

Astrochemistry

Lecture 2

Basic Processes (cont'd)



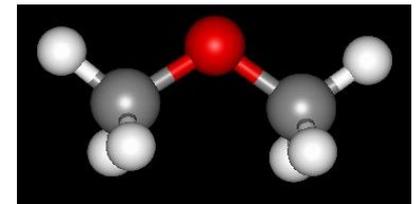
Ewine F. van Dishoeck

Leiden Observatory

May-June 2022



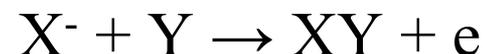
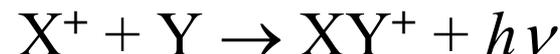
Tielens Chap. 6, 7
Water review Sect. 3
(vD 1988 review)



Types of chemical reactions

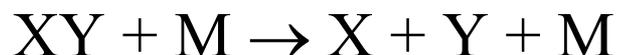
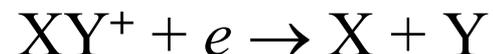
■ Formation of bonds

- Radiative association:
- Associative detachment
- **Grain surface:**



■ Destruction of bonds

- Photo-dissociation:
- Dissociative recombination:
- Collisional dissociation:



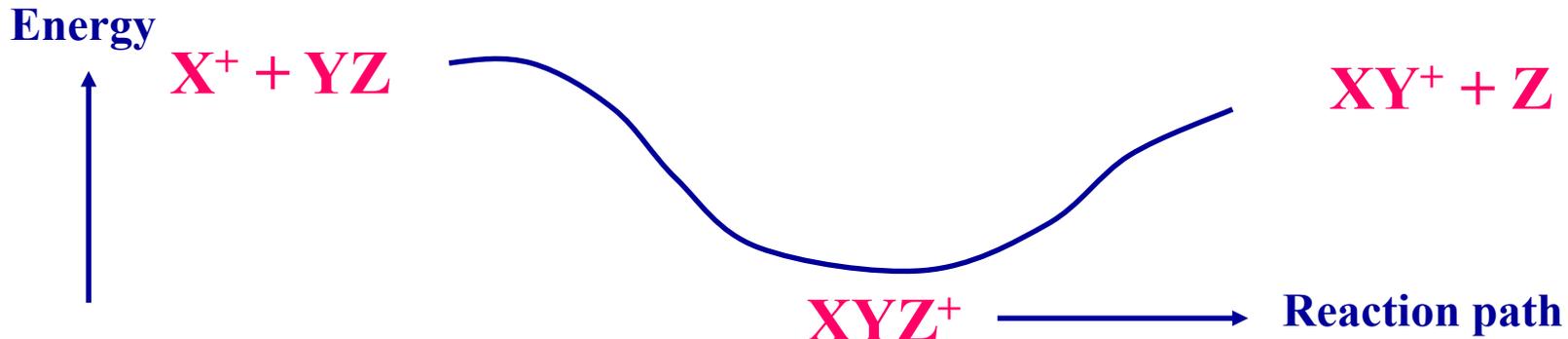
■ Rearrangement of bonds

- **Ion-molecule reactions:**
- **Charge-transfer reactions:**
- **Neutral-neutral reactions:**

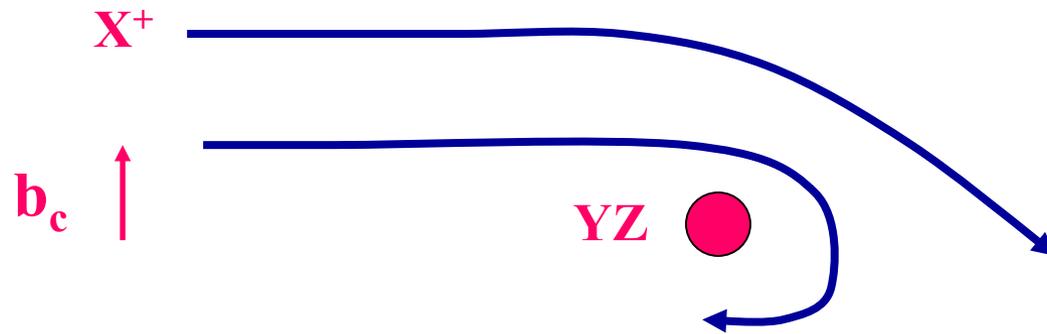


2.1 Ion-molecule reactions

- Ion induces dipole moment in molecule when it approaches it => long-range attraction which goes as $\sim 1/R^4$
- Reaction is rapid even at low T *if* the reaction is exothermic; rate can be readily computed by classical capture theory developed by Langevin 1905



Classical capture theory



- Reaction only occurs if impact parameter b is small enough that X^+ is ‘captured’, i.e., it spends enough time near YZ for reaction to take place

Langevin rate

- Interaction potential (induced dipole + centrifugal barrier):

$$V_{\text{eff}}(R) = \frac{-e^2 \alpha}{2R^4} + \frac{\mu b^2 v^2}{2R^2}$$

α =polarizability
 b =impact parameter
 v =velocity

↑
Centrifugal barrier

- V_{eff} has maximum value: $(\mu b^2 v^2)^2 / (8\alpha e^2)$
- Critical impact parameter:

$$\frac{1}{2} \mu v^2 > (\mu b^2 v^2)^2 / (8\alpha e^2) \Rightarrow b_{\text{crit}} = \left(\frac{4\alpha e^2}{\mu v^2} \right)^{1/4}$$

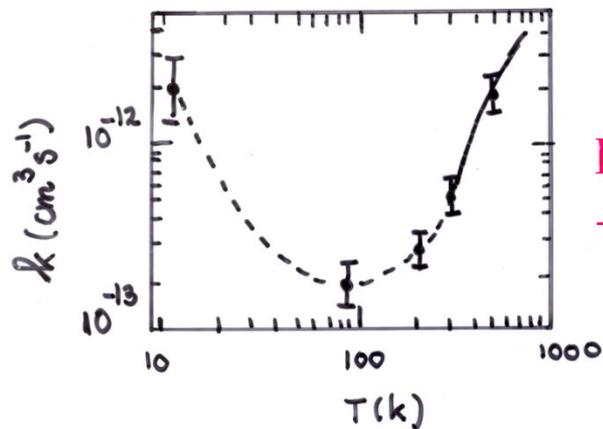
- Rate coefficient is **independent of T**:

$$k = \langle \sigma v \rangle = \langle \pi b_{\text{crit}}^2 v \rangle = 2\pi \sqrt{\frac{\alpha e^2}{\mu}} \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

