LECTURE 4

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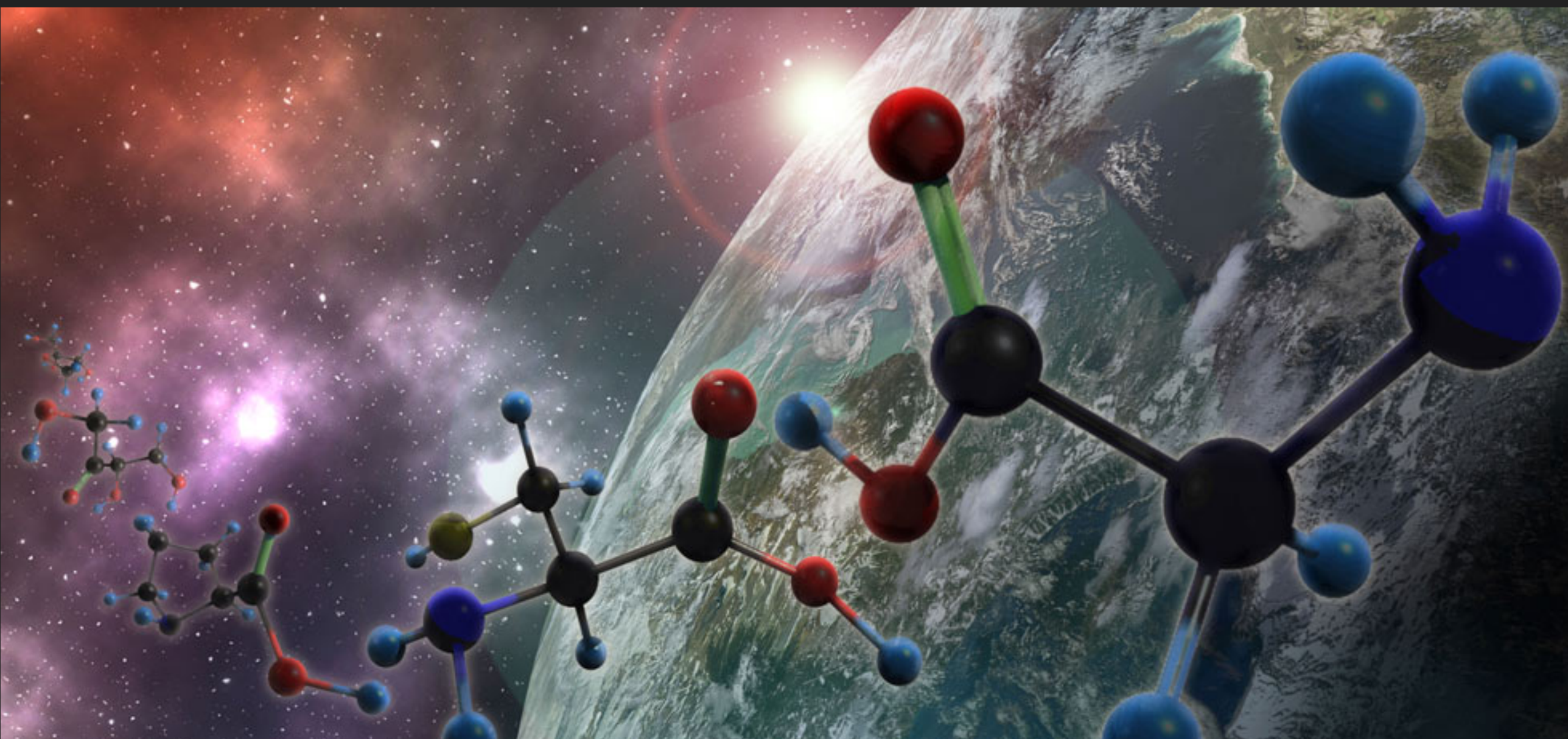


RELEVANT QUANTITIES IN ASTROCHEMICAL MODELS

- Collisions are fundamental: elastic, inelastic, and reactive processes regulate the ISM
- Astrochemical network contains thousands of reactions and hundreds of species (see KIDA)
- Knowledge of elementary reactions is required (only a few % have been studied at temperature of interest for the ISM)
- We need rate coefficients and branching ratios

COLLISIONS, CROSS SECTIONS, RATE COEFFICIENTS

Simple Collision Theory (classical): for a reaction to occur, the reactants must have:

- a sufficiently close encounter, or "collision" (→ cross section σ)
- a sufficient collision energy (→ activation energy $E_{\rm act}$)

Number of collisions per unit time and unit volume: $n_{\rm A} n_{\rm B} \sigma \langle v_{\rm rel} \rangle$

For a Maxwellian velocity distribution:

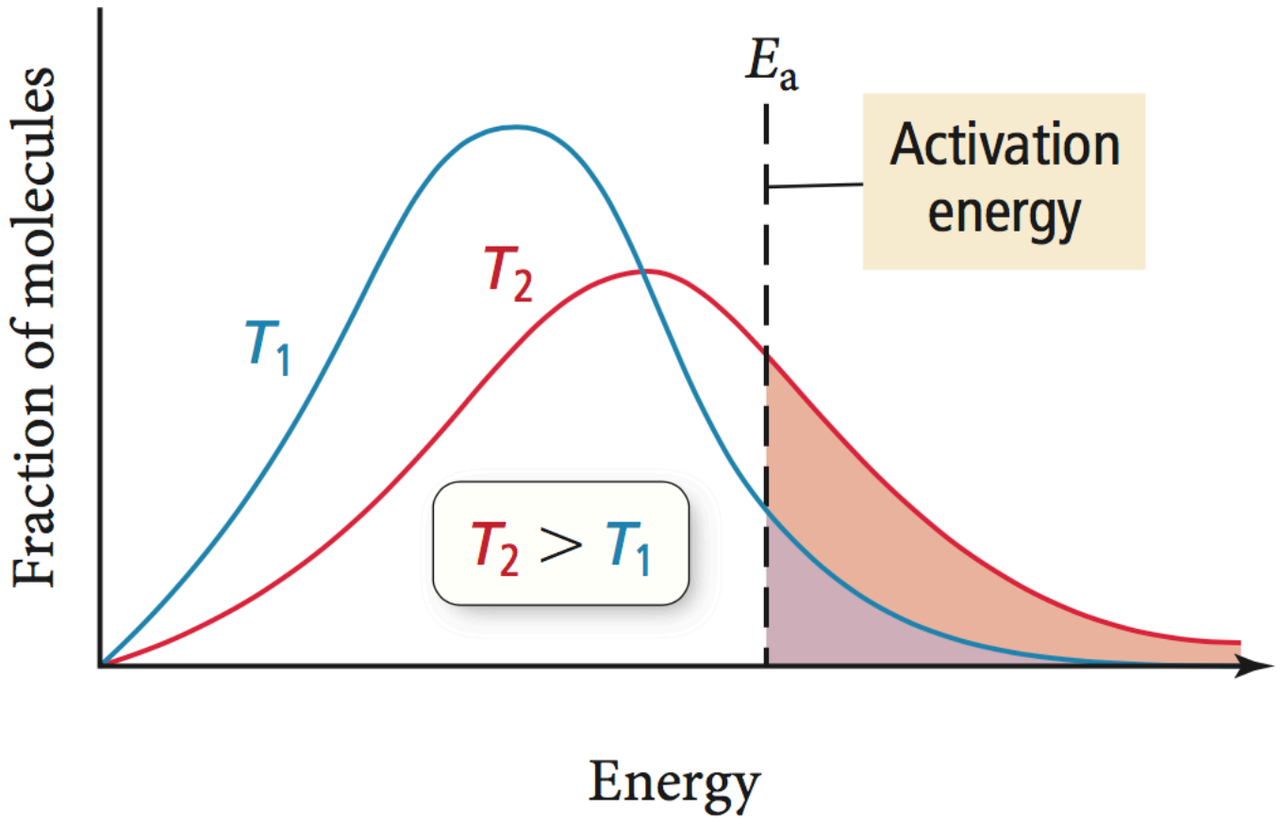
- the average thermal speed is $\langle v_{\rm rel} \rangle = \left(\frac{8 k_{\rm B} T}{\pi \mu} \right)^{1/2}$
- the fraction of particles with $E > E_{\rm act}$ is $f(E > E_{\rm act}) = \exp\left(-\frac{E_{\rm act}}{k_{\rm B} T} \right)$

DANIELE GALLI'S SLIDE (KROME SCHOOL 2018)

Collision theory (Maxwell distribution)

Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



RATE COEFFICIENTS IN GAS-PHASE (THERMAL EQ)

$$k = \sigma v$$

unimolecular reactions: $\mathrm{A} \rightarrow \mathrm{C}$

$$-\frac{d\,\mathrm{n(A)}}{d\,\mathrm{t}} = \mathrm{k\,n(A)} = \frac{d\,\mathrm{n(C)}}{d\,\mathrm{t}}$$

- The above formulation is valid if sigma is velocity-independent
- Normally: we have a distribution of speed

$$k(T) = \langle \sigma v \rangle = \int_0^\infty \sigma(v) v f(v) dv$$

RATE COEFFICIENTS IN GAS-PHASE (THERMAL EQ)

- This obeys a Maxwell-Boltzmann distribution

$$f(v)dv = 4\pi v^2 \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu v^2}{2k_B T}\right) dv$$

$$k(T) = \langle \sigma v \rangle = 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \int_0^\infty \sigma(v) v^3 \exp\left(-\frac{\mu v^2}{2k_B T}\right) dv$$

Cross sections determined quantum-mechanically or experimentally

EXPERIMENTAL/THEORETICAL PROBLEMS

- Generation of a gas at very low temperature without significant condensation or clustering
- Absolute concentration determination of species (often radicals with short lifetime)
- Theoretically is even more challenging: quantum mechanical dynamical calculations possible only for small systems… in addition at the low temperatures we have to consider tunneling effects, resonances, etc. etc.

MOLECULES FORMATION

TYPES OF GAS-PHASE CHEMICAL REACTIONS

Bond Formation Processes	
Radiative association	$X + Y \rightarrow XY + h\nu$
Grain surface formation	$X + Y{:}g \rightarrow XY + g$
Associative detachment	$X^- + Y \rightarrow XY + e$
Bond Destruction Processes	
Photodissociation	$XY + h\nu \rightarrow X + Y$
Dissociative recombination	$XY^+ + e \rightarrow X + Y$
Collisional dissociation	$XY + M \rightarrow X + Y + M$
Bond Rearrangement Processes	
Ion–molecule exchange	$X^+ + YZ \rightarrow XY^+ + Z$
Charge–transfer	$X^+ + YZ \rightarrow X + YZ^+$
Neutral–neutral	$X + YZ \rightarrow XY + Z$

TYPES OF GAS-PHASE CHEMICAL REACTIONS

Bond Formation Processes

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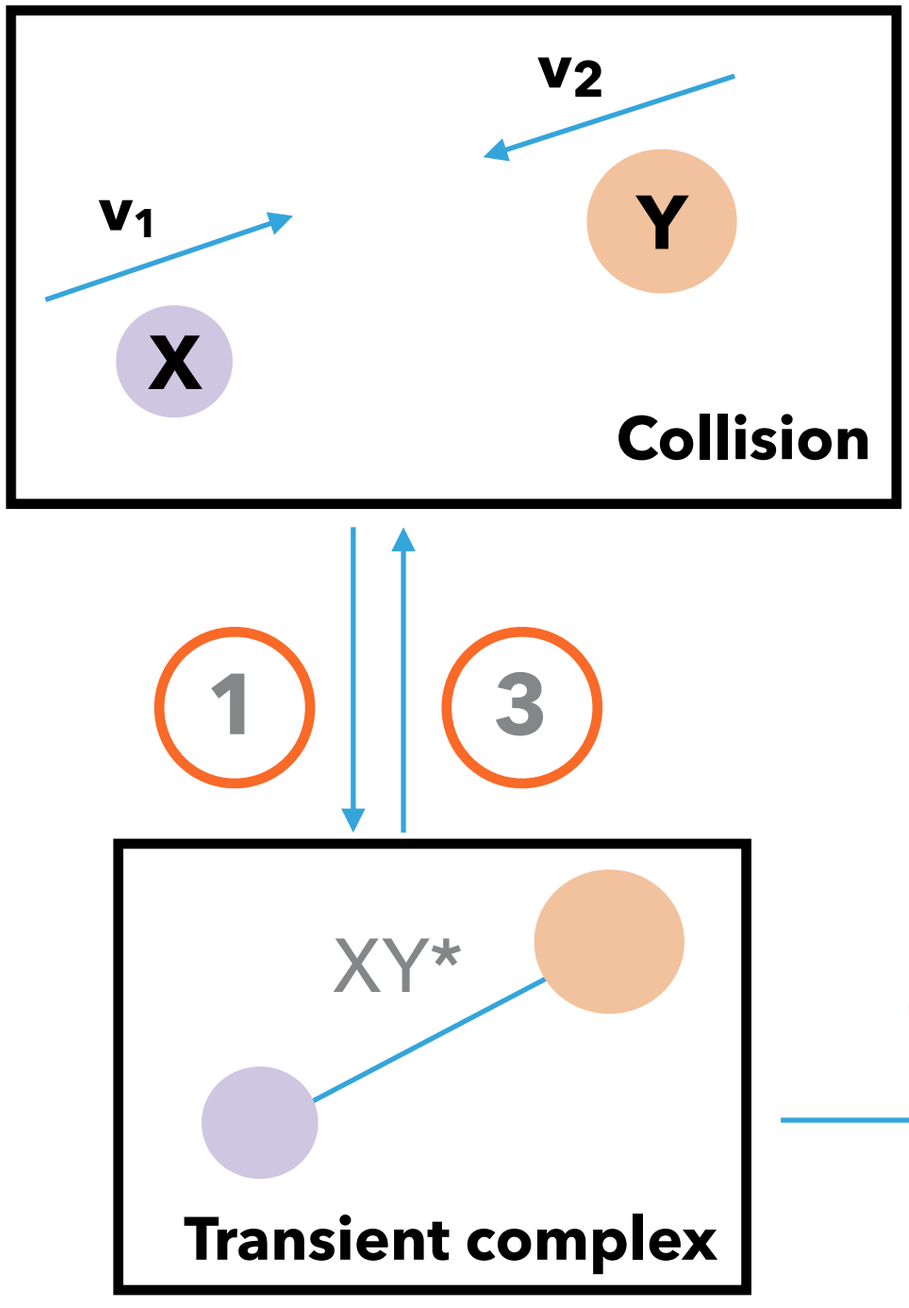
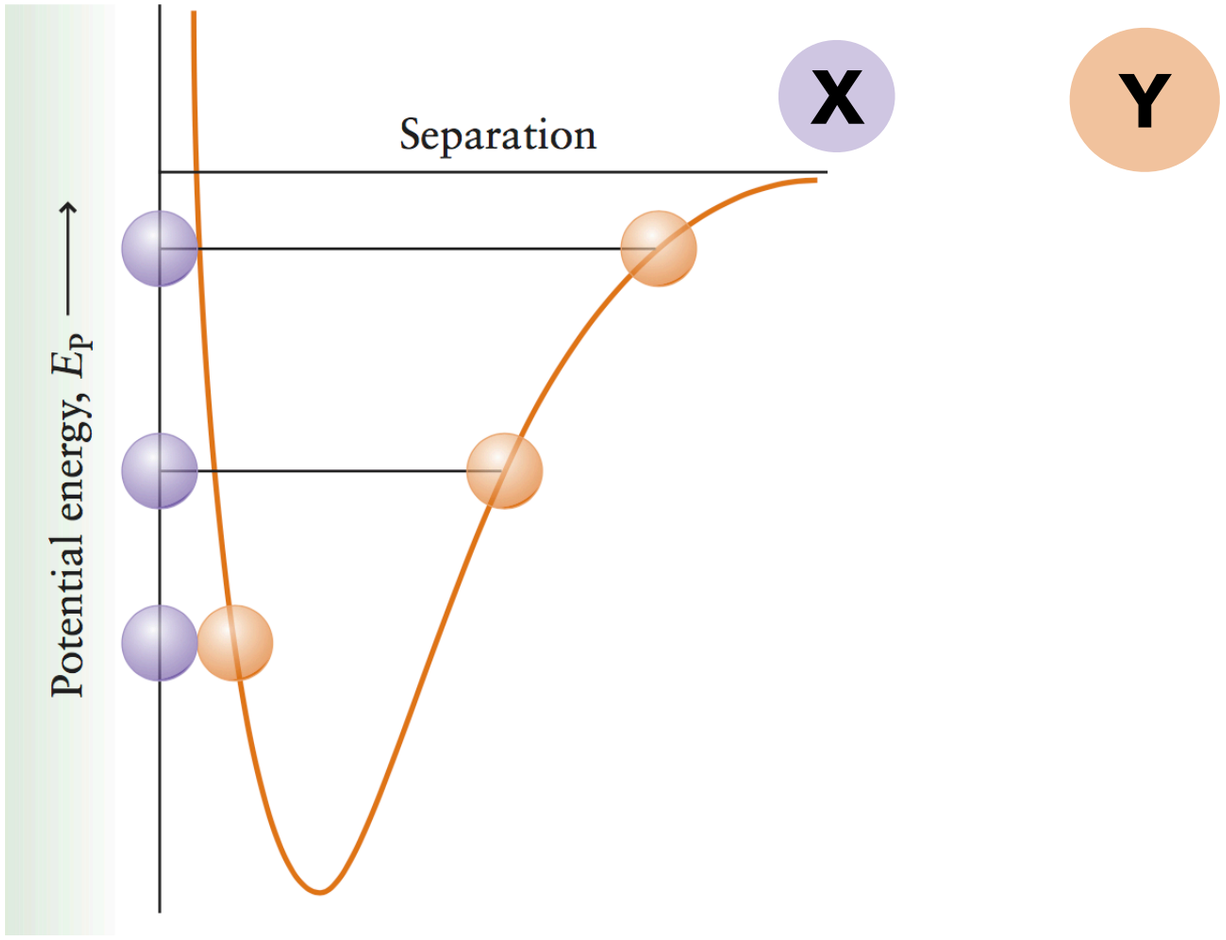
FORMATION OF BONDS

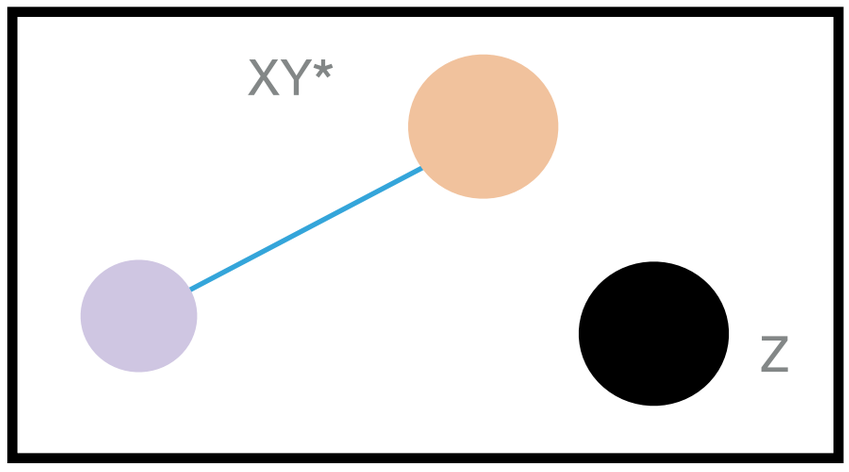




Formation of a transient complex that has to loose the excess of kinetic energy to stabilize the molecule

FORMATION OF BONDS

2



$$\mathrm{X} + \mathrm{Y} \rightarrow \mathrm{XY}^*$$

$$\mathrm{XY}^* + \mathrm{Z} \rightarrow \mathrm{XY} + \mathrm{Z}$$

Normally done by a third body under Earth conditions

FORMATION OF BONDS: RADIATIVE ASSOCIATION

- In the ISM 3B collisions very rare (density is low)
- Formation of molecules can proceed through photon-emission

$$X + Y \underset{3}{\overset{1}{\rightleftarrows}} XY^* \xrightarrow{2} XY + \gamma$$

