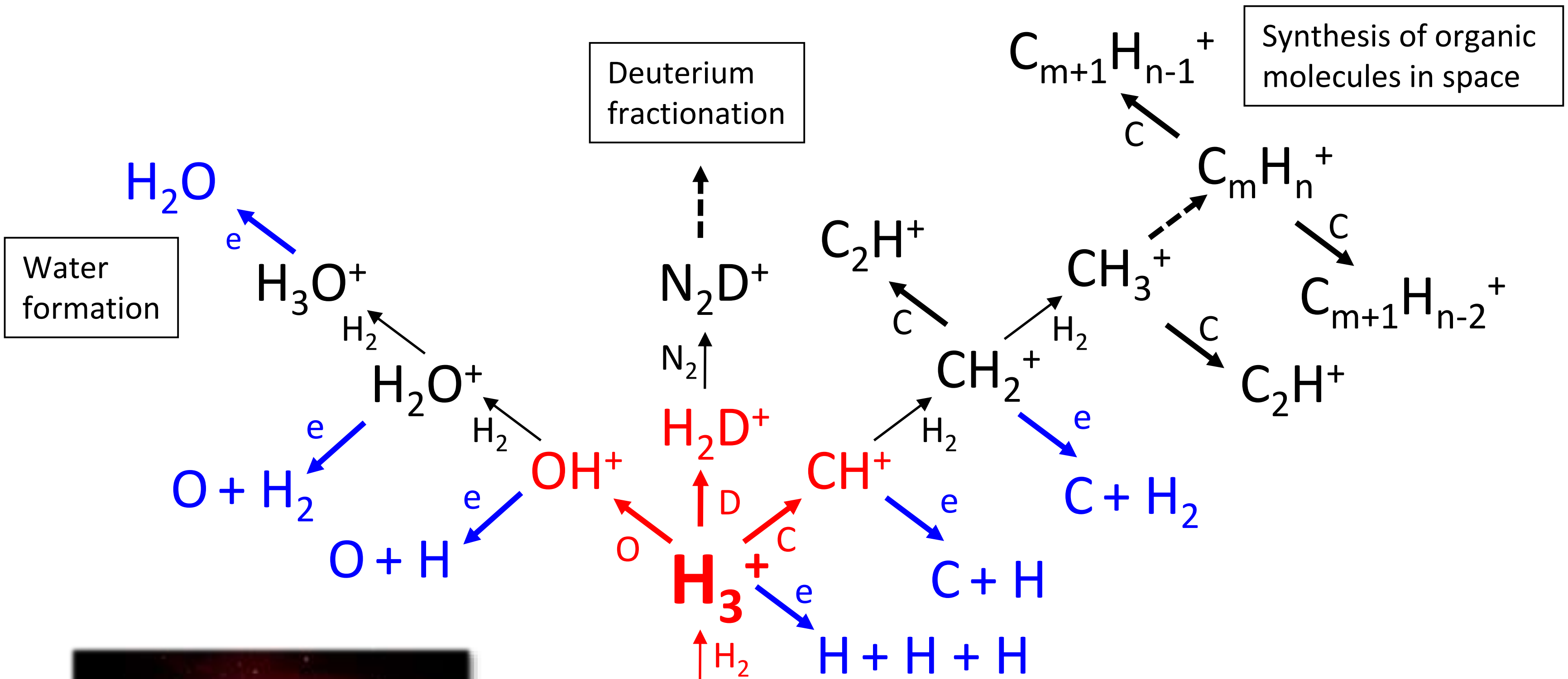
Recap: Molecules Everywhere!

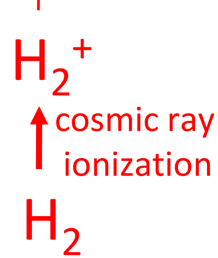
Almost 300 today!



McGuire, ApJS 259, 30 (51pp), 2022

Recap: Ion-Neutral Reactions drive Gas Phase Chemistry





Ion-neutral reactions

Competition

Dissociative electron Recombination (DR)

Different classes of reactions relevant for Interstellar Chemistry

Type of process	Example	Number in model
Gas-grain interactions	$H + H + grain \rightarrow H_2 + grain$	14
Direct cosmic ray processes	$H_2 + \zeta \rightarrow H_2^+ + e$	11
Cation-neutral reactions	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2933
Anion-neutral reactions	$C^- + NO \rightarrow CN^- + O$	11
Radiative associations (ion)	$C^+ + H_2 \rightarrow CH_2^+ + h\nu$	81
Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46
Chemi-ionization	$O + CH \rightarrow HCO^+ + e$	1
Neutral-neutral reactions	$C + C_2H_2 \rightarrow C_3\ H + H$	382
Radiative association (neutral)	$C + H_2 \rightarrow CH_2 + h\nu$	16
Dissociative recombination	$N_2H^+ + e \rightarrow N_2 + H$	539
Radiative recombination	$H_2CO^+ + e \rightarrow H_2CO + h\nu$	16
Anion-cation recombination	$HCO^+ + H^- \rightarrow H_2 + CO$	36
Electron attachment	$C_6H + e \rightarrow C_6H^- + h\nu$	4
External photo-processes[a]	$C_3N + h\nu \rightarrow C_2 + CN$	175
Internal photo-processes[a]	$CO + h\nu \rightarrow C + O$	192

Number of reactions of different types that are included in the OSU kinetic database (osu-09-2008)

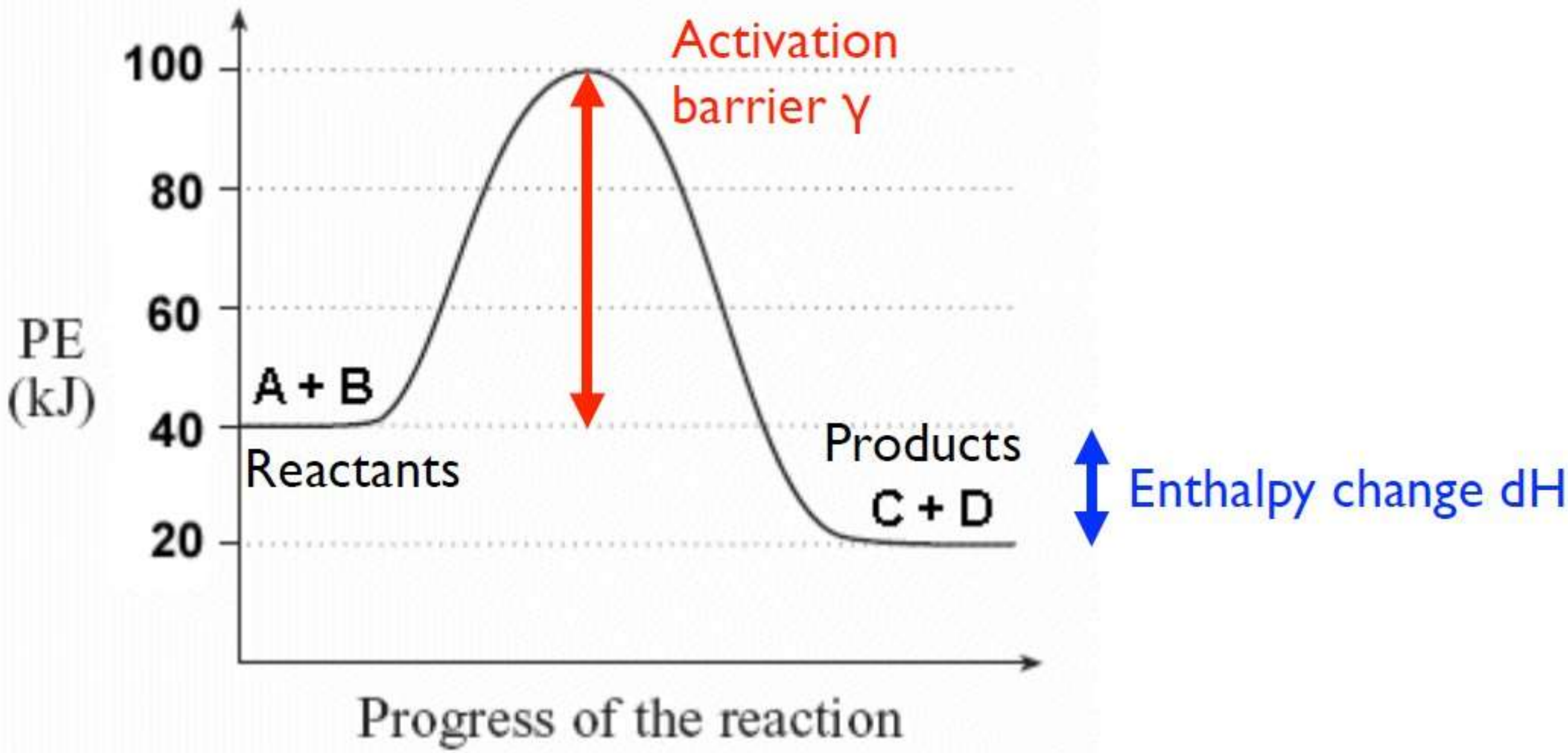
4500 reactions in total

In most reactions, charged particles are involved

I. Smith, Annu. Rev. Astron. Astrophys. **49**, 29 (2011)

Chemical potential energy (enthalpy)

Collision A + B ⇒ Activated complex AB^* ⇒ Stabilization ⇒ C + D



- Exothermic reaction: dH < 0 (energy is released)
- Endothermic reaction: dH > 0 (energy is absorbed)

General concepts: rate coefficient

Generic reaction: **A + B ⟶ C + D**

Example: $H_2 + O \rightarrow OH + \mathrm{H}$ ← $\boldsymbol{k = 9\ x\ 10^{-12}}$ **cm³ s⁻¹ at high temperature**

Rate coefficient [cm³ s⁻¹]

Product formation rate: $$\mathrm{R} = \frac{d\,n_C}{dt} = k(T)n_A n_B$$

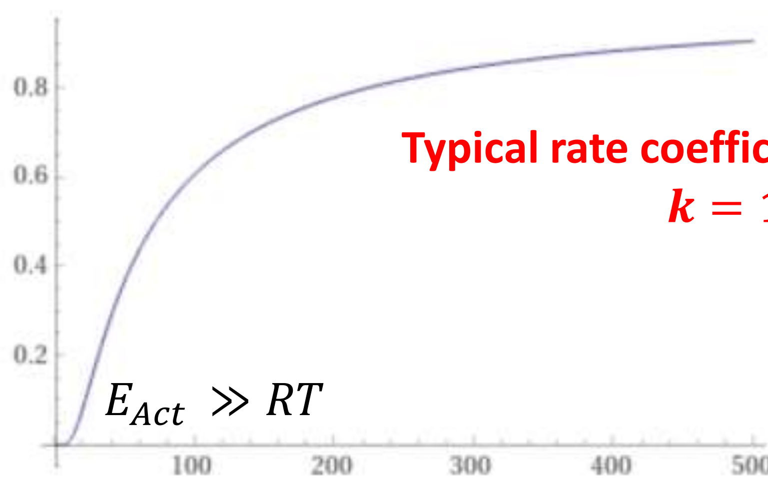
[cm⁻³ s⁻¹] [cm⁻³] [cm⁻³]

Arrhenius law: $$k(T) = M\,e^{-\frac{E_{Act}}{RT}}$$

Activation energy E_{Act}

Pre-exponential rate factor M

$k(T)$ in units of M



$E_{Act} \ll RT$

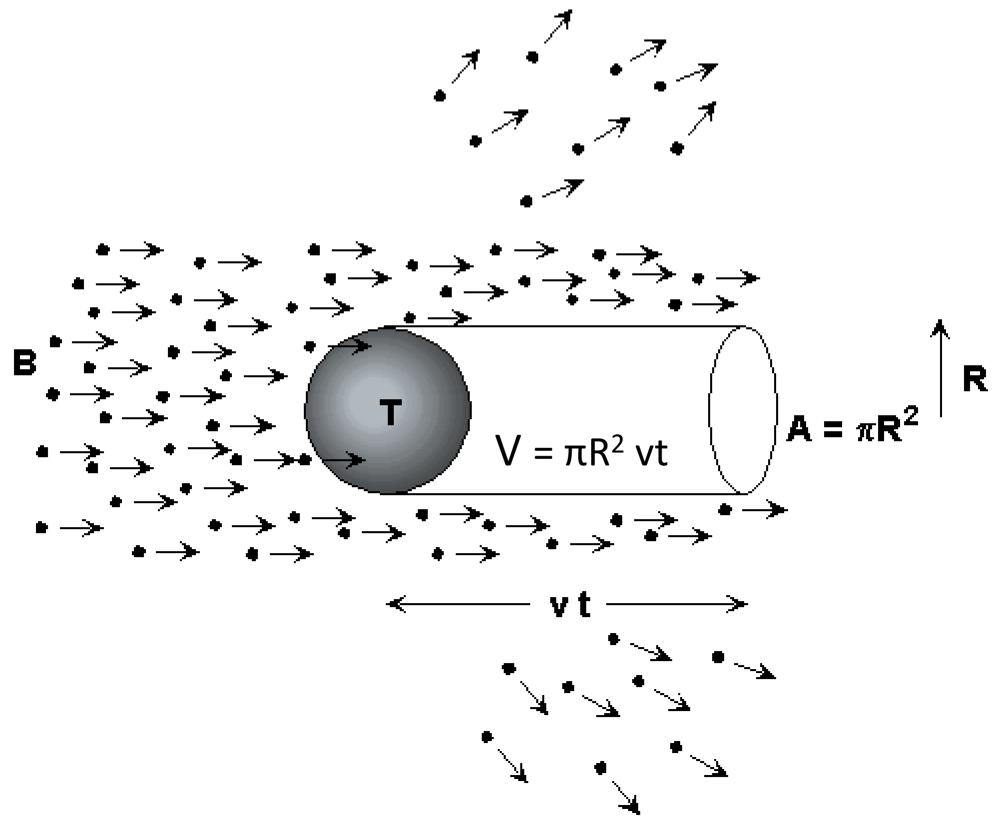
Temperature T

Typical rate coefficient Neutral-Neutral reaction:
$\boldsymbol{k = 1\ x\ 10^{-11}}$ **cm³ s⁻¹**

General concepts: cross section and rate coefficient

- Consider point-like bullets B colliding with a spherical Target T with diameter R
- The number of interactions is the number of particles scattered out of the „shadow“ volume V times the beam density n_B

$$N_{int} = n_B \pi R^2 vt$$

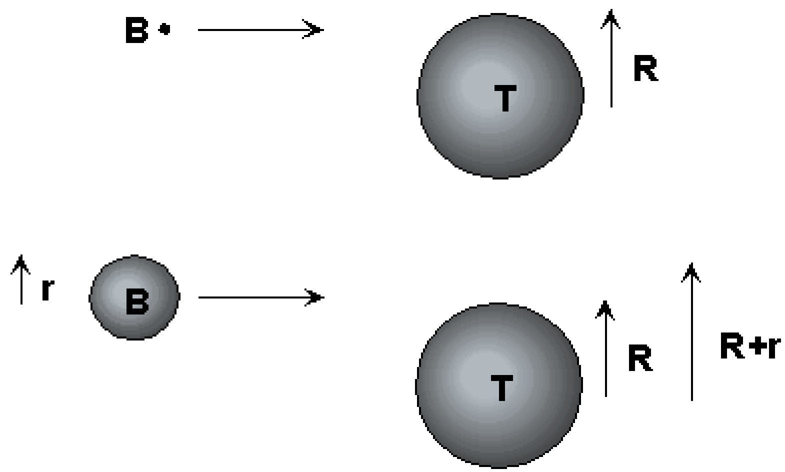


Geometric cross section:
$\sigma = \pi R^2$

Rate coefficient:
$k = \langle \sigma v \rangle = \pi R^2 v$

Cross section averaged over relative energies

General concepts: cross section and rate coefficient



Point vs. sphere

Geometric cross section:
$\sigma = \pi R^2$

Sphere vs. sphere

Geometric cross section:
$\sigma = \pi(r + R)2$

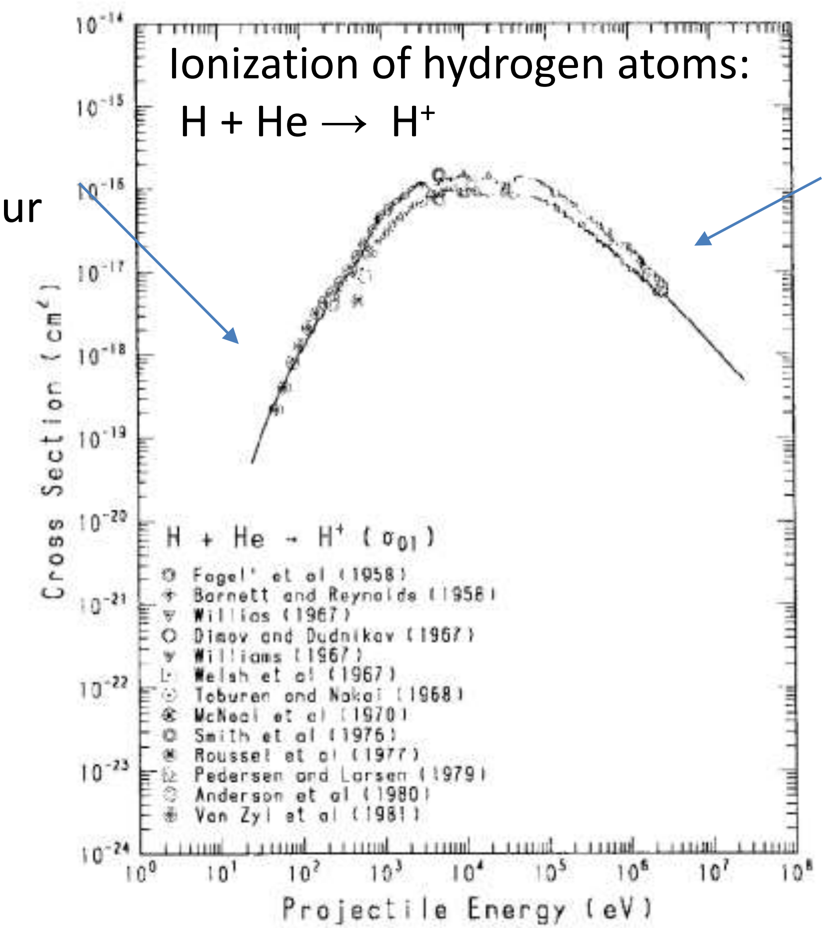
In atomic and molecular physics particles can not really be represented by hard spheres, especially when attractive forces are at play.
Effective cross sections depend on the type of interaction.

Estimate: Atom-Atom collision cross section: $\sigma = \pi(2a_0)^2 = \pi(1\ x\ 10^{-8}\ \text{cm})^2$

$\sigma = 3\ x\ 10^{-16}\ \text{cm}^2$

General concepts: cross section and rate coefficient

not enough energy
for ionization to occur

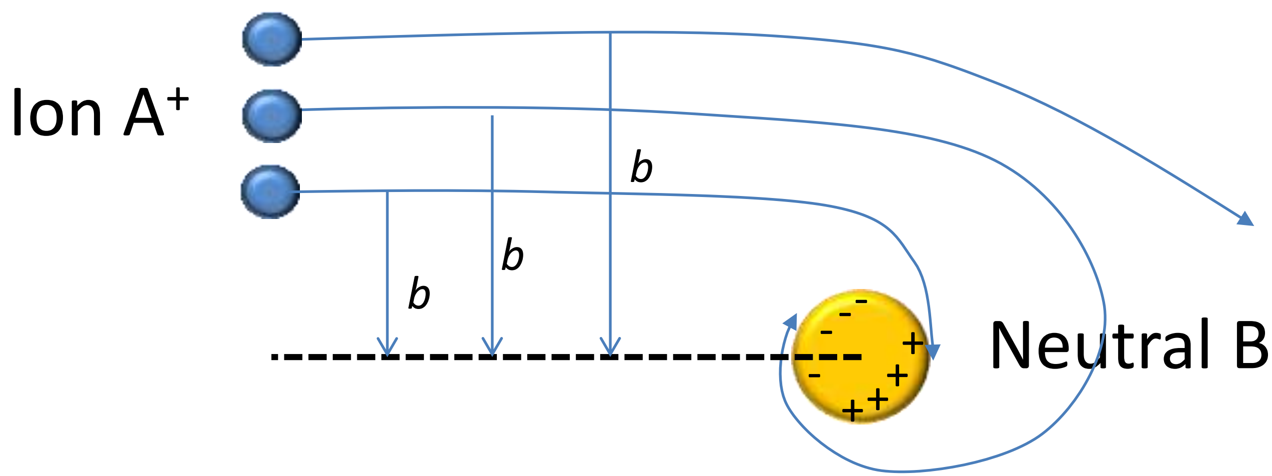


Cross section drops at higher energies because the interaction time is not long enough for ionization

Estimate: Atom-Atom collision cross section: $\sigma = \pi(2a_0)^2 = \pi(1\,x\,10^{-8}\text{ cm})^2$

$\sigma = 3\,x\,10^{-16}\text{ cm}^2$

Examples beyond the geometric cross section: classic capture theory for ion-neutral reactions



b: impact parameter
r: distance between particles

Charge-induced Dipole potential

$$V_{eff} = \frac{-1}{8\pi\varepsilon_0}\frac{e^2\,\alpha}{r^4}$$

Attractive **induced dipol potential** between singly charged reactant A^+ and neutral reactant **B with polarizability α**

Reactions only happen if impact parameter b is small enough,
Particle A^+ then can be captured and spends enough time around B to react

Ion-neutral reactions: the Langevin rate coefficient

Generic reaction: $A^+ + B \rightarrow C^+ + D$

Table 4.7 *Ion–molecule reactions*

reaction	α
$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.1 (–9)
$H_3^+ + O \rightarrow OH^+ + H_2$	8.0 (–10)
$H_3^+ + CO \rightarrow HCO^+ + H_2$	1.7 (–9)
$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	5.9 (–9)
$OH^+ + H_2 \rightarrow H_2O^+ + H$	1.1 (–9)
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	6.1 (–10)
$C^+ + OH \rightarrow CO^+ + H$	7.7 (–10)
$C^+ + H_2O \rightarrow HCO^+ + H$	2.7 (–9)
$CO^+ + H_2 \rightarrow HCO^+ + H$	2.0 (–9)
$He^+ + CO \rightarrow C^+ + O + He$	1.6 (–9)
$He^+ + O_2 \rightarrow O^+ + O + He$	1.0 (–9)
$He^+ + H_2O \rightarrow OH^+ + H + He$	3.7 (–10)
$He^+ + H_2O \rightarrow H_2O^+ + He$	7.0 (–11)
$He^+ + OH \rightarrow O^+ + H + He$	1.1 (–9)

[a] Reaction rates are of the form $k = \alpha$.

[in units of $cm^3\ s^{-1}$]

Attractive potential between induced dipole of the neutral and the charged reactant

$$V_{eff} = \frac{-1}{8\pi\varepsilon_0}\frac{e^2\alpha}{r^4} + E\left(\frac{b}{r}\right)^2$$

Centrifugal barrier

Effective cross section

$$\sigma(E) = \pi\, b_{crit}{}^2$$

polarizability of the neutral

$$k_L = \langle v\, \pi b_{crit}{}^2 \rangle = e\sqrt{\frac{\pi\,\alpha}{\varepsilon_0 \mu}}$$

reduced mass

Independent of *E, T, v* !

Tielens: Physics and Chemistry of the interstellar medium

Example: estimates of collision time scales

Reaction rate (for a particular particle) = Rate coefficient x number density (target)

$$R = k\,n$$

Example 1) *Neutral N_2 molecule with other N_2 molecules in Earth's atmosphere*

Neutral-neutral collision in Earth's atmosphere: $k = 10^{-11}$ cm^3 s^{-1} , n = 3 x 10^{19} cm^{-3}

R = 3 x 10^{8} s^{-1}

(3 million collisions per second)

Example 2) *H_2^+ ion colliding with H_2 atoms in the diffuse ISM*

Ion-neutral collision in diffuse ISM: $k = 10^{-9}$ cm^3 s^{-1} , n_{H2} = 10 cm^{-3}

R = 1 x 10^{-8} s^{-1}

(1 collision every 3 years)

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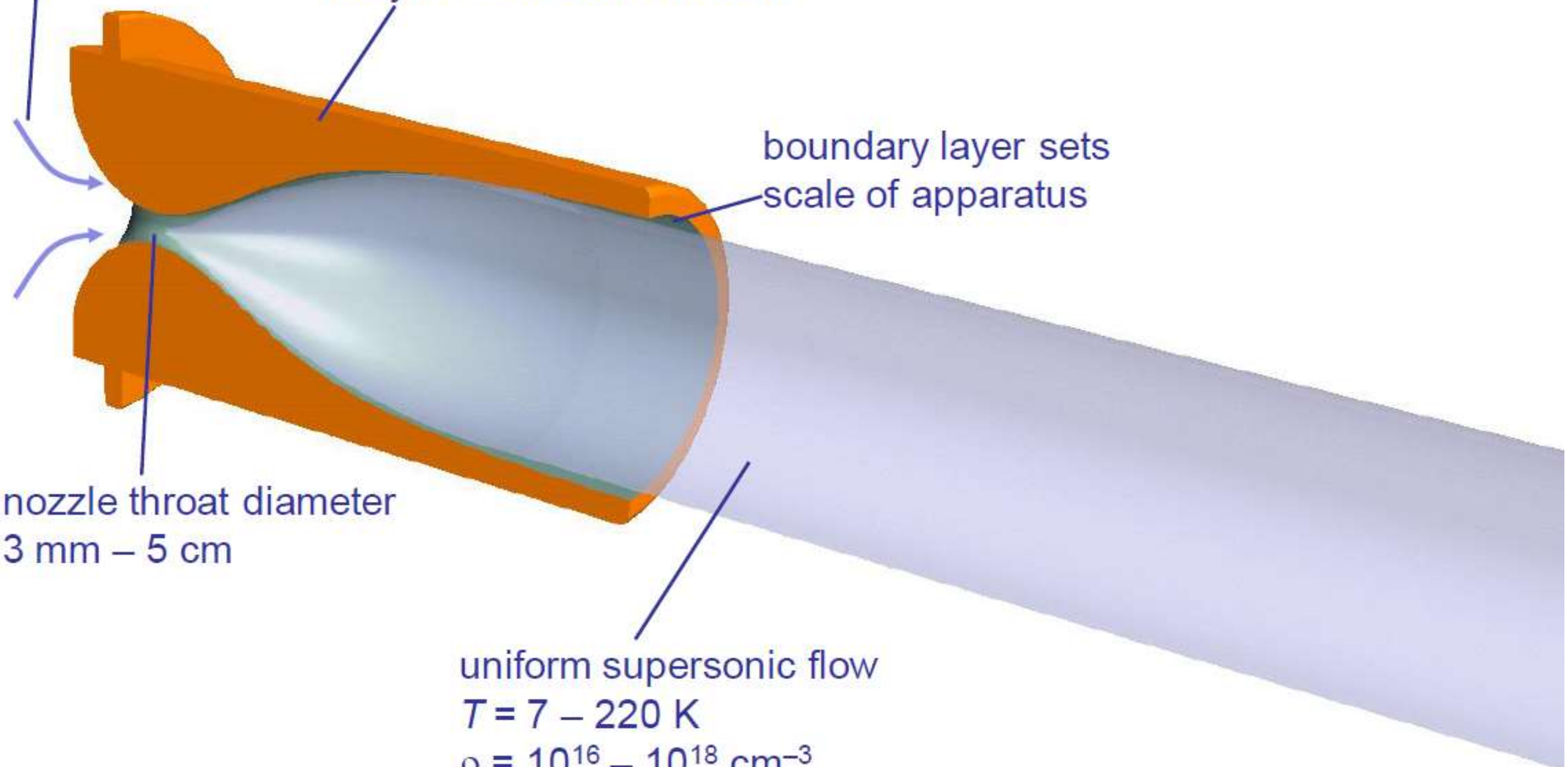
I. Smith, Annu. Rev. Astron. Astrophys. **49**, 29 (2011)