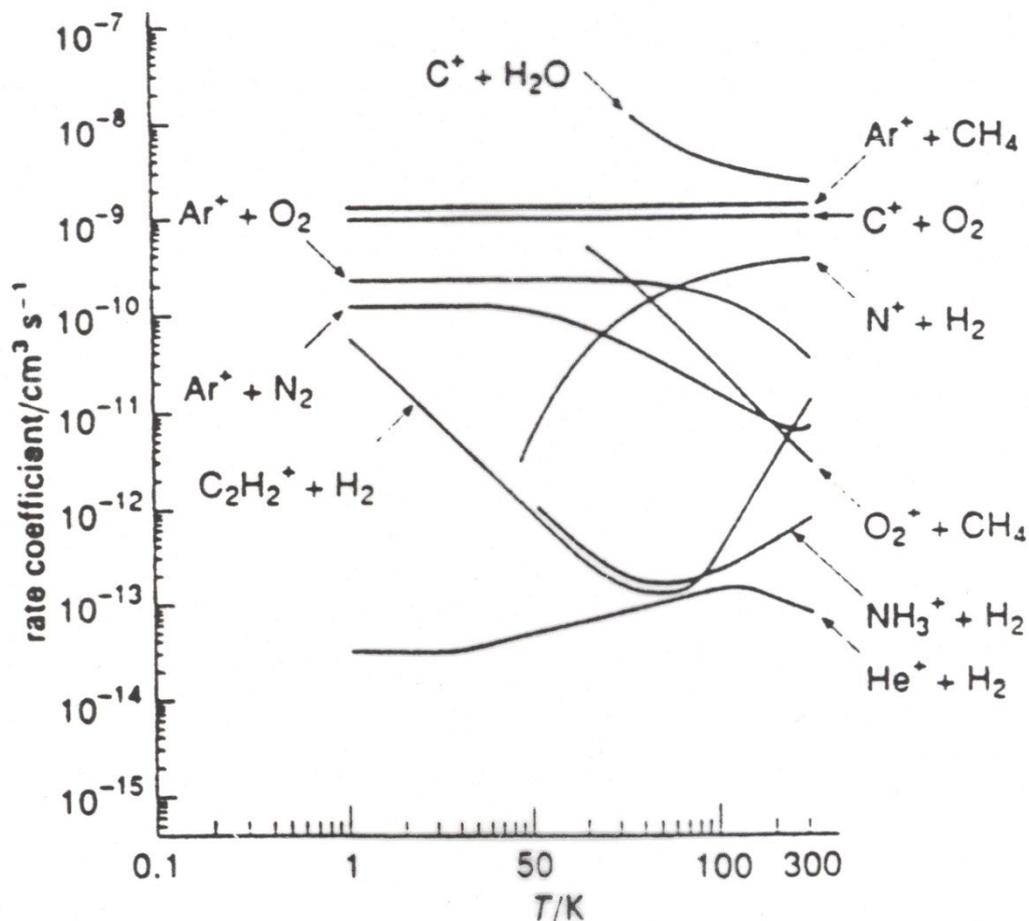
Langevin rate

Ion-molecule processes

- $X^+ + YZ \rightarrow XY^+ + Z$ exchange
 $\rightarrow X + YZ^+$ charge transfer
- Many experiments performed at room T , some at low T . Most reactions (>90%) indeed proceed at Langevin rate, but some exceptions known



Experiments

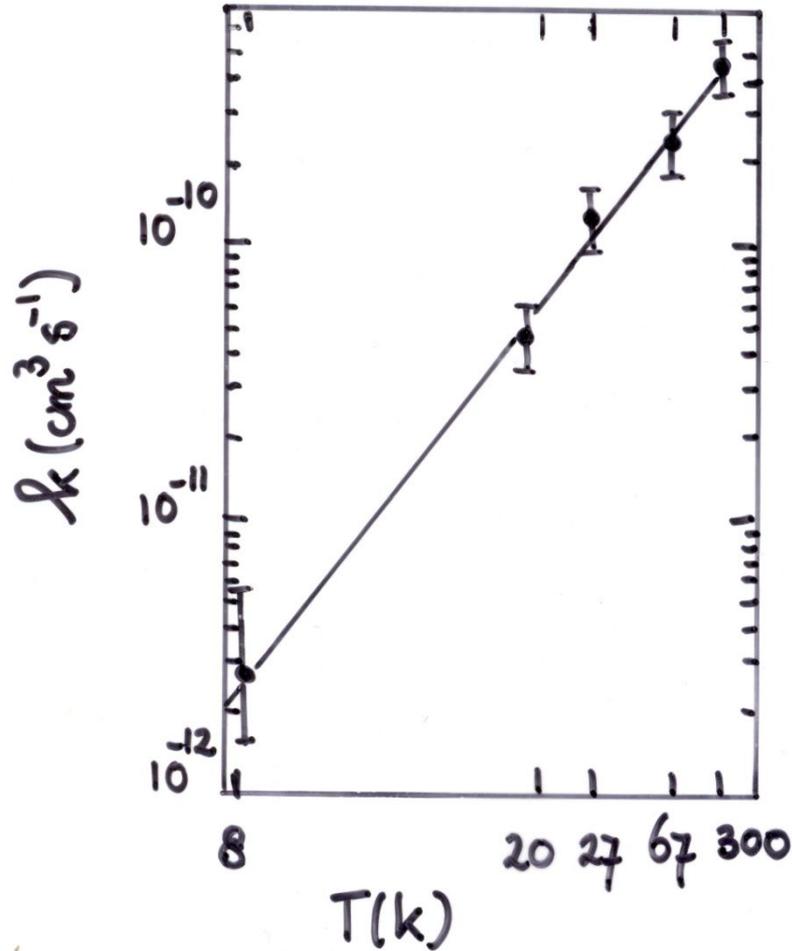


M. Smith 1993

-Rate coefficients for ion-polar reactions may be factors of 10-100 larger than Langevin values at low T , because $V(R) \propto R^{-2}$