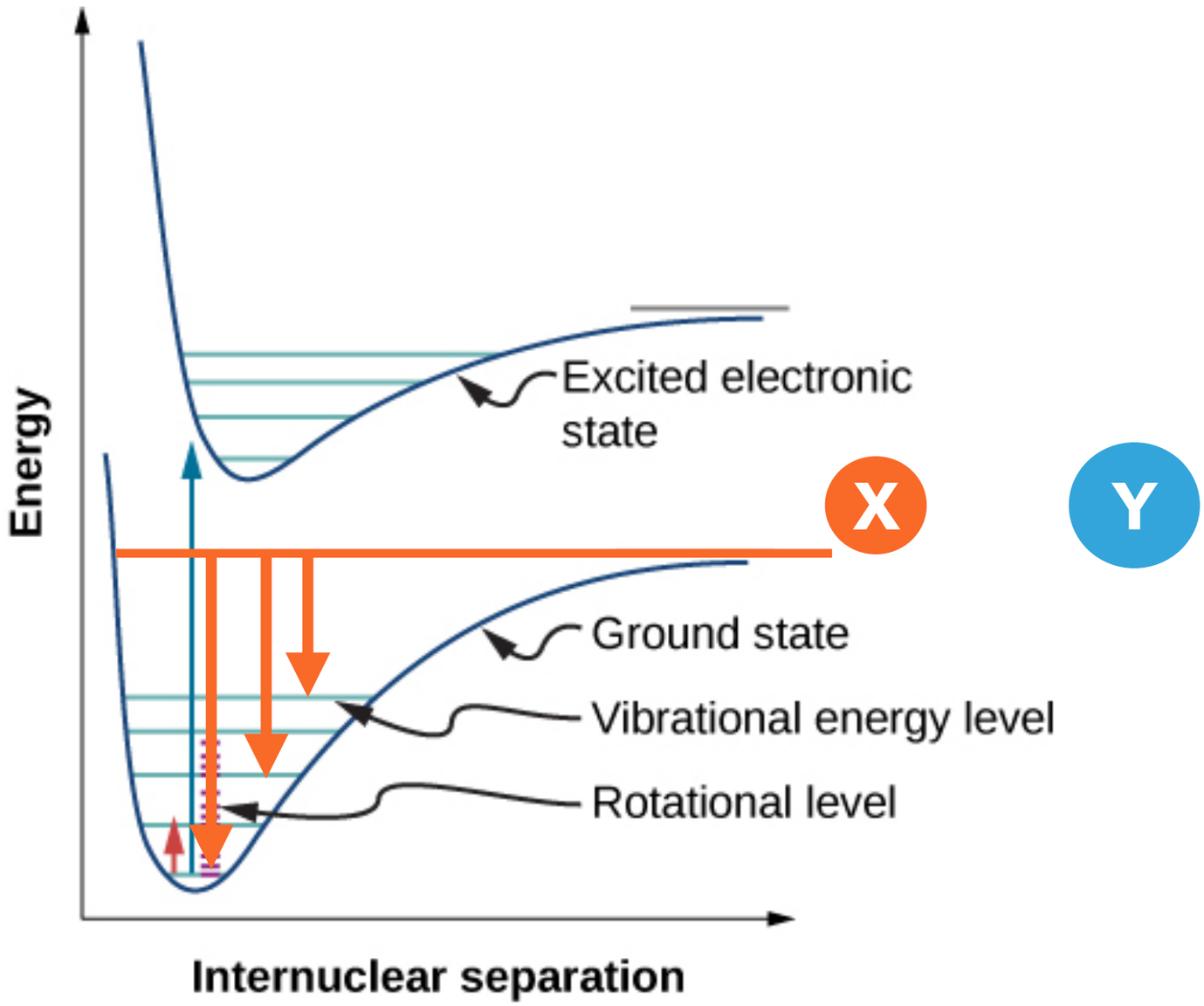
- The complex XY* relaxes through the emission of radiation to yield a stable reaction product (2)
- Most probable scenario XY* re-dissociates (3)

FORMATION OF BONDS: RADIATIVE ASSOCIATION

- Only long-lived activated complexes will lead to efficient radiative association reactions
- More energy levels available better the kinetic energy can be distributed

$$X + Y \rightleftarrows XY^* \rightarrow XY + \gamma$$

FORMATION OF BONDS: RADIATIVE ASSOCIATION



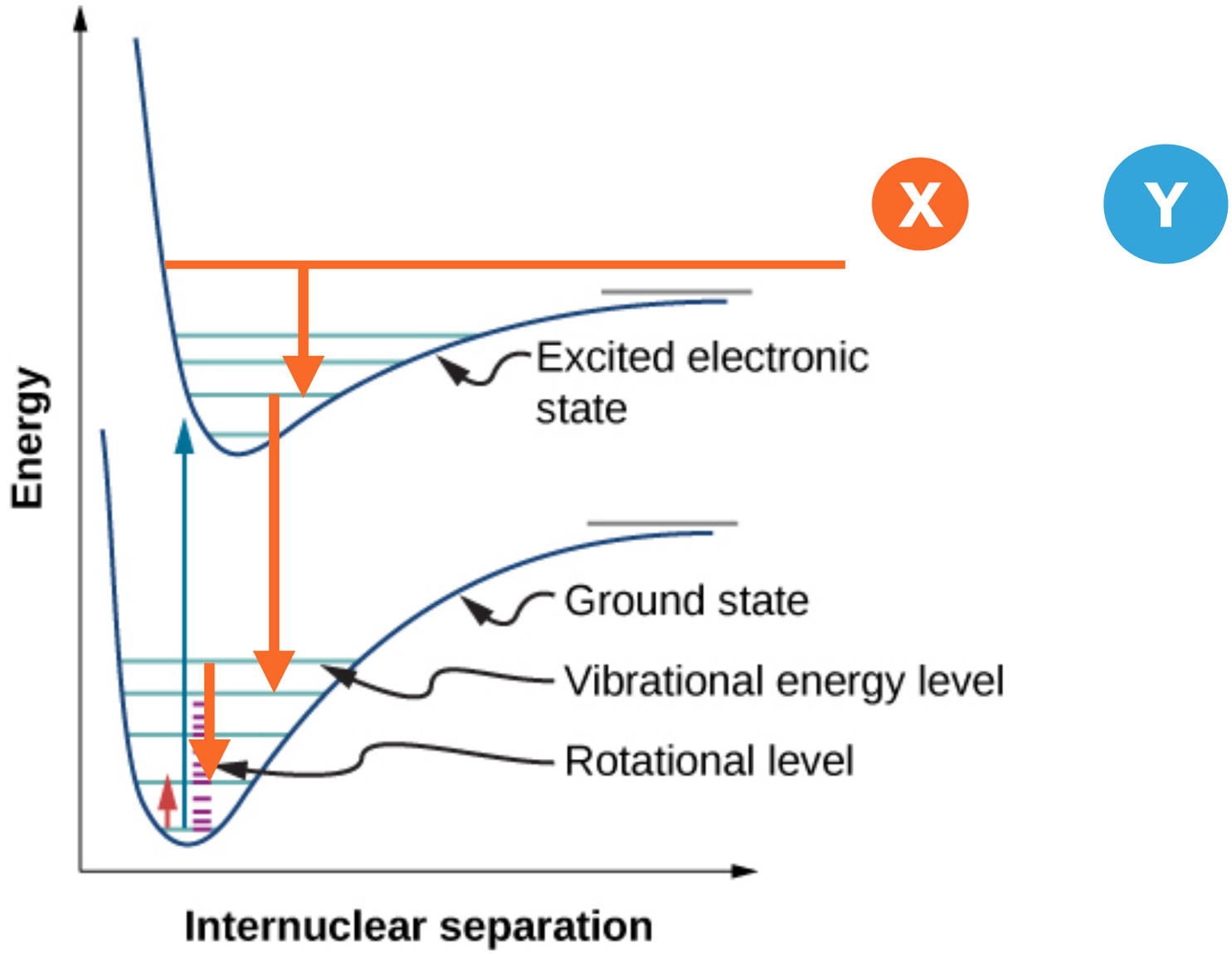
FORMATION OF BONDS: RADIATIVE ASSOCIATION

$$X + Y \underset{\tau_d}{\overset{\tau_c}{\rightleftarrows}} XY^* \xrightarrow{\tau_r} XY + h\nu$$

- The excess energy is distributed across electronic or vibrational states
- Via **vibrational** decay (radiative time: $A_{ul}^{-1} \sim 10^{-3}$ s)
- Collision time ($\sim 10^{-13}$ s with v ~ 0.5 km/s)
- (molecules form every 1:10^{10} collisions)

FORMATION OF BONDS: RADIATIVE ASSOCIATION

$$X + Y \rightleftarrows XY^* \rightarrow XY + \gamma$$



FORMATION OF BONDS: RADIATIVE ASSOCIATION

$$X + Y \rightleftarrows XY^* \rightarrow XY + \gamma$$

- Via **electronic** decay (lifetime: $A_{ul}^{-1} \sim 10^{-8}$ s)
- Collision time ($\sim 10^{-13}$ s)
- efficiency increased $1:10^5$ collisions

RADIATIVE ASSOCIATION: WHEN IS IT BOOSTED?

- If electronic states available
- Entrance channel has a barrier (dissociation longer)
- Molecules with large dipole moment faster $A_{ij} \propto \nu^3 |\mu_d|^2$
- Larger molecules, longer collision time

Reaction	k
$C + H \longrightarrow CH + h\nu$	1.0×10^{-17}
$C + C \longrightarrow C_2 + h\nu$	4.4×10^{-18}
$C + N \longrightarrow CN + h\nu$	1.4×10^{-18}
$C + H_2 \longrightarrow CH_2 + h\nu$	1.0×10^{-17}
$C^+ + H \longrightarrow CH^+ + h\nu$	1.7×10^{-17}
$C^+ + H_2 \longrightarrow CH_2^+ + h\nu$	4.0×10^{-16}
$O + O \longrightarrow O_2 + h\nu$	4.9×10^{-20}

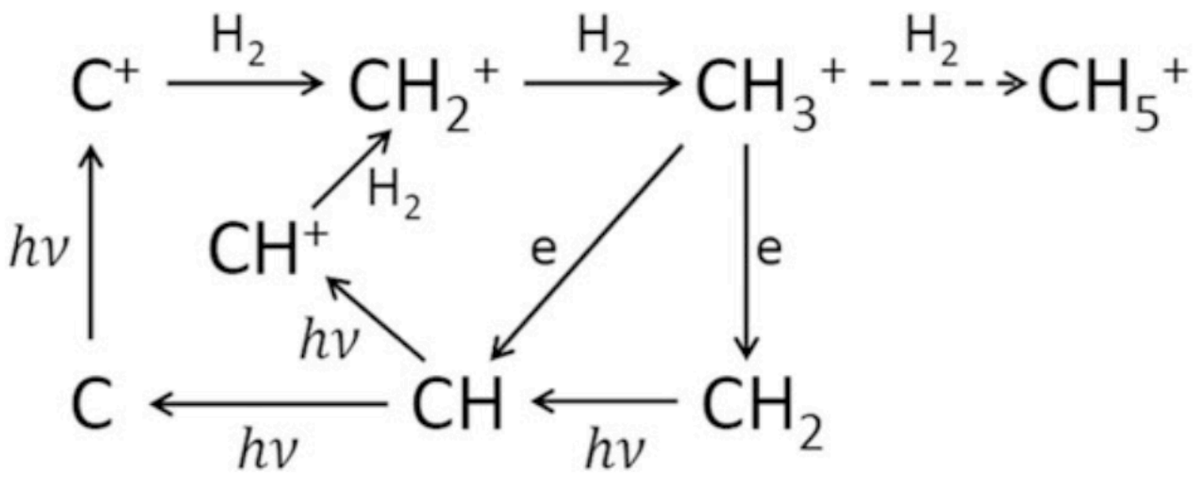
RADIATIVE ASSOCIATION: WHERE WE GET THE RATES?

- Difficult to measure in laboratory as three-body collisions dominate under typical lab conditions
- Mostly based on theory with uncertainties of 1-2 orders of magnitudes

RADIATIVE ASSOCIATION: EXAMPLES

Well known R.A. rate, initiates the carbon chemistry: ~10^{-15} cm^3s^{-1}

$$C^+ + H_2 \rightarrow CH_2^+ + \gamma$$



Larger molecules ~10^{-11} cm^3s^{-1}:

$$CH_3^+ + HCN \rightarrow CH_3CNH^+ + \gamma$$

RADIATIVE ATTACHMENT + ASSOCIATIVE DETACHMENT

$$\mathrm{X} + \mathrm{e}^- \rightarrow \mathrm{X}^- + \gamma$$ **Slow (faster for large molecules)**

$$\mathrm{X}^- + \mathrm{Y} \rightarrow \mathrm{XY} + \mathrm{e}^-$$ **Fast**

Takes away the excess of energy

Example: radiative attachment followed by associative detachment

$$\mathrm{H} + \mathrm{e}^- \rightarrow \mathrm{H}^- + \gamma$$ **Slow**

$$\mathrm{H}^- + \mathrm{H} \rightarrow \mathrm{H}_2 + \gamma$$ **Fast**

In general important if ionization fraction is high (early Universe!!)

ANIONS ARE RARE IN THE ISM

- In very dense environments excess of electrons can favor this process
- However the large densities will allow more collisions inducing the removal of all the electrons until **neutralization**
- In highly ionized environment photoionization will be dominant
- Polyatomic species that can stabilize the charge are more likely to be observed
- CN^- anion in the circumstellar envelope of IRC +10216 (Agundez et al., 2010).

TYPES OF GAS-PHASE CHEMICAL REACTIONS

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Bond Rearrangement Processes		
Ion–molecule exchange	$X^+ + YZ \rightarrow XY^+ + Z$	
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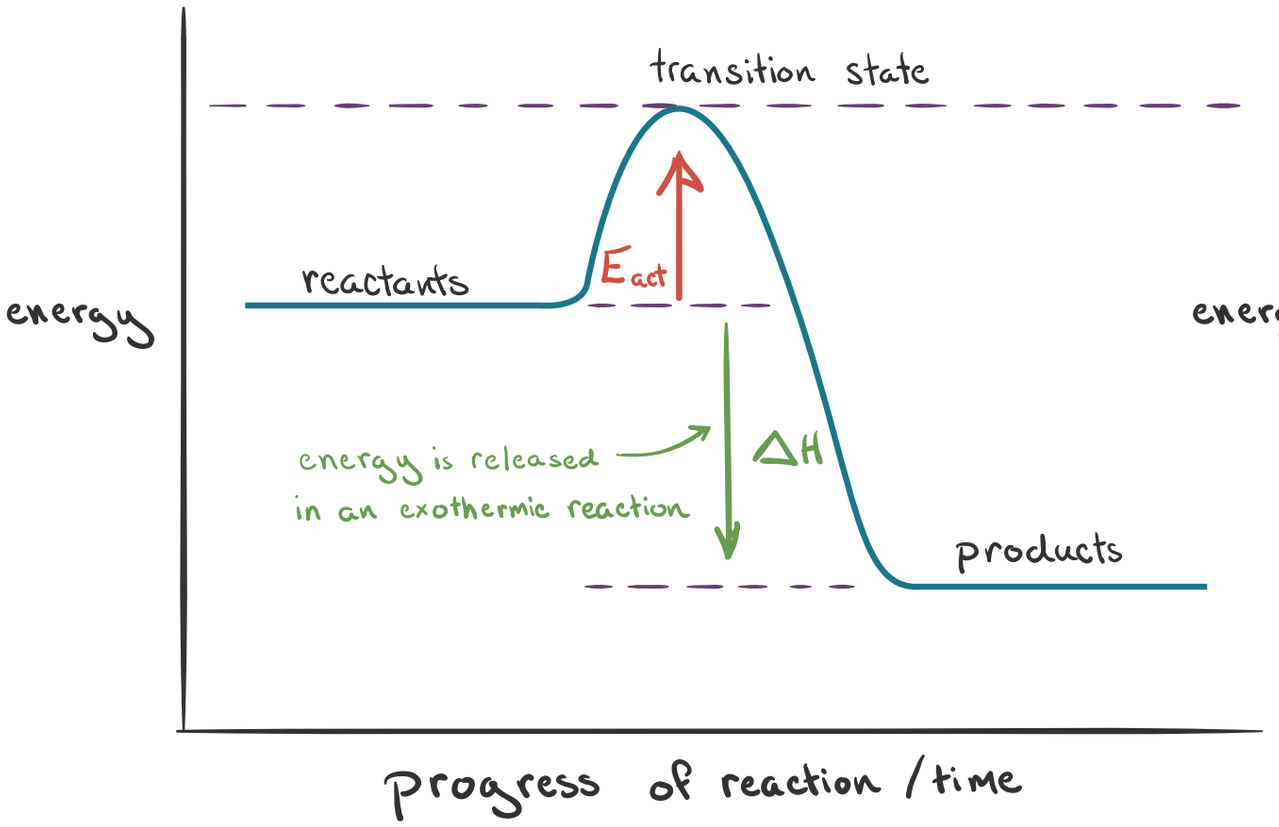
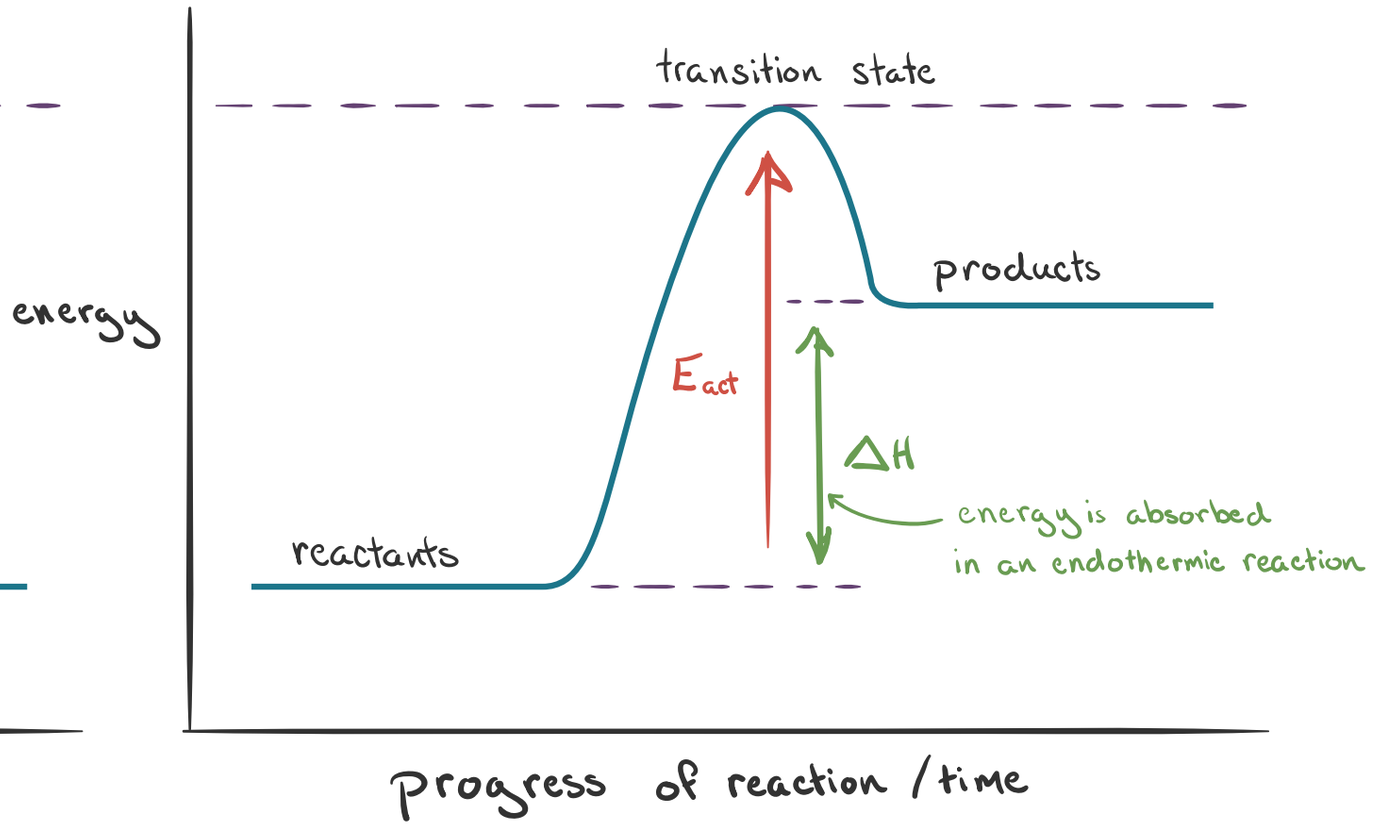
REARRANGEMENT