CRESU technique



Laval nozzle and isentropic flow

Gustave de Laval (1845-1913)

Space shuttle

The Cresu Technique

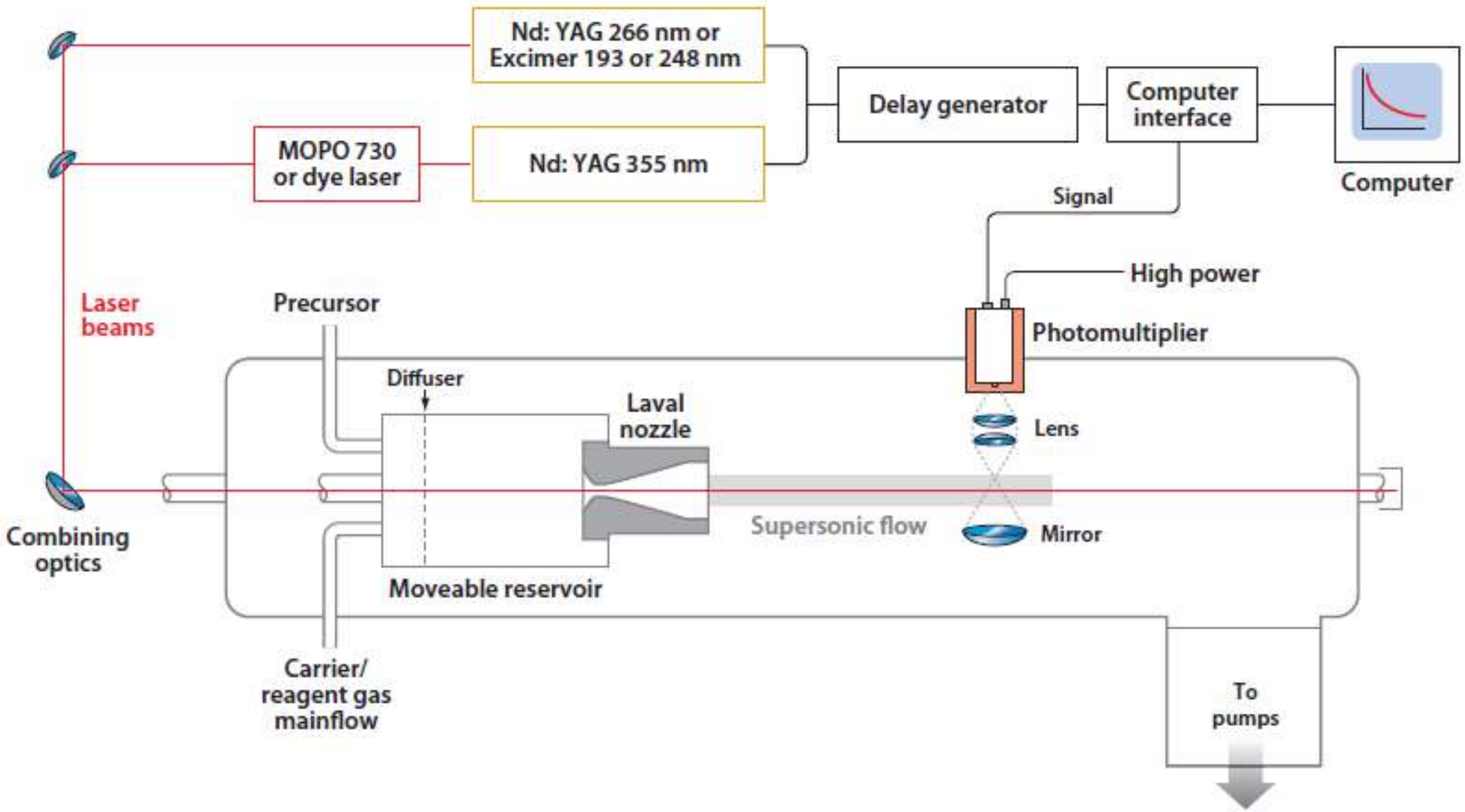
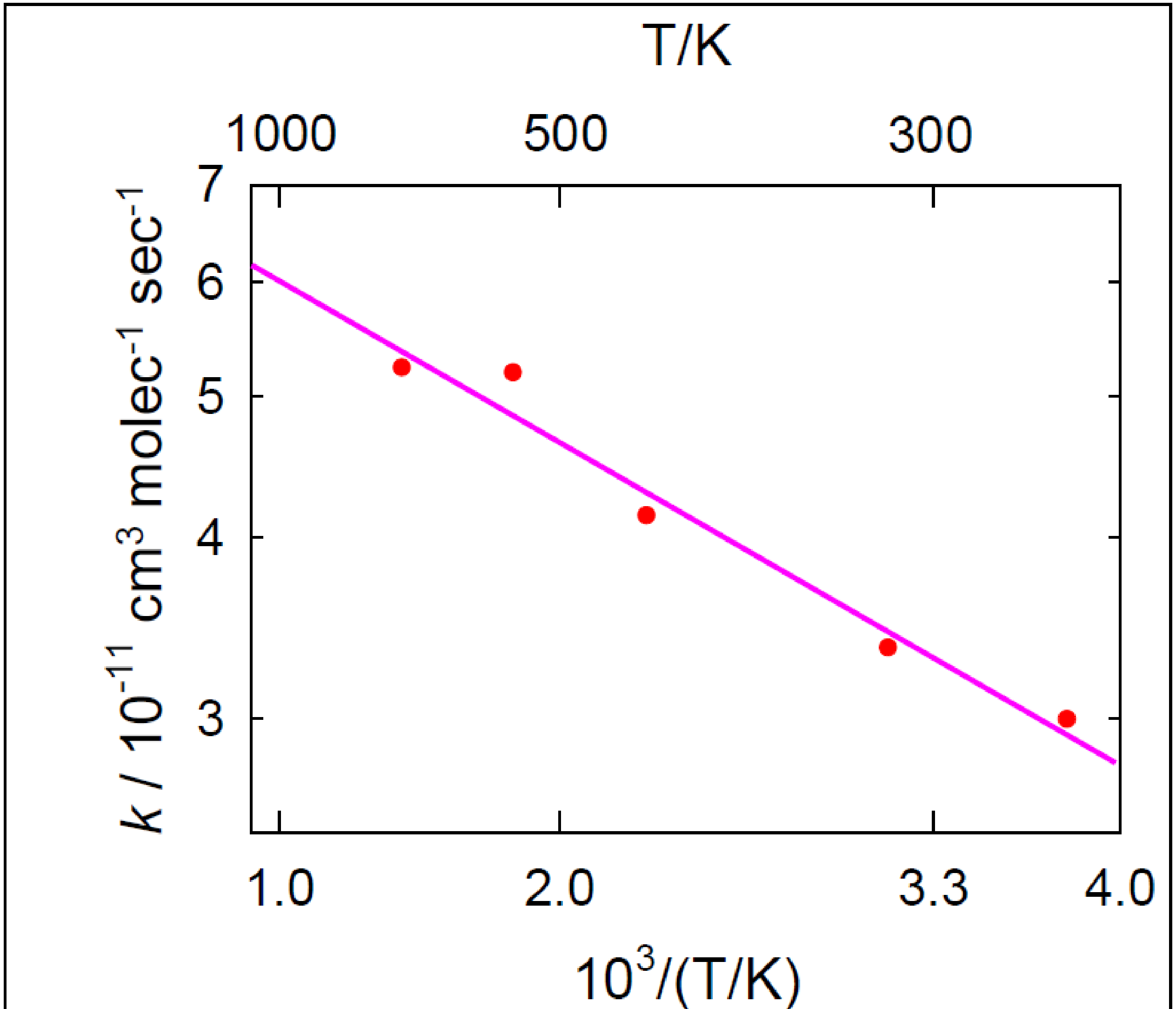


Figure 3

Sketch of a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus configured for the study of radical-neutral reactions. In this arrangement, radicals are generated by photolysis of a suitable precursor using radiation from a fixed-frequency pulsed laser operating at one of the three wavelengths, 226, 248, or 193 nm, and are detected by laser-induced fluorescence excited by tunable radiation from a dye laser or a master oscillator parametric oscillator (MOPO). (Reproduced, with permission, from Canosa et al. 2008.)

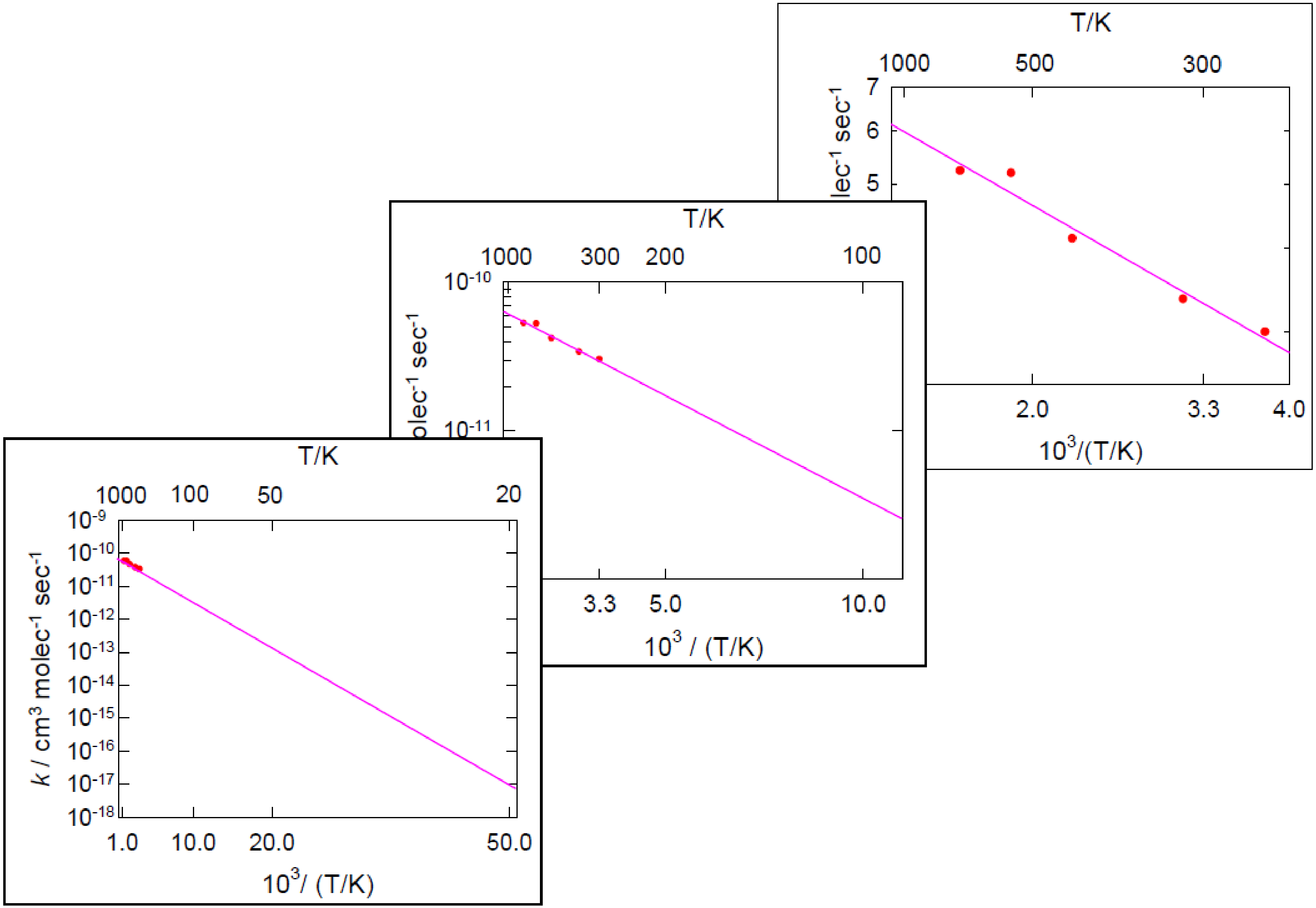
I. Smith, Annu. Rev. Astron. Astrophys. **49**, 29 (2011)

CN + C_2H_6: or why extrapolation is unreliable



I. Sims et al. Rennes/Birmingham

$CN + C_2H_6$: or why extrapolation is unreliable



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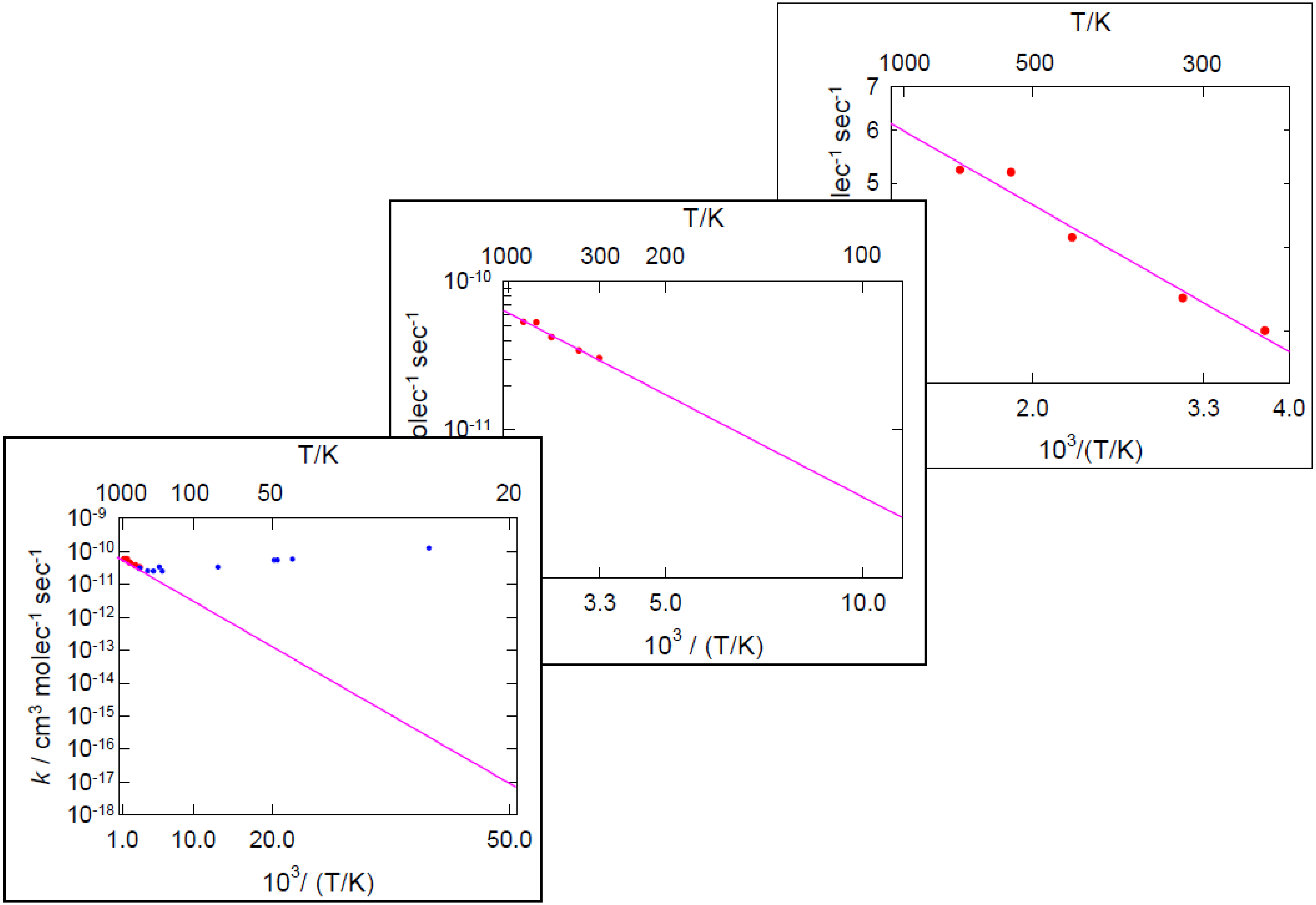
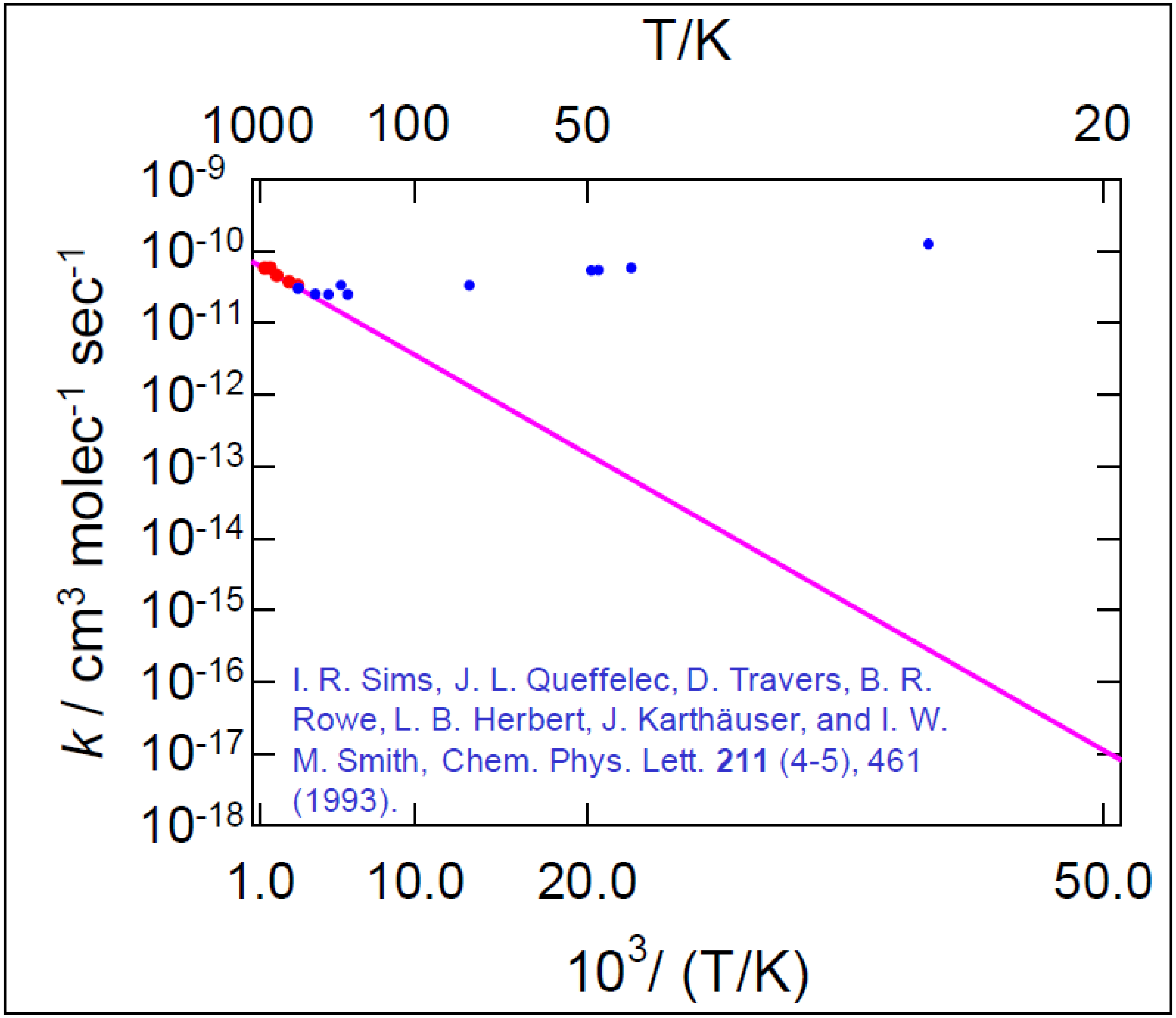
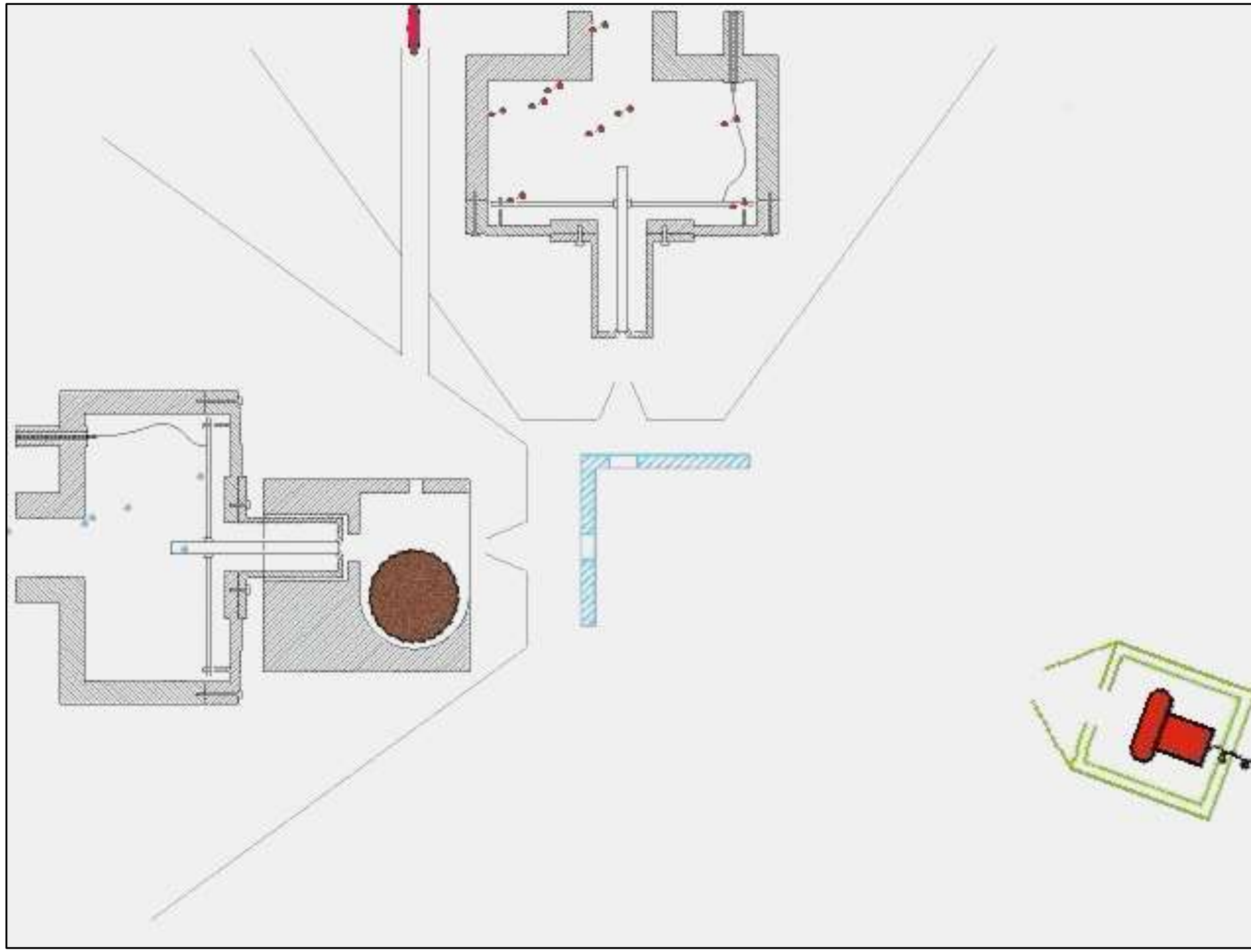


$CN + C_2H_6$: reaction stays rapid at low *T*!