Example: $\text{C}^+ + \text{OH} \rightarrow \text{CO}^+ + \text{H}$

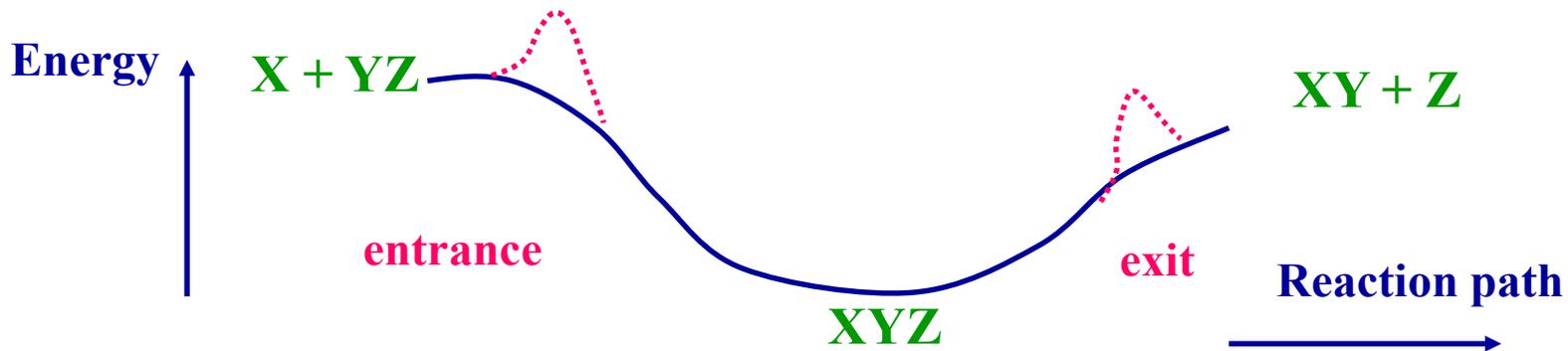
Unusual case: $\text{N}^+ + \text{H}_2$



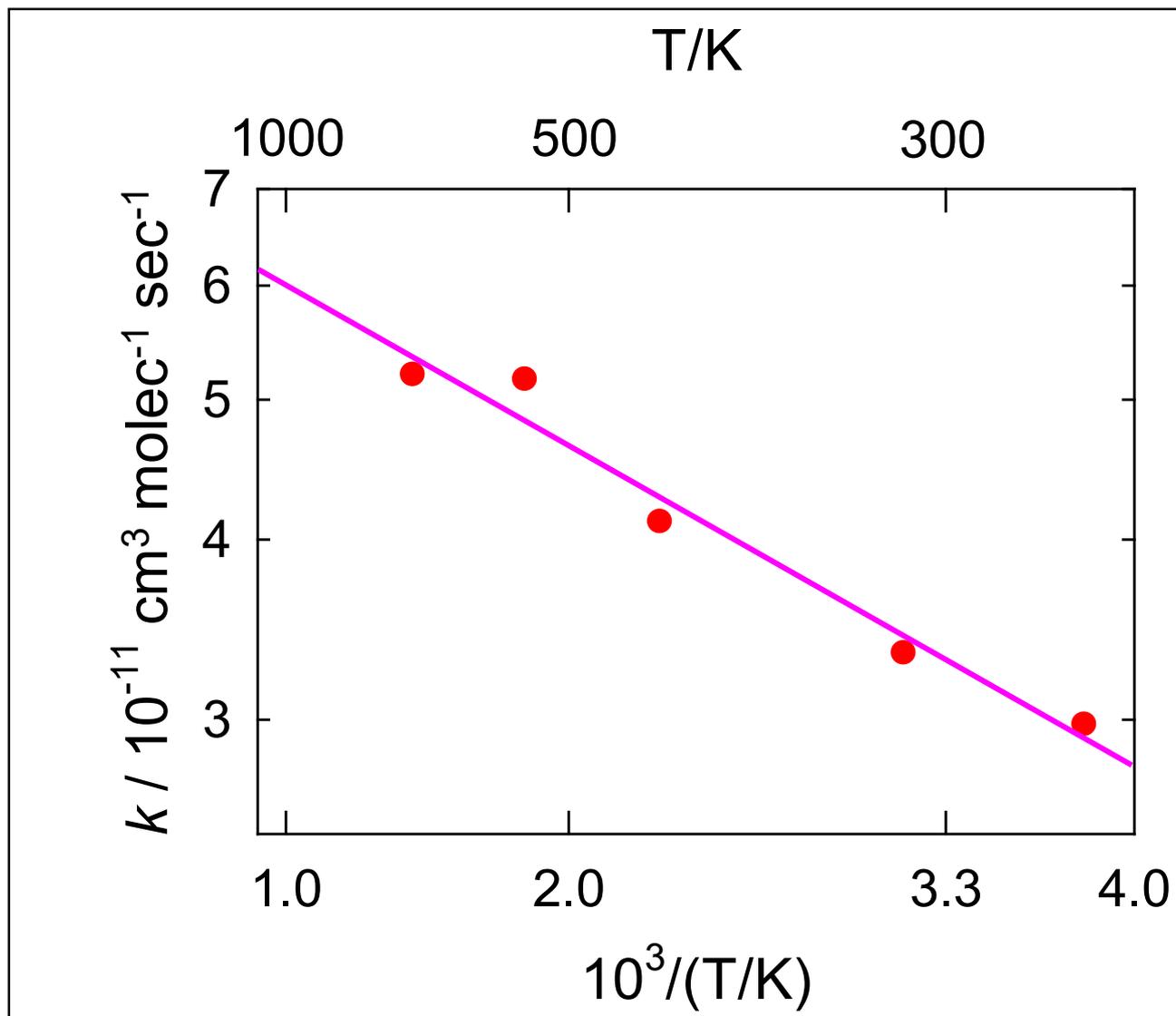
- Potentially initiates much of nitrogen chemistry: forms $\text{NH}^+ + \text{H}$
- Rate decreases rapidly at low T , however, because reaction slightly endothermic at $T < 100$ K

2.2 Neutral-neutral reactions

- Long-range attraction weak: van der Waals interaction $\sim 1/R^6$
- Potential barriers may occur in entrance and exit channels \Rightarrow reactions thought to be slow at low T
- Experiments: reactions can be fast at low T !