EXOTHERMIC AND ENDOTHERMIC



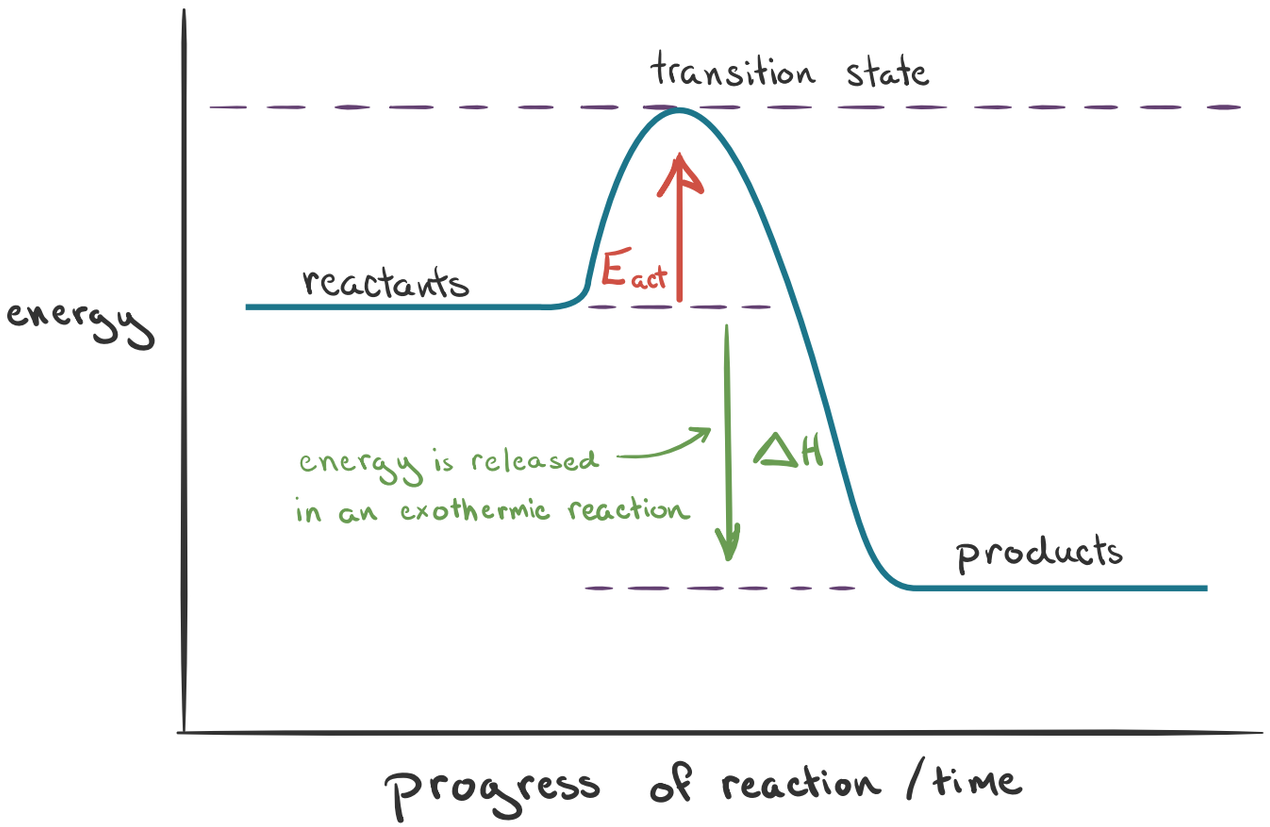


Bulk of molecules discovered in cold clouds (T < 100 K)

NEUTRAL-NEUTRAL REACTIONS

- Normal type of reaction on Earth atmosphere
- No attractive forces (“hard-spheres” models)

$$AB + C \rightarrow AC + B$$



Interaction potential

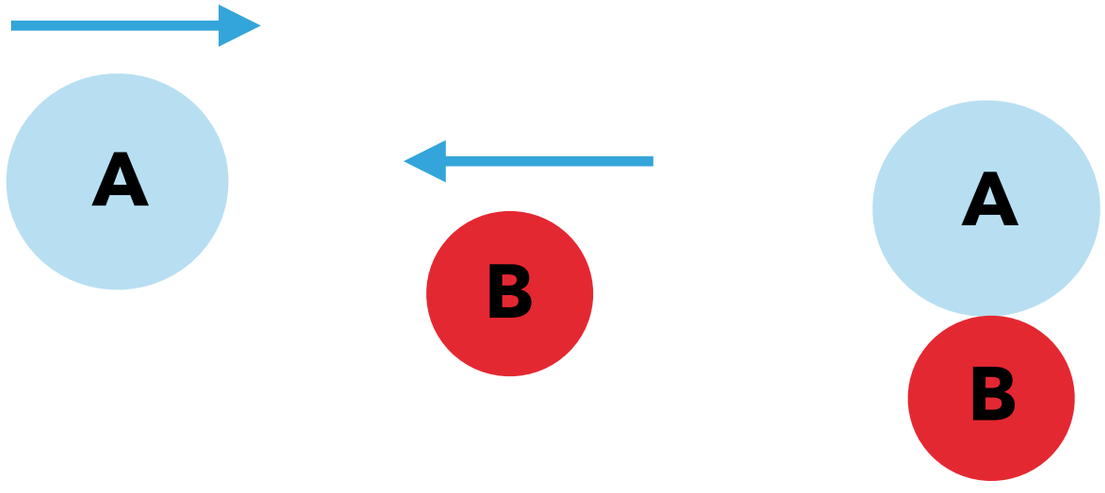
$V \sim r^{-6}$

NEUTRAL-NEUTRAL REACTIONS: HARD-SPHERES

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$$

$$\sigma = \pi(r_A + r_B)^2$$

$$k = \sigma v_{AB} = \pi(r_A + r_B)^2 \left(\frac{8k_B T}{\pi\mu}\right)^{1/2}$$



NEUTRAL-NEUTRAL REACTIONS: HARD-SPHERES

$$k = \sigma v_{AB} = \pi(r_A + r_B)^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}$$

Calculate the rate at T = 10 K

$$\sigma = \pi(R_\mathrm{A} + R_\mathrm{B})^2 \approx 10^{-15}\mathrm{cm}^2$$

$$\langle\sigma v\rangle = \pi(R_\mathrm{A} + R_\mathrm{B})^2 \left(\frac{8k_\mathrm{B}T}{\pi\mu_\mathrm{AB}}\right)^{1/2} \approx 10^{-10}\left(\frac{T}{100\ \mathrm{K}}\right)^{1/2}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$$

k ~ 10^{-11}-10^{-13} cm^3 s^{-1}

NEUTRAL-NEUTRAL REACTIONS: HARD-SPHERES

	$A(cm^3s^{-1})$	$E_a(K)$
$H + H_2CO = H_2 + HCO$	$2.7\ 10^{-11}$	1300
$H + H_2S = H_2 + SH$	$1.3\ 10^{-11}$	860
$H + O_2 = OH + O$	$3.7\ 10^{-10}$	8500
$O + H_2 = OH + H$	$1.0\ 10^{-11}$	5700
$O + H_2S = OH + SH$	$6.6\ 10^{-13}$	900
$OH + CO = H + CO_2$	$5.1\ 10^{-13}$	300

$$k(T) = A(T) \exp\left(-\frac{E_a}{k_B T}\right)^{1/2}$$

NEUTRAL-NEUTRAL REACTIONS: HARD-SPHERES

$$\mathrm{CH} + \mathrm{O} \rightarrow \mathrm{CO} + \mathrm{H},$$

$$\mathrm{NO} + \mathrm{N} \rightarrow \mathrm{N_2} + \mathrm{O},$$

$$\mathrm{C_2H_2} + \mathrm{CN} \rightarrow \mathrm{HC_3N} + \mathrm{H}.$$

A few exothermic, rare examples

NEUTRAL-NEUTRAL REACTIONS:

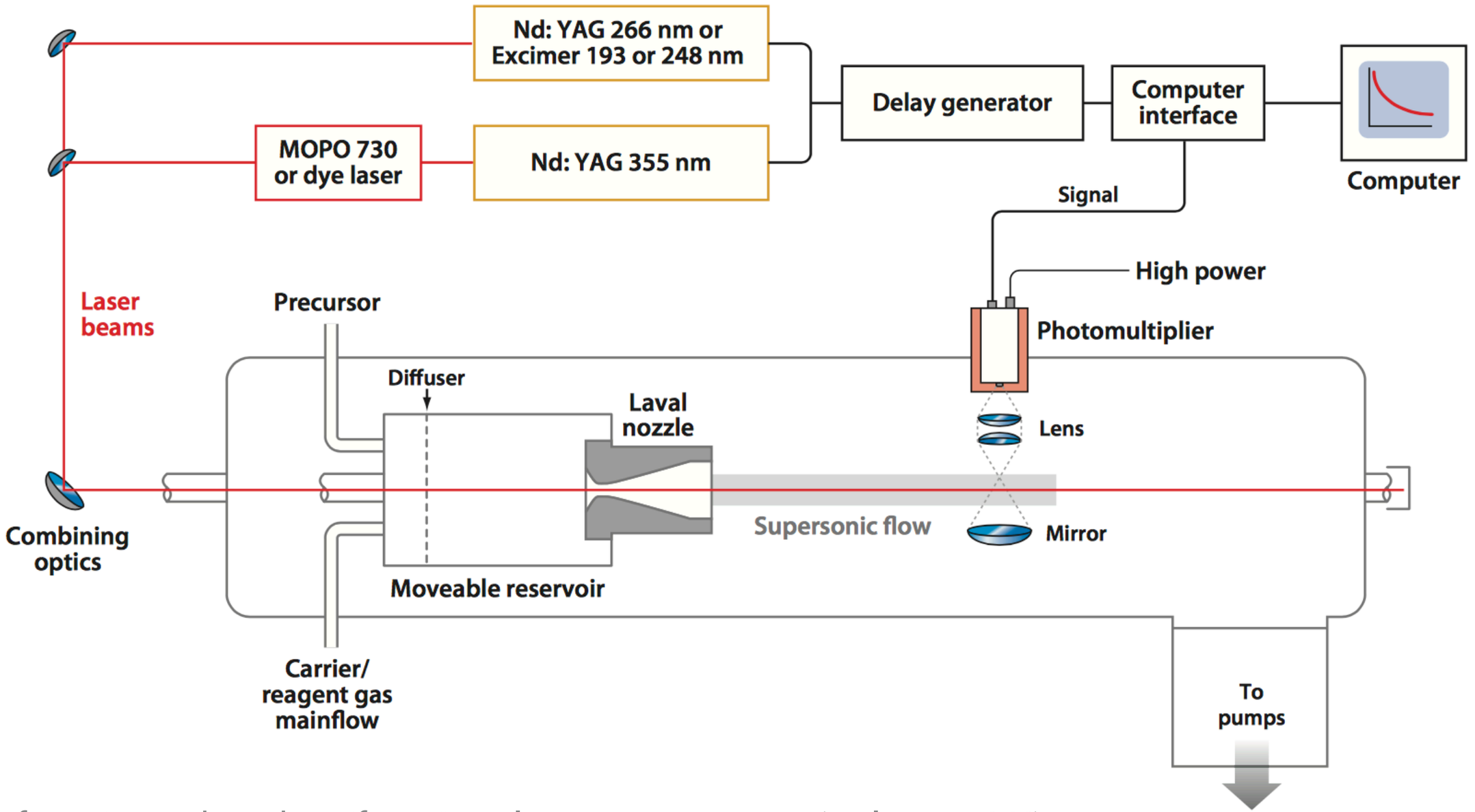
- Large activation energies
- neutral-neutral reactions involving atoms or radicals* can occur significantly because they have only small or no activation barriers
- Need high-T to overcome the barrier
- Important in shocks, outflows, stellar ejecta, hot cores…

*Radical: a chemical species with one unpaired electron, highly reactive, important examples in astrochemistry CH_3O, CH_3, OH, CH…

NEUTRAL-NEUTRAL REACTIONS: CRESU EXPERIMENT

Cinétique de Réaction en Ecoulement Supersonique Uniforme

Developed by Rowe 1985



*flow of gas is produced: uniform in velocity, temperature (as low as 6 K), and density and persists for tens of centimeters

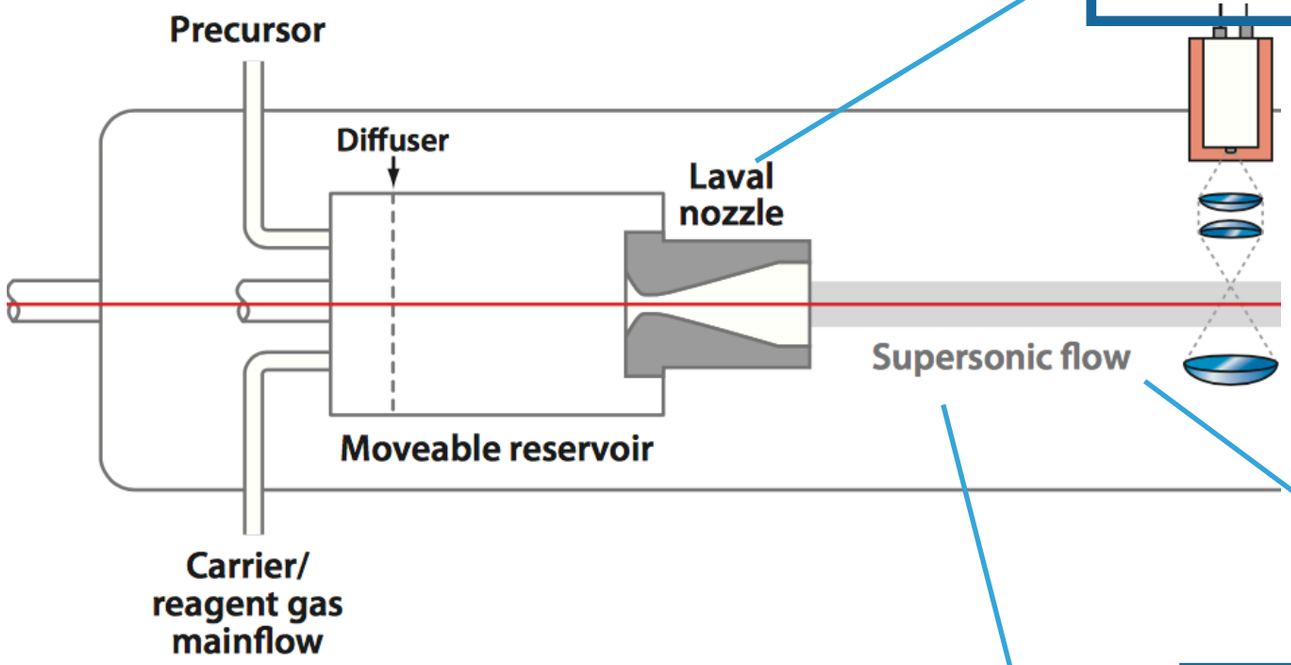
Smith+2011

NEUTRAL-NEUTRAL REACTIONS: CRESU EXPERIMENT

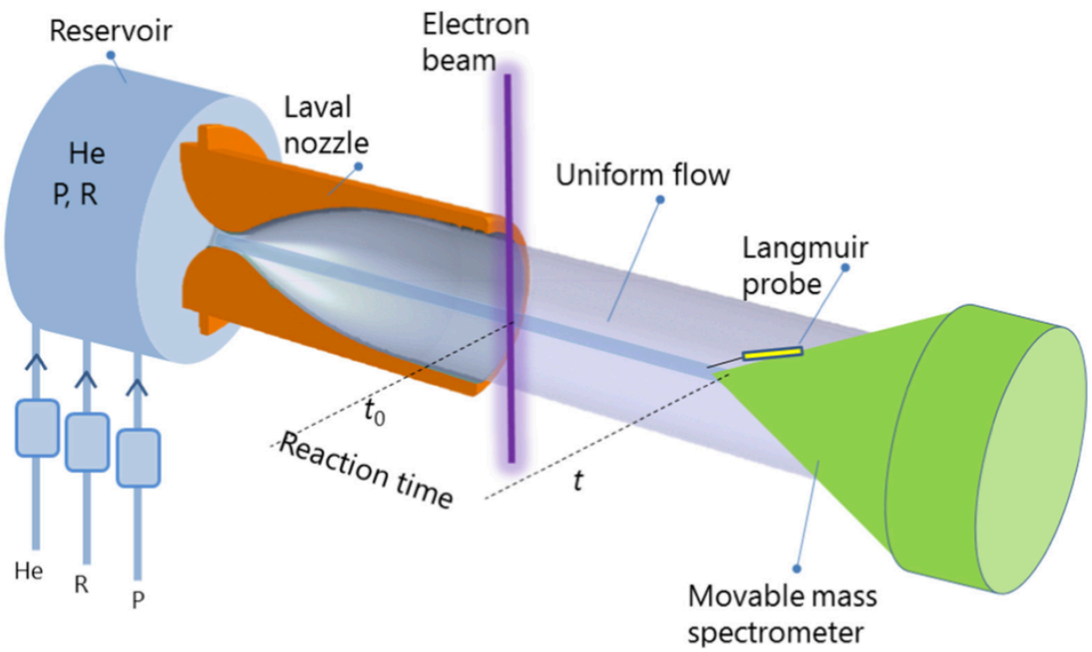
Isentropic expansion

Design of the nozzle defines T, n
Throat diameter: 3mm-5cm

T_0, u_0, p_0



T-range:
Ambient - 10 K
In few microseconds



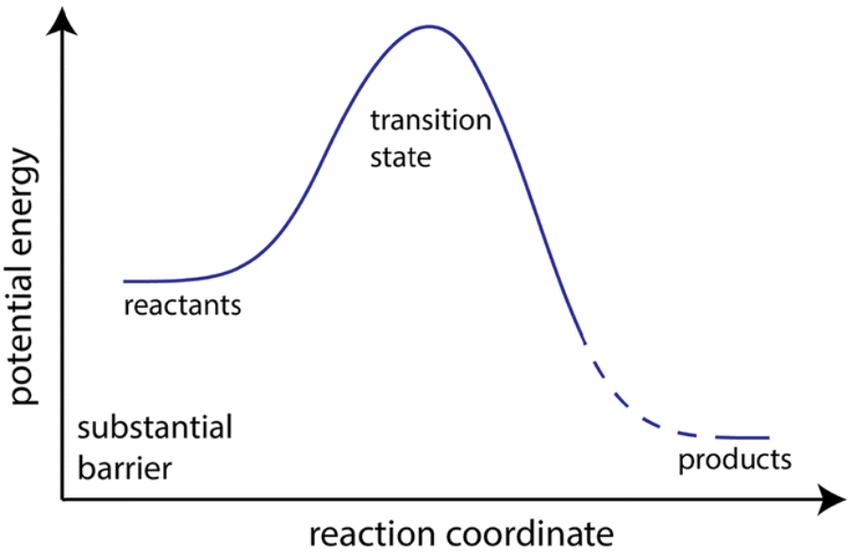
Low pressures (pumps @ 30,000 m^3/h)