Neutral-Neutral Experiments: Crossed Beams

Group of Ralf I. Kaiser
Department of Chemistry, University of Hawai'i at Manoa



Examples:
HCCCCH on CN (molecular clouds, Titan)
B on C_2H_2, C_2H_4, CH_3CCH, etc …

(Y. T. Lee: Nobel prize in Chemistry 1986)

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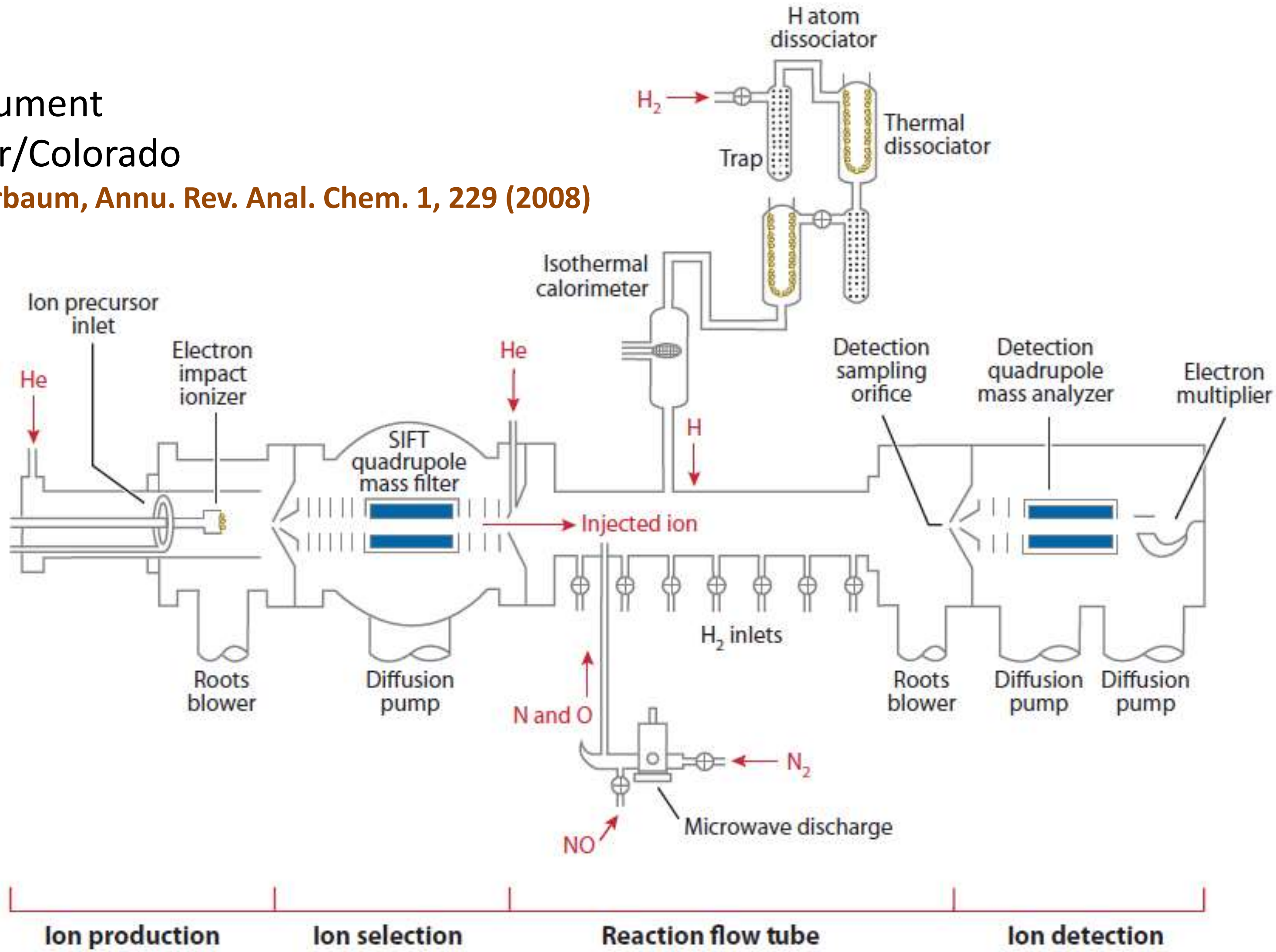
I. Smith, Annu. Rev. Astron. Astrophys. **49**, 29 (2011)

Ion-neutral reactions and electron recombination: The Flowing Afterglow / Selected Ion Flow Tube (SIFT)Technique

SIFT Instrument
In Boulder/Colorado
Snow & Bierbaum, Annu. Rev. Anal. Chem. 1, 229 (2008)



Problem: measurement in flow of helium gas (1 mbar), usually at room temperature

Ion-neutral reactions and electron recombination: The Flowing Afterglow / Selected Ion Flow Tube (SIFT)Technique

Table 5 Experimental results for the reactions of positive ions[a] with O-atoms at 298 (± 5) K

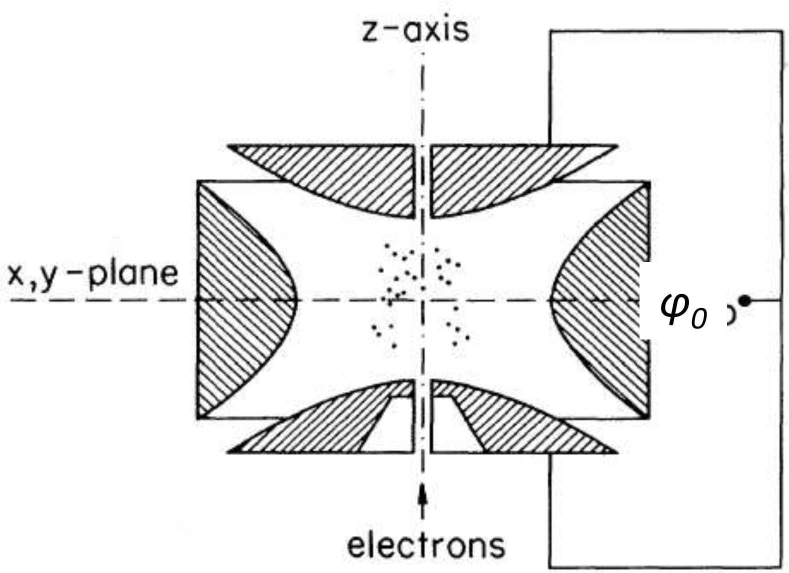
Ionic reactant	Reaction products	Branching ratio	Rate constant ($cm^3 s^{-1}$)	Reference
$C_6H_6^+$ (benzene)	$C_5H_6^+ + CO$	1.0	9.5×10^{-11}	71
$C_6H_6^+$ (benzene)	$C_5H_6^+ + CO$	0.9	1.4×10^{-10}	82
	$C_4H_4O^+ + C_2H_2$	0.1		
$C_{10}H_8^+$ (naphthalene)	$C_9H_8^+ + CO$	0.55	1.0×10^{-10}	71
	$C_{10}H_8O^+$	0.45		
$C_{16}H_{10}^+$ (pyrene)	$C_{15}H_{10}^+ + CO$	<0.05	9.5×10^{-11}	72
	$C_{16}H_{10}O^+$	>0.95		
$C_{24}H_{12}^+$ (coronene)	$C_{24}H_{12}O^+$	1.0	1.3×10^{-10}	73
$C_{16}H_9^+$	$C_{15}H_9^+ + CO$	~0.5	$\sim 2 \times 10^{-10}$	72
	$C_{16}H_9O^+$	~0.5		
CH_3^+	$HCO^{+b} + H_2$	1.0	4.1×10^{-10}	82
$C_2H_2^+$	$HCO^{+b} + CH$	0.5	2.0×10^{-10}	82
	$HC_2O^+ + H$	0.5		
$C_2H_3^+$	$H_2CCO^+ + H$	0.85	1.0×10^{-10}	82
	$C_2H_3O^+$	0.10		
	$CH_3^+ + CO$	0.05		
$C_2H_4^+$	$CH_3^+ + HCO$	0.45	2.4×10^{-10}	82
	$HCO^+ + CH_3$	0.35		
	$HC_2O^+ + H_2 + H$	0.10		
	$CH_3CO^+ + H$	~0.05		
	$H_2CCO^+ + H_2$	~0.05		
ac-$C_3H_3^+$	$C_3H_2O^+ + H$	0.30	1.5×10^{-10}	82
	$C_2H_3^+ + CO$	0.30		
	$C_2H_2^+ + HCO$	0.25		
	$HC_3O^+ + H_2$	0.15		
$C_4H_2^+$	$C_4HO^+ + H$	0.50	2.7×10^{-10}	82
	$C_3H_2^+ + CO$	0.40		
	$C_3HO^+ + CH$	~0.05		
	$C_4H_2O^+$	~0.05		
c-$C_6H_5^+$	$C_5H_5^+ + CO$	0.6	1.0×10^{-10}	82
	$C_3H_3^+ + C_3H_2O$	0.4		
HC_3N^+	$C_3NO^+ + H$	0.50	4.1×10^{-10}	83
	$HC_2N^+ + CO$	0.40		
	HC_3NO^+	0.10		
N_2^+	$NO^+ + N$	0.95	1.4×10^{-10}	83
	$O^+ + NO$	0.05		
H_3^+	$OH^+ + H_2$	0.70	1.2×10^{-9}	84
	$H_2O^+ + H$	0.30		

Room temperature,
High pressure

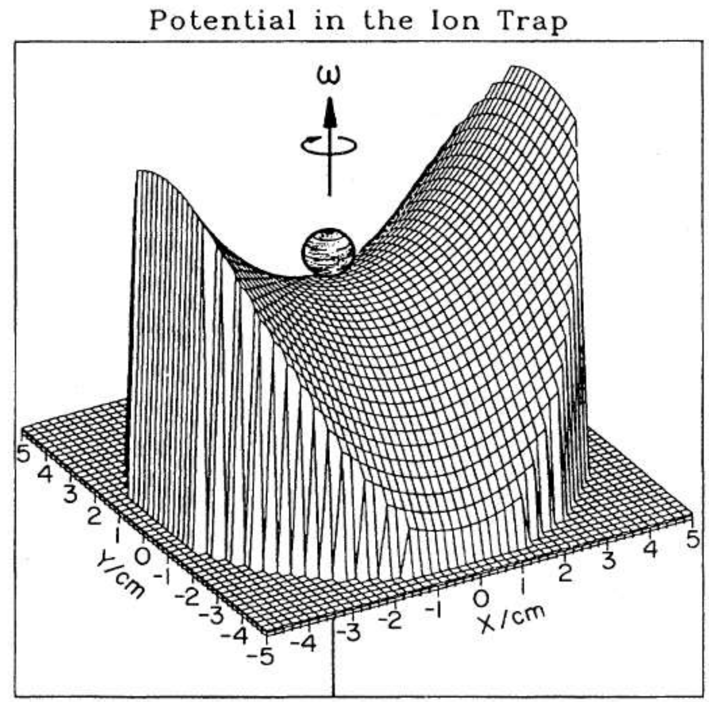
Snow & Bierbaum, Annu. Rev. Anal. Chem. 1, 229 (2008)

Radiofrequency Ion Traps

The original “Ionenkäfig”



$\varphi_0 = U + V \cos \omega t$



Trapping potential created by radiofrequency applied to the electrodes

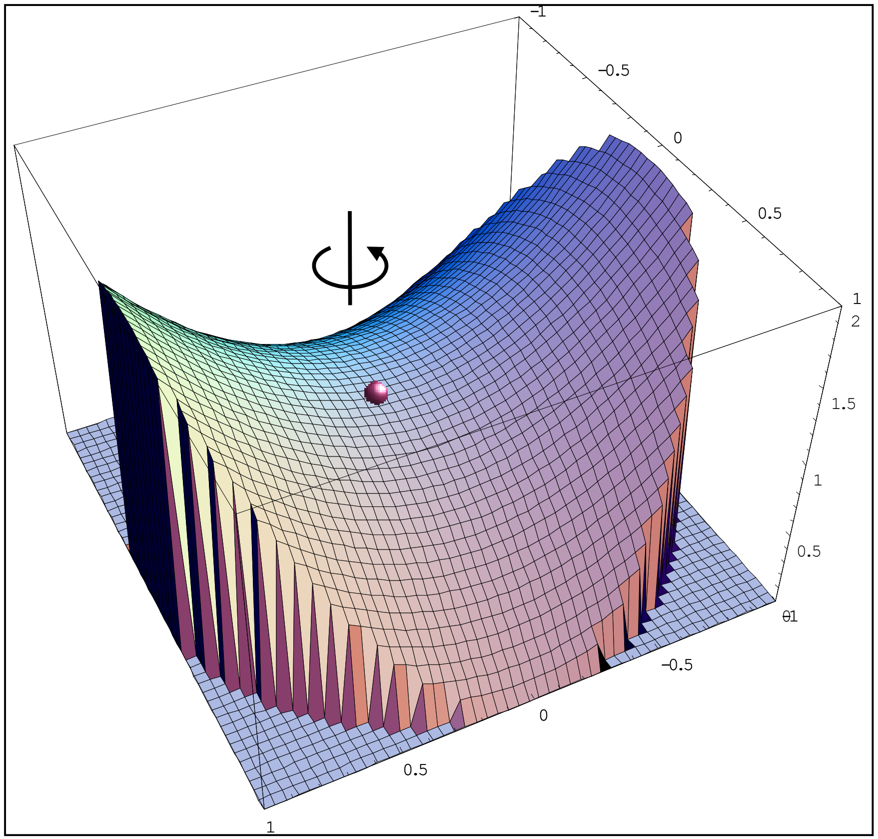
- Cooling with a **buffer gas** possible
- Problem: Radiofrequency heating

Wolfgang Paul, Rev. Mod. Phys. 62, 531 (1990)

Nobel prize 1989

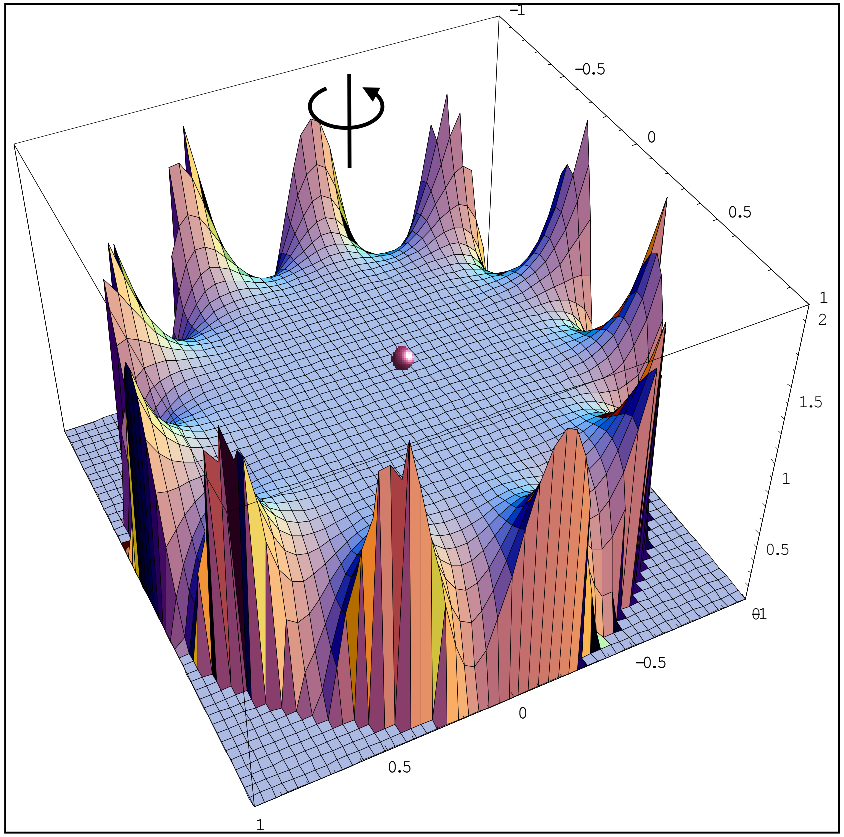
Field Geometry: higher order multipoles

Quadrupole



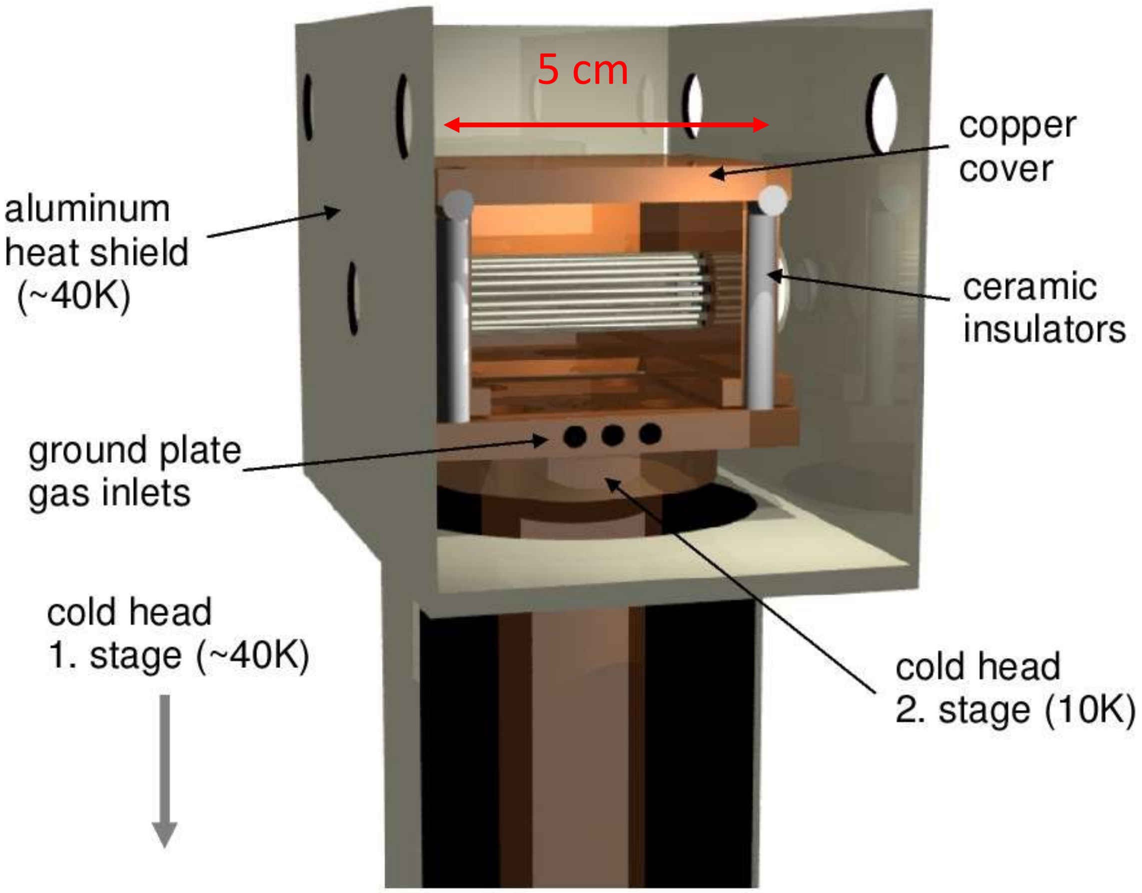
Problem for light ions:
Radiofrequency heating

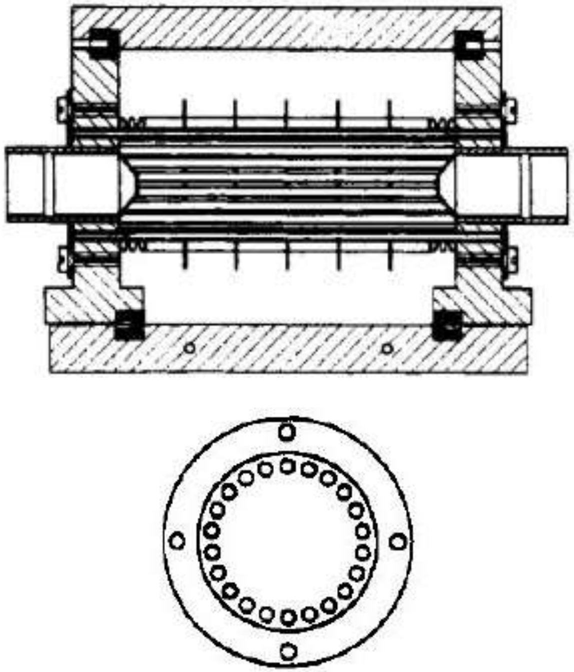
22-Pole



Advantage:
Large field free zone reduces RF heating

Cold ion-neutral reactions:
Cryogenic Ion Traps with helium buffer gas cooling

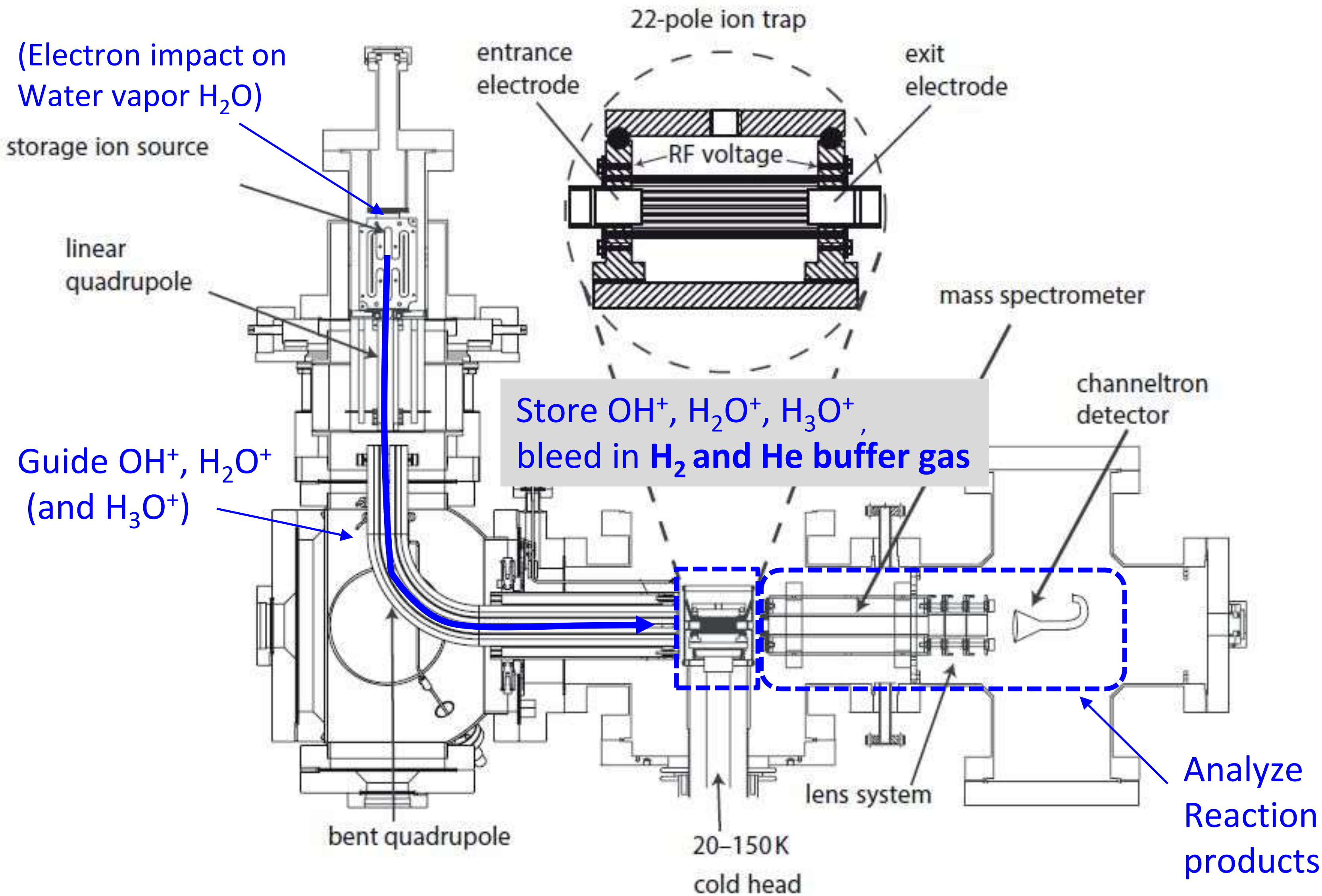




Dieter Gerlich
1944 - 2020

Gerlich, Physica Scripta, T59, 256, (1995)

Study $OH^+ + H_2$ and $H_2O^+ + H_2$ in Temperature-Variable Ion Trap

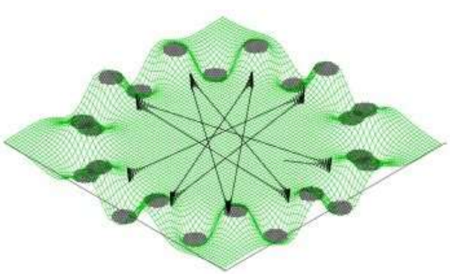


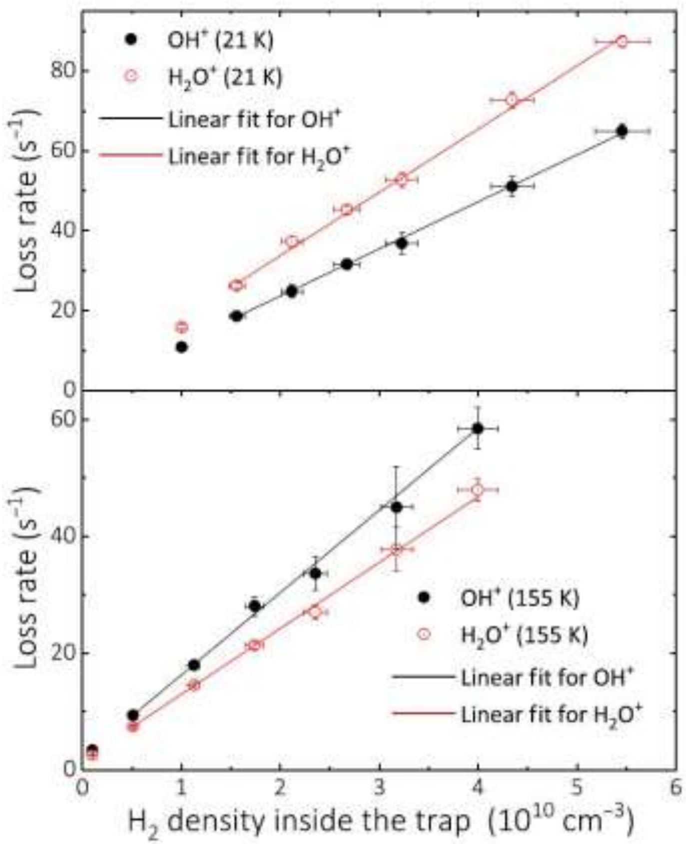
Precise rate coefficients for gas phase water formation

Water in Space: Gas Phase Formation Route

$$H_3^+ \xrightarrow{O} OH^+ \xrightarrow{H_2} H_2O^+ \xrightarrow{H_2} H_3O^+ \xrightarrow{e} \begin{cases} H_2O + H \\ OH + H_2 \end{cases}$$

Store **OH^+** and **H_2O^+** in **temperature-variable** ion trap and bleed in H_2

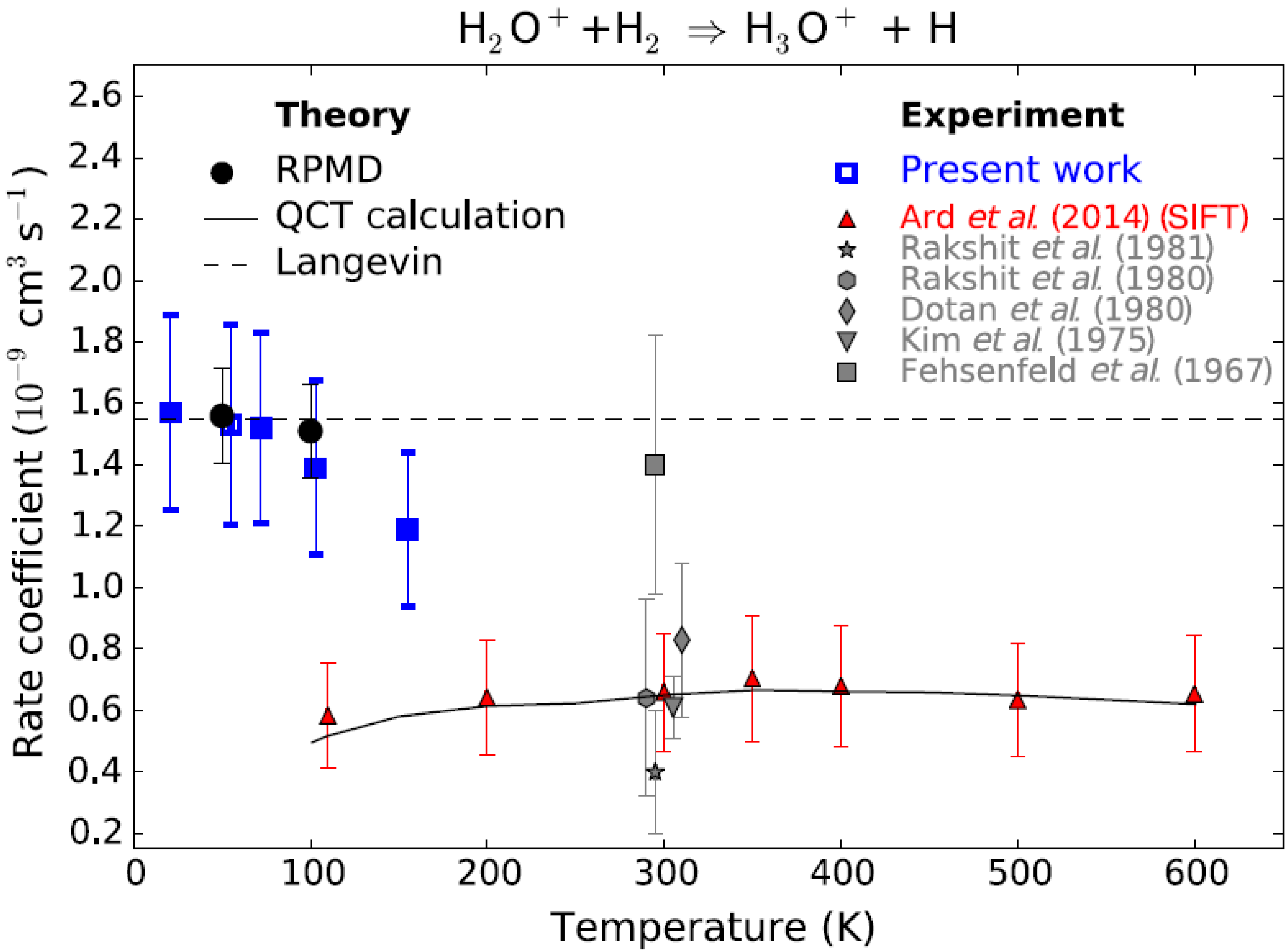




HERSCHEL found Surprising abundances of **OH^+, H_2O^+ and H_3O^+**

Kumar et al., *Science Advances 4*: eaar3417 (2018)