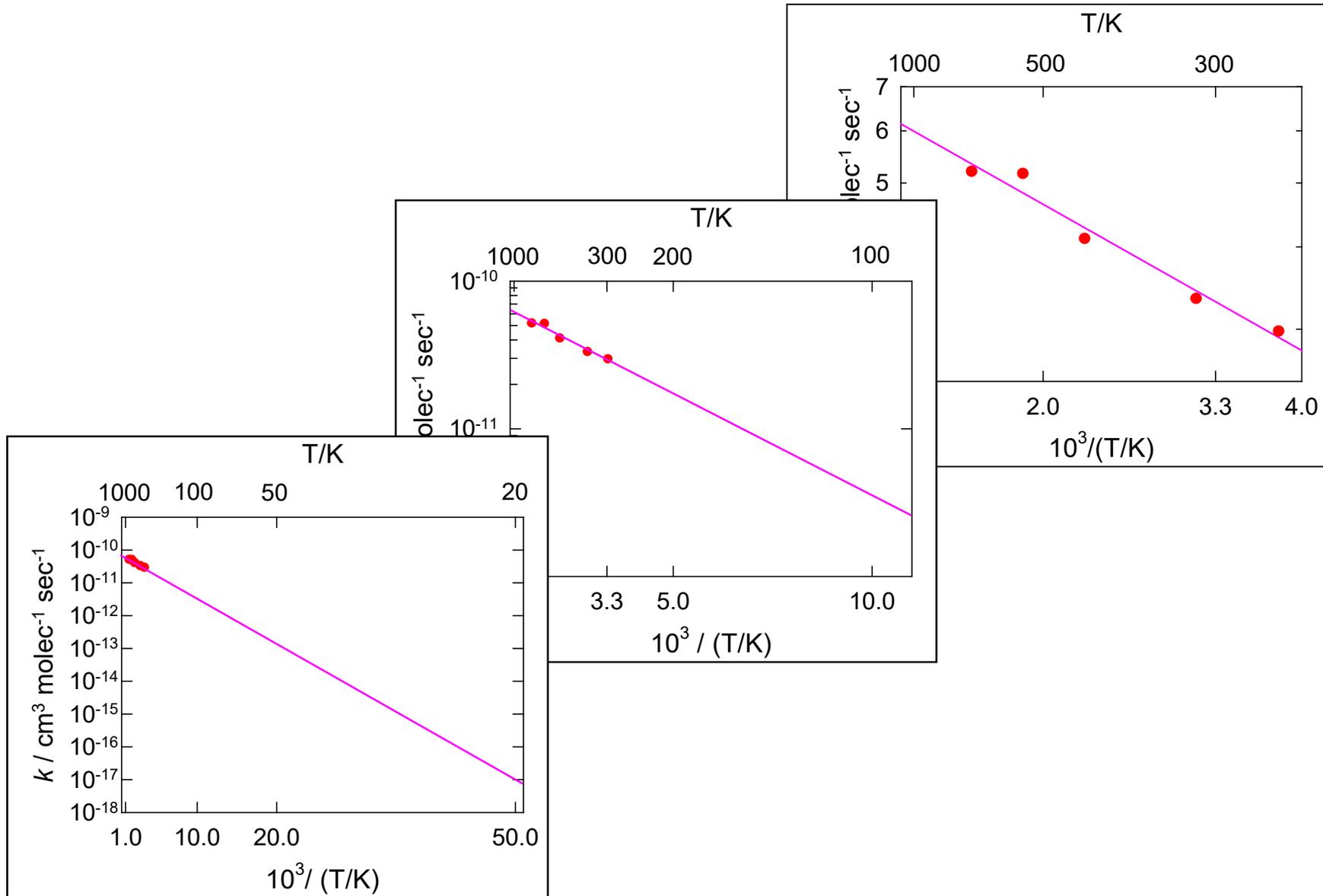


CN + C₂H₆: or why extrapolation is unreliable

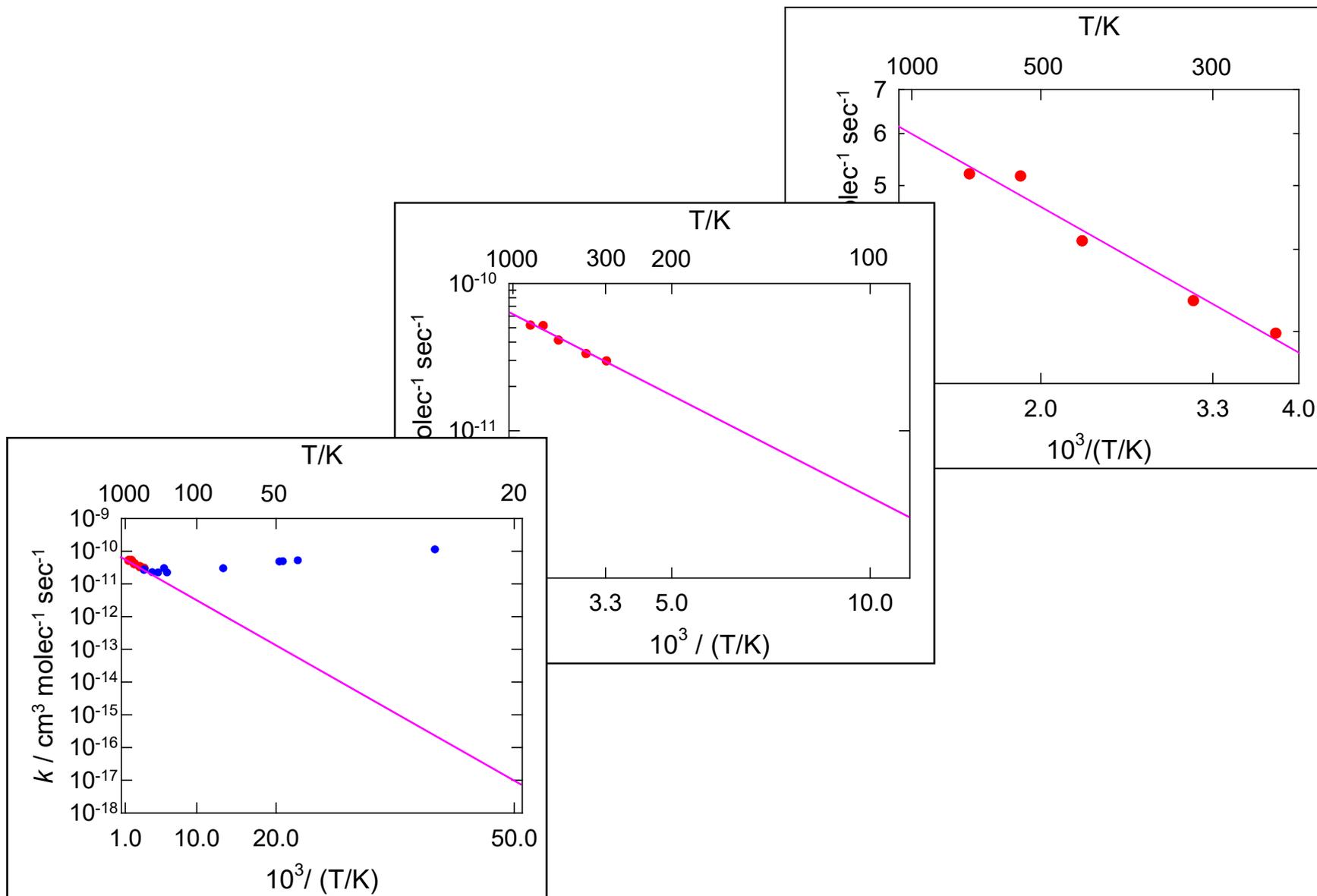


I. Sims et al. Rennes/Birmingham

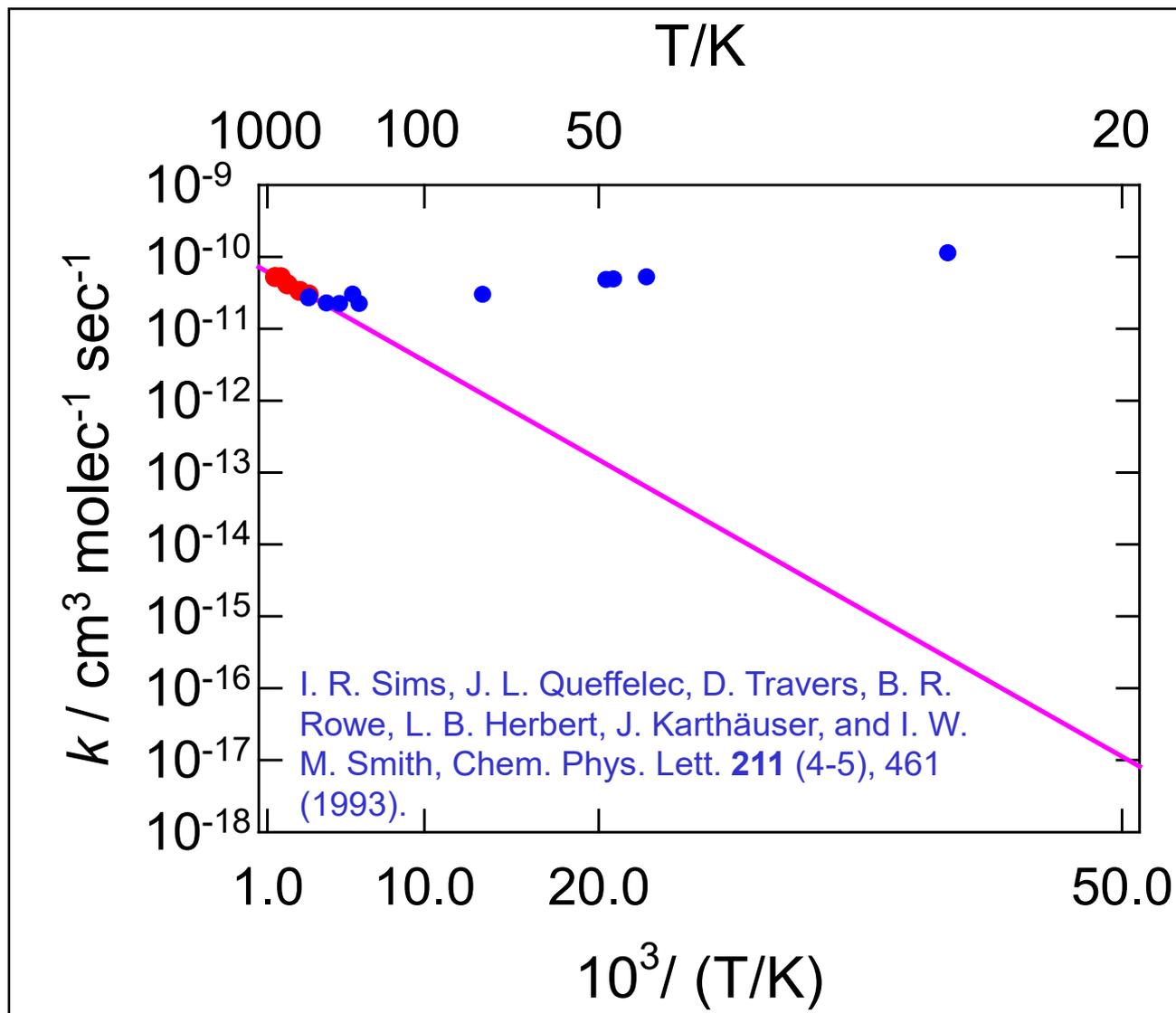
CN + C₂H₆: or why extrapolation is unreliable



CN + C₂H₆: or why extrapolation is unreliable



CN + C₂H₆: reaction stays rapid at low *T*!