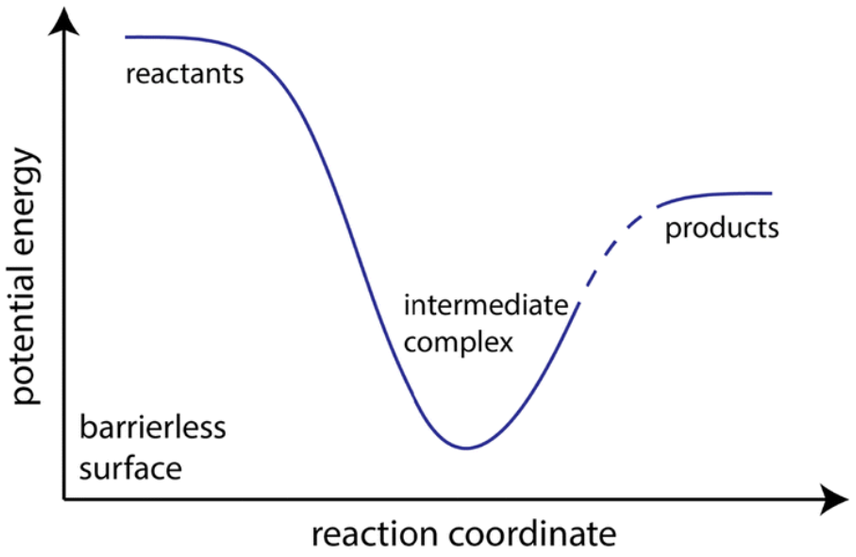
Densities (typically 10^{16}–10^{17} cm^3)

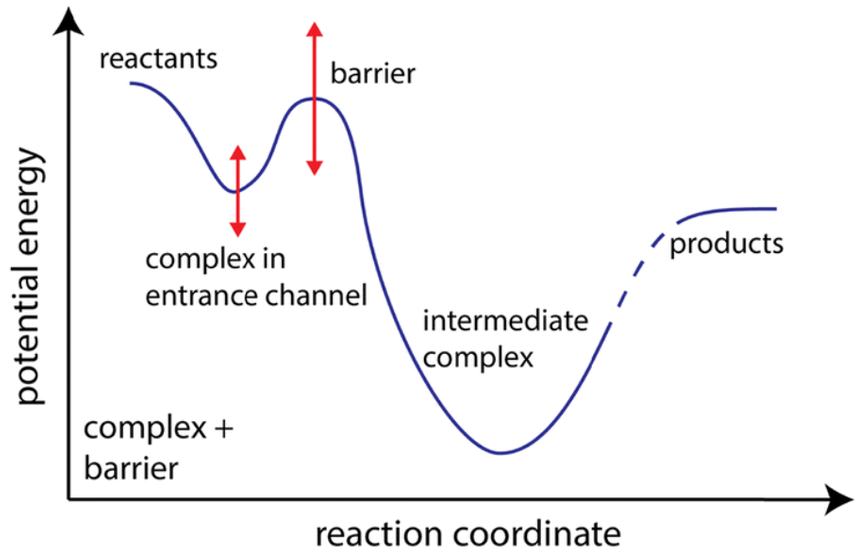
Thermal equilibrium (T well defined)

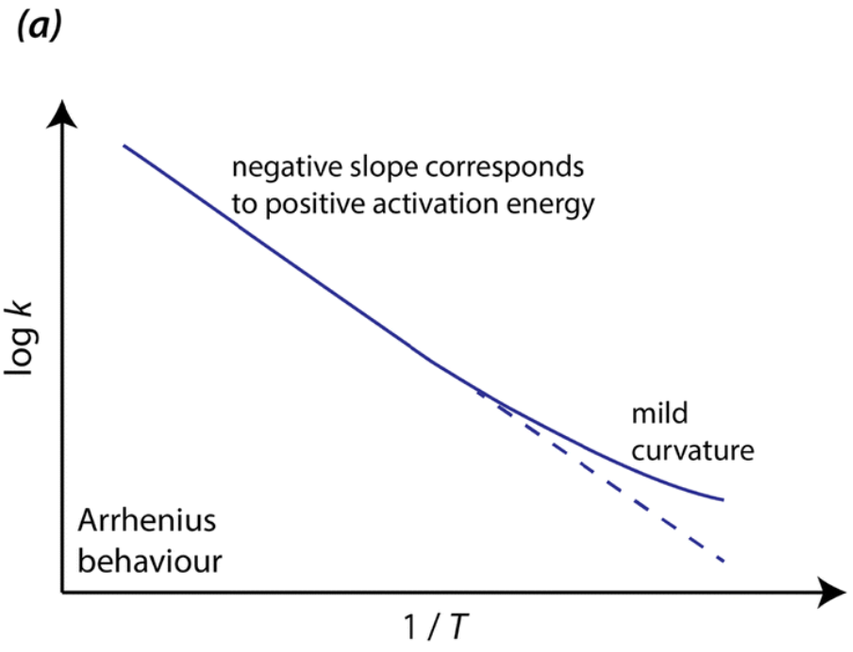
Large flow rates (50 L/min) are needed to maintain the uniformity of the continuous flow for long distances (tens of centimeters)