Water in Space: Gas Phase Formation Route

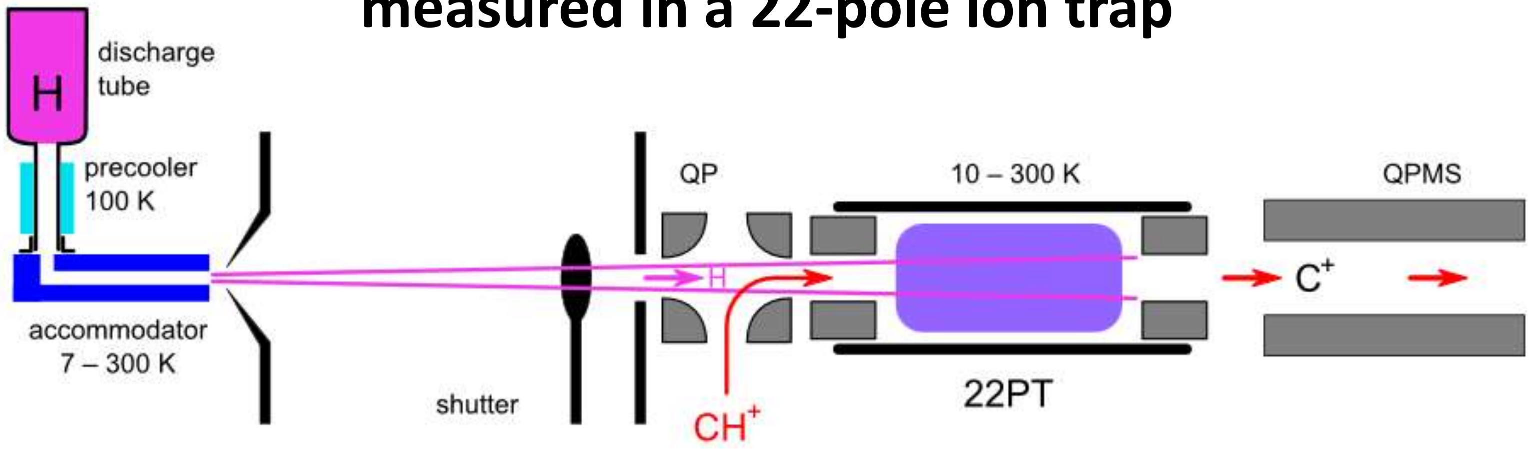


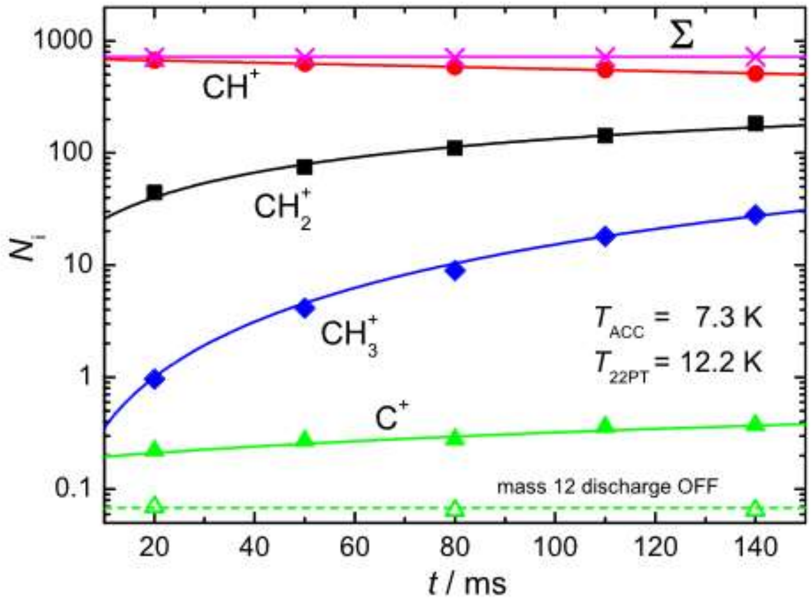
Theory: Ring Polymer Molecular Dynamics

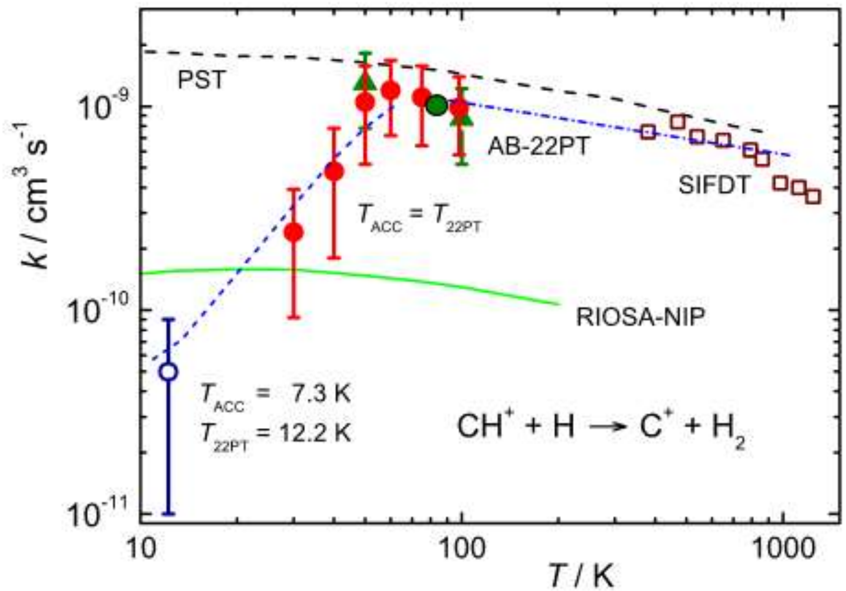
Y. Suleimanov

Kumar et al., *Science Advances 4*: eaar3417 (2018)

Example: $CH^+ + H \rightarrow C^+ + H_2$ measured in a 22-pole ion trap







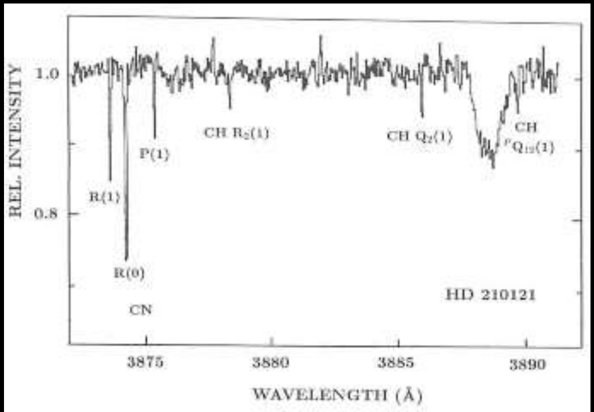
The rate coefficient is a **factor of 50 smaller** than the classical Langevin value at low energy!

Plasil et al, ApJ 737, 60 (2011)

History of molecular observations in space I

Sharp absorption bands (optical):

- CH: Swings & Rosenfeld (1937)
- CN: McKellar (1940)
- CH^+: Douglas & Herzberg (1941)

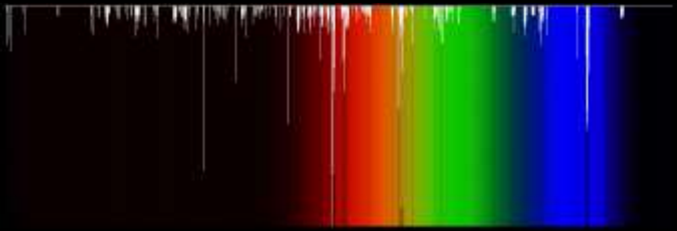


G. Herzberg, J. Roy. Soc. Can. 82, 115, (1988)

"Historical Remarks on the discovery of interstellar molecules"

Diffuse Interstellar Bands (DIBs), optical:

- Discovered by Mary L. Heger (1922)
- Probably molecular carriers
- Remain (largely) unidentified to date



B.J. McCall, R.E. Griffin, Proc. R. Soc. A 469, 0604 (2012)

"On the discovery of the diffuse interstellar bands"

Action spectroscopy in ion traps: C_{60}^+ as carrier of diffuse interstellar bands?

Detection of two interstellar absorption bands coincident with spectral features of C_{60}^+

B. H. Foing* & P. Ehrenfreund†

* Solar System Division, ESA Space Science Department, ESTEC/SO, 2200 Noordwijk AG, The Netherlands
† Leiden Observatory, PO Box 9513, NL-2300 RA Leiden, The Netherlands

MORE than a hundred well-defined absorption bands, arising from diffuse gas in the interstellar medium, have been observed in the visible and near-infrared spectra of stars[1–4]. The identity of the species responsible for these bands has remained unclear, although many possibilities have been suggested[5,6]. Carbon-based molecules ubiquitous in the interstellar medium have been widely favoured as potential carriers of some of the diffuse interstellar bands[7–10,29]; in particular, C_{60}^+ has been thought to be a promising candidate[9,29]. Here we present the results of a search for C_{60}^+ in the near-infrared spectra of seven stars, based on recent laboratory measurements of the absorption spectrum of this species[11–13]. We find two diffuse bands that are coincident (within 0.1%) with laboratory measurements on C_{60}^+ in a Ne matrix[11]. From this observation and the total absorption, we estimate that 0.3–0.9% of interstellar carbon is in the form of C_{60}^+. The molecule is very stable, which should allow it to survive in the interstellar medium for a long time[14], but the inhibition of C_{60} formation by hydrogen probably limits its abundance.

The C_{60} molecule has attracted much attention since Kratschmer *et al.*[15] succeeded in synthesizing it in macroscopic quantities by vaporizing graphite in a He atmosphere. C_{60} is expected to be the most stable and dominant fullerene during clustering[14], but the visible absorption spectrum of neutral C_{60}

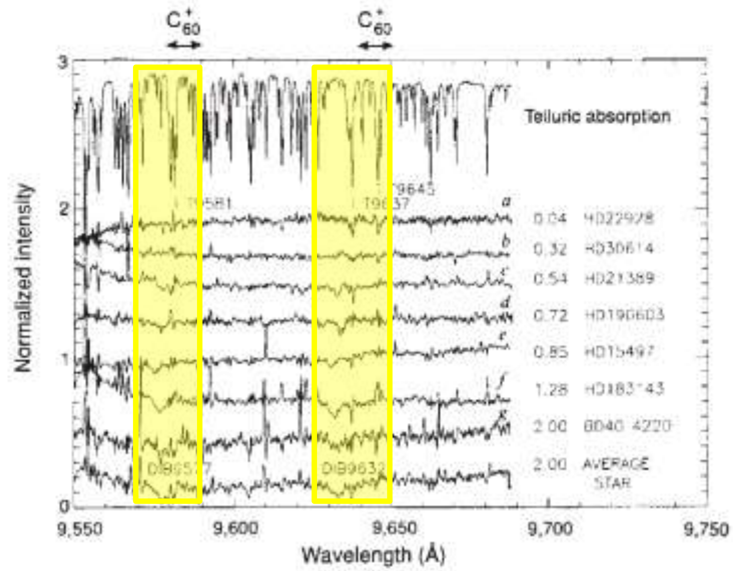
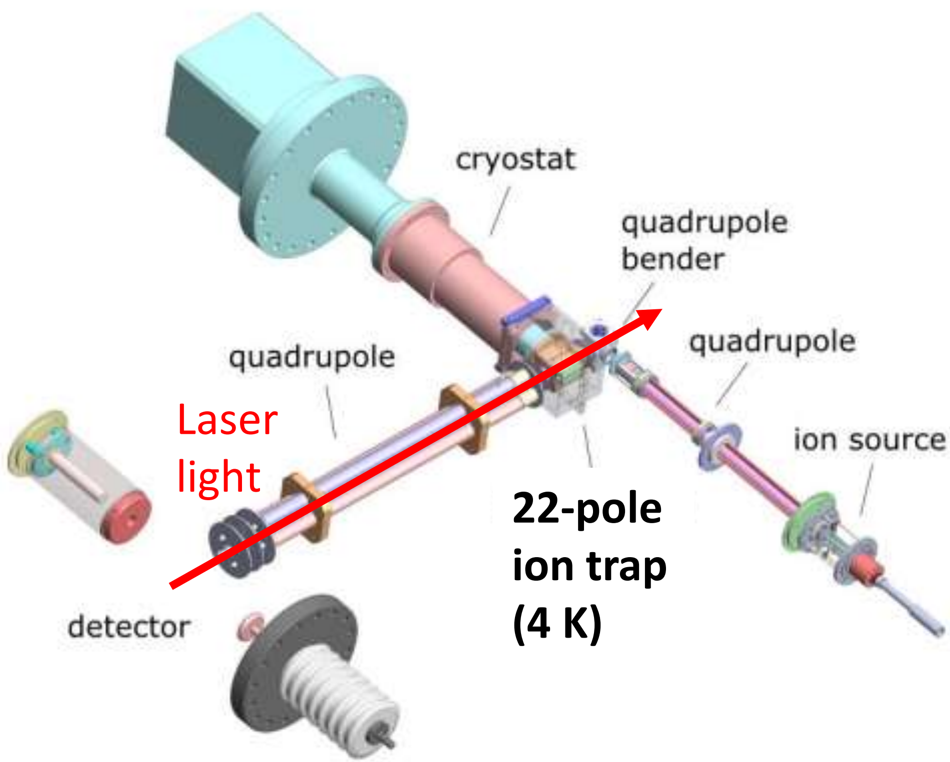


FIG. 1 *a–g*. Spectra of the seven stars studied, in order of increasing reddening. To the right of each trace are shown the associated $E_{(B-V)}$ value, and the star name. Each observed star spectrum has been, after instrumental corrections, divided by a spectrum of a reference star (of similar spectral type) observed immediately at the same airmass. This divided out both the telluric water absorption bands and the stellar lines. The top trace is a reference spectrum of η Ursae Majoris (with offset of 2), showing the strength of the telluric water bands. Slight residuals from telluric corrections are indicated (T). Two new diffuse interstellar bands (DIBs) are detected at 9,577 and 9,632 Å, increasing with $E_{(B-V)}$. The slight wavelength shifts, up to 1.3 Å, and different line profiles are associated with the velocity distribution of interstellar clouds along the line of sight. The bottom trace is an average composite spectrum corresponding to $E_{(B-V)} = 2$. We also give the positions of the two C_{60}^+ main bands measured in Ne matrix by Fulara *et al.*[11].

Action spectroscopy in ion traps: helium tagging identifies C_{60}^+ as carrier of diffuse interstellar bands

Form C_{60}^+-He compounds at low temperature, detach He by laser light and detect the pure C_{60}^+



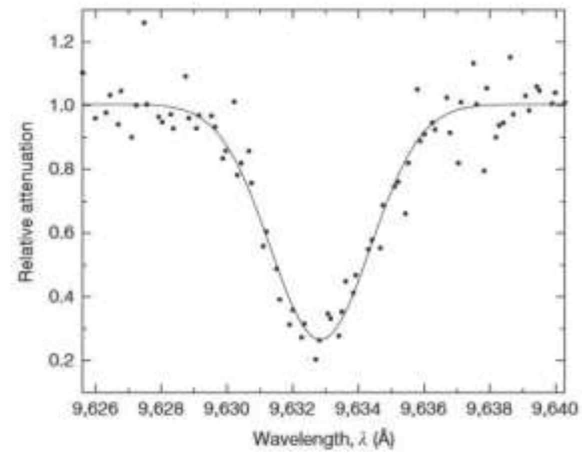
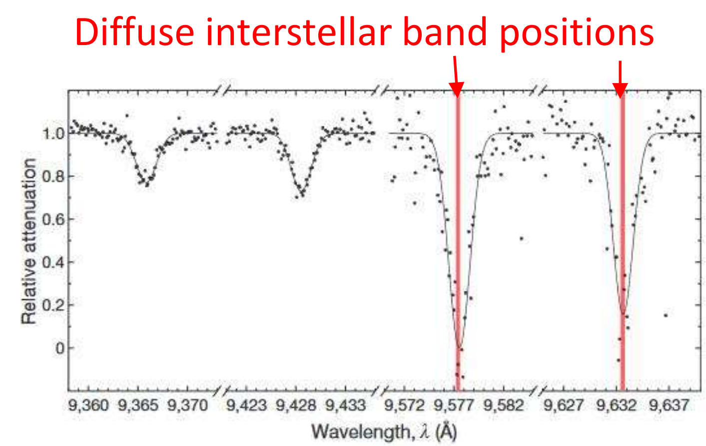


Figure 2 | C_{60}^+–He_2 spectrum. This spectrum was recorded by monitoring the depletion on the C_{60}^+–He_2 mass channel. A Gaussian fit to the experimental data (circles) is represented by the solid line. The fit yields a band maximum at 9,632.8 ± 0.1 Å and a FWHM of 3.6 ± 0.2 Å.



Campbell et al., Nature 528, 321 (2015)

Different classes of reactions relevant for Interstellar Chemistry

Type of process	Example	Number in model
Gas-grain interactions	$H + H + grain \rightarrow H_2 + grain$	14
Direct cosmic ray processes	$H_2 + \zeta \rightarrow H_2^+ + e$	11
Cation-neutral reactions	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2933
Anion-neutral reactions	$C^- + NO \rightarrow CN^- + O$	11
Radiative associations (ion)	$C^+ + H_2 \rightarrow CH_2^+ + h\nu$	81
Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46
Chemi-ionization	$O + CH \rightarrow HCO^+ + e$	1
Neutral-neutral reactions	$C + C_2H_2 \rightarrow C_3H + H$	382
Radiative association (neutral)	$C + H_2 \rightarrow CH_2 + h\nu$	16
Dissociative recombination	$N_2H^+ + e \rightarrow N_2 + H$	539
Radiative recombination	$H_2CO^+ + e \rightarrow H_2CO + h\nu$	16
Anion-cation recombination	$HCO^+ + H^- \rightarrow H_2 + CO$	36
Electron attachment	$C_6H + e \rightarrow C_6H^- + h\nu$	4
External photo-processes[a]	$C_3N + h\nu \rightarrow C_2 + CN$	175
Internal photo-processes[a]	$CO + h\nu \rightarrow C + O$	192

Number of reactions of different types that are included in the OSU kinetic database (osu-09-2008)

4500 reactions in total

In most reactions, charged particles are involved

I. Smith, Annu. Rev. Astron. Astrophys. **49**, 29 (2011)

Dissociative Recombination (DR):

Important neutralization process in space (and Earth´s atmosphere)

Molecular ion → $AB^+ + e^- \rightarrow A + B$

Solar radiation produces a lot of electrons in the **Ionosphere** by photoionization.
How are these electrons removed?

$O_2^+ + e^- \rightarrow O^* + O$

1st step: DR of O_2^+

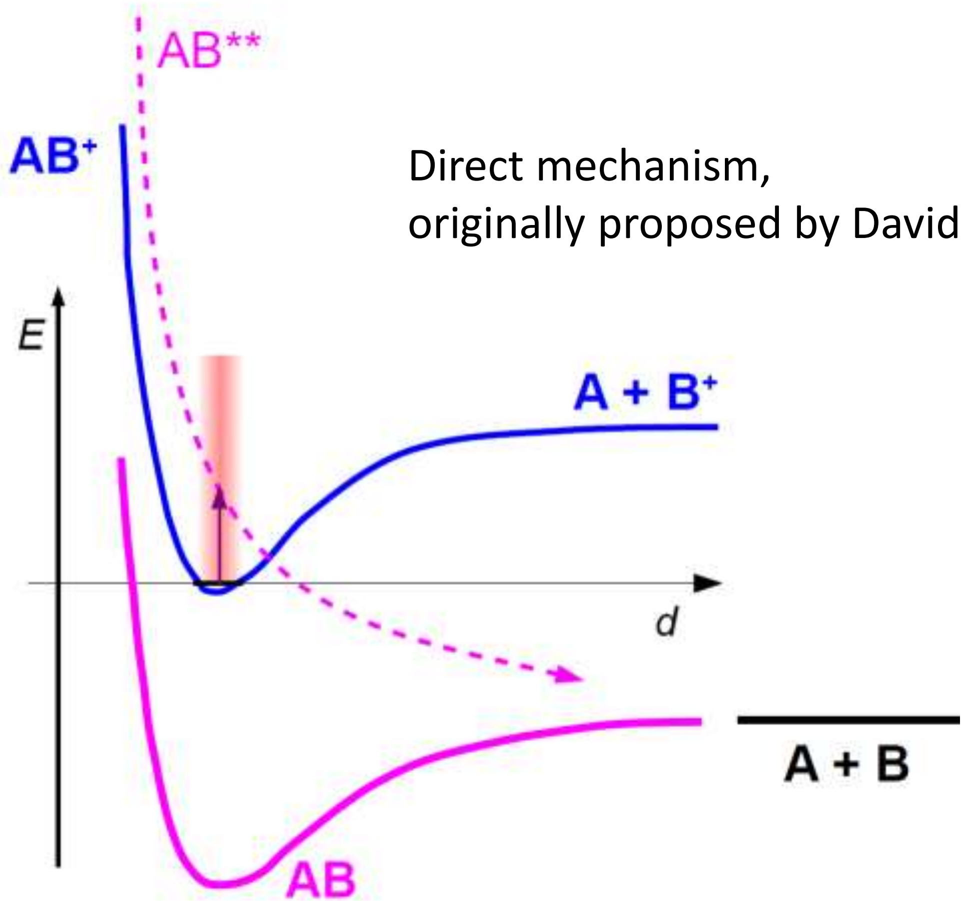
$O\ (^1S \rightarrow {}^1D)$ emission at 5577 Å

2nd step: emission from excited atomic products

Molecular Ions: Dissociative Electron Recombination

$$AB^+ + e^- \longrightarrow AB^{**} \longrightarrow A + B$$

Molecular ion Free electron Atomic or molecular fragments (neutral)

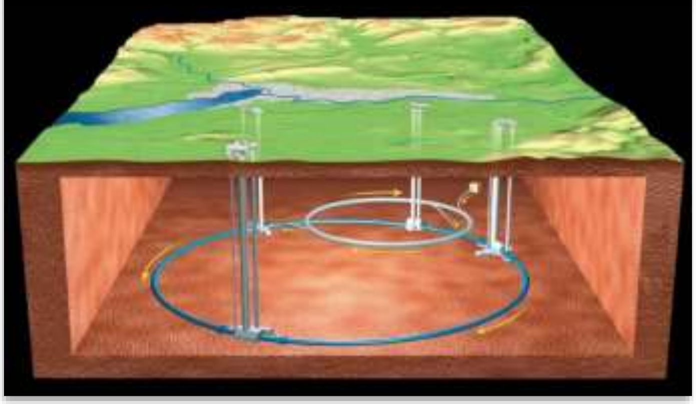


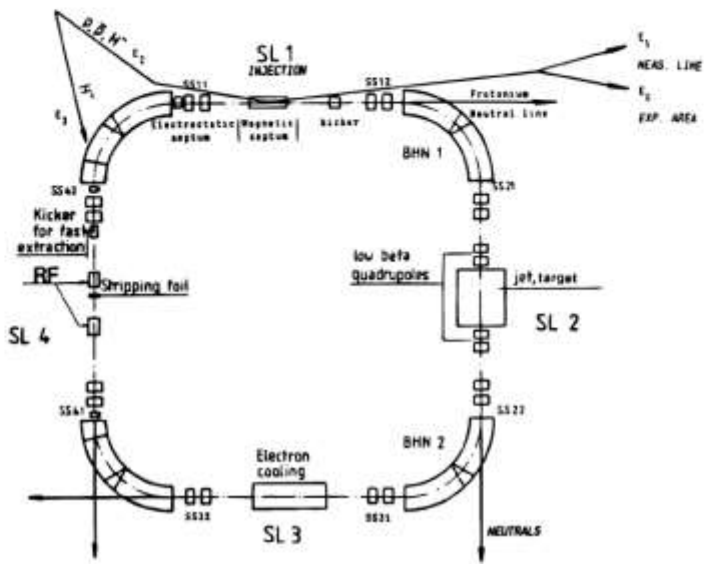
Direct mechanism,
originally proposed by David Bates

Non-resonant electron capture into a dissociative neutral state

Heavy Ion Storage Rings: Historical Remarks

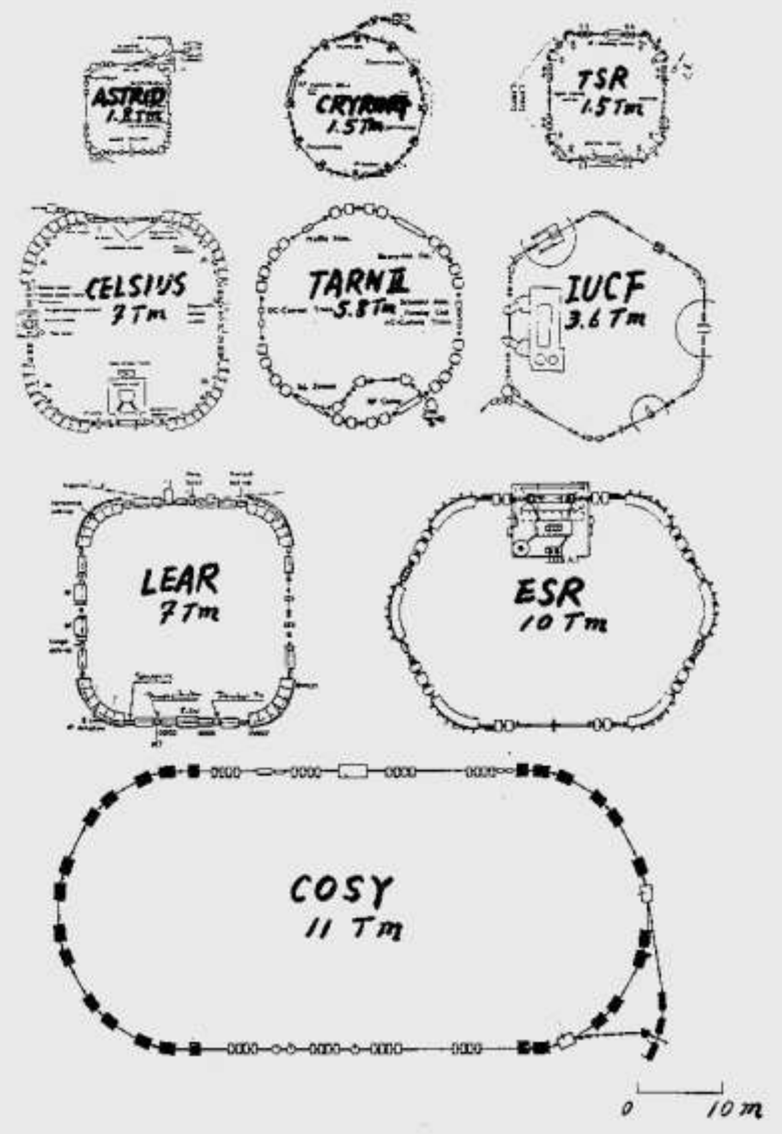
Large Hadron Collider / CERN (27 km)





Low Energy Antiproton Ring (LEAR)
CERN (1982-1996) **Cooler ring!**

LEAR and its heritage



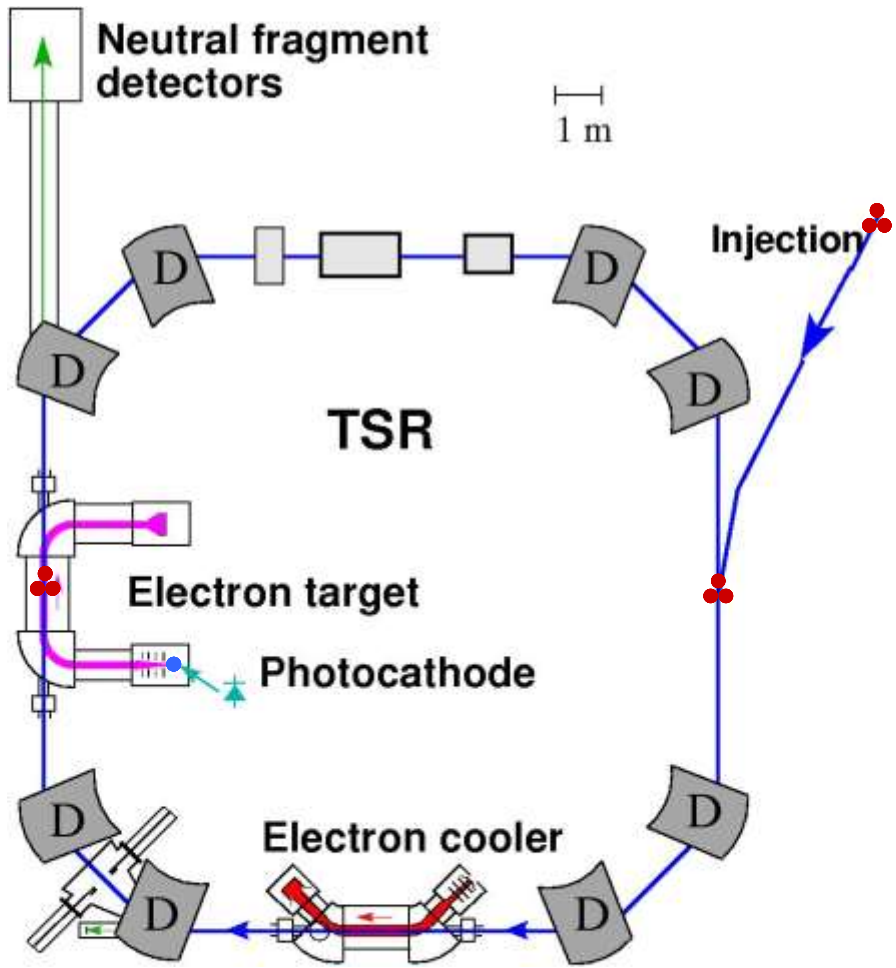
Heavy Ion Storage Ring Technique

Merged electron-ion beams for recombination studies

Very powerful technique!