CRESU technique

50-100 slm carrier gas (He, Ar or N₂) + precursor + reagent

axisymmetric Laval nozzle

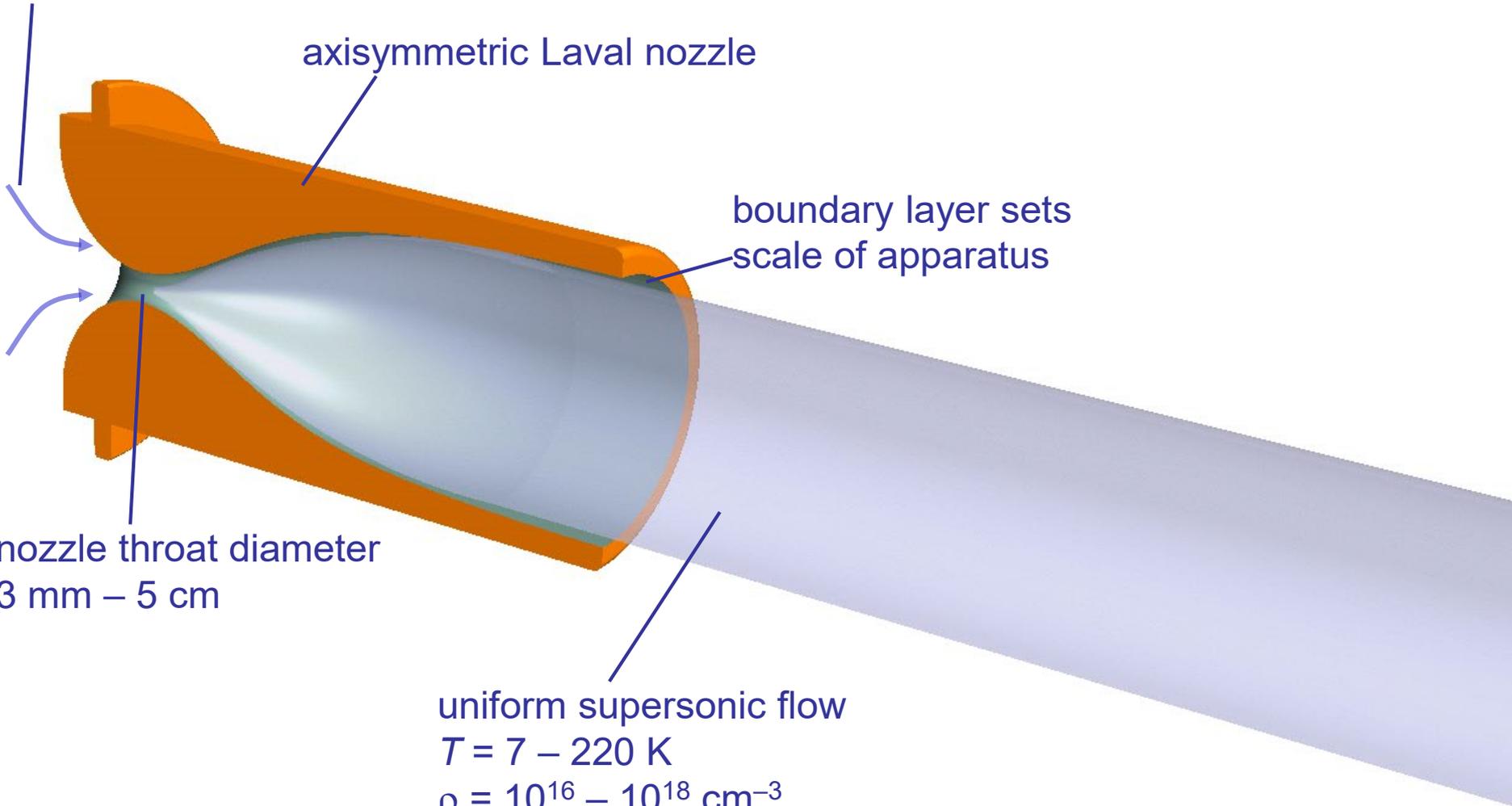
boundary layer sets scale of apparatus

nozzle throat diameter
3 mm – 5 cm

uniform supersonic flow
 $T = 7 - 220 \text{ K}$
 $\rho = 10^{16} - 10^{18} \text{ cm}^{-3}$