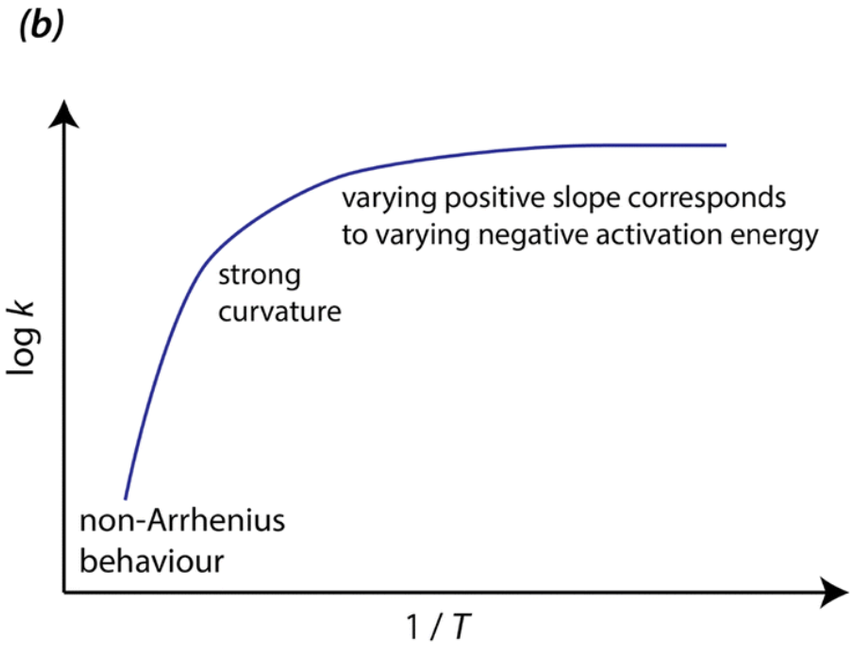
Smith+2011

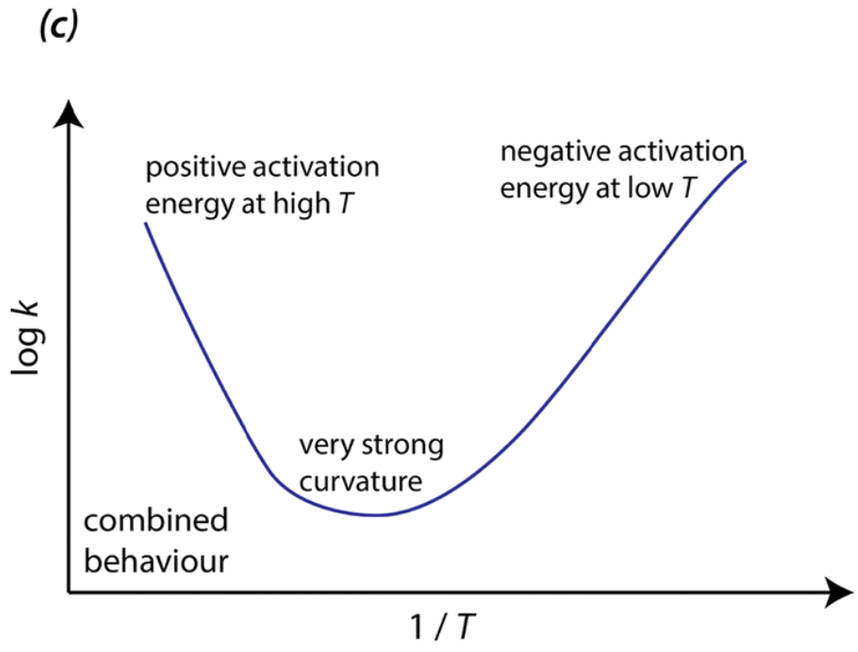




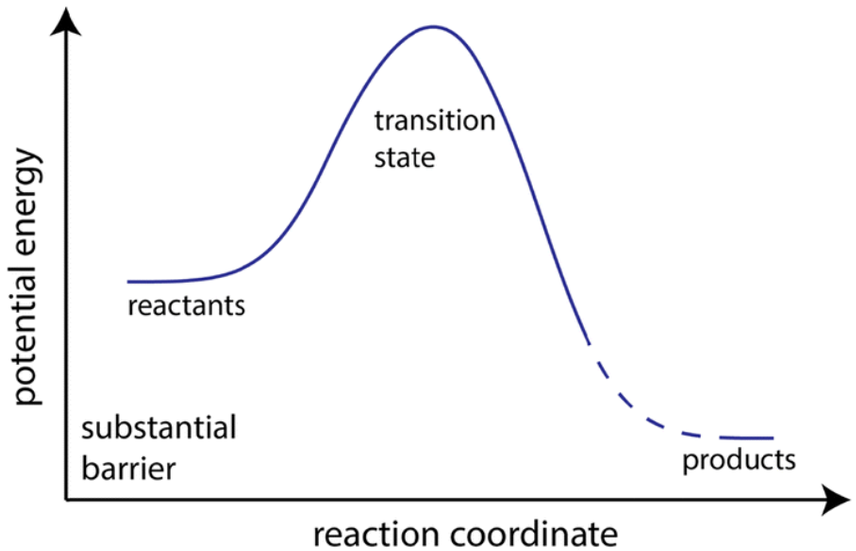


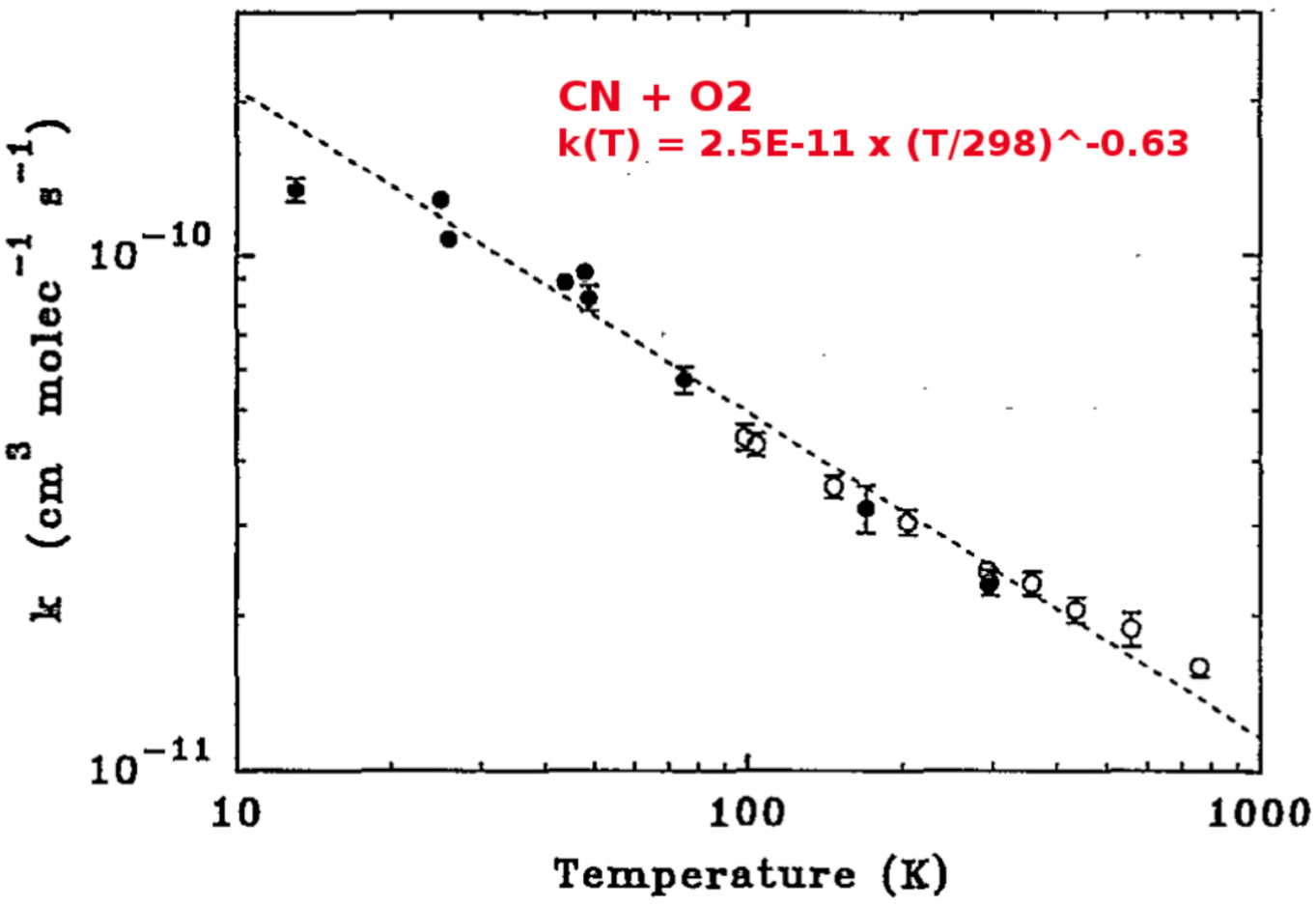






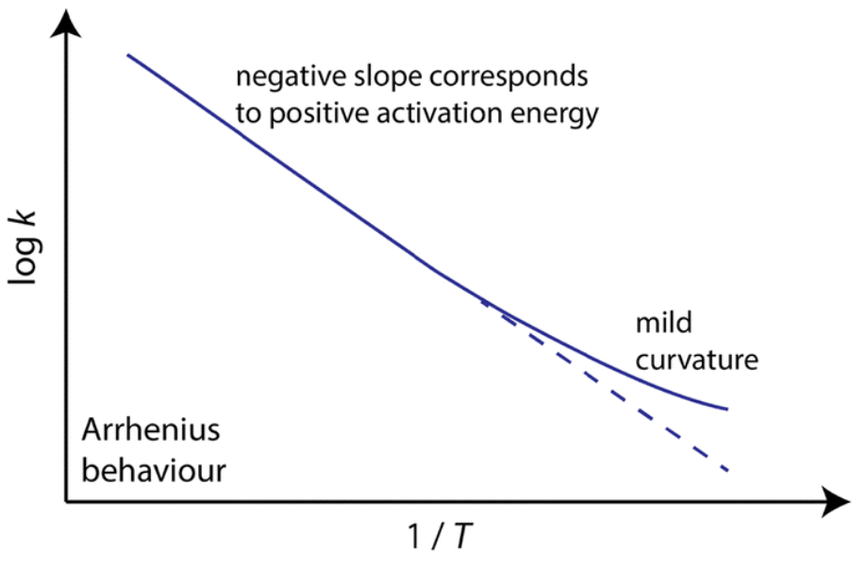
Fournier+2017



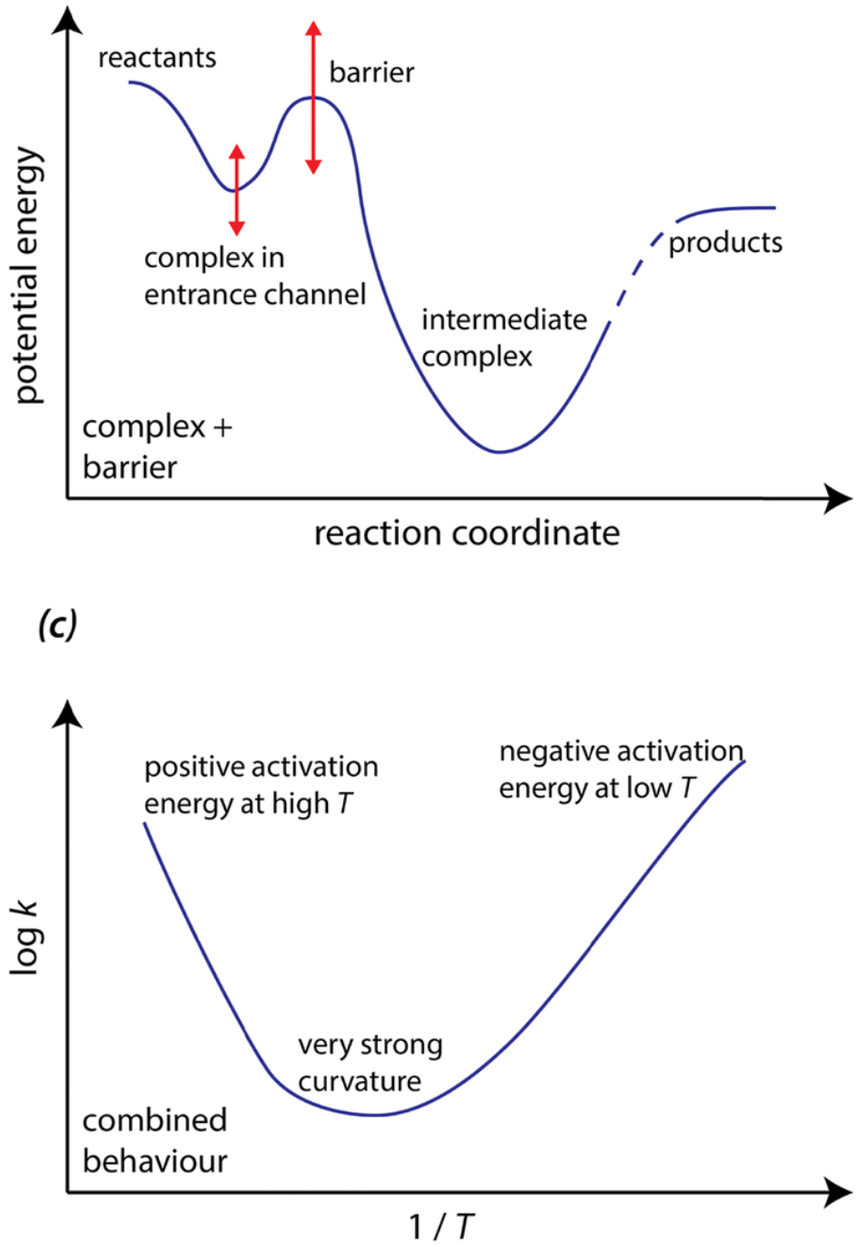


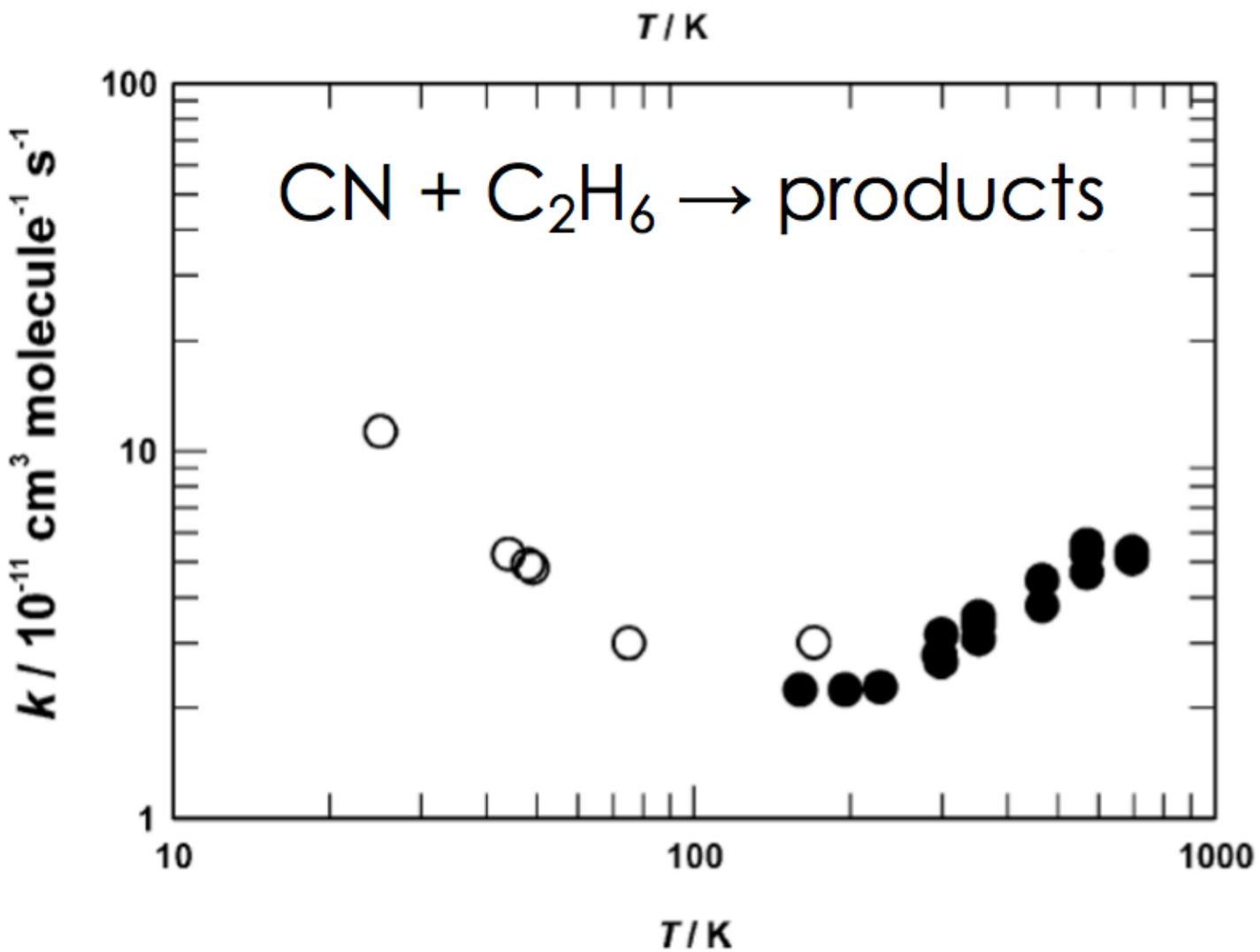
Sims I. R. et al, J Chem Phys 1994

(a)



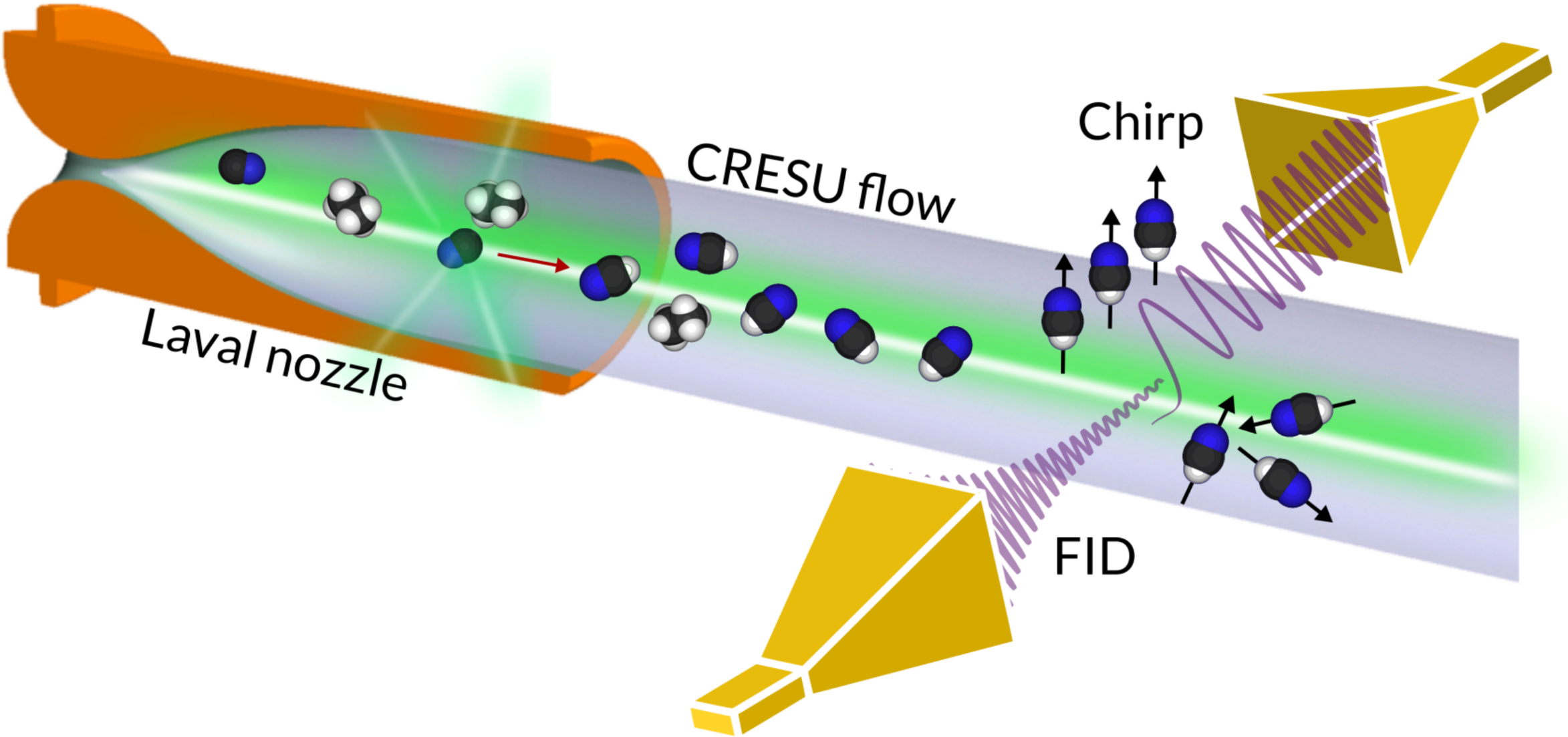
Fournier+2017





Fournier+2017

NEUTRAL-NEUTRAL REACTIONS: THE NEW CRESUCHIRP



Each molecule has a unique microwave spectral fingerprint that can be detected by the chirped-pulse Fourier-transform microwave spectrometer within a single pulse (https://cresuchirp.wordpress.com/research/).

NEUTRAL-NEUTRAL REACTIONS: THE NEW CRESUCHIRP

TYPES OF GAS-PHASE CHEMICAL REACTIONS

Bond Formation Processes		Typical rate coefficient ($cm^3\ s^{-1}$)
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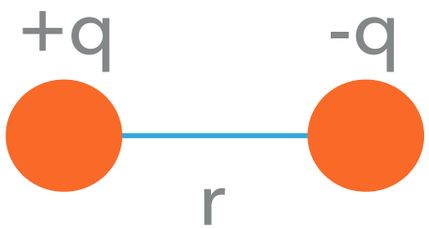
Charge–transfer	$X^+ + YZ \rightarrow X + YZ^+$	
Neutral–neutral	$X + YZ \rightarrow XY + Z$	$10^{-11} - 10^{-9}$

ION-NEUTRAL REACTIONS

$$\mathrm{AB} + \mathrm{C}^+ \rightarrow \mathrm{AC}^+ + \mathrm{B}$$
$$\mathrm{A}^+ + \mathrm{B} \rightarrow \mathrm{C}^+ + \mathrm{D}$$

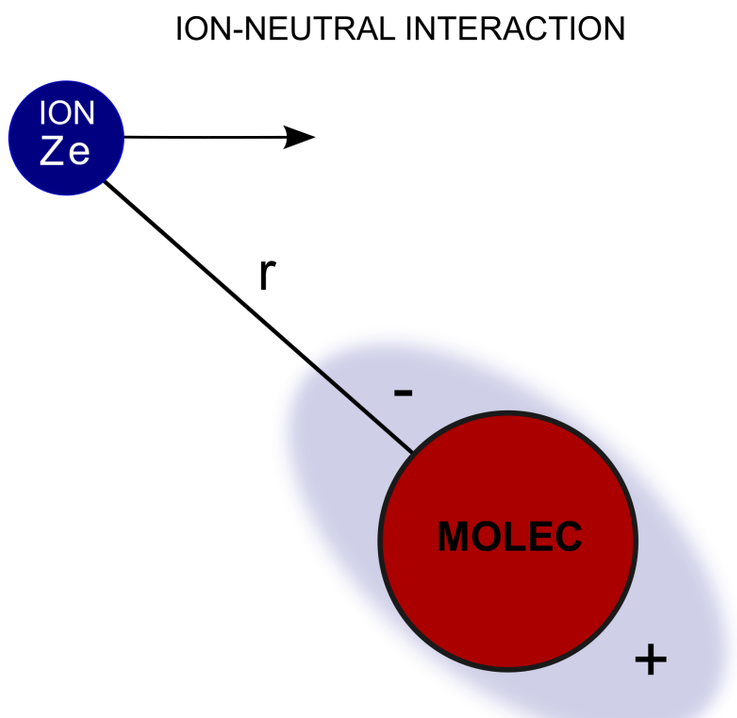


dipole moment

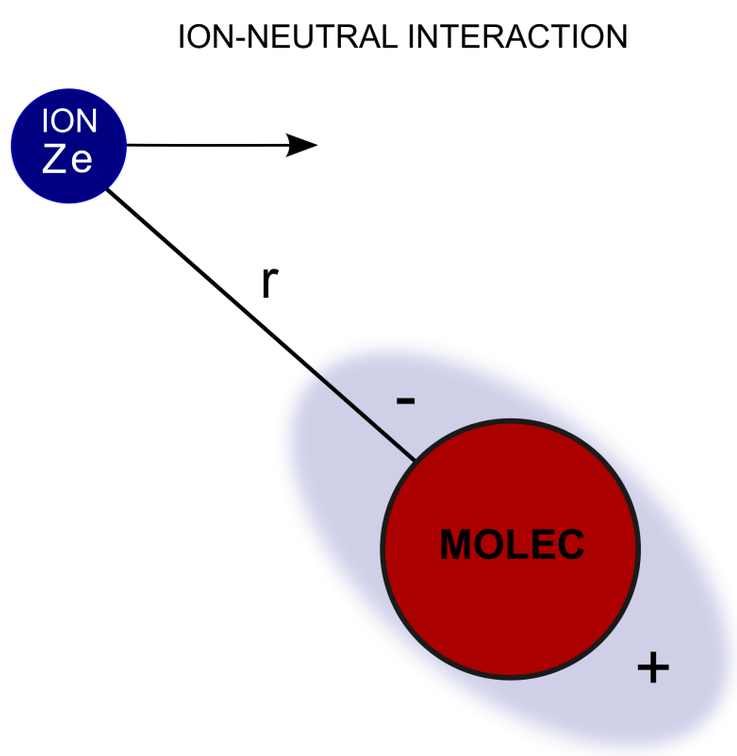
$$\mu_D = \sum_i q_i \vec{r}_i$$

1. Polar molecules (e.g. water) have permanent dipole moment

2. Charges can induce dipole moment in non-polar molecules



ION-NEUTRAL REACTIONS



$$\mu_D^{\text{induced}} = \alpha E$$

$$U(r) = -\frac{\alpha Z^2 e^2}{2r^4}$$

Long-range attractive potential

Polarizability indicates how easily the molecule electrons can be displaced by an electric field. Usually of the order of r_B^3

ION-NEUTRAL REACTIONS: CAPTURE THEORY

- Interaction between ion-neutral can be weak or strong
- Comparison between kinetic and interaction energy
- Angular momentum is conserved ($L = \mu b v$)
- Critical Impact parameter b_0

$$U(r) = -\frac{\alpha Z^2 e^2}{2r^4}$$

ION-NEUTRAL REACTIONS: CAPTURE THEORY

$$L = \mu v b$$

$b > b_0$ **No collisions: recoils**

$b < b_0$ **Reactive collisions**

Centrifugal force

$$U(r) = -\frac{\alpha Z^2 e^2}{2r^4} + \frac{\mu b^2 v^2}{2r^2}$$

ION-NEUTRAL REACTIONS: CAPTURE THEORY

$$b_0^2 = \sqrt{\frac{4\alpha e^2}{\mu v^2}}$$

$$k = \sigma v = \pi b_0^2 v = 2\pi e v \sqrt{\frac{\alpha}{\mu v^2}}$$

$$k = k_L = 2\pi e \sqrt{\frac{\alpha}{\mu}} \simeq 10^{-9} \mathrm{cm}^3\,\mathrm{s}^{-1}$$

Langevin rate (1905)

ION-NEUTRAL REACTIONS: FINAL COMMENTS

- Generally more rapidly than neutral-neutral because of the strong polarization-induced interaction potential (~r^{-4})
- A small amount of ions in a given medium can have a strong impact on the interstellar chemistry.
- If one of the two species has a permanent dipole moment the reactions are even faster
- $k \sim 10^{-9}\ cm^3\ s^{-1}$

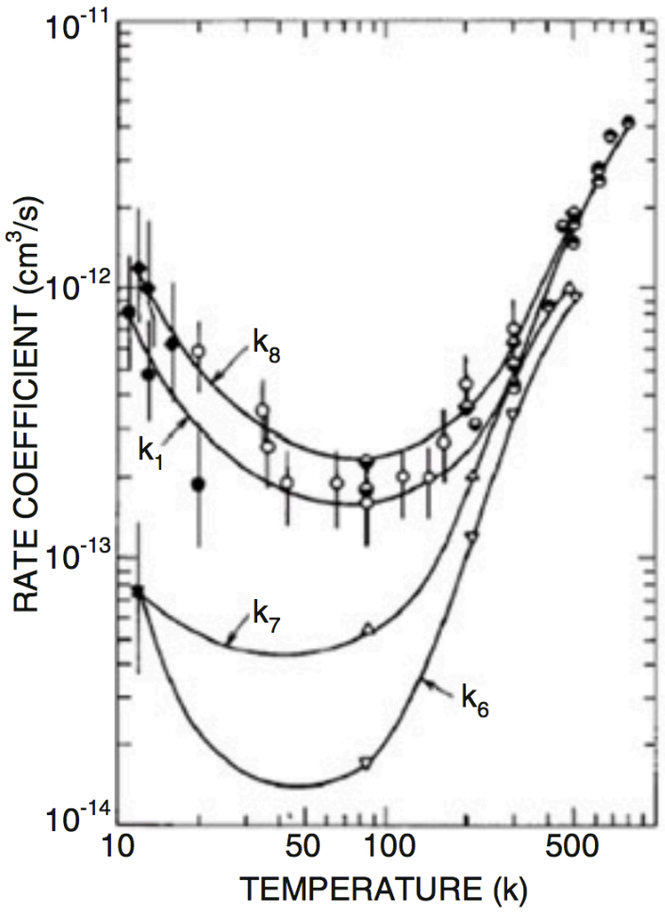
ION-NEUTRAL REACTIONS: DEVIATIONS FROM LANGEVIN

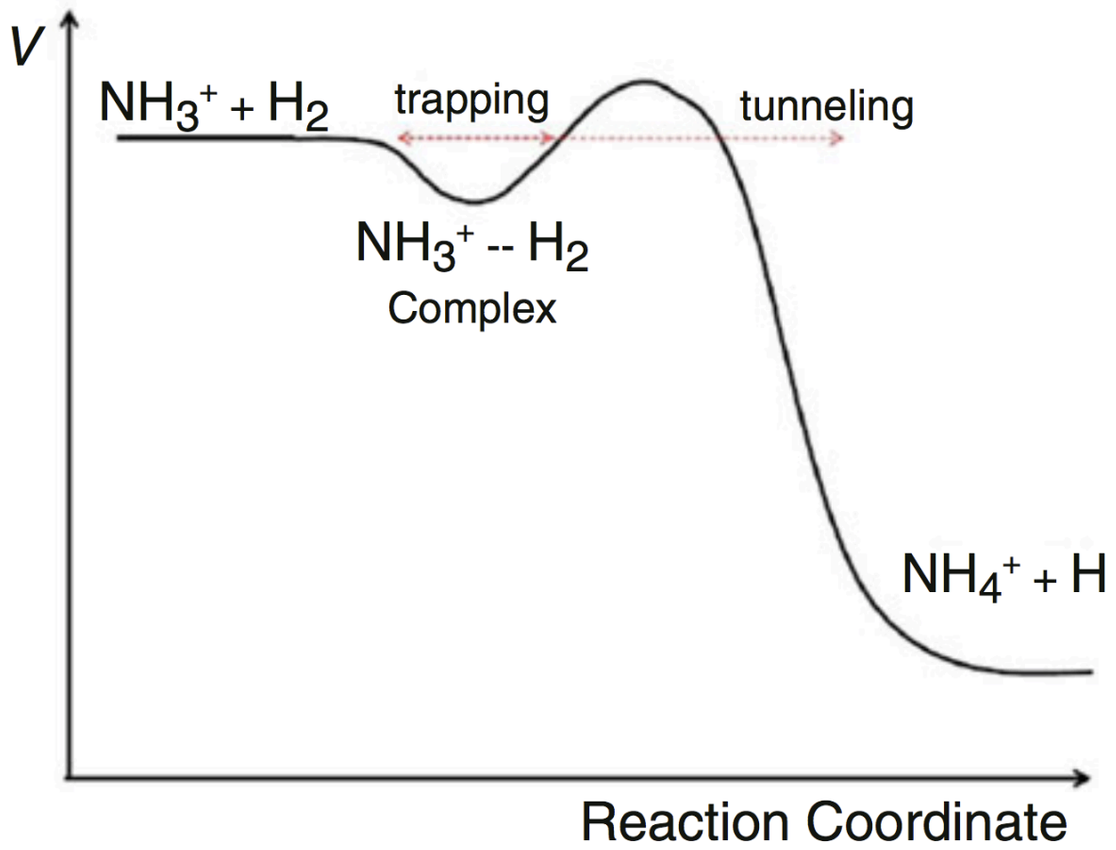
- So far we considered exothermic reactions (no barrier)
- If we have slightly endothermic or reactions with barrier there is a dependence on T
- Example $N^+ + H_2$ (decreases for T < 100 K)

$$k(T) = k_L \exp\left(-\frac{E_a}{k_B T}\right)$$

ION-NEUTRAL REACTIONS: DEVIATIONS FROM LANGEVIN

$NH_3^+ + H_2$ exothermicity: 0.9 eV (with a small barrier)