But:

- Ion temperature ≥ 300K
- Limited to small molecules



Merged beams 101: electron-ion collisions $H_3^+ + e^-$

$$E_r = \frac{1}{2}\mu v_r^2 = \mu\left[\frac{E_1}{m_1} + \frac{E_2}{m_2} - 2\left(\frac{E_1 E_2}{m_1 m_2}\right)^{\frac{1}{2}} \cos\theta\right]$$

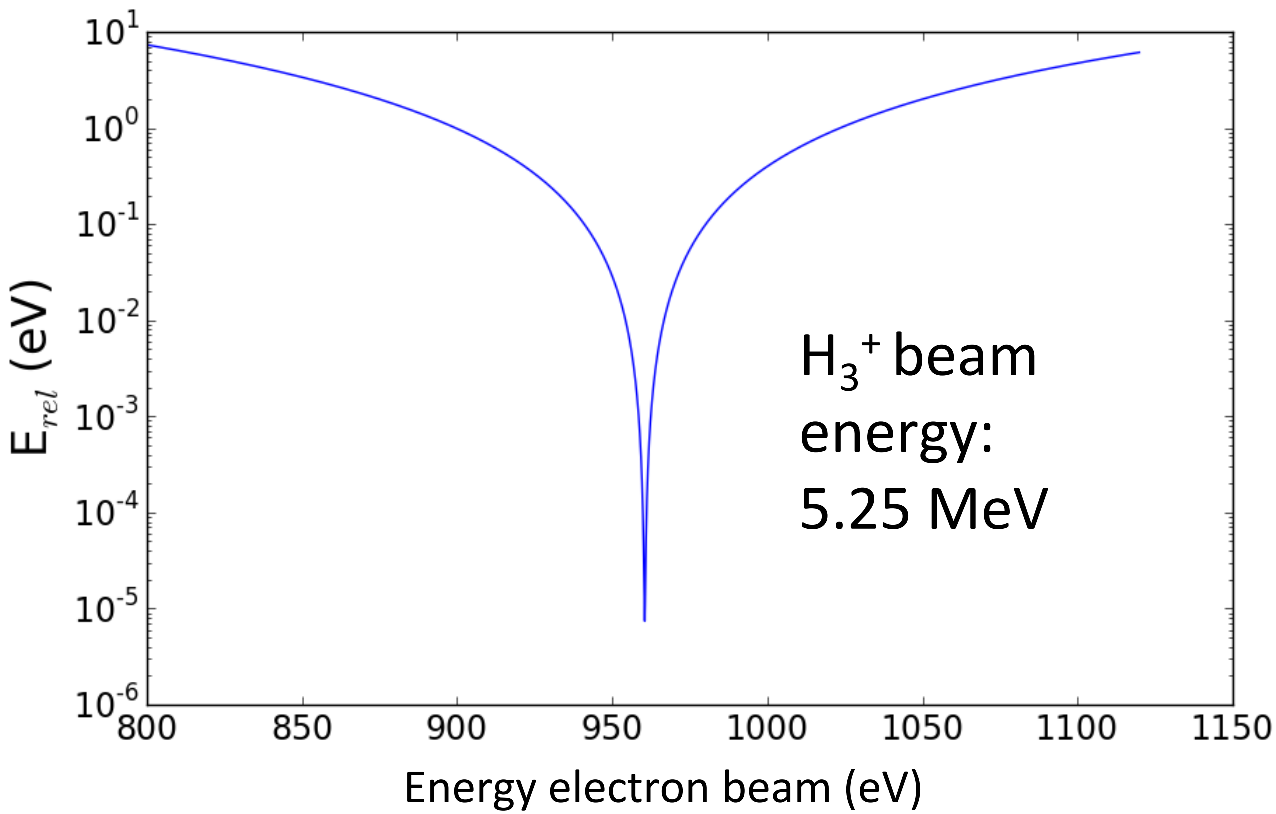
Relative collision energy

Reduced mass

Beam 1

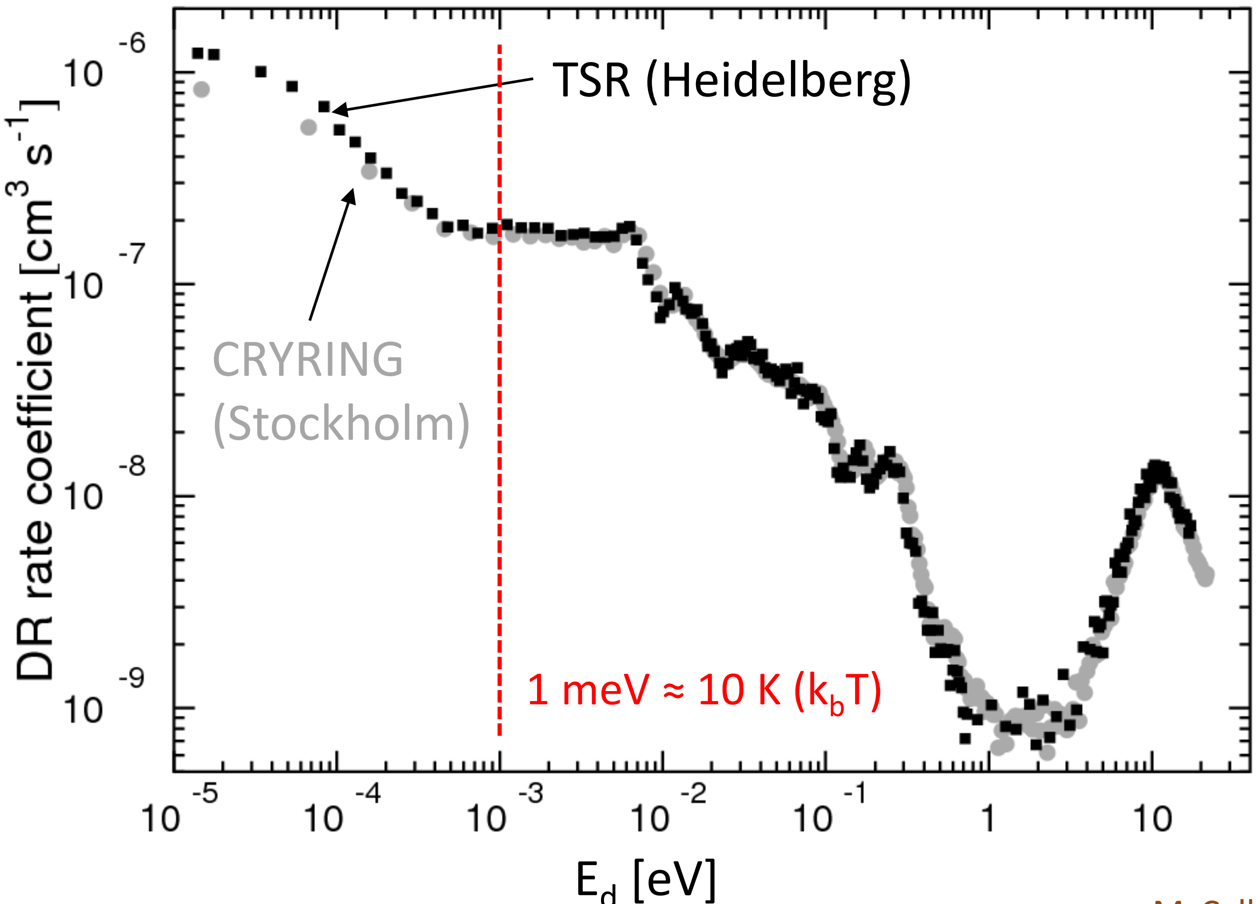
Beam 2

Angle between beams



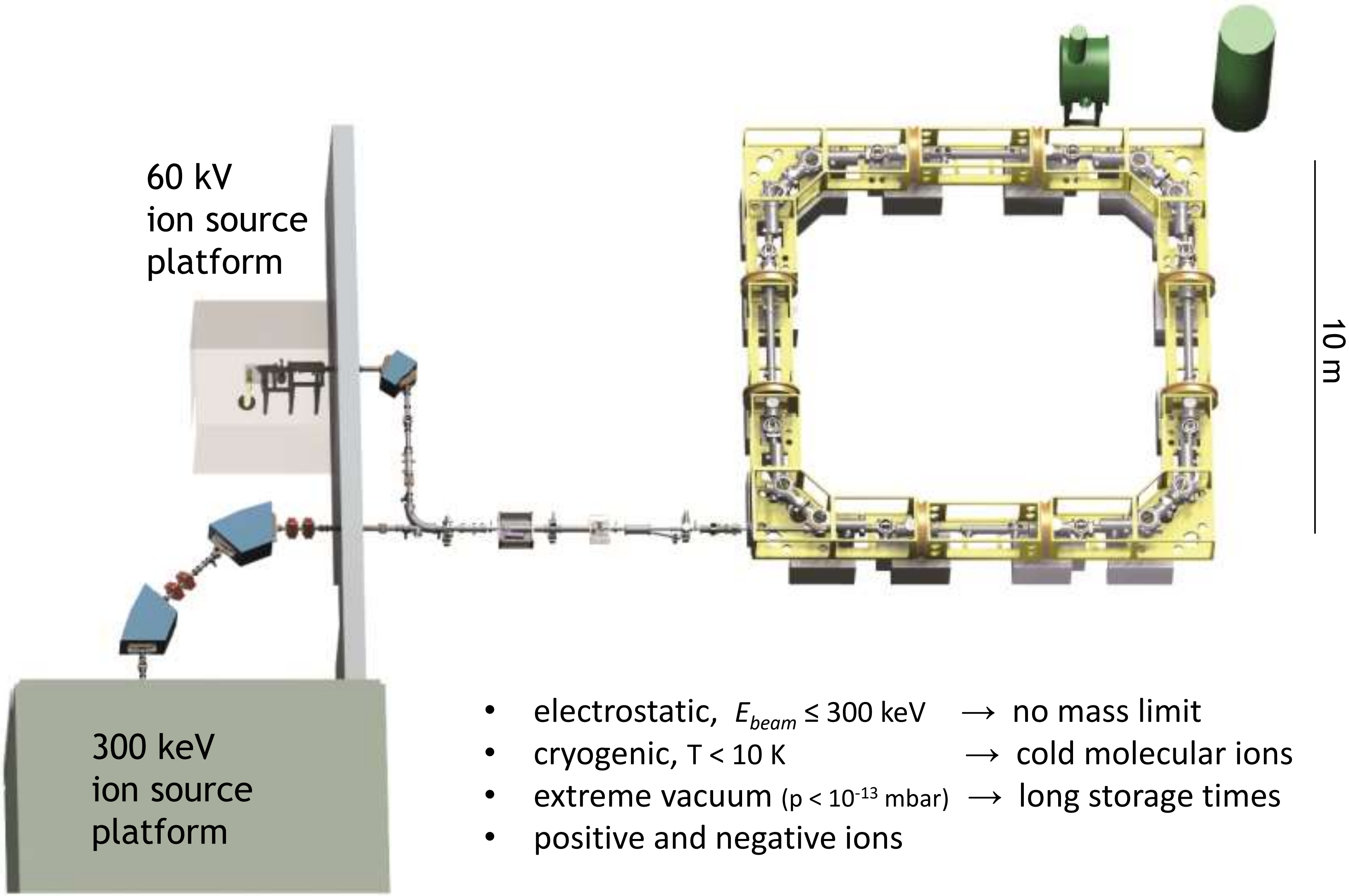
Electron recombination of the most simple polyatomic ion: H_3^+

$$H_3^+ + e^- \longrightarrow \begin{cases} H_2 + H \\ H + H + H \end{cases}$$



McCall, Nature **422**, 500 (2003)
Kreckel, Phys. Rev. Lett. **95**, 263201 (2005)
Kreckel, Phys. Rev. A **82,** 042715 (2010)

Toward colder molecular ions: the Cryogenic Storage Ring (CSR)

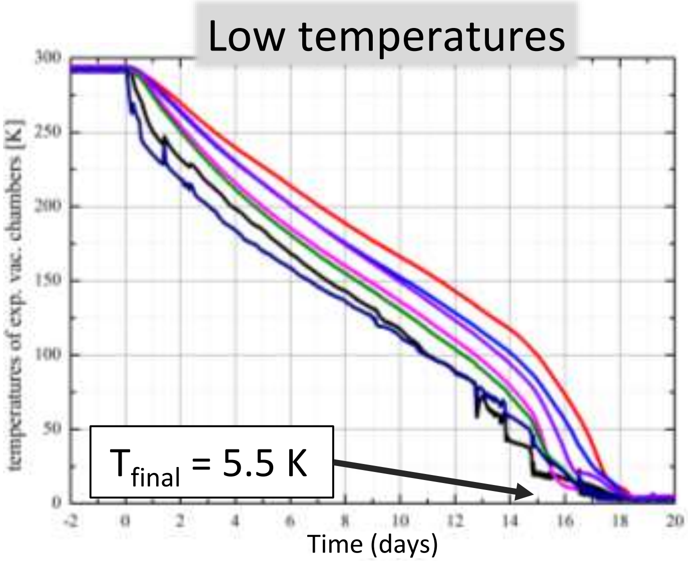


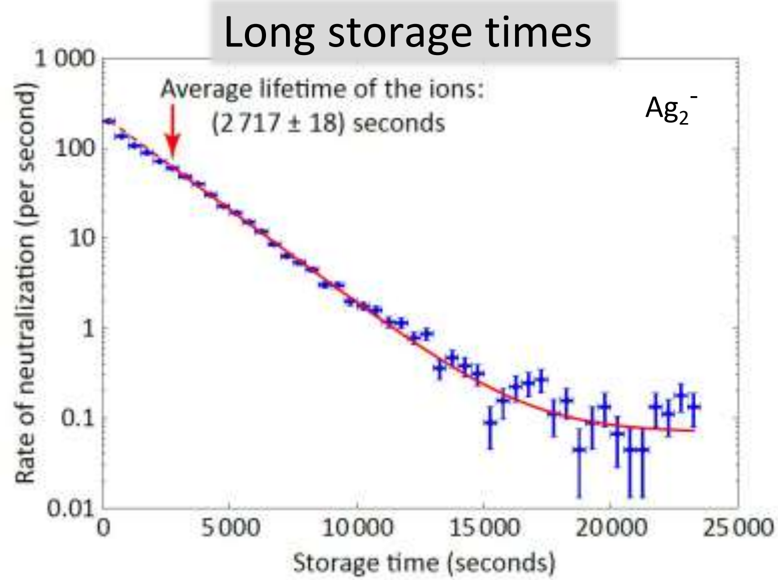
- electrostatic, $E_{beam} \leq 300$ keV → no mass limit
- cryogenic, T < 10 K → cold molecular ions
- extreme vacuum (p < 10^{-13} mbar) → long storage times
- positive and negative ions

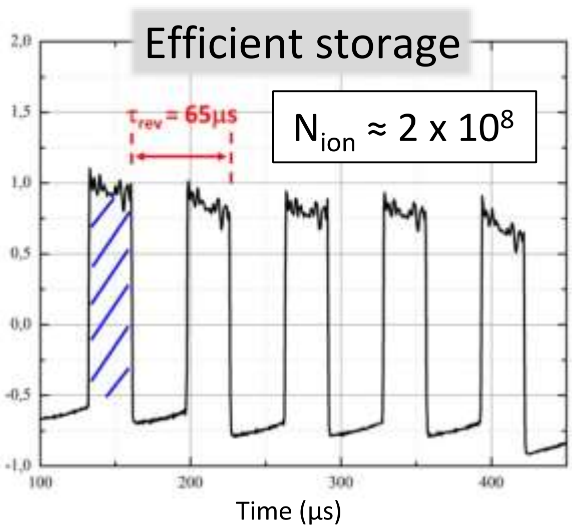
The Cryogenic Storage Ring CSR at MPIK (Heidelberg)

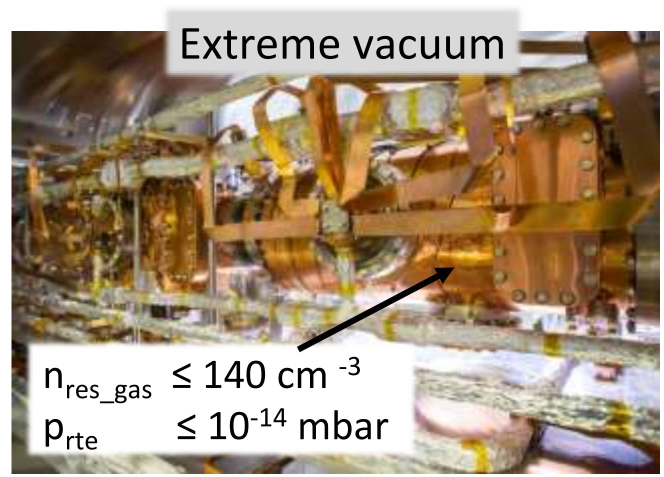
The CSR in February 2015

CSR: Commissioning and Performance Milestones









R. von Hahn et al., „The Cryogenic Storage Ring CSR“, Rev. Sci. Instrum. **87**, 063115 (2016)

CH^+ : The first molecular ion identified in space

CH^+ IN INTERSTELLAR SPACE AND IN THE LABORATORY

At a recent conference on interstellar molecules at the Yerkes Observatory, P. Swings called attention to three sharp interstellar lines—λλ 4232.58, 3957.72, and 3745.33—for which no identification was available. He suggested that the three lines belong to a light-ionized molecule such as CH^+, CN^+, C_2^+, NH^+, or NO^+. The molecule should have a small energy of dissociation in the excited state. E. Teller and G. Herzberg suggested the CH^+ molecule as most likely, by analogy to BH. However, at the time no laboratory data were available. Since then we have investigated the spectrum of a discharge through helium to which a trace of C_6H_6 vapor was added. This spectrum shows three bands with heads at λλ 4225.3, 3954.0, and 3743.4 A. They have a very widely spaced fine structure which can be readily analyzed. Each band consists of three singlet branches—P, Q, and R—corresponding to a $^1\Pi - {}^1\Sigma$ transition. The numbering of the lines is found by inspection. The R(0) lines of the three bands have the wave lengths λλ 4232.57, 3957.71, and 3745.30 A, which agree with those of the three interstellar lines given above. Since it is known that in interstellar absorption practically only the lines coming from the lowest rotational level of the lower state occur and since just these lines [R(0)] of the new bands agree with the interstellar lines, we consider it as proved that *the three interstellar lines belong to the three new bands* observed by us in the laboratory and are therefore *due to the same molecule*.

A $^1\Pi - {}^1\Sigma$ system with a 0–0 band at about 4300 A is to be expected for the CH^+ molecule, since the isoelectronic BH molecule has such a system in this region. CH^+ is also strongly suggested by the conditions of excitation. The rotational constant B_0'' in the lower state of the new bands was found to be 14.0 cm.$^{-1}$, which is close to that of CH ($B_0 = 14.189$), as one would expect if CH^+ is the emitter. At any rate the value of B_0'' shows that the emitter must be a hydride molecule belonging to the second period of the periodic system ($Li - F$). The observation of the band system in interstellar space shows that the lower state is the electronic ground state of the molecule. Now the ground states of all neutral and singly ionized diatomic hydrides of the second period are known with the exception of LiH^+, CH^+, NH^+, and FH^+. Since the observed B_0'' value does not agree with that of any of the known hydrides and since of the four unknown ionized hydrides, only CH^+ can have singlet bands, we conclude that *the new bands and the interstellar lines are due to the* CH^+ *molecule.*

The presence of CH^+ in interstellar space, thus established, appears very plausible in view of the known presence of CH as well as of comparatively large amounts of H^+.

A more complete report on this work including a full discussion of the structure of the CH^+ molecule will be submitted later.

A. E. Douglas
G. Herzberg

Douglas and Herzberg, ApJ **94**, p.381 (1941)

Summary: Molecular Levels and Transitions

Electronic Transitions:

ΔE = 1-15 eV

Visible-UV

Vibrational Transitions:

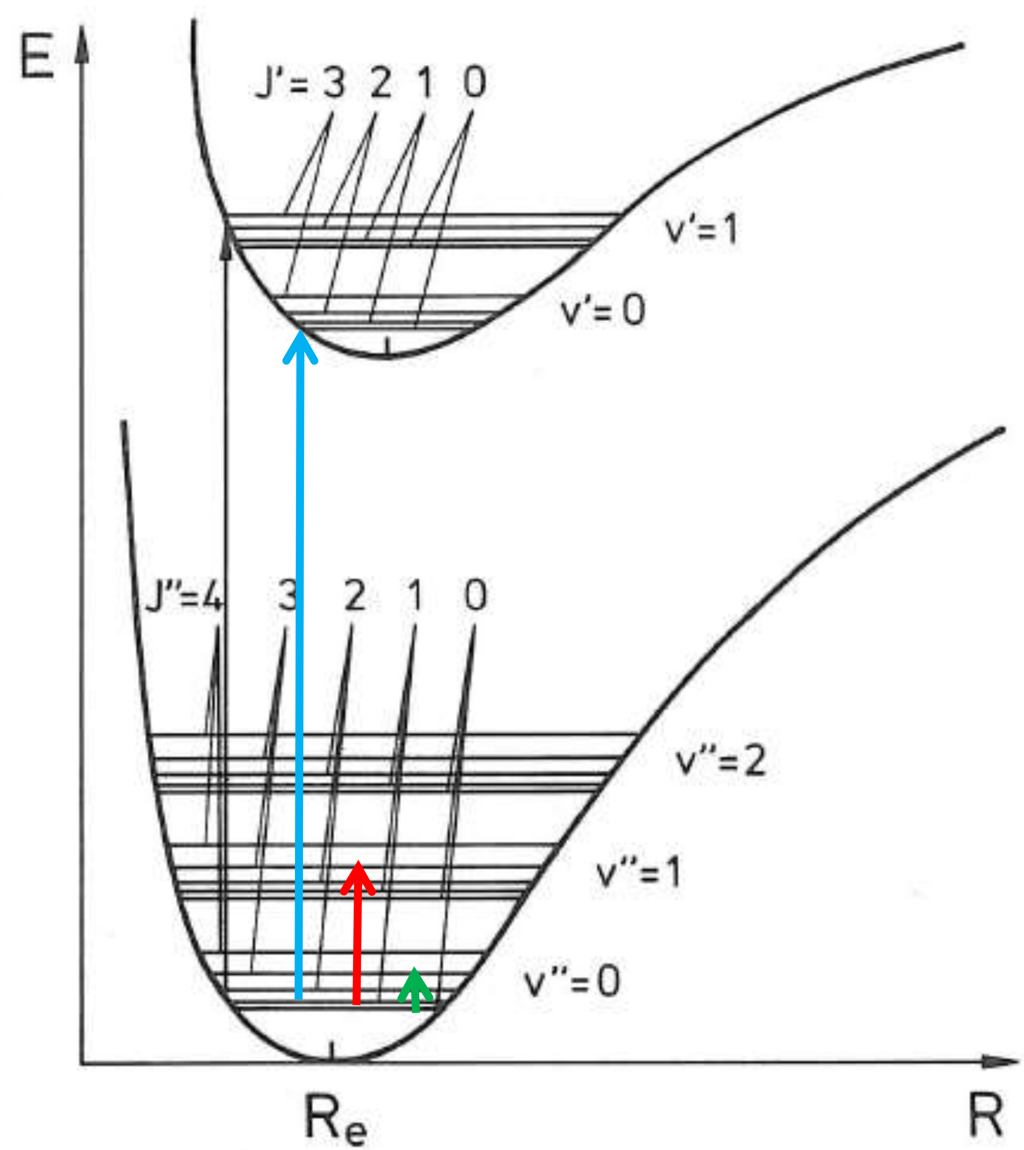
$\Delta E \approx$ 0.1 eV

Infrared

Rotational Transitions:

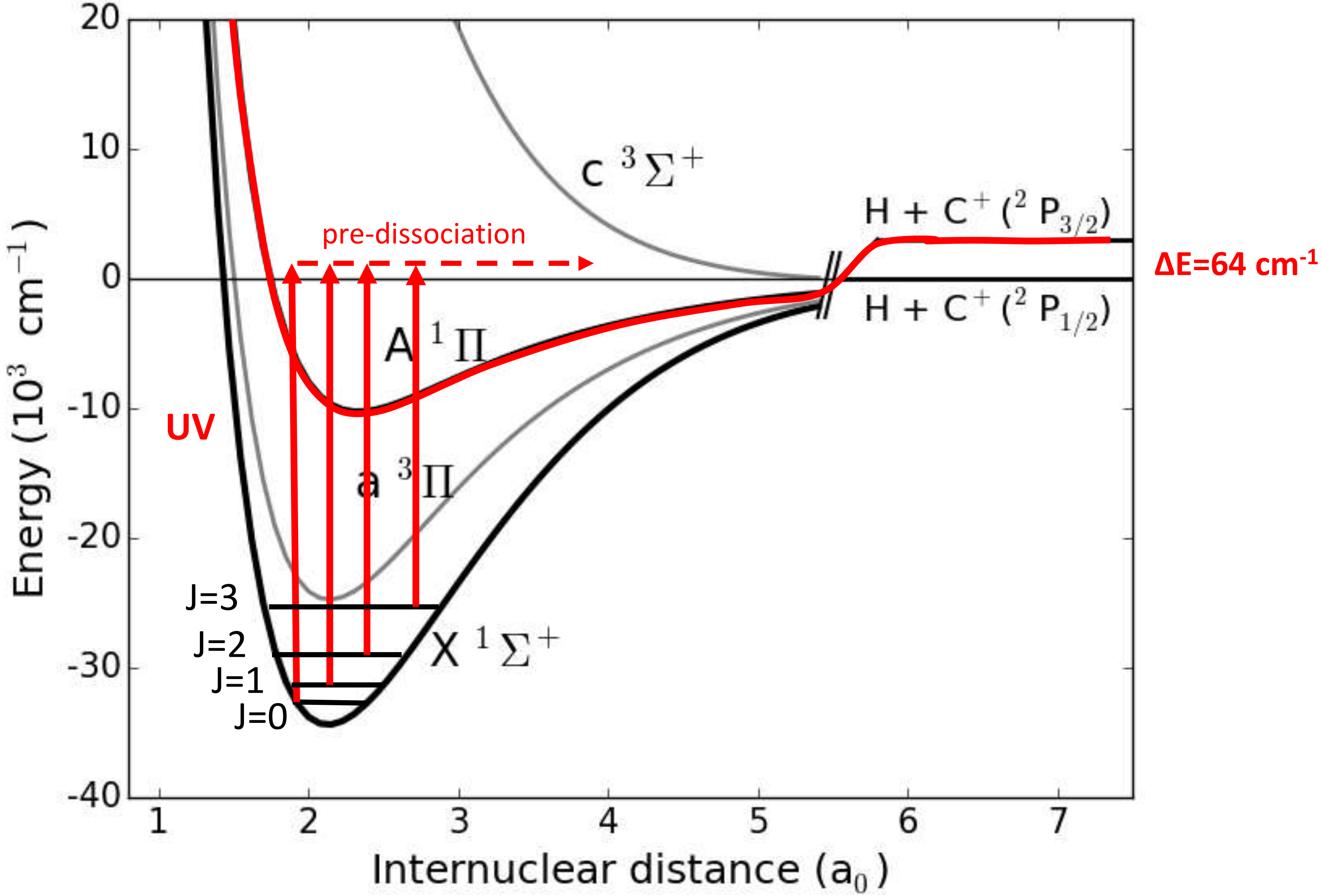
$\Delta E \approx$ 0.001-0.01 eV

(sub)-Millimeter



CH^+ Photodissociation

$$CH^+ + UV \longrightarrow C^+ + H$$



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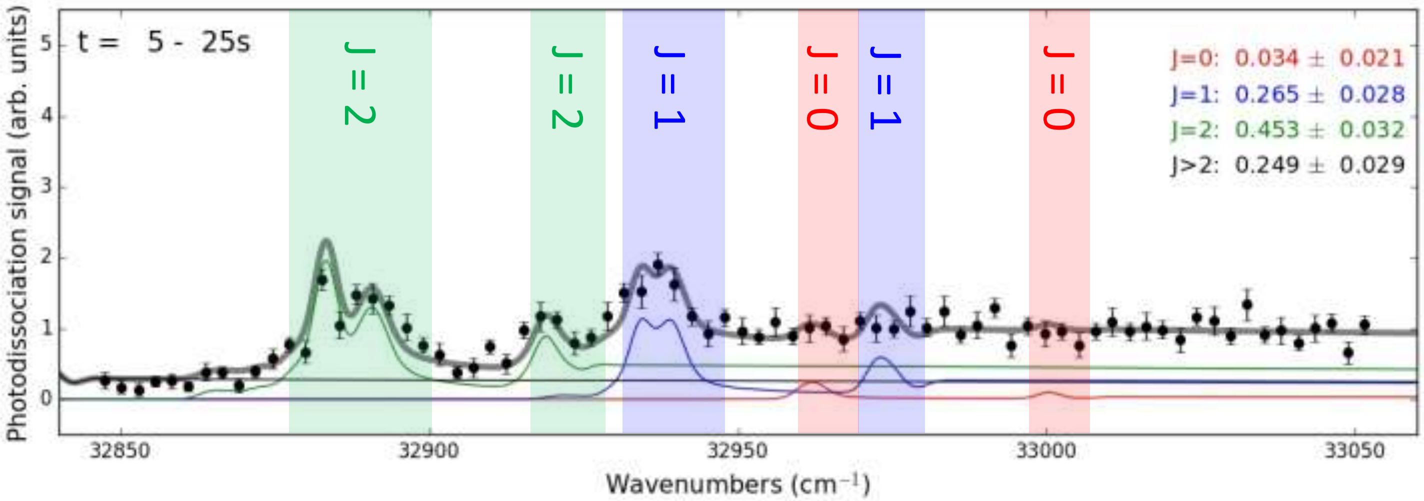

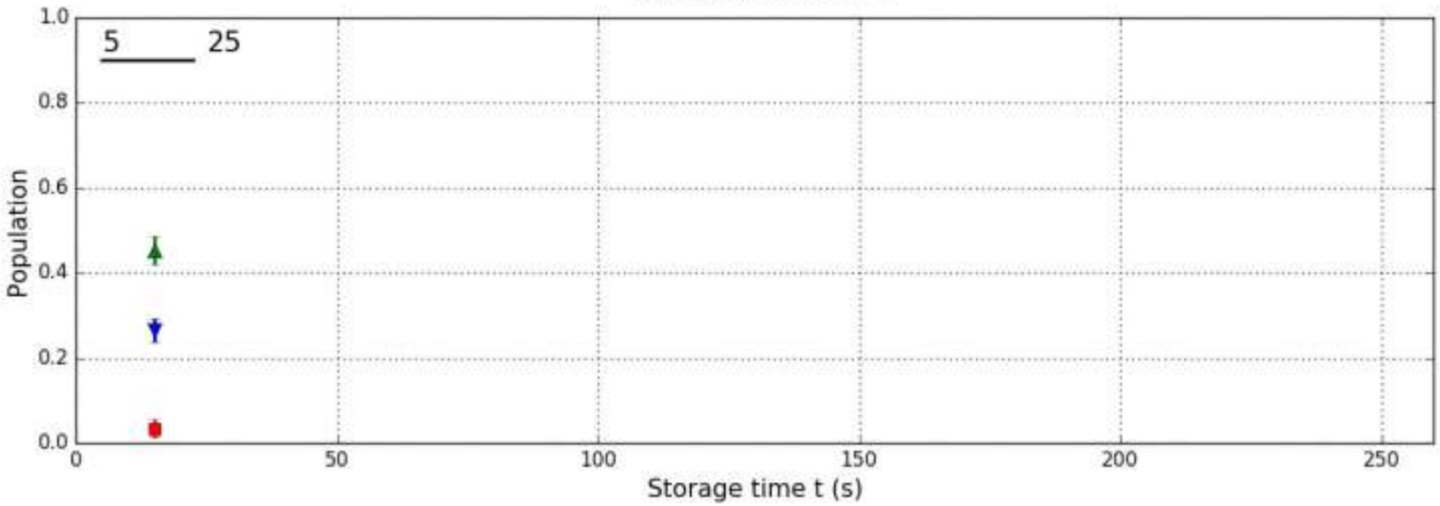

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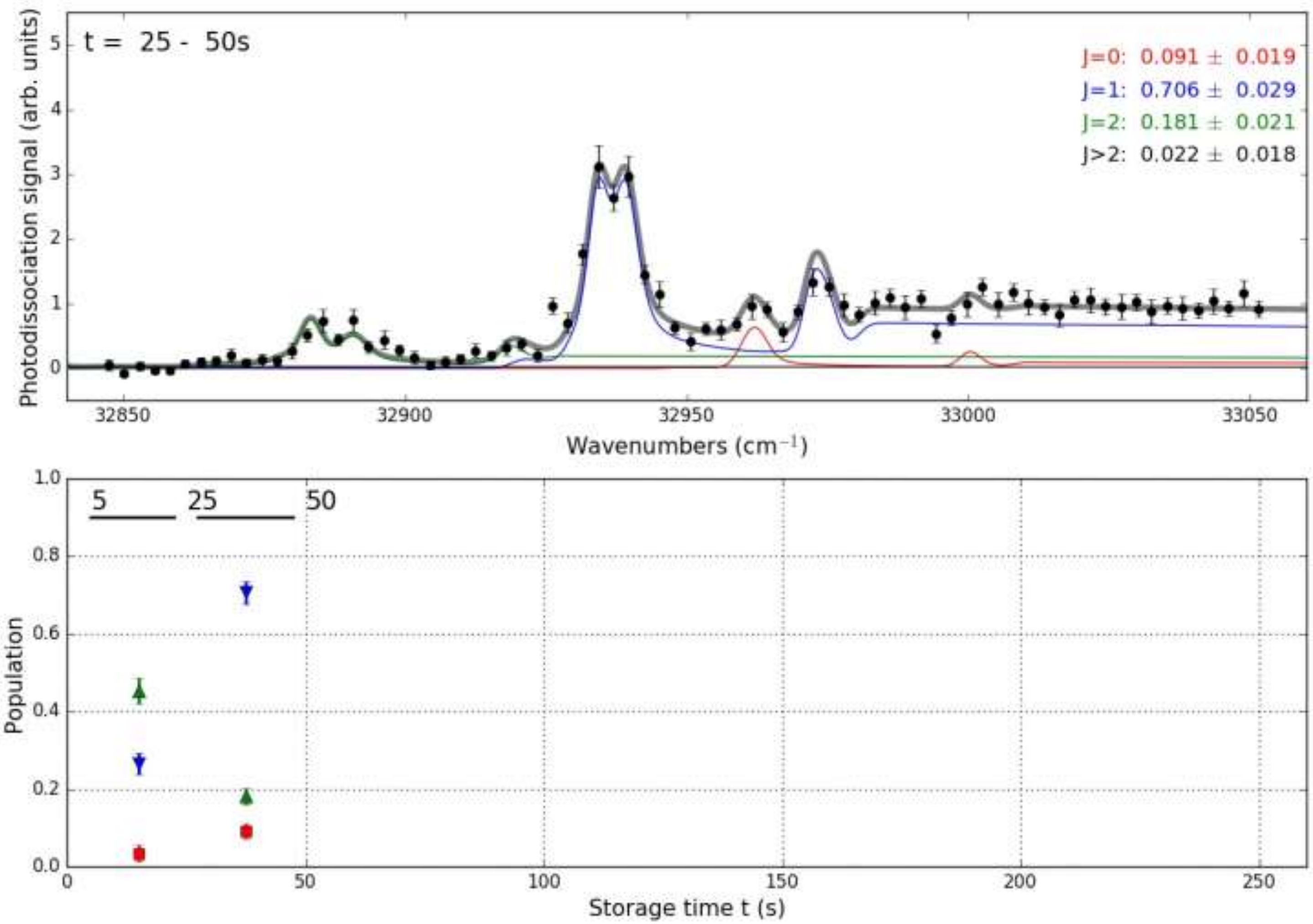

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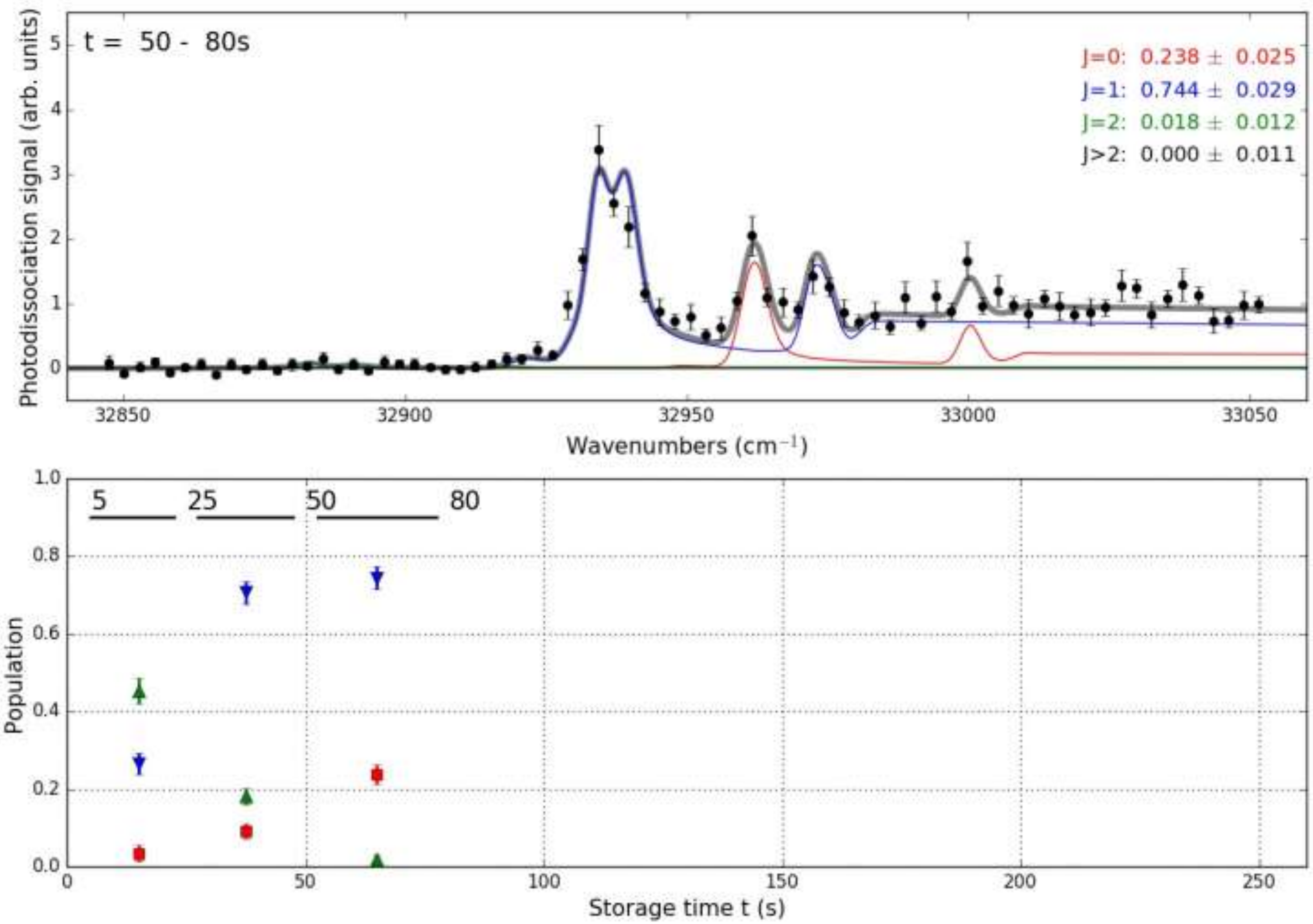

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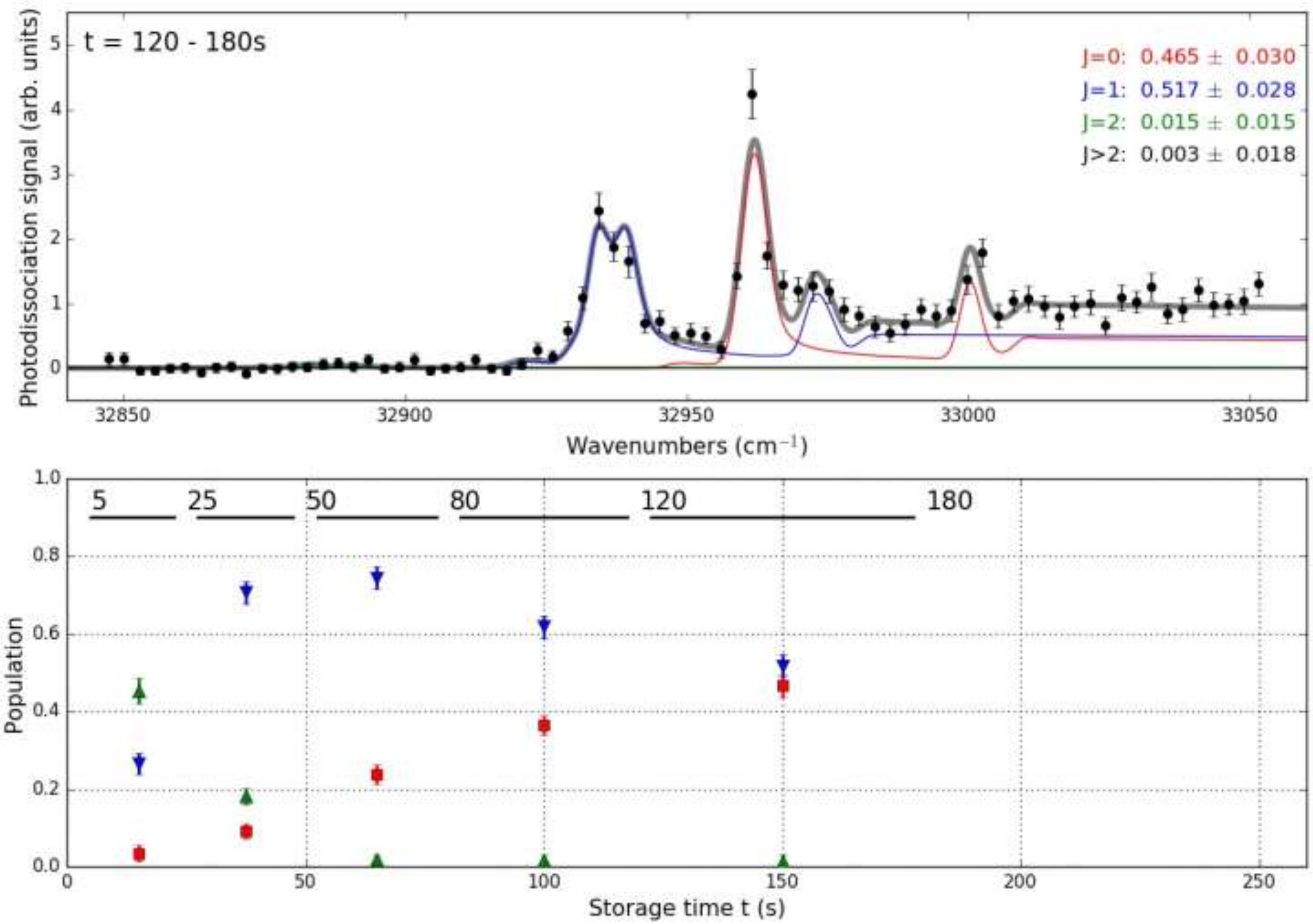

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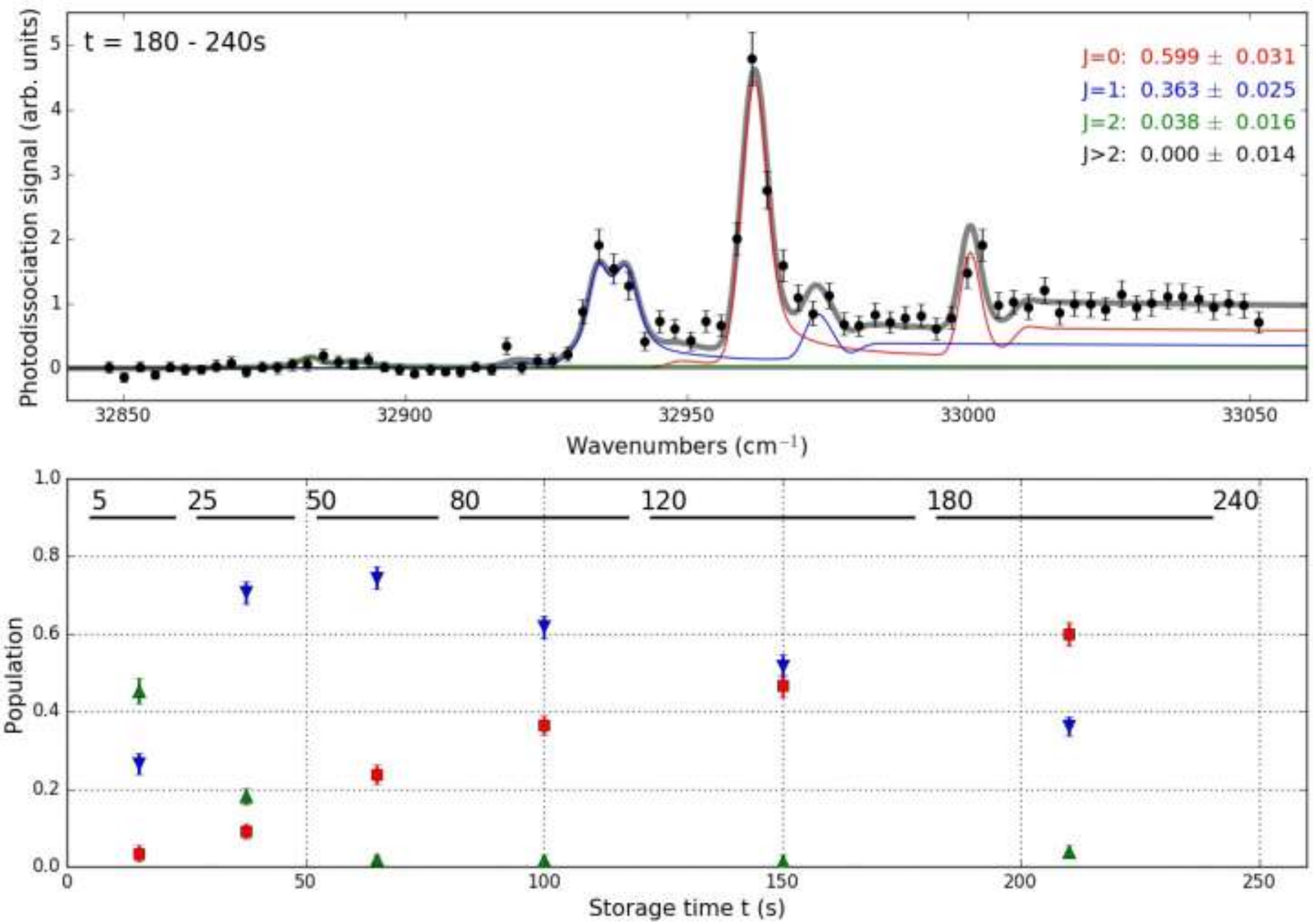

CH^+ Photodissociation

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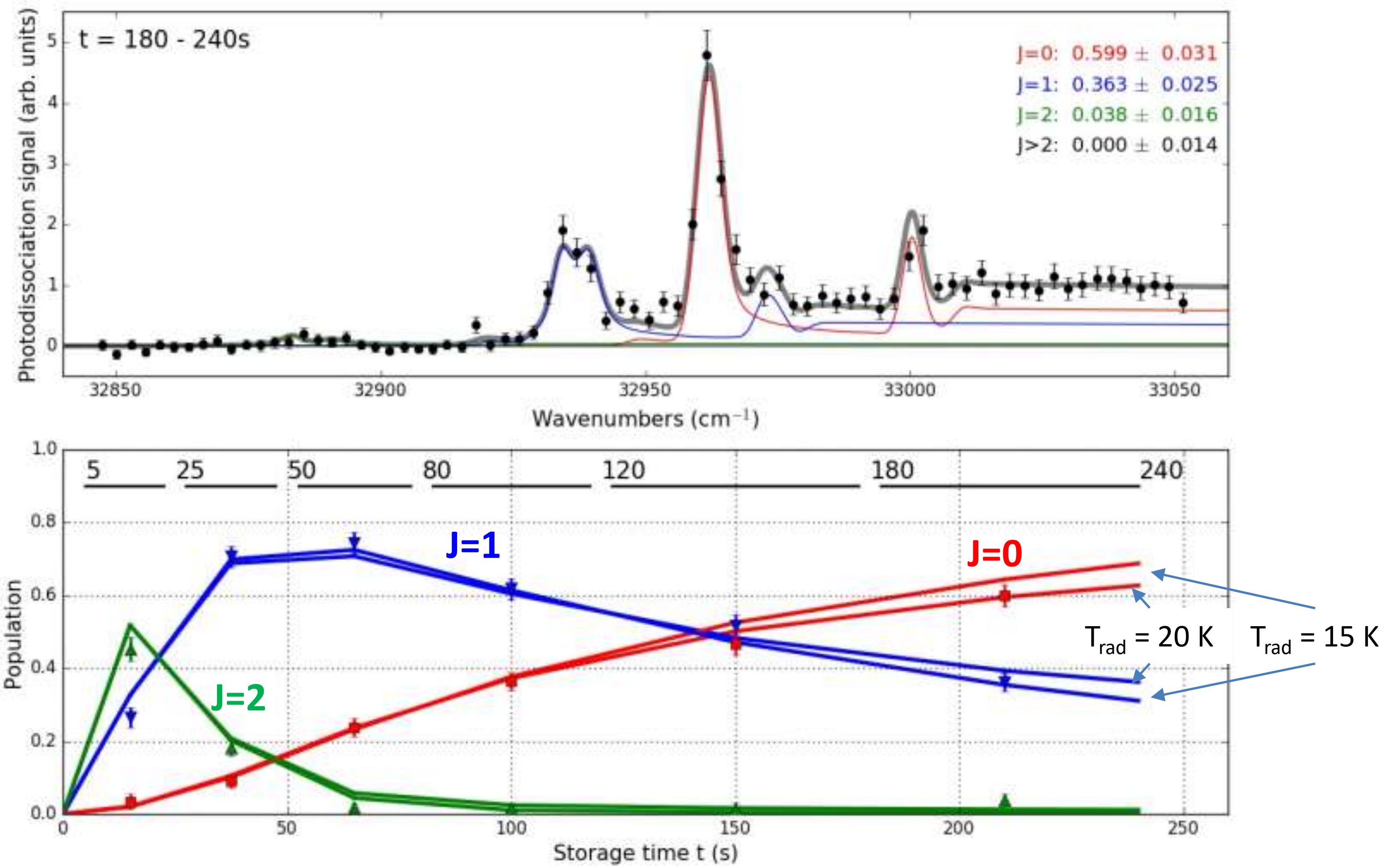
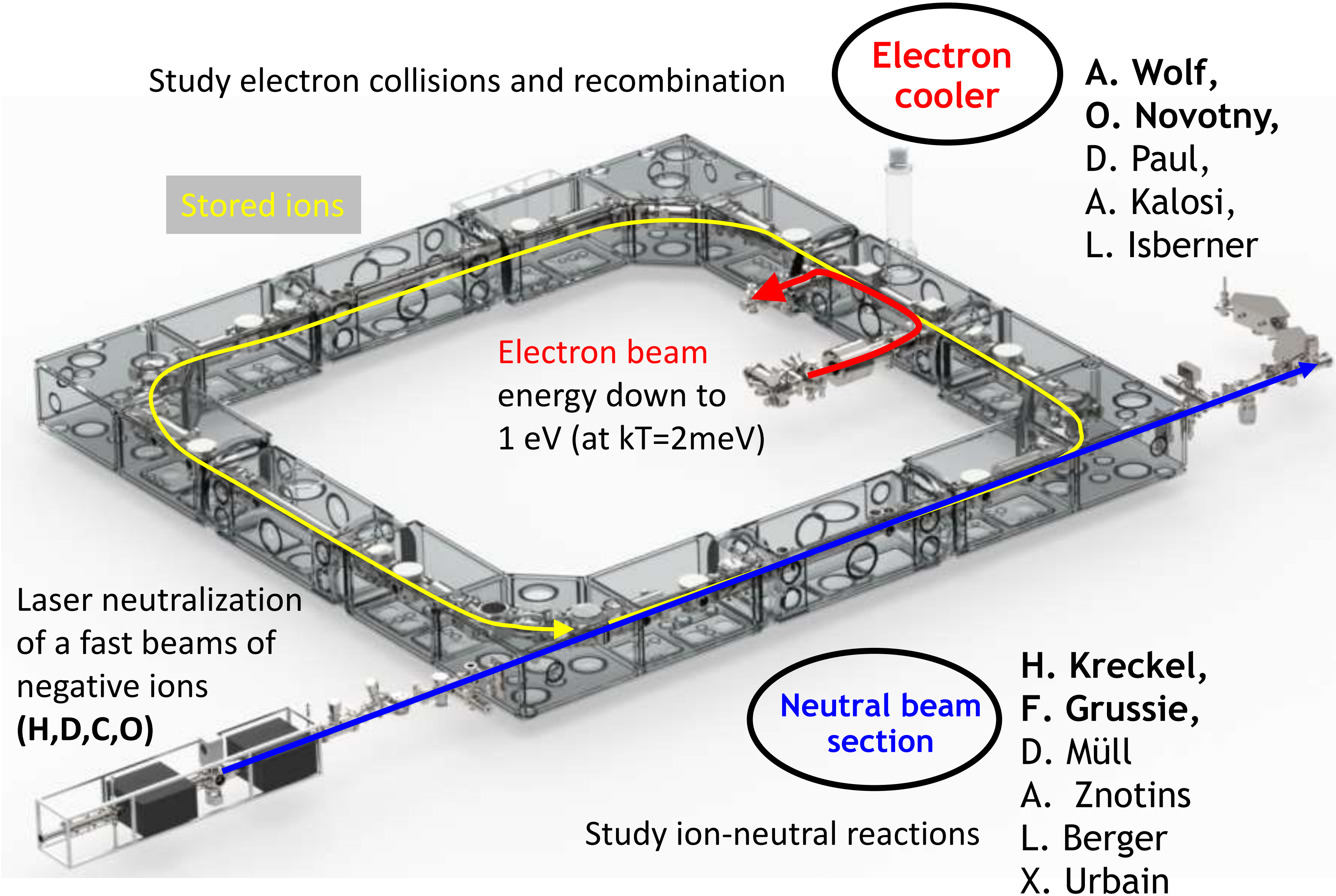