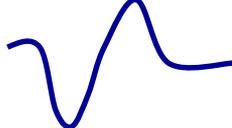
chamber pressure 0.1 – 0.25 mbar
pumping speed $\sim 30000 \text{ m}^3 \text{ hr}^{-1}$

Laval nozzle and isentropic flow



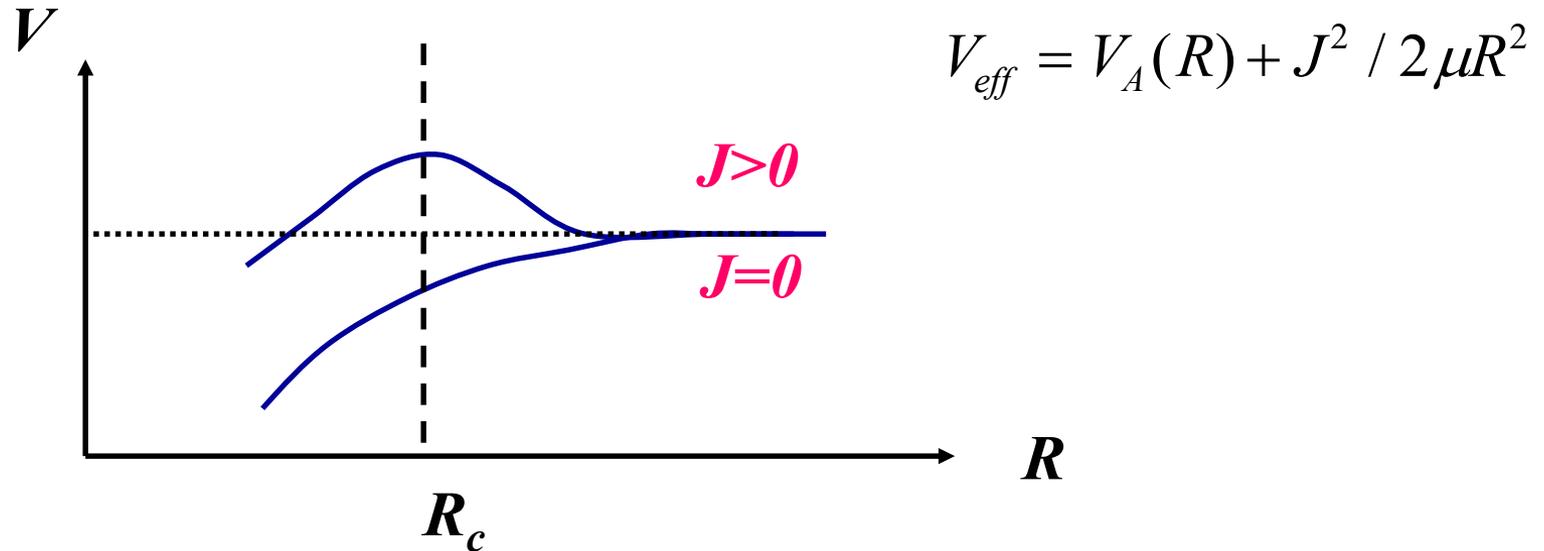


Types of neutral-neutral reactions

	E_A/k	$V(R)$
■ Molecule-molecule ■ E.g., $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$	$>10^4$ K	
■ Radical-saturated mol ■ E.g., $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	~ 2000	
■ Radical-unsaturated mol ■ E.g., $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	~ 0	
■ Radical-radical ■ E.g., $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	-100	

Rate coefficient

Blow-up entrance channel



- Determined by shape entrance potential
- Low energy collisions: R_c large

Adiabatic capture approximation

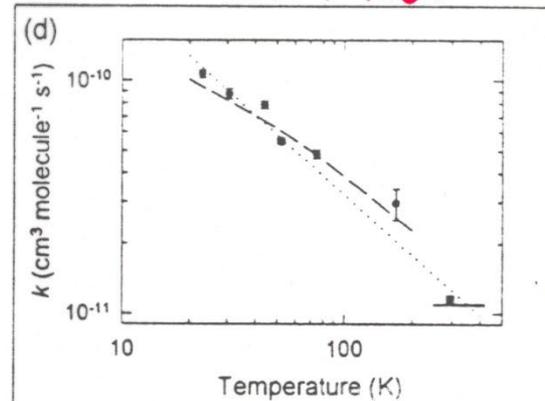
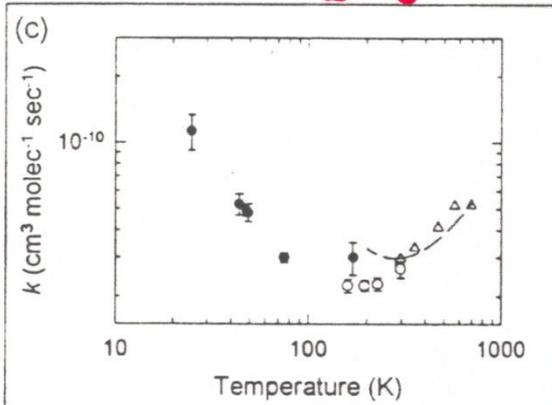
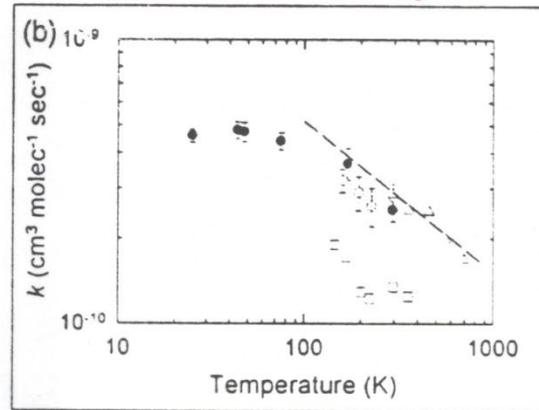
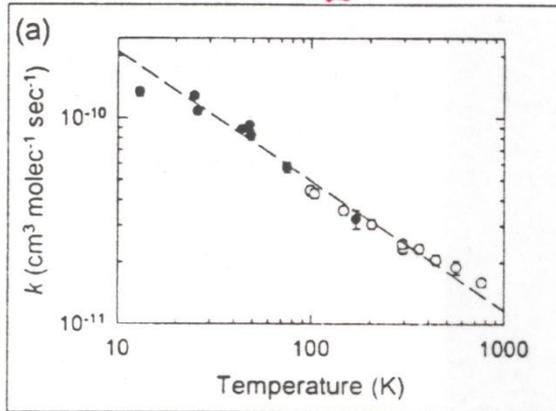
- If collision energy $< V_{\text{eff}}(R_c)$: reaction probability=0
- If collision energy $> V_{\text{eff}}(R_c)$: reaction probability=1
- This implies that one needs to know the potential surface in the entrance channel very well!
- Advantages
 - Analytical formulae for rate constants for easy use in chemical networks
- Disadvantages
 - Ignores angular dependence potential
 - Ignores short range forces
 - Ignores quantum effects (e.g., tunneling)
 - Assumes no activation energy