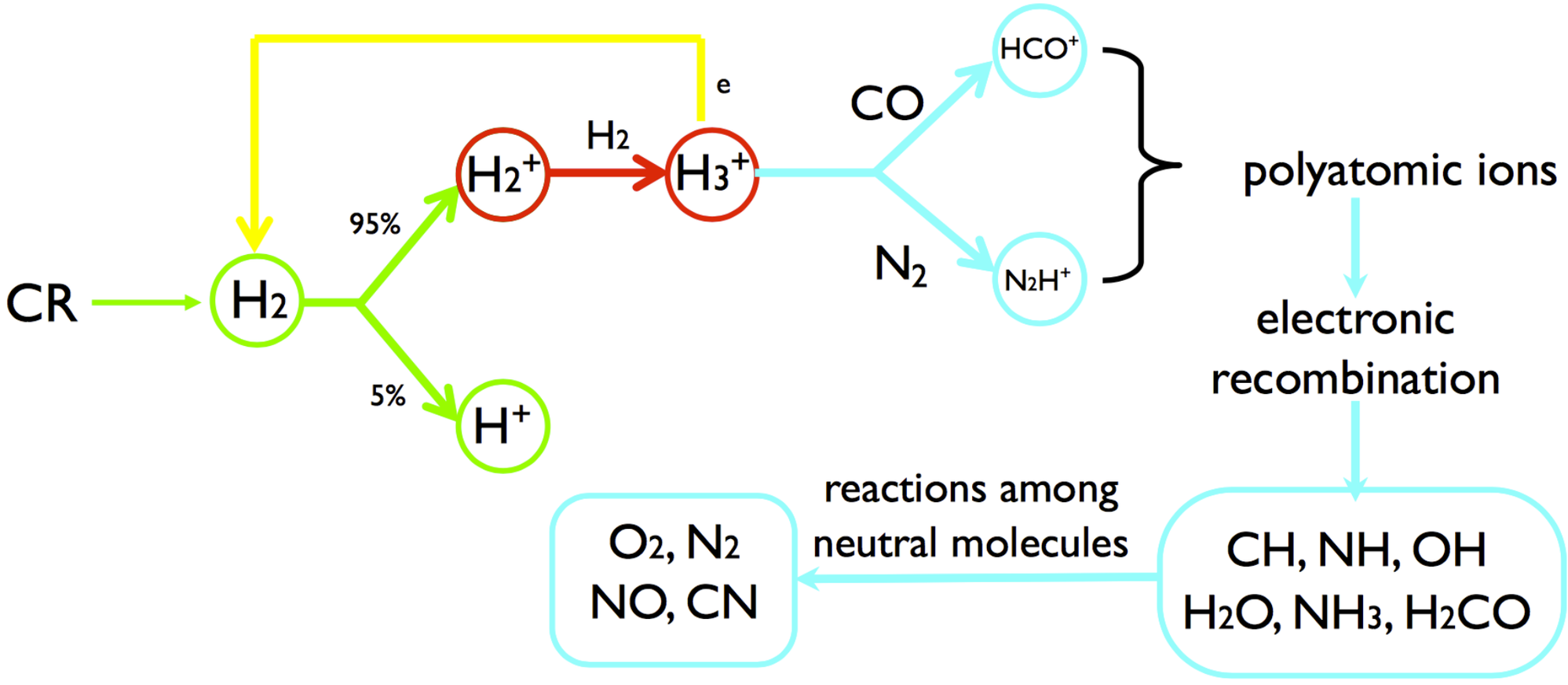




Example: $H_2^+ + H_2 \rightarrow H_3^+ + H$

- a "cornerstone" reaction in molecular clouds:

H_2 ionized by photons, CRs, X-rays, reacts with ambient H_2



DANIELE GALLI'S SLIDE (KROME SCHOOL 2018)

OXYGEN CHEMISTRY

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

$$H_3^+ + O \rightarrow H_2O^+ + H$$

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H$$

$$OH^+ + H_2 \rightarrow H_2O^+ + H$$

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

CARBON-NITROGEN CHEMISTRY

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

$$H_3^+ + C \rightarrow CH_2^+ + H$$

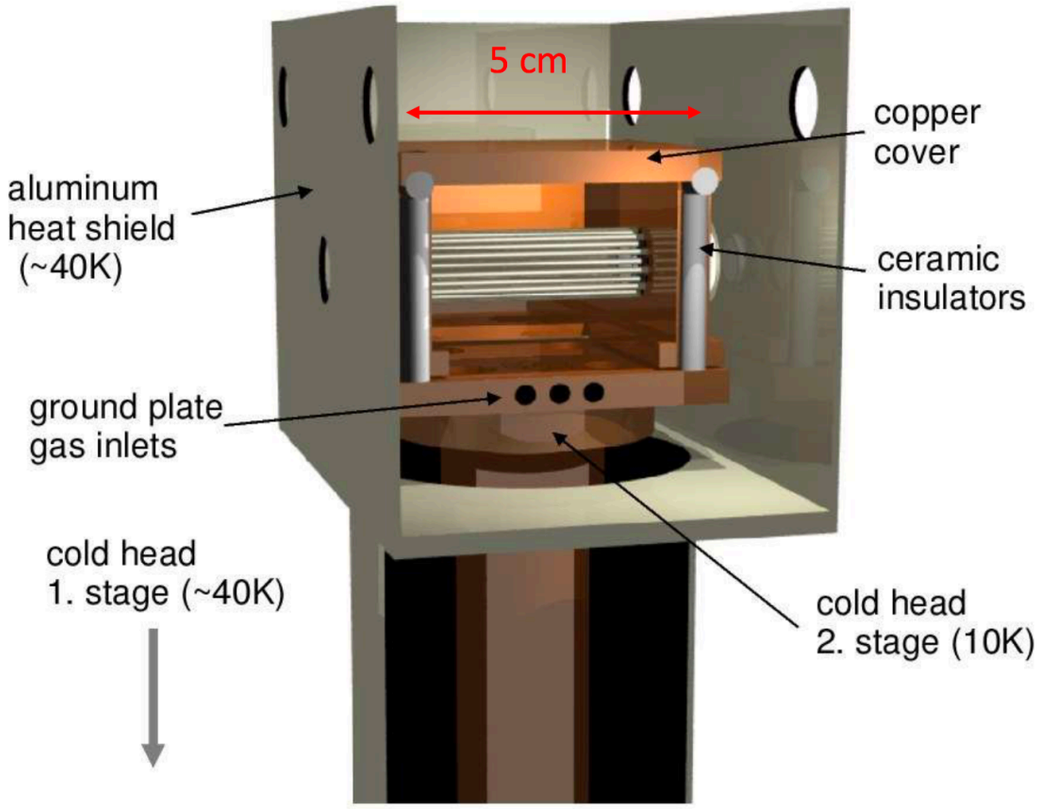
$$H_3^+ + N \rightarrow NH_2^+ + H$$

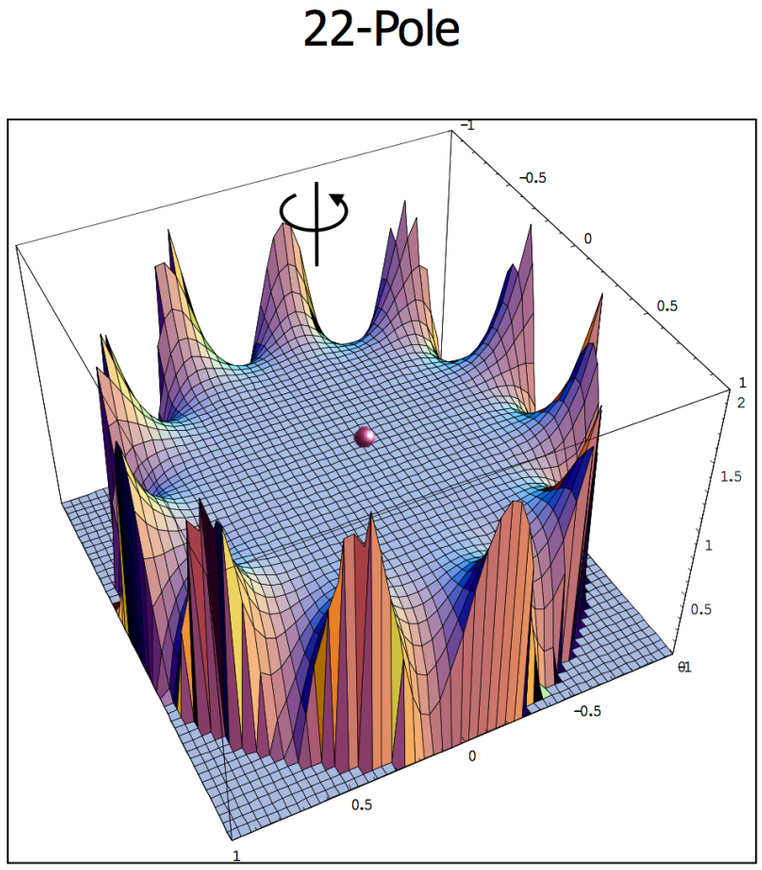
$$NH_2^+ + H_2 \rightarrow NH_3^+ + H,$$
$$NH_3^+ + H_2 \rightarrow NH_4^+ + H,$$
$$NH_4^+ + e^- \rightarrow NH_3 + H,$$

ION-NEUTRAL REACTIONS: EXPERIMENTAL WORK

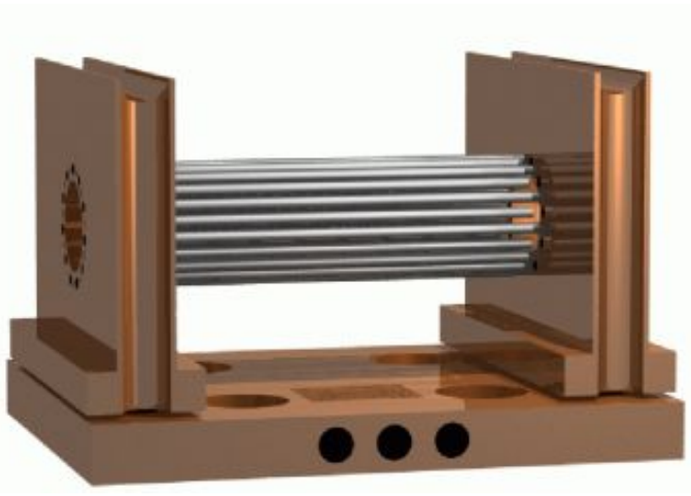
- Ion traps: observe the charge loss while the reactant is introduced ($n \sim 10^{11}$ cm^{-3})
- Ion injected into a flowing gas and the loss is observed at a fixed point downstream when a neutral is added to the gas flow ($n \sim 10^{16}$ cm^{-3})

ION-NEUTRAL REACTIONS: TRAPPING EXPERIMENT





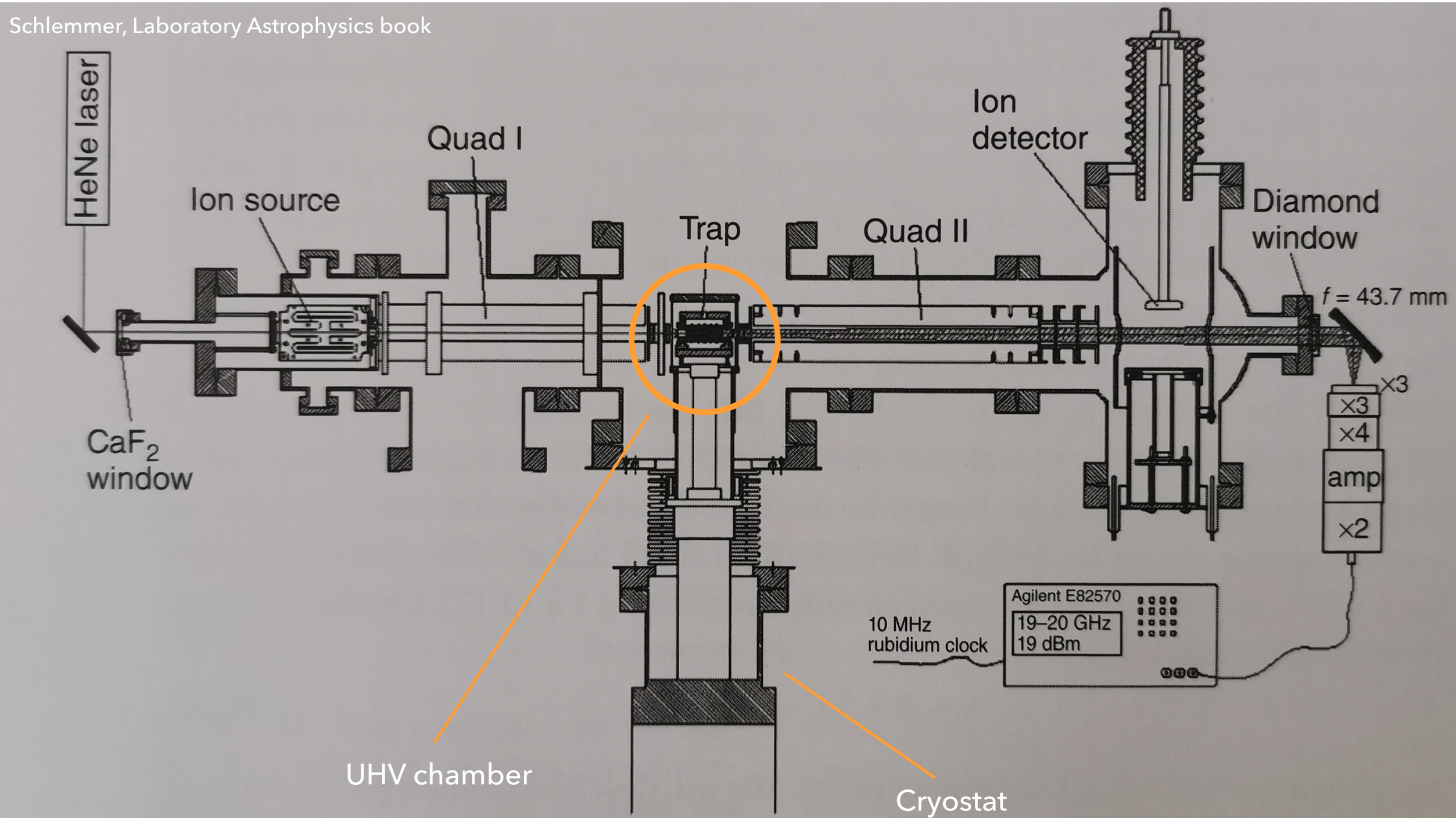
Gerlich, Physica Scripta, T59, 256, (1995)



http://www.hkreckel.de/ion_trap.html

Neutral density: 10^{9}-10^{14} cm^{-3}
Ion source: e.g. electron impact
Quadrupole mass filter: to select a certain m/z
Detector: to analyse the outcome of the reaction

Schlemmer, Laboratory Astrophysics book

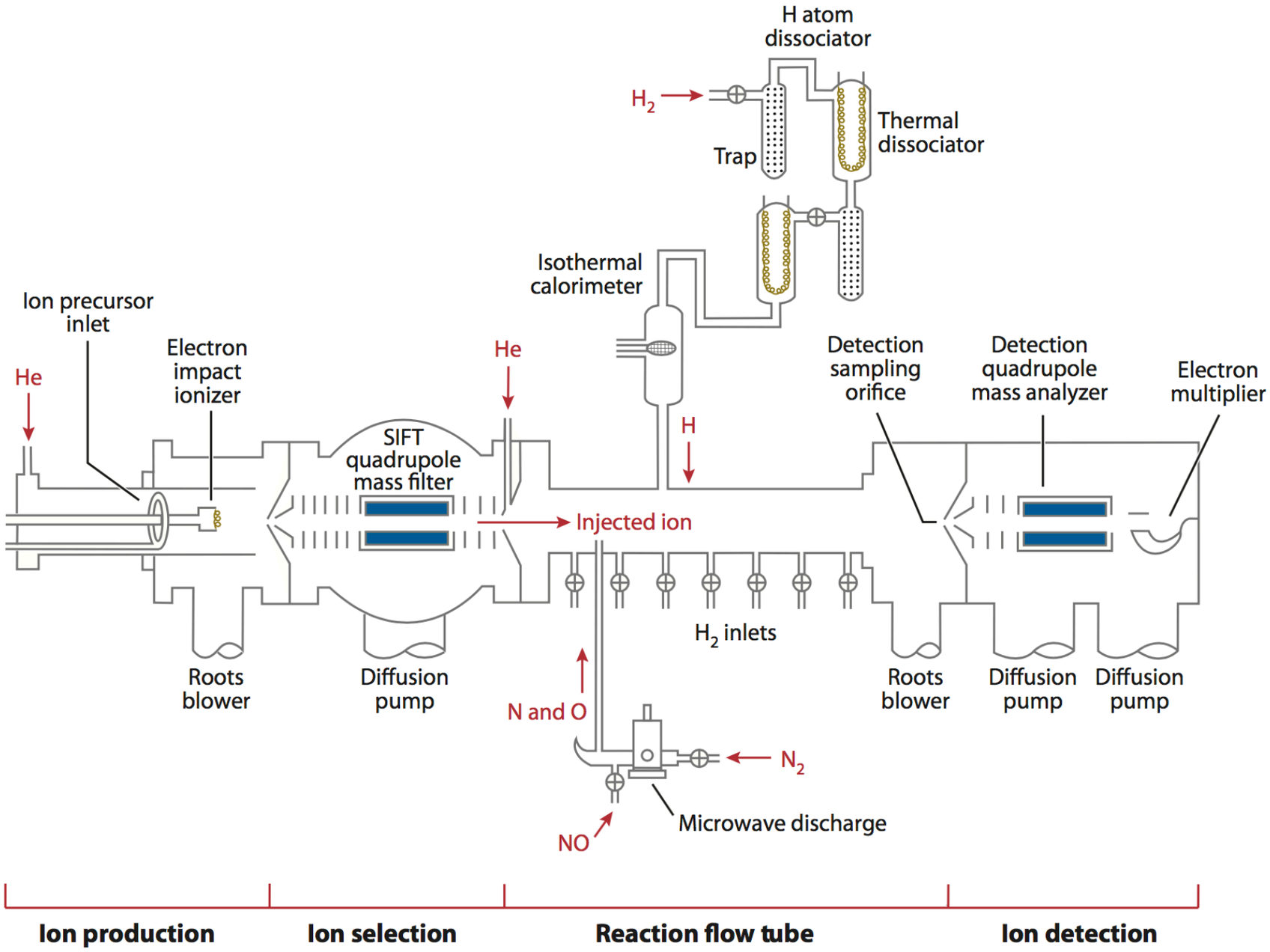


ION-NEUTRAL REACTIONS: EXPERIMENTAL WORK

- Flowing-afterglow (Ferguson et al. 1969):
- Ion produced at the upstream end of a tubular reactor (via discharge for N and O atoms or thermal dissociation for H)
- Diluted with a buffer gas (He), thermalization
- Neutrals introduced further away
- Mixture flows through mass spectrometric detection

ION-NEUTRAL REACTIONS: FA-SIFT EXPERIMENT

Working from room temperature down to 80 K max



*The flowing afterglow (FA)-selected ion flow tube (SIFT) instrument in Boulder Smith+2011

ION-NEUTRAL REACTIONS: CHARGE TRANSFER

$$A^+ + B \rightarrow A + B^+$$

- In this reaction no break of chemical bonds
- Requires exothermicity
- Rate fast (10^{-9} cm^3 s^{-1}) and T-independent

Reaction	k
$H^+ + OH \longrightarrow H + OH^+$	2.1×10^{-9}
$N_2^+ + H_2O \longrightarrow N_2 + H_2O^+$	2.3×10^{-9}
$C^+ + CH \longrightarrow C + CH^+$	3.8×10^{-10}
$C^+ + CH_2 \longrightarrow C + CH_2^+$	5.2×10^{-10}
$C^+ + C_2H_4 \longrightarrow C + C_2H_4^+$	3.0×10^{-10}
$N^+ + CH_2 \longrightarrow N + CH_2^+$	1.0×10^{-9}
$O^+ + CH \longrightarrow O + CH^+$	3.5×10^{-10}
$O^+ + H_2O \longrightarrow O + H_2O^+$	3.2×10^{-9}