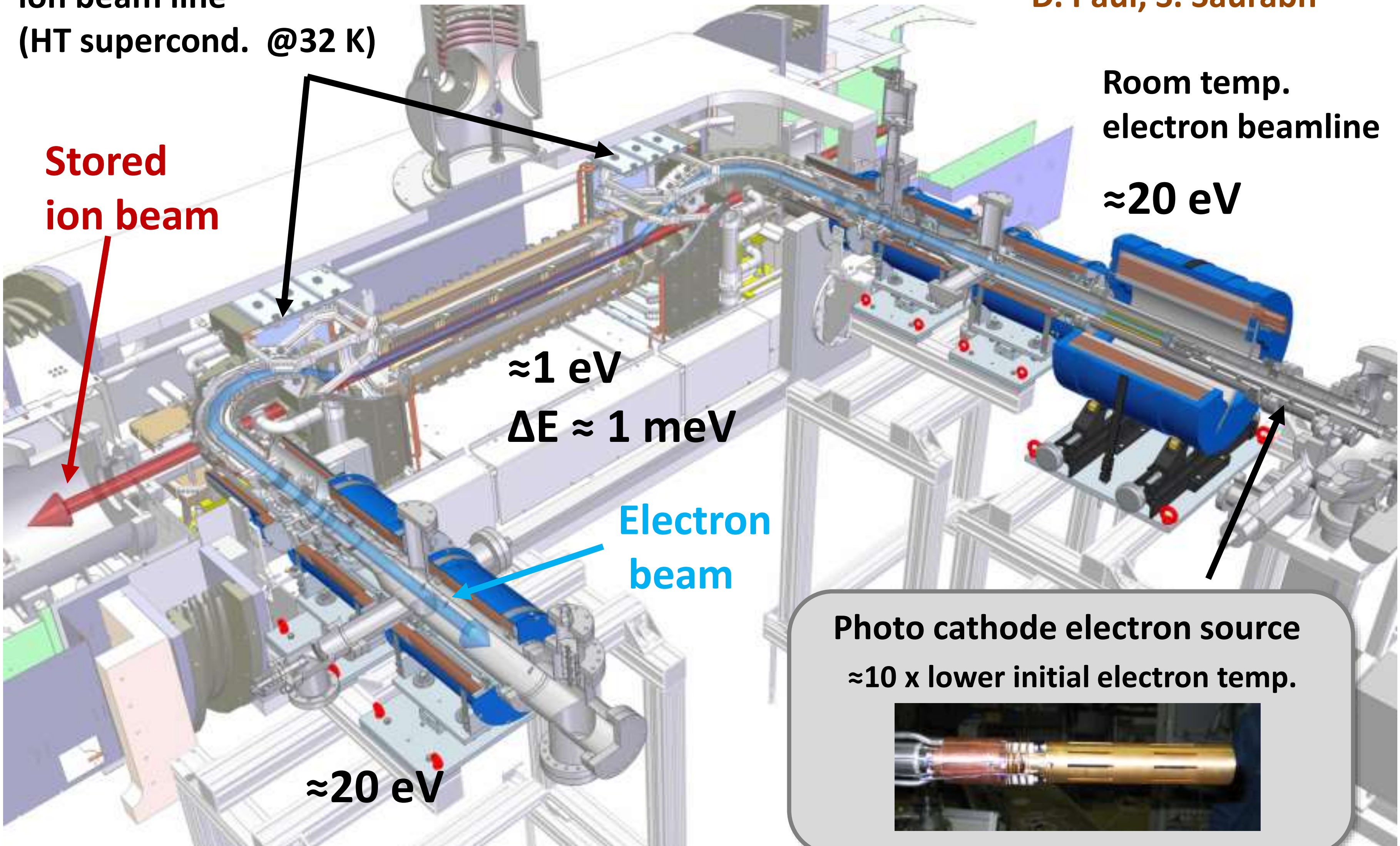
O'Connor et al., Phys. Rev. Lett., **116**, 113002 (2016)

Merged Beam Sections to study Gas Phase Processes

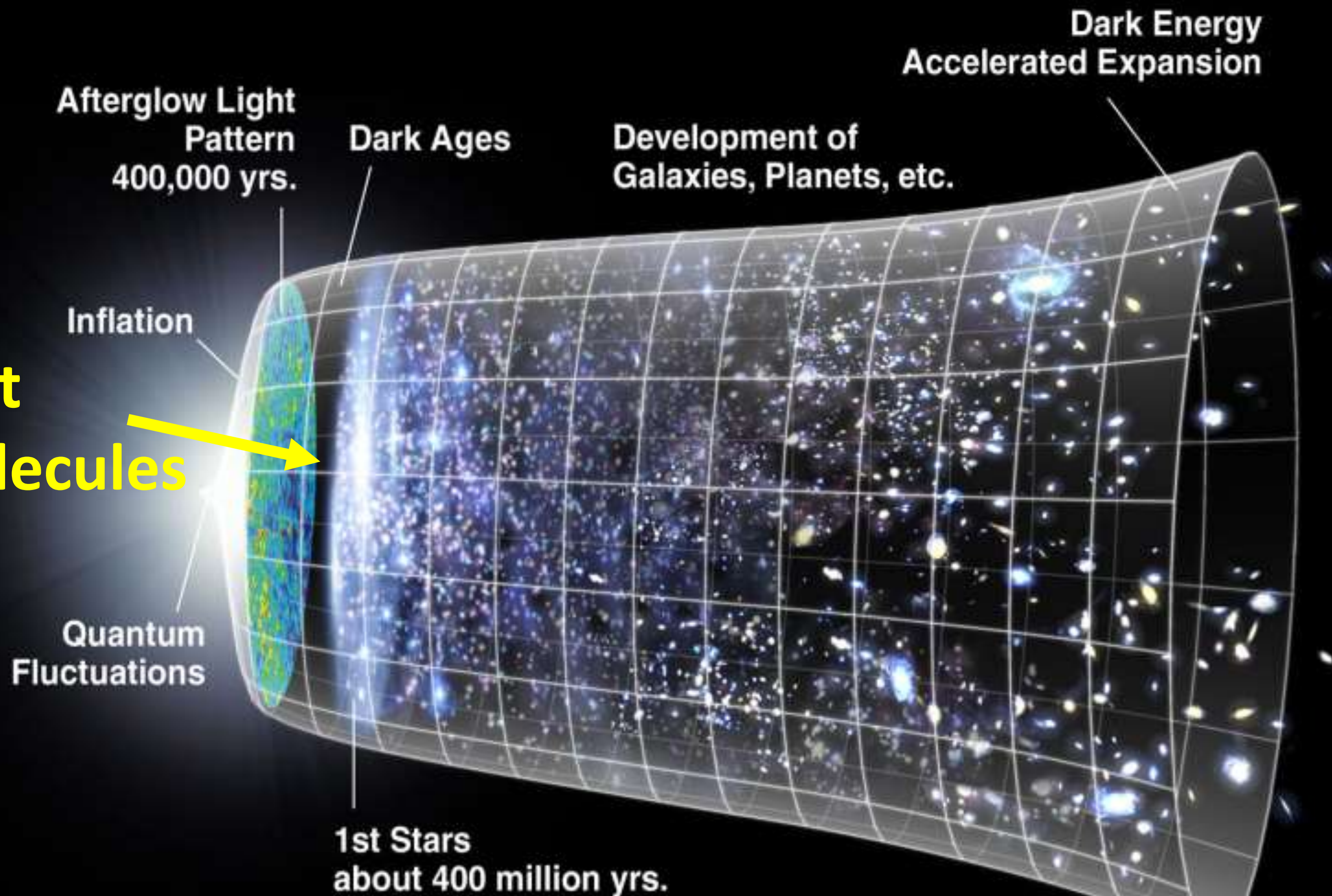


The CSR Electron Cooler

A. Wolf, O. Novotny,
C. Krantz, P. Wilhelm,
D. Paul, S. Saurabh



Molecules in the Early Universe



First molecules

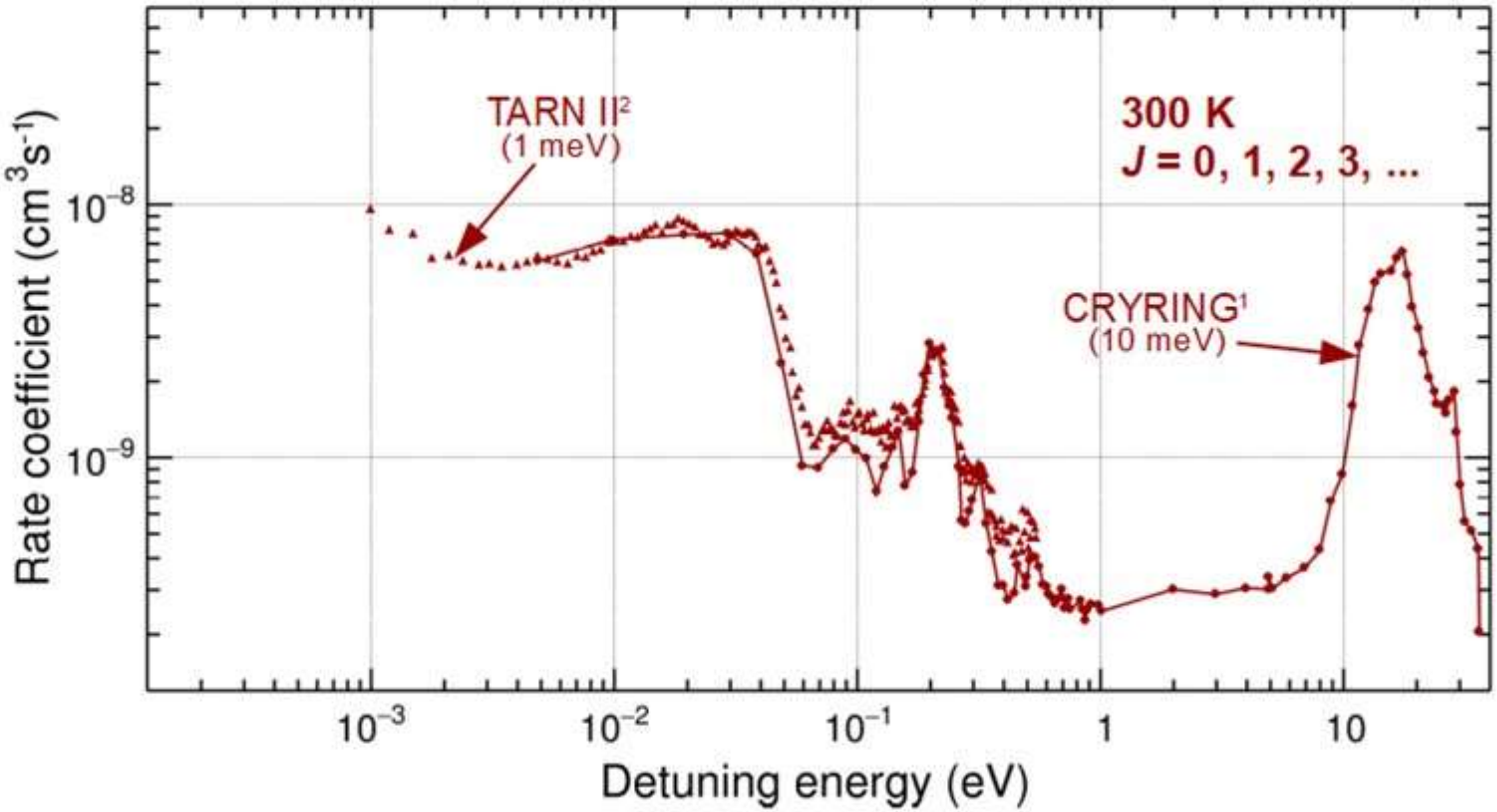
HeH^+, H_2^+, H_2, HD^+, HD, H_3^+, LiH^+...

Güsten et al, Nature 568, 357 (2019)

NASA/WMAP Science Team

Previous studies: Electron Recombination of HeH^+

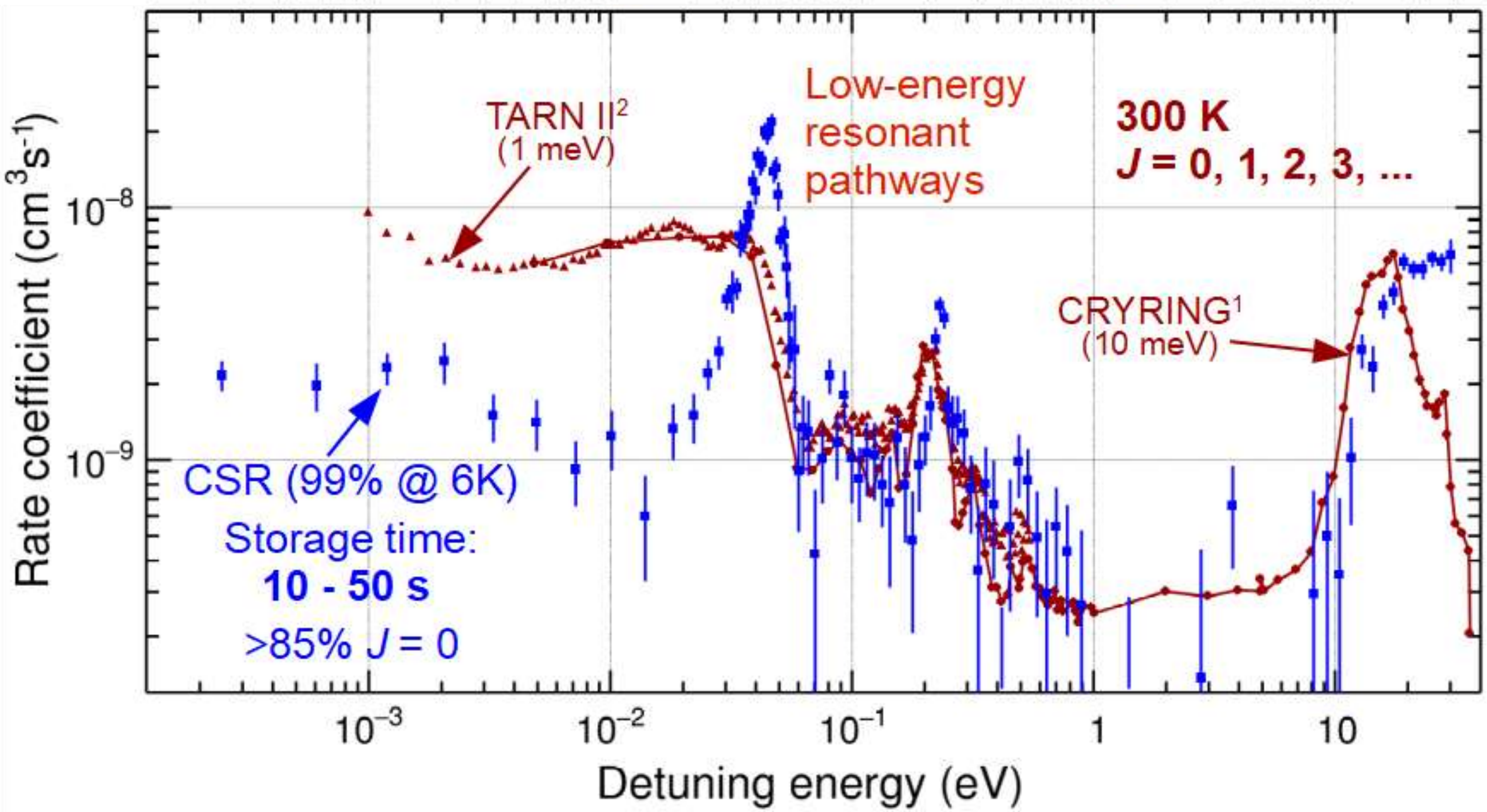
$HeH^+(J) + e^- \rightarrow He + H$



C. Strömholm et al., Phys. Rev. A **54**, 3086 (1996)
T. Tanabe et al., J. Phys. B **31**, L297 (1998)

Electron Recombination of cold HeH^+

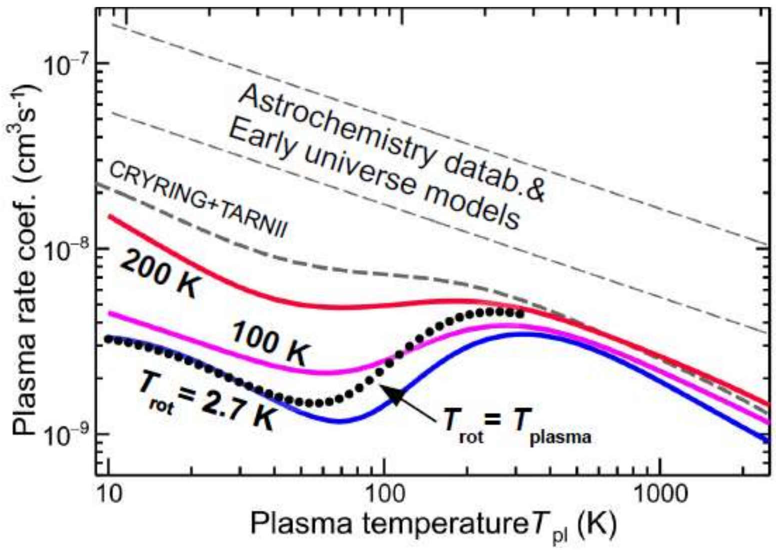
$$HeH^+(J) + e^- \rightarrow He + H$$



O. Novotný et al.,
Science **365**, 676–679 (2019)

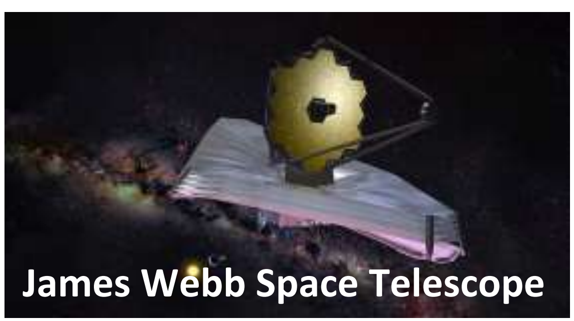
C. Strömholm et al., Phys. Rev. A **54**, 3086 (1996)
T. Tanabe et al., J. Phys. B **31**, L297 (1998)

PART III Rate coefficients for Astrochemical Models

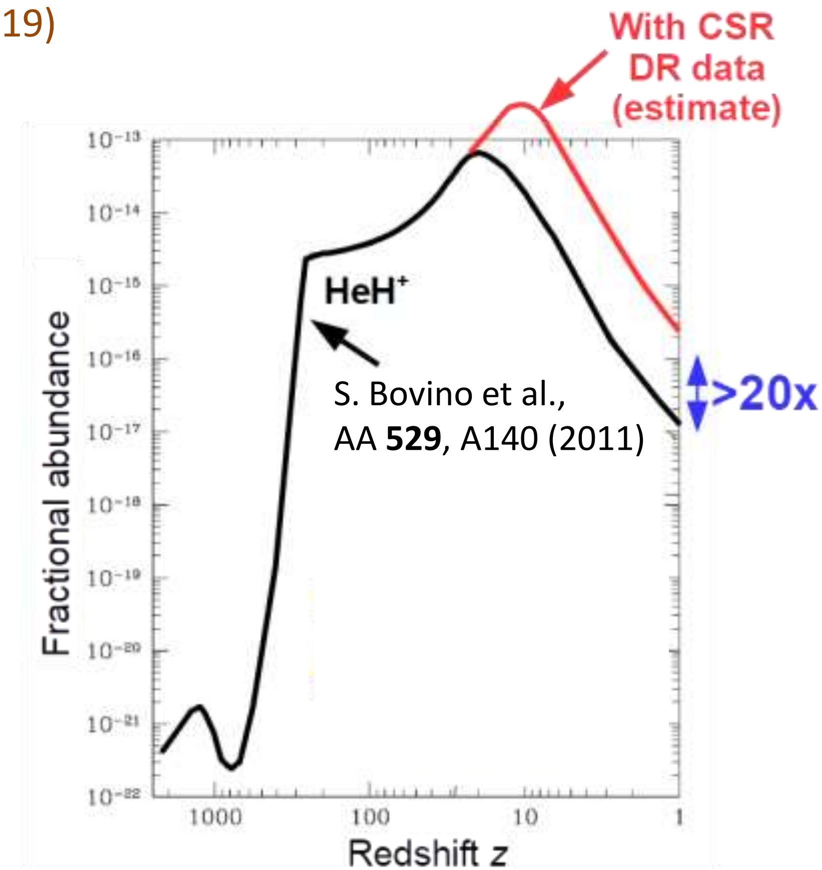


Fixed rotational temperature

Fully thermal rate coefficients



O. Novotný et al., *Science* **365**, 676–679 (2019)



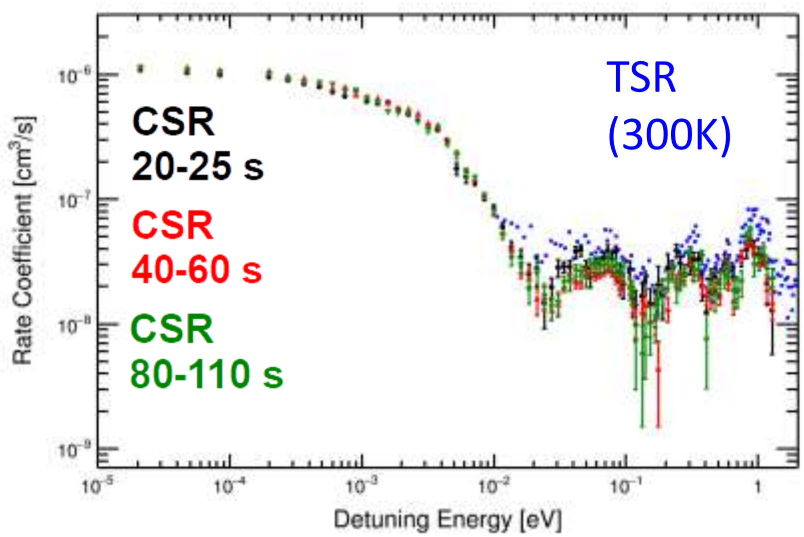
S. Bovino et al., AA **529**, A140 (2011)

Expect Early Universe Abundance of HeH^+ to be much higher!

Another first: Inelastic electron collisions of $CH^+ + e^-$

Dissociative recombination

$CH^+ + e^- \rightarrow C + H$



D. Paul et al., ApJ **939** 122 (2022)

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Dissociative recombination

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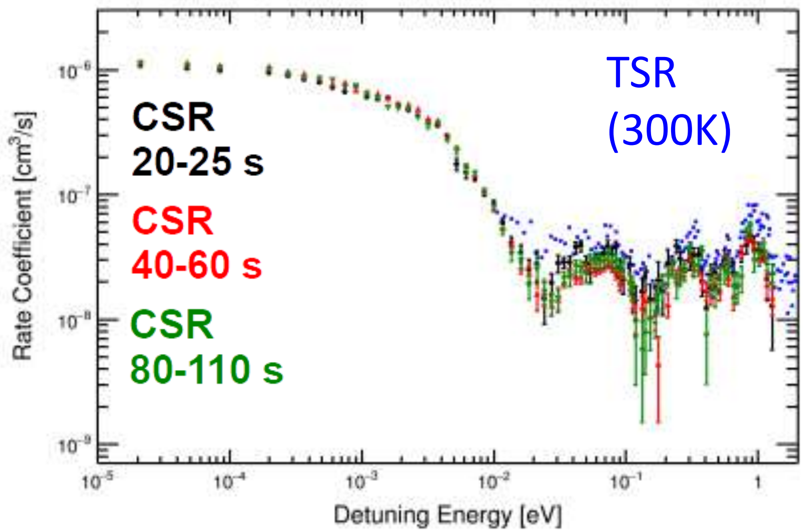

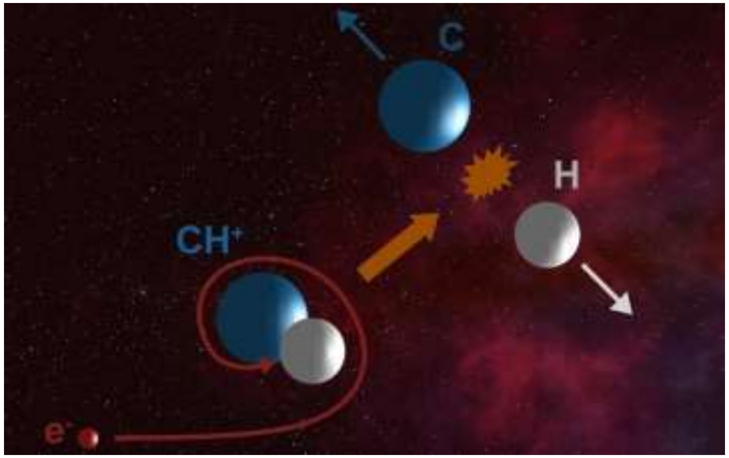

D. Paul et al., ApJ **939** 122 (2022)

Another first: Inelastic electron collisions of $CH^+ + e^-$

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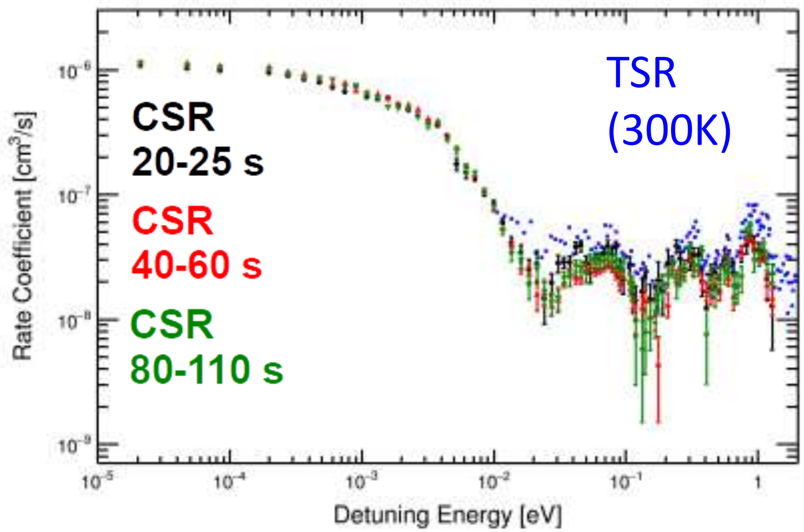
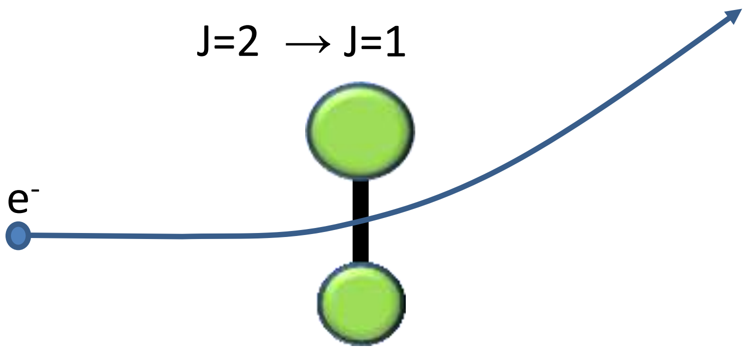
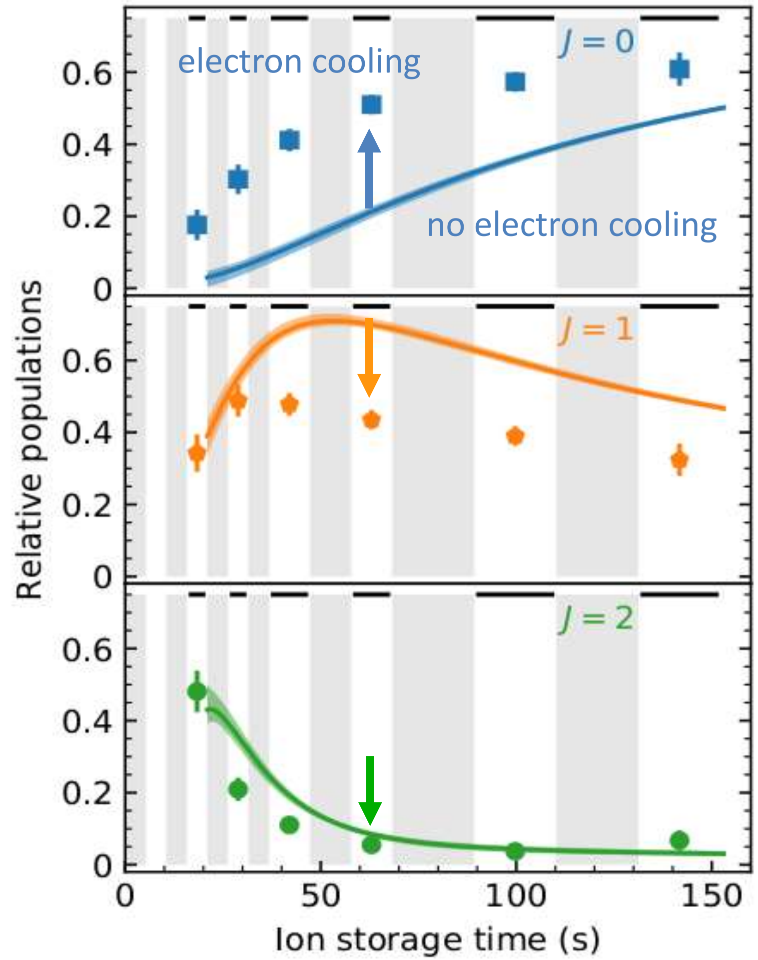
$CH^+ + e^- \rightarrow C + H$