Adiabatic capture theory

- Rate coefficient $k(T) \propto T^{\frac{-2}{n} + \frac{1}{2}}$ as $T \rightarrow 0$
for potentials of the form R^{-n}

Interaction	Potential	Low T dep.
Charge-induced dipole	R^{-4}	T^0
Charge-dipole	R^{-2}	$T^{-1/2}$
Charge-quadrupole	R^{-3}	$T^{-1/6}$
Dipole-dipole	R^{-3}	$T^{-1/6}$
Dipole-quadrupole	R^{-4}	T^0
Dispersion	R^{-6}	$T^{1/6}$

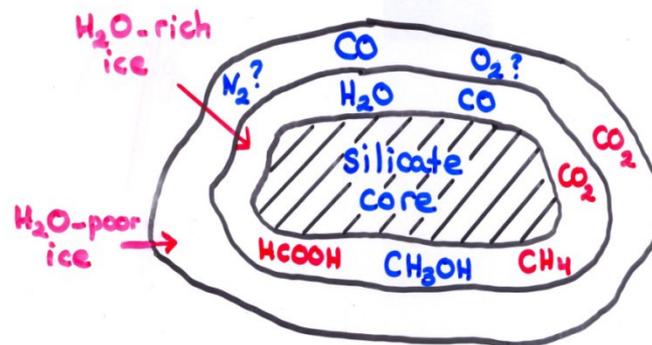
Experiments: examples



- Some reactions are faster at low T than at high T
- These neutral-neutral reactions are typically only a factor of 5 slower than ion-molecule reactions at low T => cannot be neglected in networks!

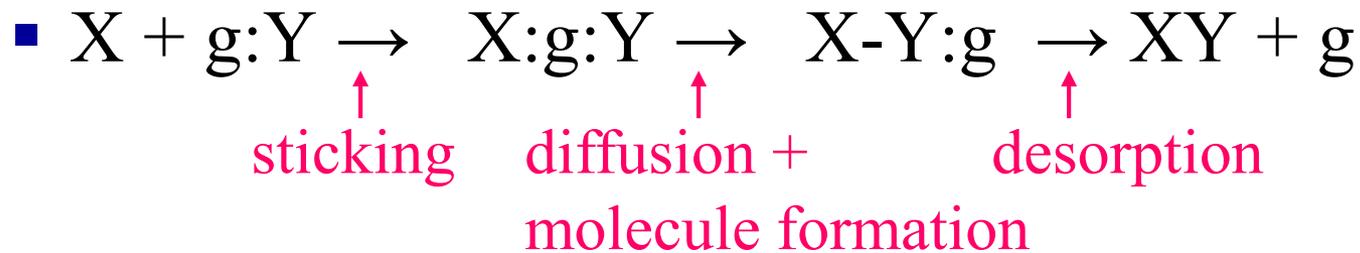
2.3 Gas-grain chemistry: H₂

- Evidence for gas-grain chemistry
 - H₂ in interstellar clouds
 - NH in diffuse clouds
 - Abundances H₂O, CO₂, CH₃OH, ... in ices higher than expected from freeze-out of gas phase

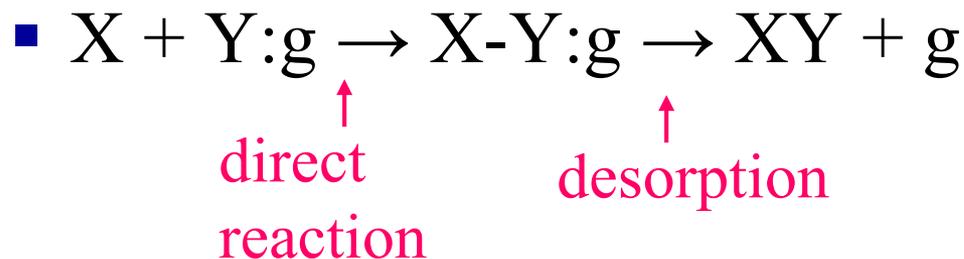


Formation mechanisms

- *Diffusive mechanism* (Langmuir-Hinshelwood)