DESTRUCTION

RADIATIVE/DISSOCIATIVE RECOMBINATION

A reaction between an electron and an ion or molecular ion

$$X^+ + e^- \rightarrow X + \gamma$$

$$XY^+ + e^- \rightarrow XY + \gamma$$ Slow: as usual requires emission of a photon

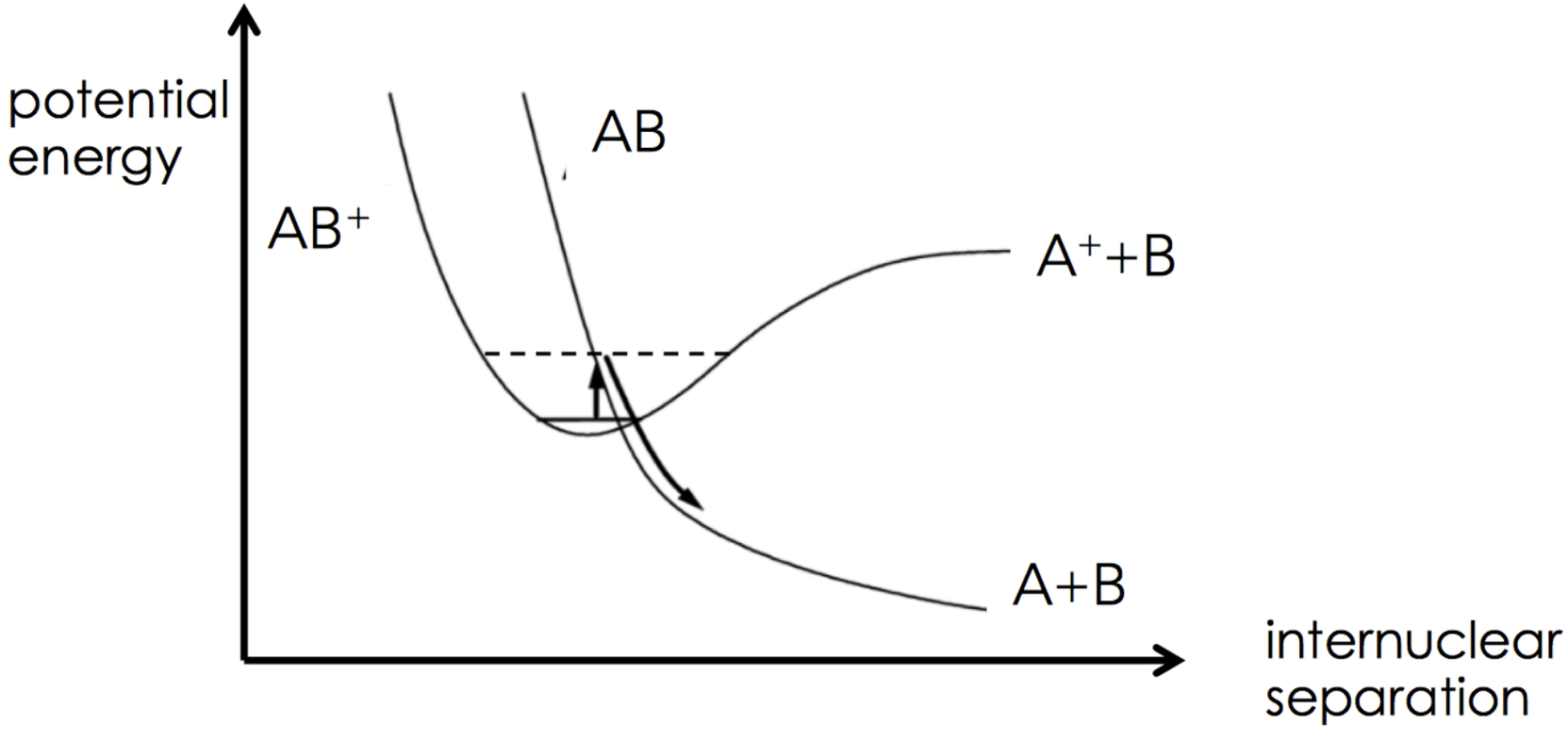
$$XY^+ + e^- \rightarrow X + Y$$ Fast: if curves crossing occurs

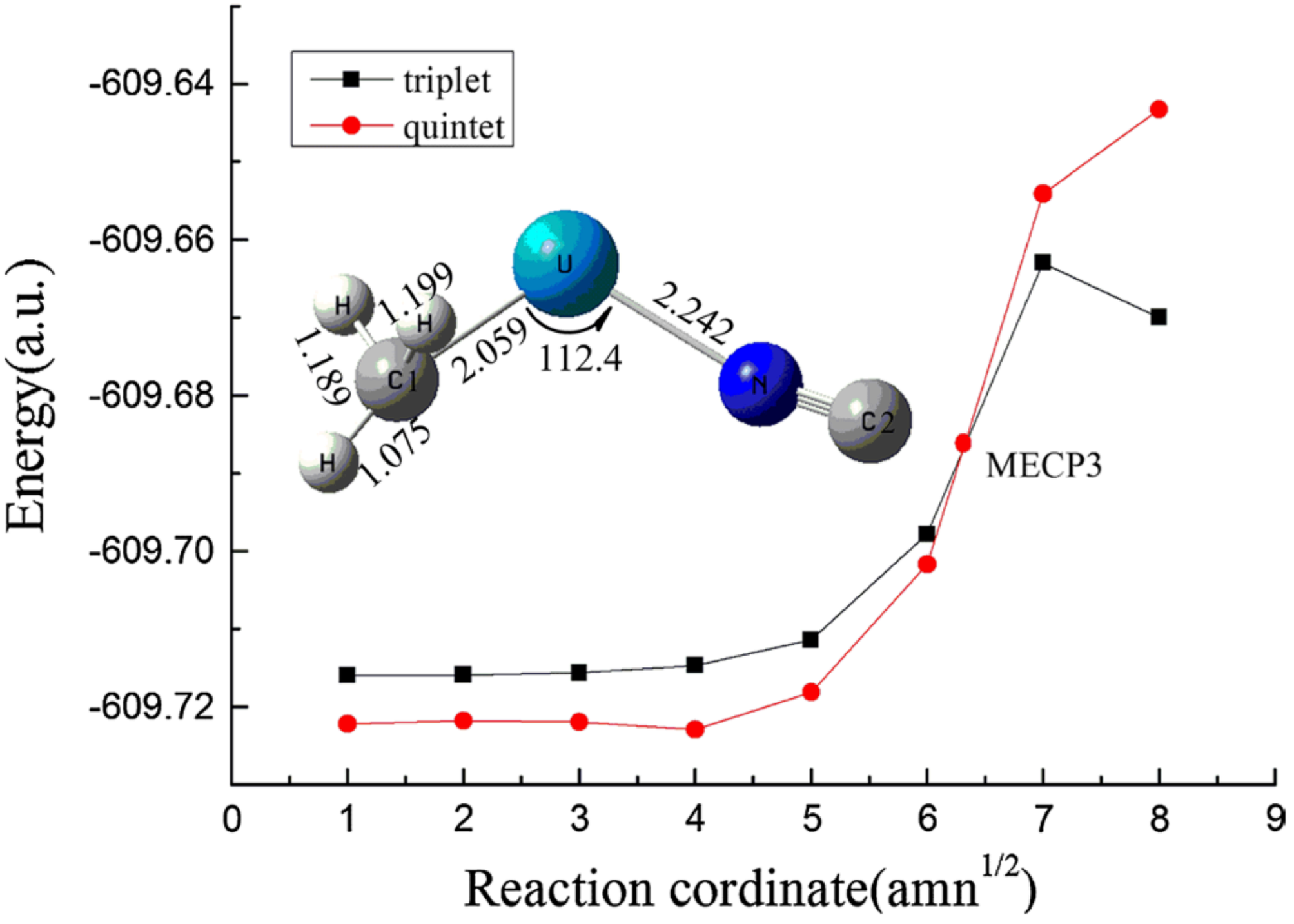
Major role is to create stable neutrals by dissociating molecular ions

$$CH_5^+ + e \rightarrow CH_4 + H$$

RADIATIVE/DISSOCIATIVE RECOMBINATION

Electron excites transition of stable AB^+ ion to a repulsive state of AB molecule which crosses the energy curve of the ion AB^+.




triplet
quintet
-609.64
-609.66
-609.68
-609.70
-609.72
Energy(a.u.)
0
1
2
3
4
5
6
7
8
9
Reaction cordinate(amn^1/2)
U
H
H
C1
H
N
C2
1.199
1.189
2.059
112.4
2.242
1.075
MECP3

DISSOCIATIVE RECOMBINATION (CONT'D)

- Important source of neutral molecules
- Initiated by ions formed via ion-molecule reactions
- Very fast process: rates of the order of 10^{-7} cm^3s^{-1} (@ 10 K)
- Usually rate goes as $T^{-1/2}$
- Difficult to measure/calculate, multiple products (need to know both the rate coefficient and the branching ratios)

DISSOCIATIVE RECOMBINATION: EXAMPLES

Branching ratios? Normally: same branching ratios assumed!

For this specific reaction Jensen+2000

$$\mathrm{OH_3^+ + e^- \rightarrow H_2O + H} \quad \textbf{0.25}$$
$$\mathrm{OH_3^+ + e^- \rightarrow OH + H_2} \quad \textbf{0.14}$$
$$\mathrm{OH_3^+ + e^- \rightarrow OH + H + H} \quad \textbf{0.60}$$
$$\mathrm{OH_3^+ + e^- \rightarrow O + H_2 + H} \quad \textbf{0.013}$$

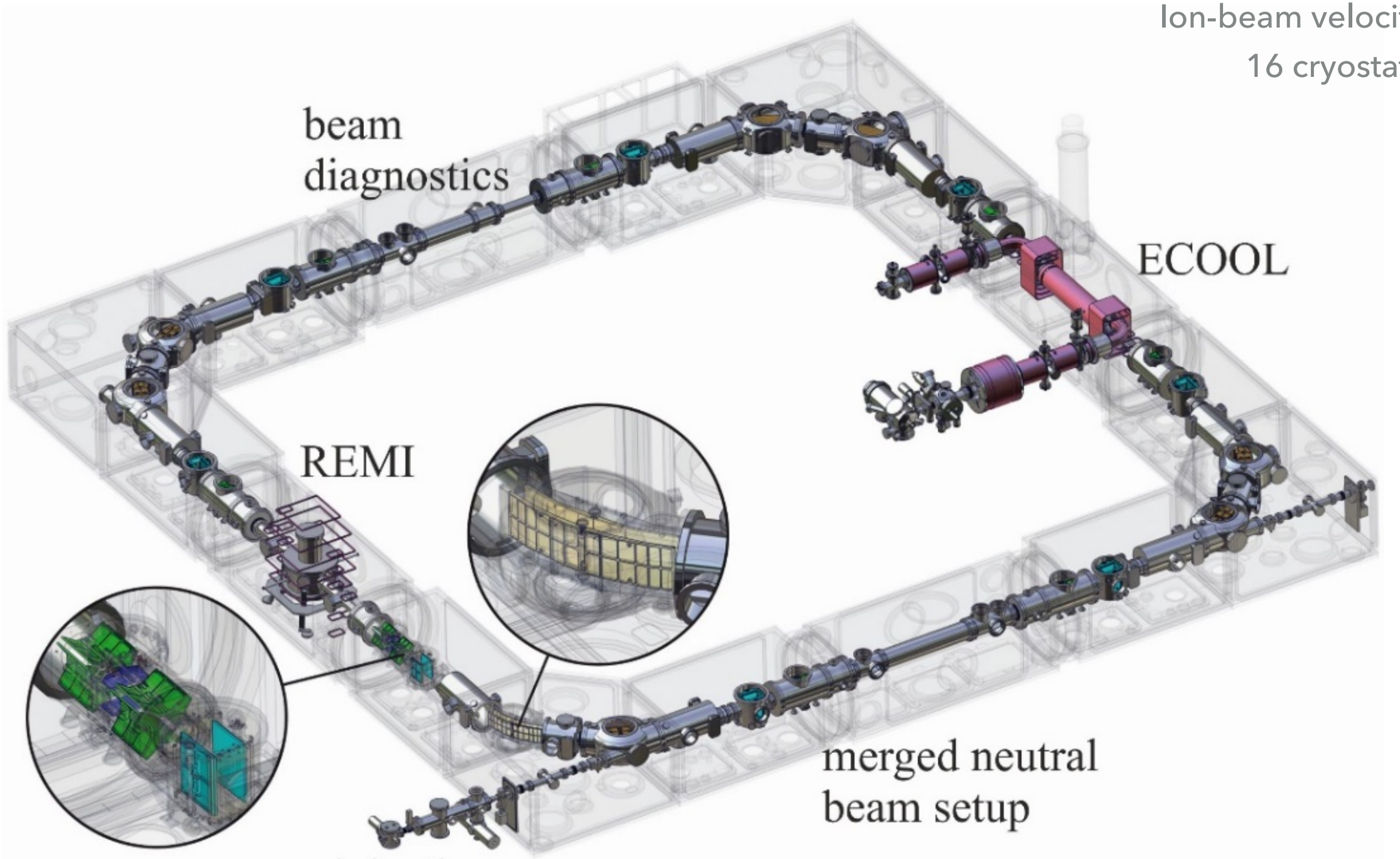
BR major uncertainty!

DISSOCIATIVE RECOMBINATION (CONT'D)

Reaction	α	β
$H_2^+ + e^- \longrightarrow H + H$	1.6×10^{-8}	-0.43
$H_2O^+ + e^- \longrightarrow O + H + H$	3.1×10^{-7}	-0.5
$H_2O^+ + e^- \longrightarrow OH + H$	8.6×10^{-8}	-0.5
$H_3O^+ + e^- \longrightarrow OH + H_2$	6.0×10^{-8}	-0.5
$H_3O^+ + e^- \longrightarrow O + H + H_2$	5.6×10^{-9}	-0.5
$H_3^+ + e^- \longrightarrow H_2 + H$	2.3×10^{-8}	-0.52
$HCN^+ + e^- \longrightarrow CN + H$	2.0×10^{-7}	-0.5
$HCO^+ + e^- \longrightarrow CO + H$	2.4×10^{-7}	-0.69
$HNO^+ + e^- \longrightarrow NO + H$	3.0×10^{-7}	-0.69
$C_2^+ + e^- \longrightarrow C + C$	3.0×10^{-7}	-0.5
$CH^+ + e^- \longrightarrow C + H$	1.5×10^{-7}	-0.42
$CH_2^+ + e^- \longrightarrow CH + H$	1.4×10^{-7}	-0.55
$CH_2^+ + e^- \longrightarrow C + H + H$	4.0×10^{-7}	-0.6
$CH_3^+ + e^- \longrightarrow CH + H + H$	2.0×10^{-7}	-0.4
$CH_3^+ + e^- \longrightarrow CH + H_2$	2.0×10^{-7}	-0.5
$CH^+ + e^- \longrightarrow C + H$	1.5×10^{-7}	-0.42
$CN^+ + e^- \longrightarrow C + N$	1.8×10^{-7}	-0.5

DISSOCIATIVE RECOMBINATION: ION STORAGE RING

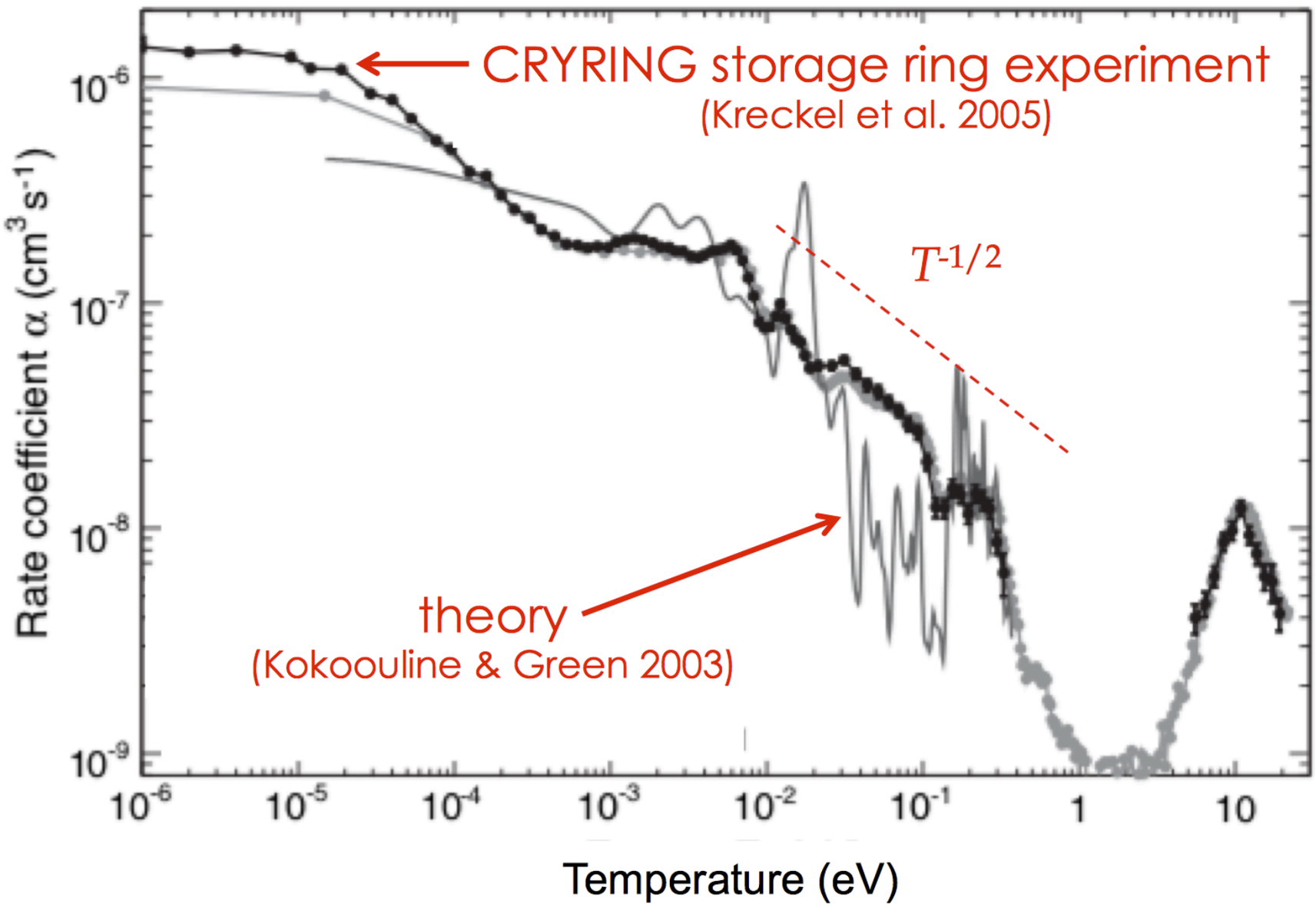
Length=40-60 m
Ion-beam velocities control
16 cryostat chambers