Laser-monitored populations



First ever inelastic electron cooling rates for CH^+

D. Paul et al., ApJ **939** 122 (2022)

A. Kalosi, Phys. Rev. Lett. **128**, 183402 (2022)

Choosing the Right Targets: Key Reactions Identified by Sensitivity Studies

Protoplanetary Disks

Among most problematic reactions:

$H_3^+ + C \longrightarrow CH^+ + H$

$HCO^+ + C \longrightarrow CH^+ + CO$

$H_3^+ + O \longrightarrow OH^+ + H_2$

$H^+ + O \longrightarrow O^+ + H$

$H_3O^+ + e \longrightarrow H_2O + H$

$CH_2^+ + O \longrightarrow HCO^+ + H$

Vasyunin et al., ApJ **672**, 629 (2008)

Dense Interstellar Clouds

Among the Top 15 most influential reactions:

$H_3^+ + O \longrightarrow OH^+ + H_2$

$H_3^+ + C \longrightarrow CH^+ + H_2$

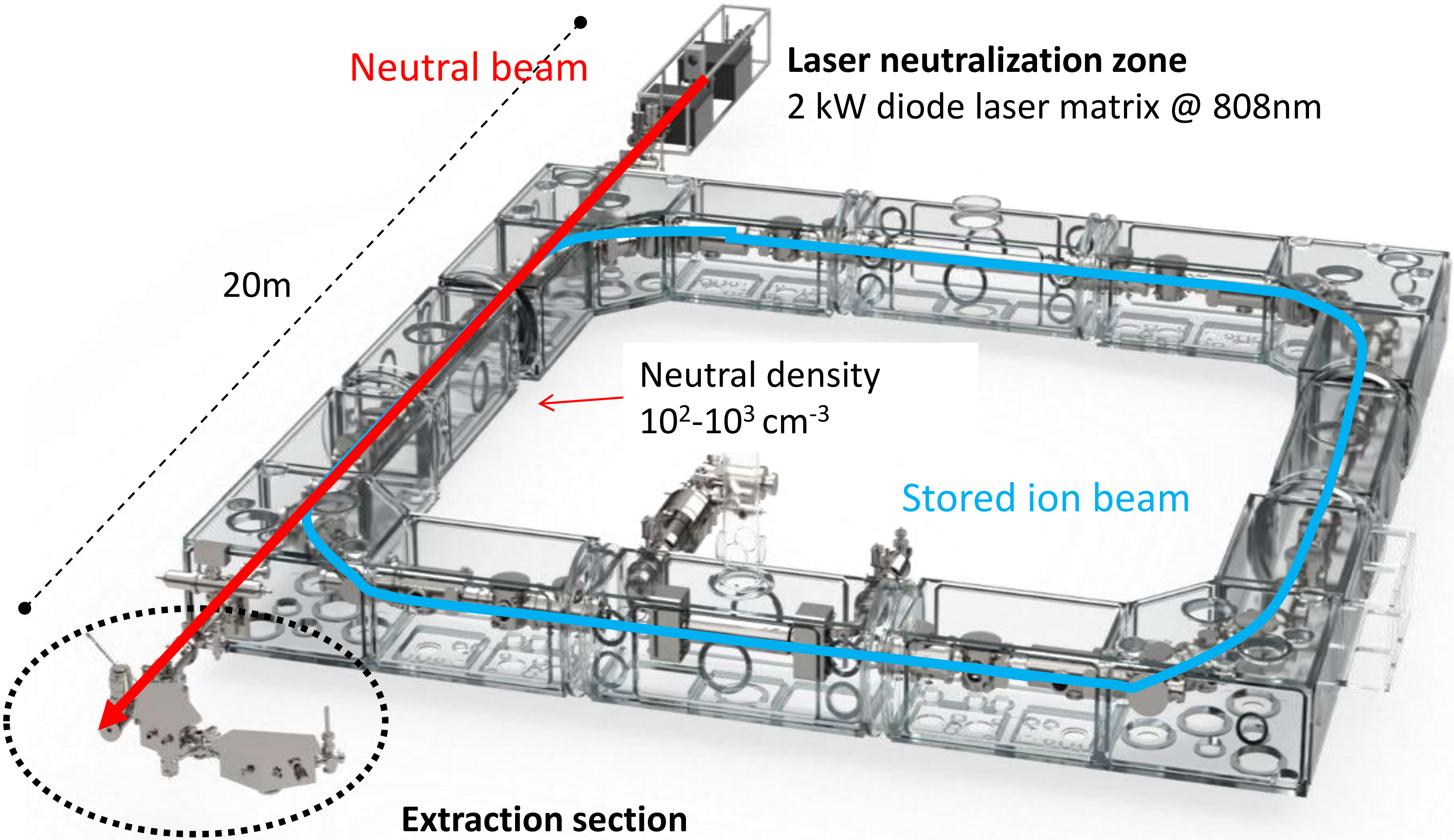
$HCO^+ + C \longrightarrow CH^+ + CO$

$H_3O^+ + e \longrightarrow H_2O + H$

$HCO^+ + e \longrightarrow CO + H$

Wakelam et al., A&A **495**, 513 (2009)

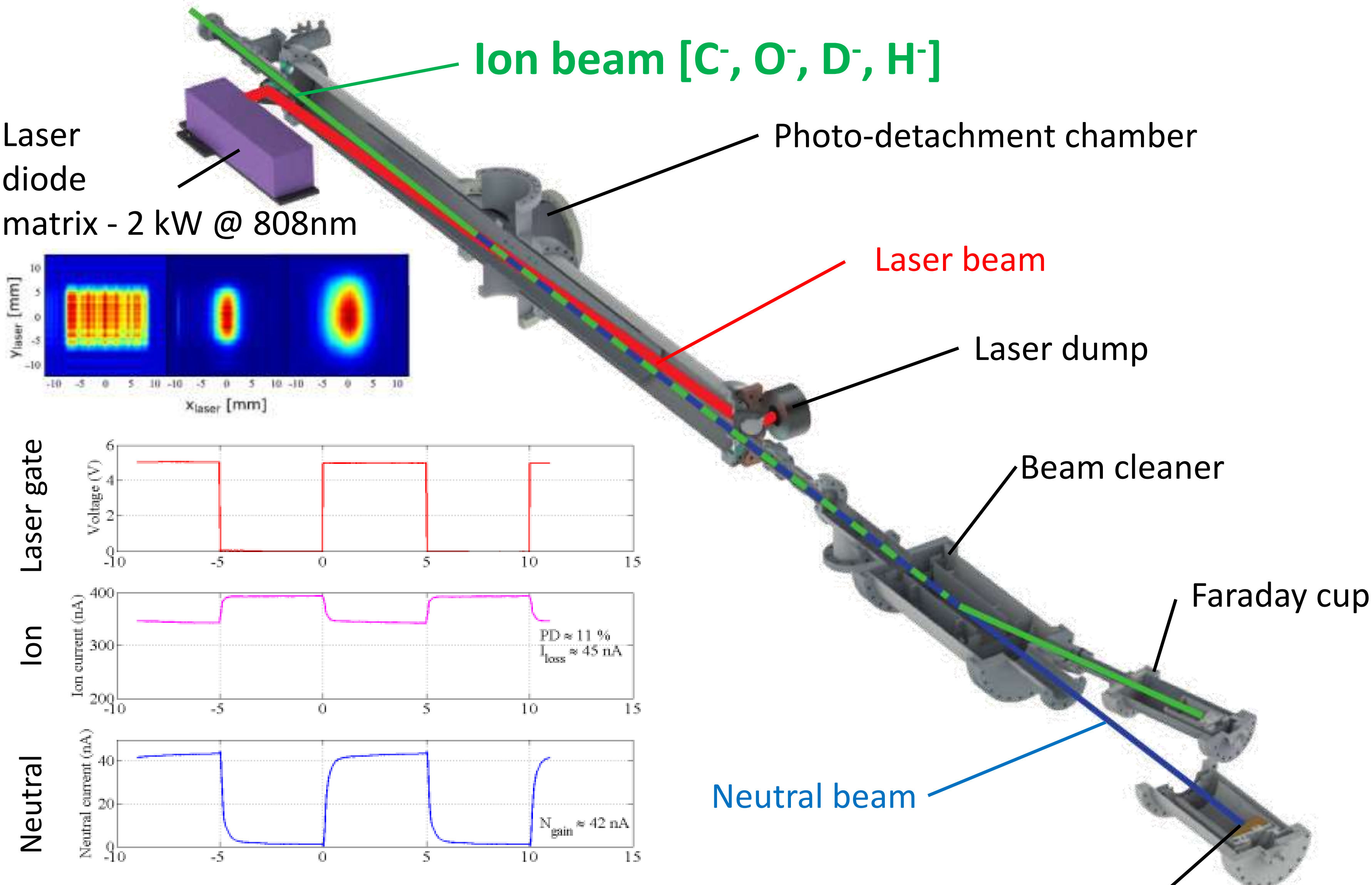
Ion-Neutral Collisions at the CSR



Extraction section

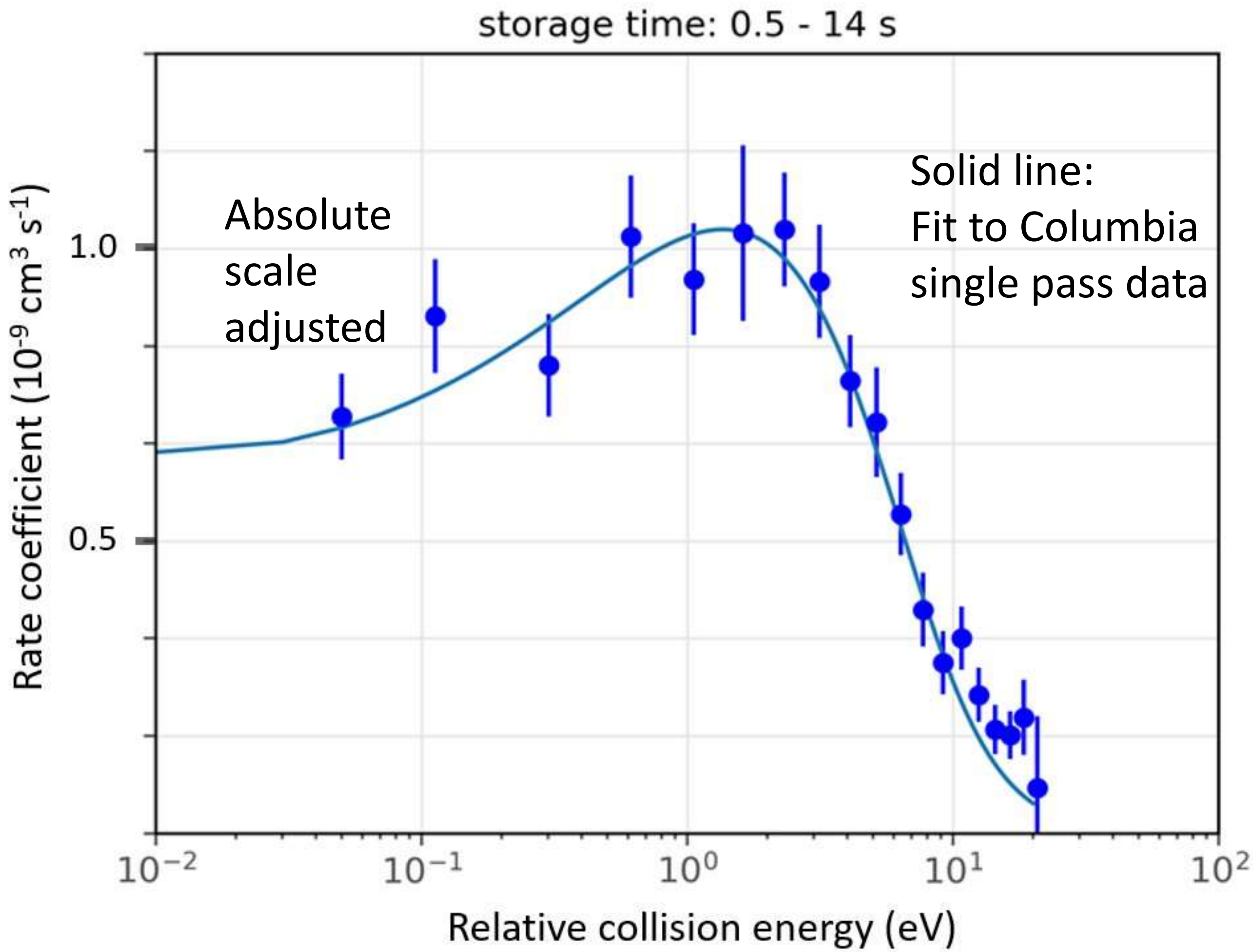
- Dump and measure neutrals
- Differential pumping
- Detect heavy products

Creation of a ground term neutral atom beam



O´Connor et al., RSI **86**, 113306 (2015)

Proof of principle data:
H_3^+ (50 kV) + C (200 kV) ⟶ $CH^+ + H_2$

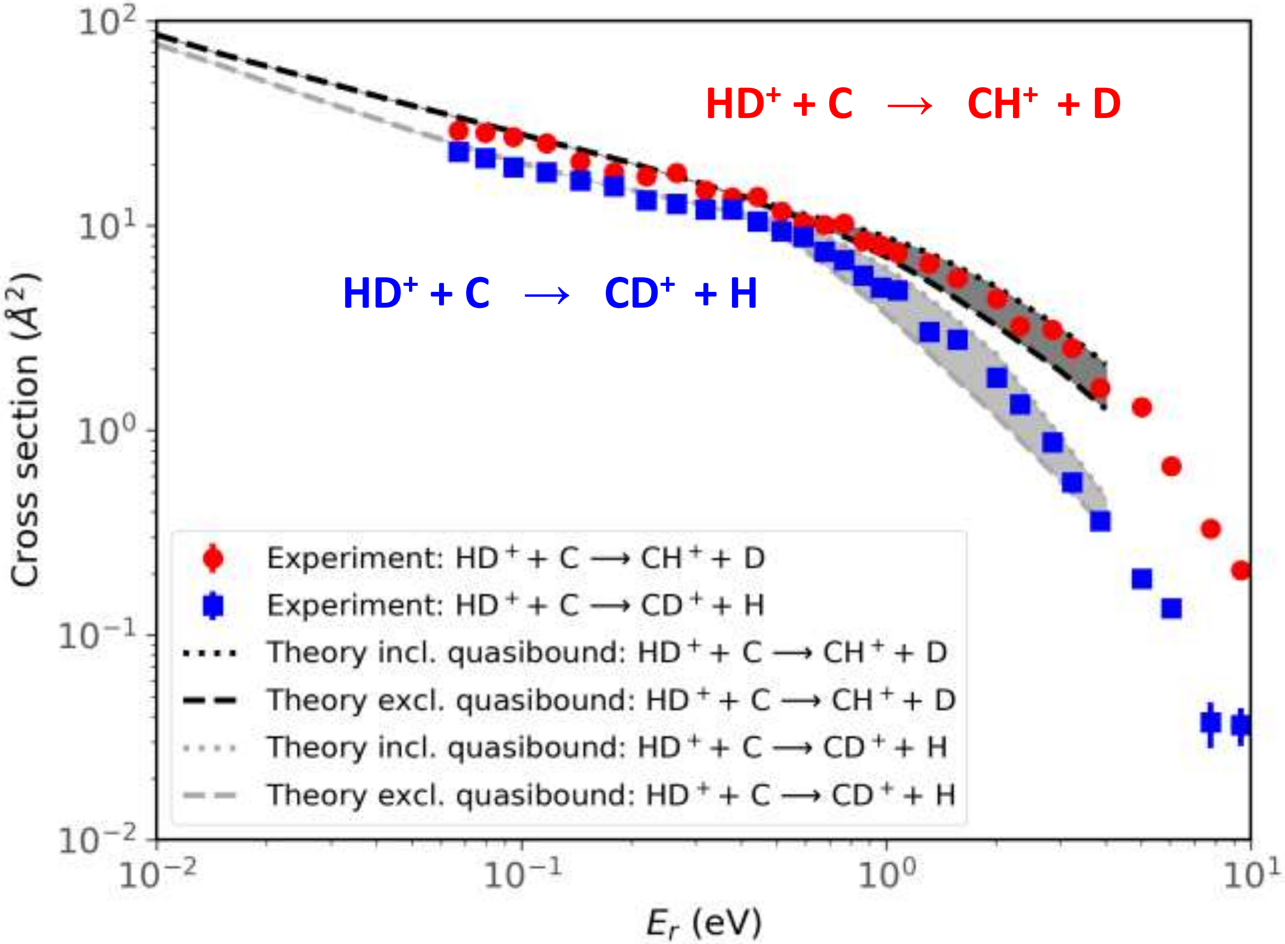


Next steps: use deuterated molecules **(H_2D^+, D_2H^+)** to monitor rates during vibrational and rotational cooling

Ion-neutral collisions

$HD^+ + C \longrightarrow CH^+/CD^+ + H/D$

Comparison to theory (150 K): absolute cross sections

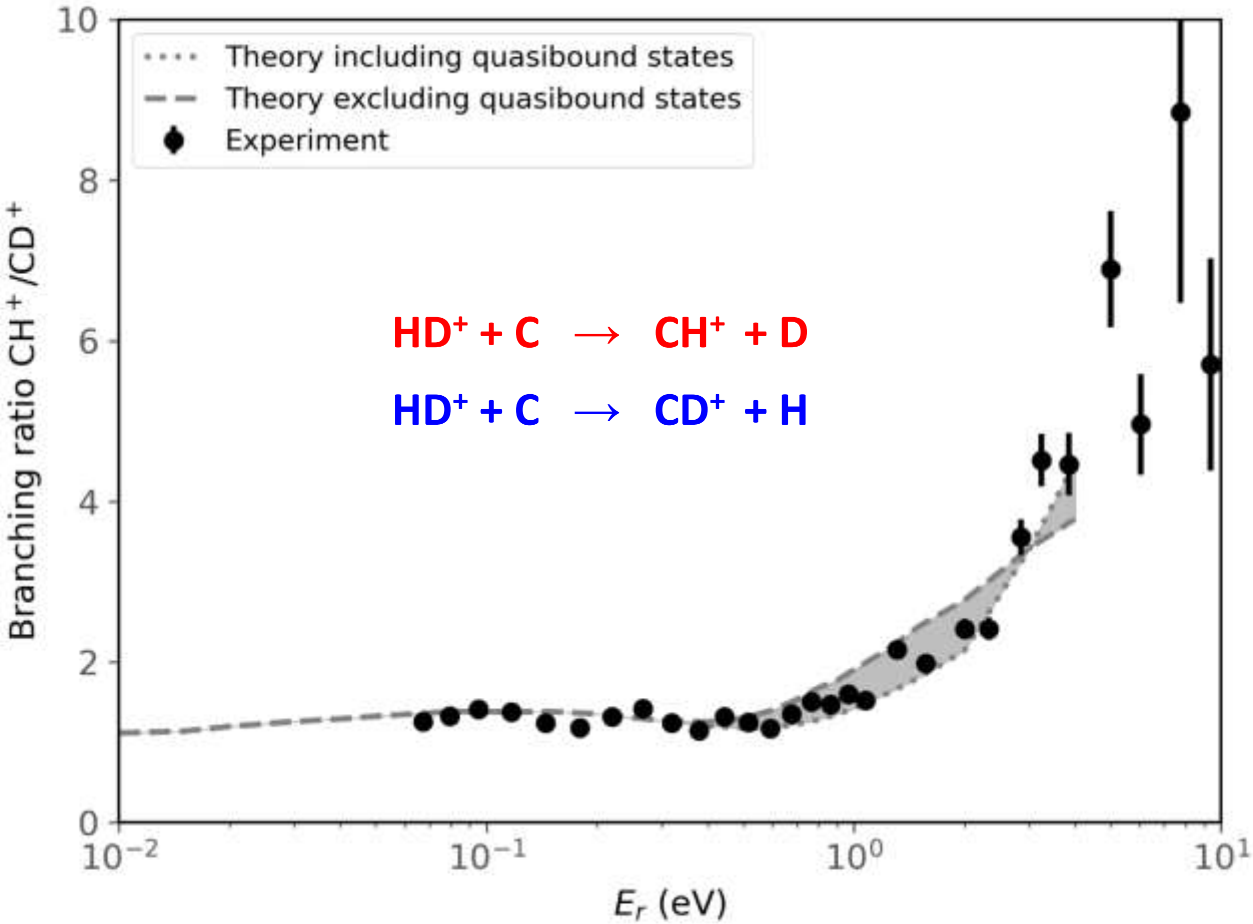


Theory: Quasi Classical Trajectory (QCT) by **Fabrice Dayou**, Paris Observatory, Meudon, France

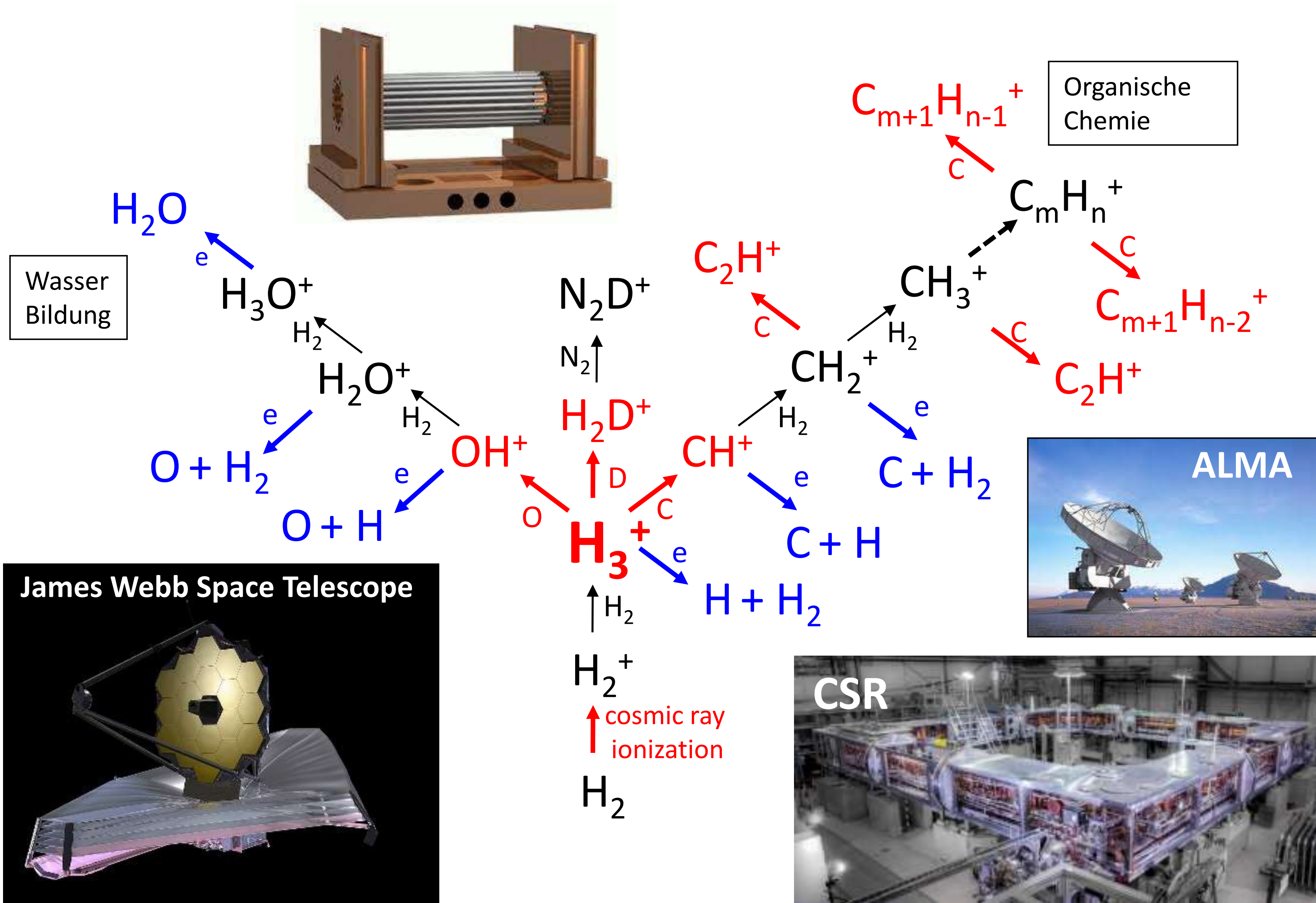
Ion-neutral collisions

$$HD^+ + C \longrightarrow CH^+/CD^+ + H/D$$

Comparison to theory: kinetic isotope effect



Summary:
Molecular Astrophyisics in the Age of ALMA and JWST



Literature

General:	Ian W.M. Smith: “Laboratory Astrochemistry: Gas-Phase Processes” Annu. Rev. Astron. Astrophys. 49, 29-66 (2011)
Ion Spectroscopy:	McGuire, Asvany, Brünken, Schlemmer „Laboratory spectroscopy techniques to enable Observations of interstellar ion chemistry“ Nature Reviews Physics, Volume 2, Issue 8, p. 402-410 (2020)
Ion-Atom Collisions:	T. Snow & V. Bierbaum “Ion Chemistry in the Interstellar Medium” Annu. Rev. Anal. Chem. 1, 229 (2008)