Supersonic nozzle

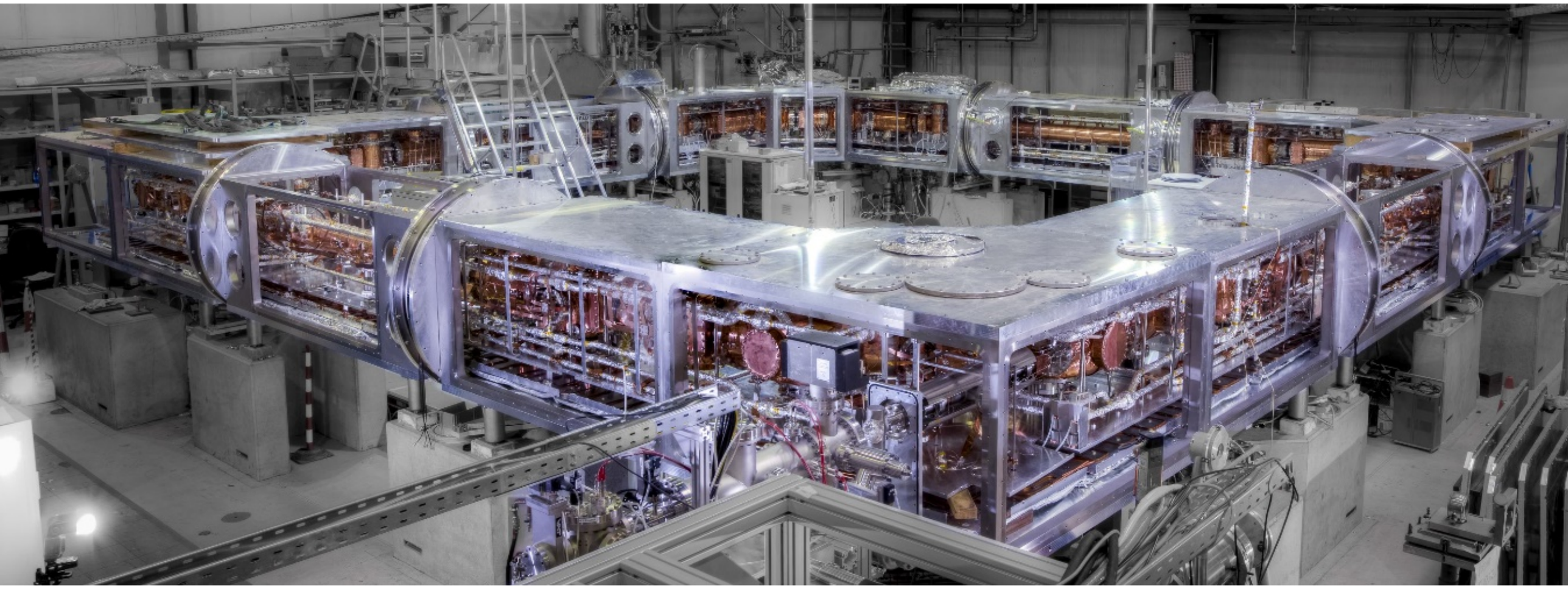
DISSOCIATIVE RECOMBINATION: EXAMPLE, H_3^+

$$H_3^+ + e^- \rightarrow H_2 + H$$
$$H_3^+ + e^- \rightarrow H + H + H$$



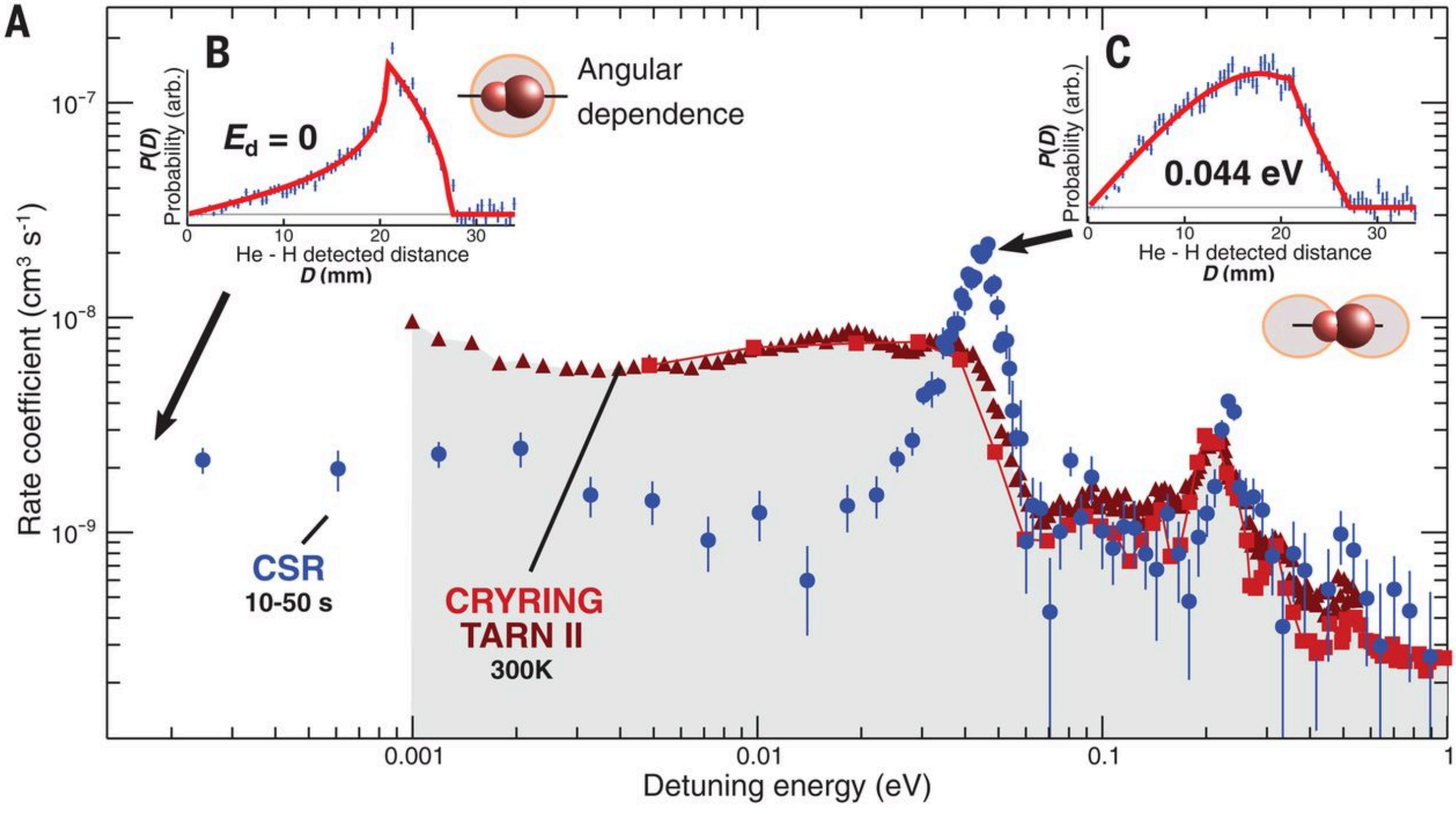
DISSOCIATIVE RECOMBINATION: CRYOGENIC ION STORAGE RING

CSR @ MAX PLANCK



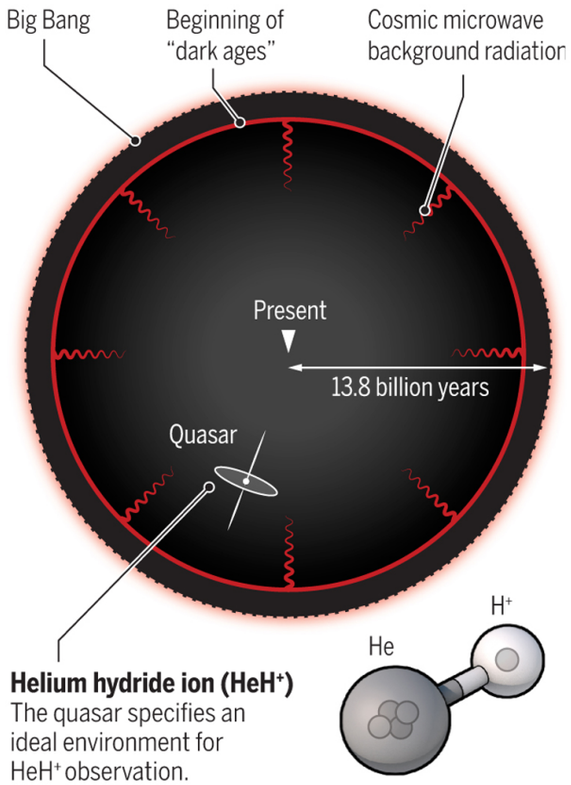
https://www.mpi-hd.mpg.de/blaum/storage-rings/csr/index.en.html

DISSOCIATIVE RECOMBINATION: EXAMPLE, HEH^+

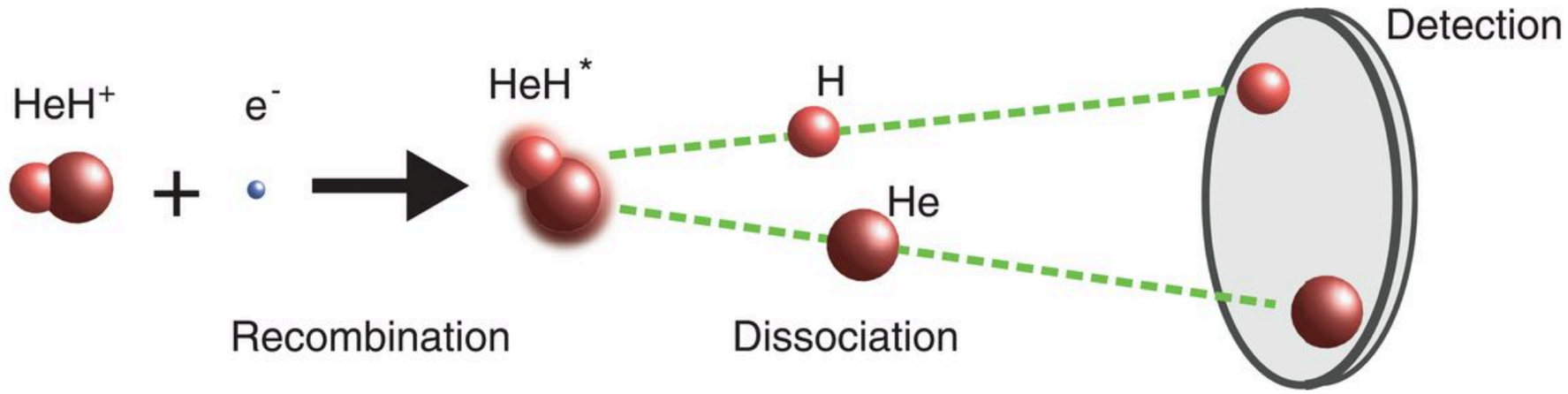


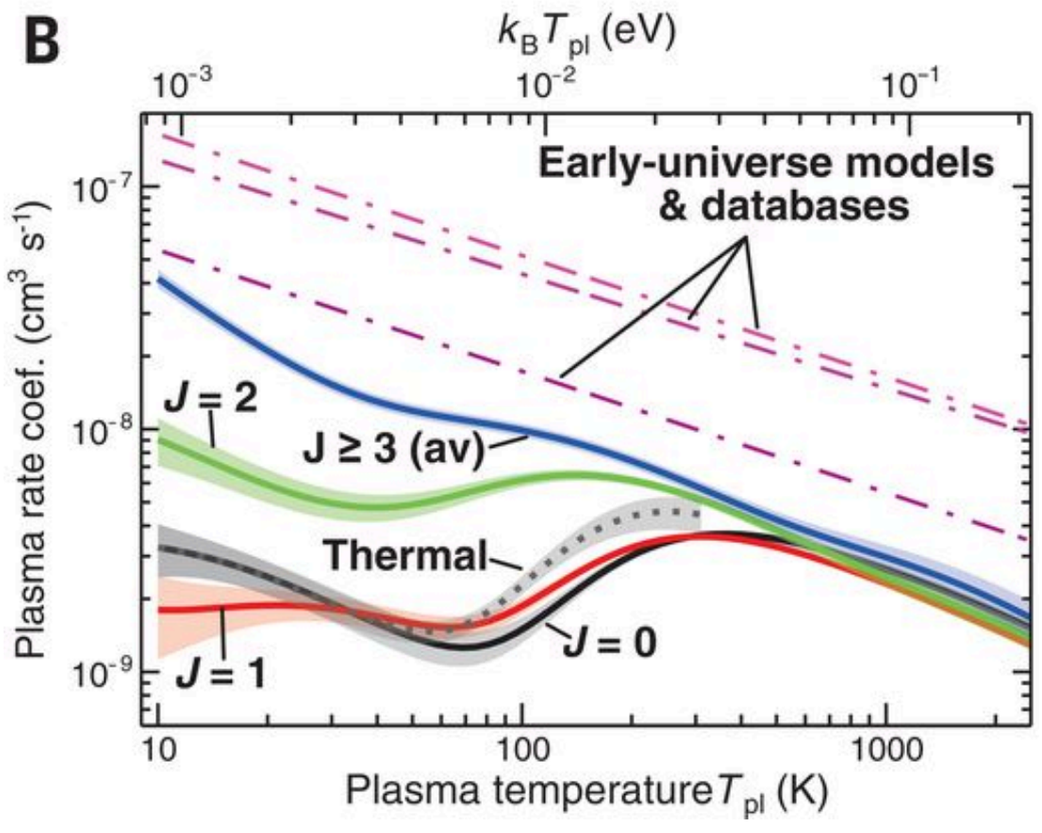
Early Universe, first molecules

Hydrogen recombination began after the generation of cosmic microwave background radiation.



Helium hydride ion (HeH^+)
The quasar specifies an ideal environment for HeH^+ observation.





Science

First molecule still animates astronomers

Stefano Bovino and Daniele Galli

Science **365** (6454), 639.
DOI: 10.1126/science.aay5825

Bond Formation Processes		Typical rate coefficient ($cm^3\ s^{-1}$)
Radiative association	$X + Y \rightarrow XY + h\nu$	$10^{-17} - 10^{-14}$
Associative detachment	$X^- + Y \rightarrow XY + e$	$\sim 10^{-9}$
Bond Destruction Processes		
Dissociative recombination	$XY^+ + e \rightarrow X + Y$	$10^{-7} - 10^{-6}$
Bond Rearrangement Processes		
Ion–molecule exchange	$X^+ + YZ \rightarrow XY^+ + Z$	$10^{-9} - 10^{-8}$
Charge–transfer	$X^+ + YZ \rightarrow X + YZ^+$	10^{-9}
Neutral–neutral	$X + YZ \rightarrow XY + Z$	$10^{-11} - 10^{-9}$

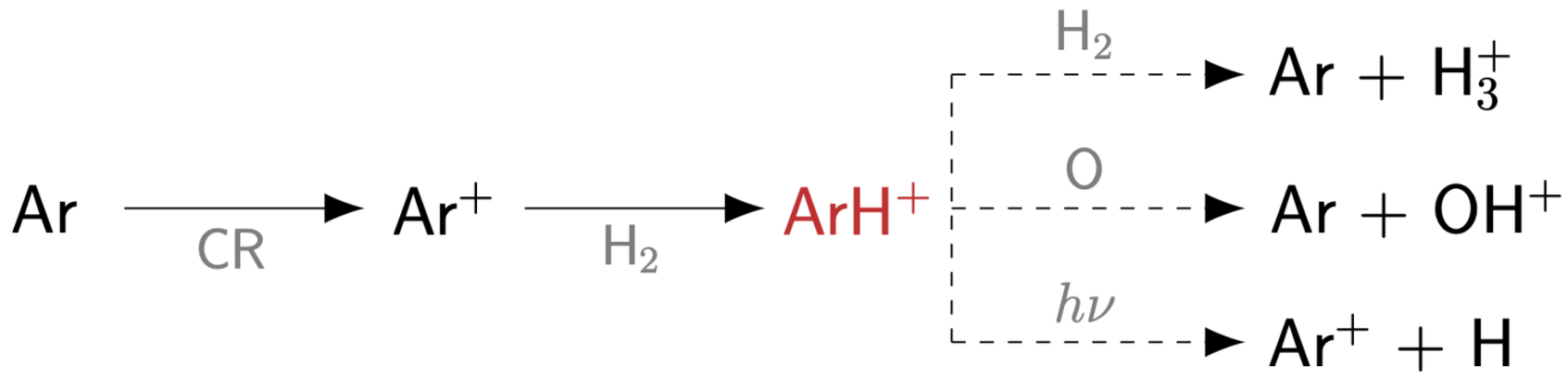
SUMMARY

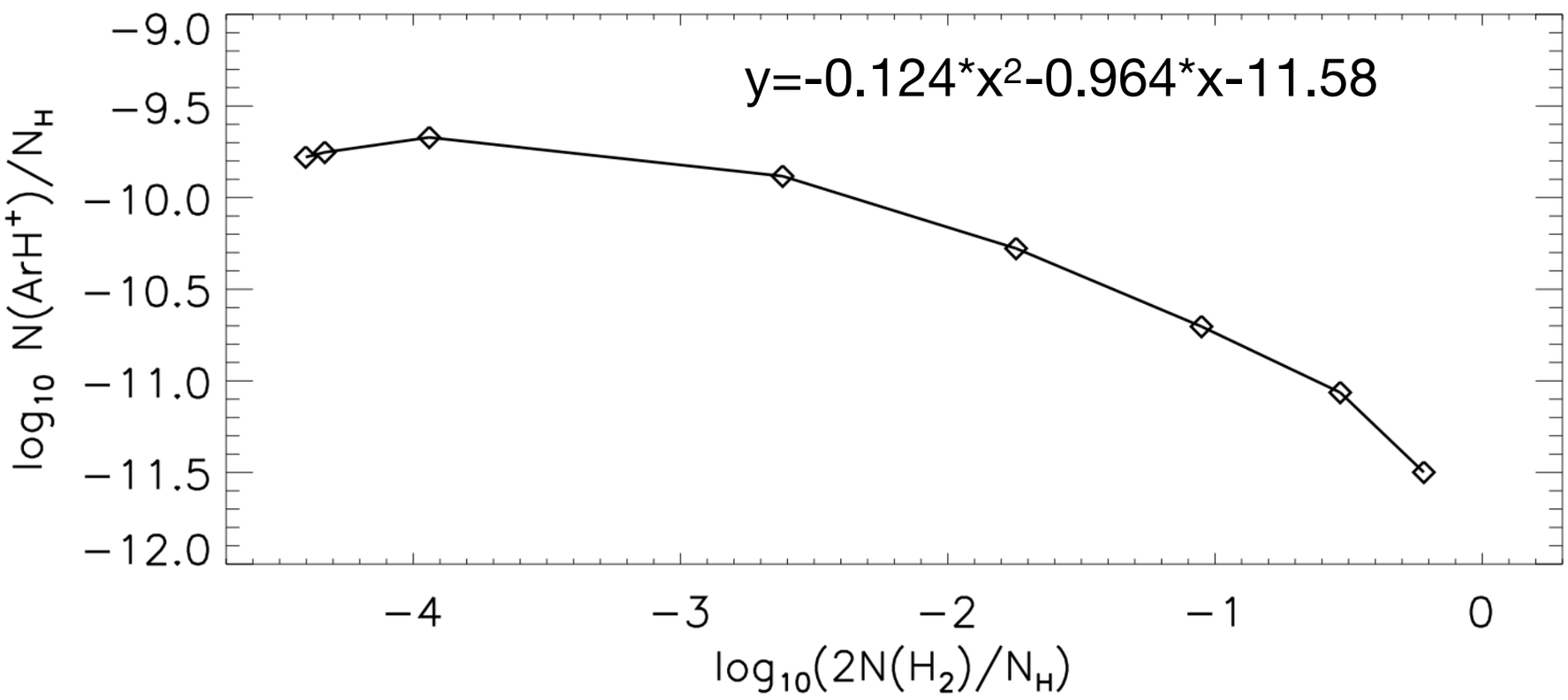
- In general exothermic reactions are the most common
- Preferably with no barrier
- Shocks and turbulence can generate warm-zones where endothermic reactions can occur
- Ion-neutral reactions very important in cold environments (MCs)
- Radiative attachment/detachment in envs with high-ionization degree (ionized regions and early Universe)
- Dissociative recombination fundamental to create stable neutrals in cold regions

What do we miss?

- Photochemistry
- Cosmic-rays induced chemistry
- Gas-grain chemistry

Exercise





x=log(f_{H2})
y=log(N[ArH^+]/N[H])