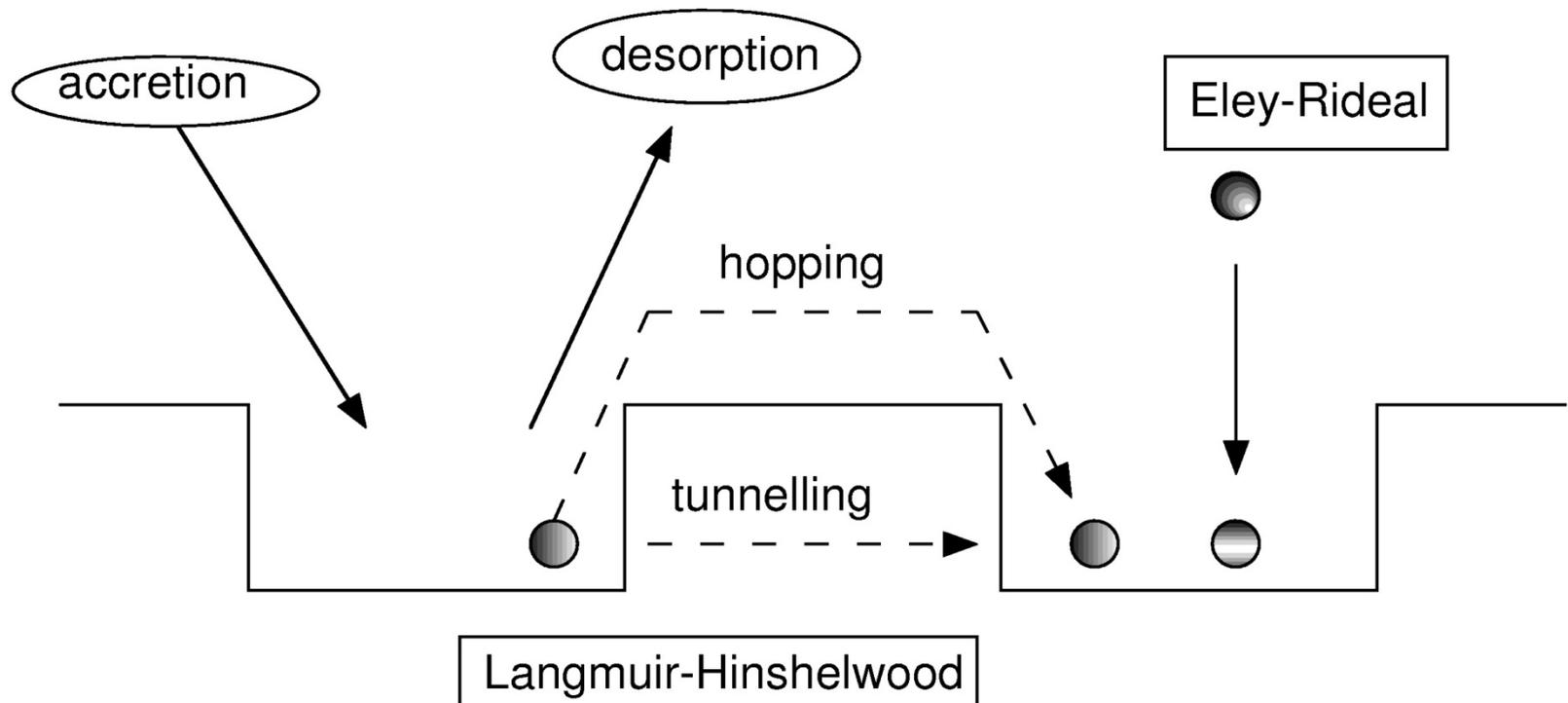


- *Direct mechanism* (Eley-Rideal)

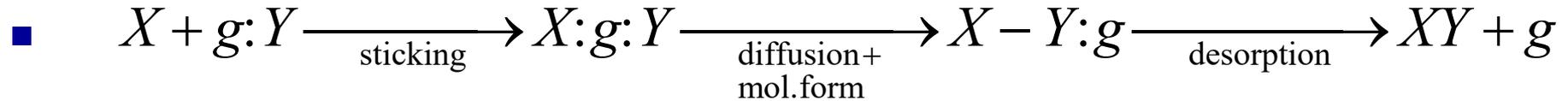


- Surface can be silicates, carbonaceous, ice, ...

Grain surface processes diffusive vs. direct



Diffusive mechanism

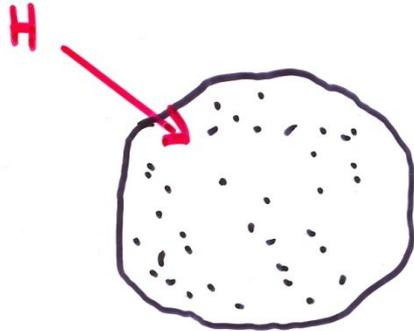


■ Process proceeds in several steps (consider case of H₂):

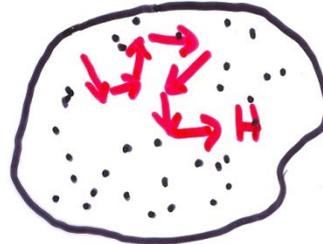
1. H atom must collide with grain: $H + g$
2. Colliding atom must stick to surface: $H + g \rightarrow H : g$
3. H atom must be retained until another atom gets absorbed:
 $H : g \rightarrow H : g : H$
4. H atoms must be mobile to find each other and form bond:
 $H : g : H \rightarrow H - H : g$
5. H₂ must be ejected from surface: $H - H : g \rightarrow H_2 + g$

Probabilities of 2, 3+4 and 5 are η_s, η_r, η_d

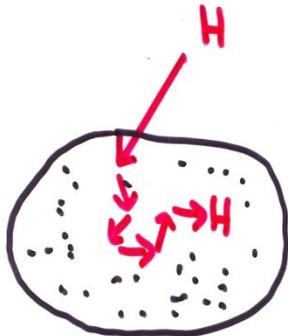
H₂ formation on grains



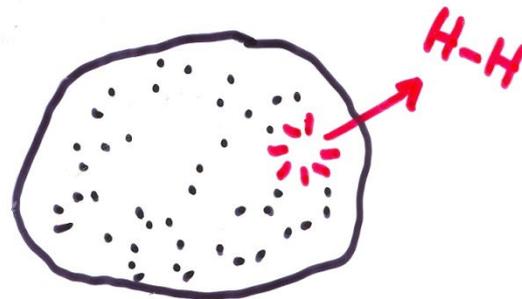
1. H collides with grain



2. H explores grain until either
| (encounter with another H)
| immobilized at enhanced binding site



3+4. second H atom collides with grain; explores surface and encounters first H atom



5. H₂ formation on surface
H₂ ejected from surface

1. Collision rate with grain

- Collision rate: $r_C = \pi a^2 v_H n_g n(\text{H})$

where πa^2 = geometrical cross section

$$v_H = 10^4 T^{1/2} \text{ cm s}^{-1} \sim 10^5 \text{ at } 100 \text{ K}$$

n_g = number density of grains

- Observations of extinction: $\pi a^2 n_g \approx 3 \times 10^{-22} n_H$

$$\Rightarrow r_C \approx 3 \times 10^{-17} n_H n(\text{H})$$

- Compare with required H_2 formation rate (from obs, Lecture 4)

$$R_f = 3 \times 10^{-17} n_H n(\text{H}) \eta_S \eta_r \eta_d$$

\Rightarrow all probabilities must be nearly unity

2. Adsorption time

- Classical expression: $t_a = \frac{1}{\nu} \exp(E_d / kT)$
 - With E_d =binding energy (also called E_{bind})
 $\nu = E_d / k \sim 10^{12} \text{ s}^{-1}$
 - Physical adsorption: $E_d \sim 400 \text{ K} \Rightarrow$
 - $t_a = 3 \times 10^5 \text{ s}$ at $T = 10 \text{ K}$
 - $t_a = 2 \times 10^{-8} \text{ s}$ at $T = 40 \text{ K}$
 - Chemisorption: $E_d \sim 20000 \text{ K} \Rightarrow$
 - $t_a = \infty$ at 100 K
- \Rightarrow H atoms will evaporate above 20 K before forming H_2 , unless the grain has strong binding sites

3. Arrival of second H atom

- Consider t_a of first H atom with time t_C for collision of second H atom with grain

$$t_C = \frac{1}{r_C n(\text{H})} = 3 \times 10^4 \text{ s for } n(\text{H}) = 1$$
$$= 3 \times 10^2 \text{ s for } n(\text{H}) = 100 \text{ cm}^{-3}$$

$\Rightarrow t_C < t_a$ if $T < 15 \text{ K}$ for physical absorption

- At higher temperatures, need chemisorption to retain first H

4. Surface hopping

- In diffuse clouds: $T > 15$ K, $T_d > 15$ K
=> need chemisorption to retain H
- Assume second H atom is physically adsorbed
- Hopping time second H atom: $t_h \sim 10^{-9}$ s
- For random 2D walk:
where r = distance between sites ~ 1.5 Å
=> $t_M < t_a$ for $T < 20$ K with
$$t_M = \frac{\pi(a/2)^2}{r^2} t_h \approx 10^{-3} \text{ s}$$
- Second H atom can find first H atom before evaporation

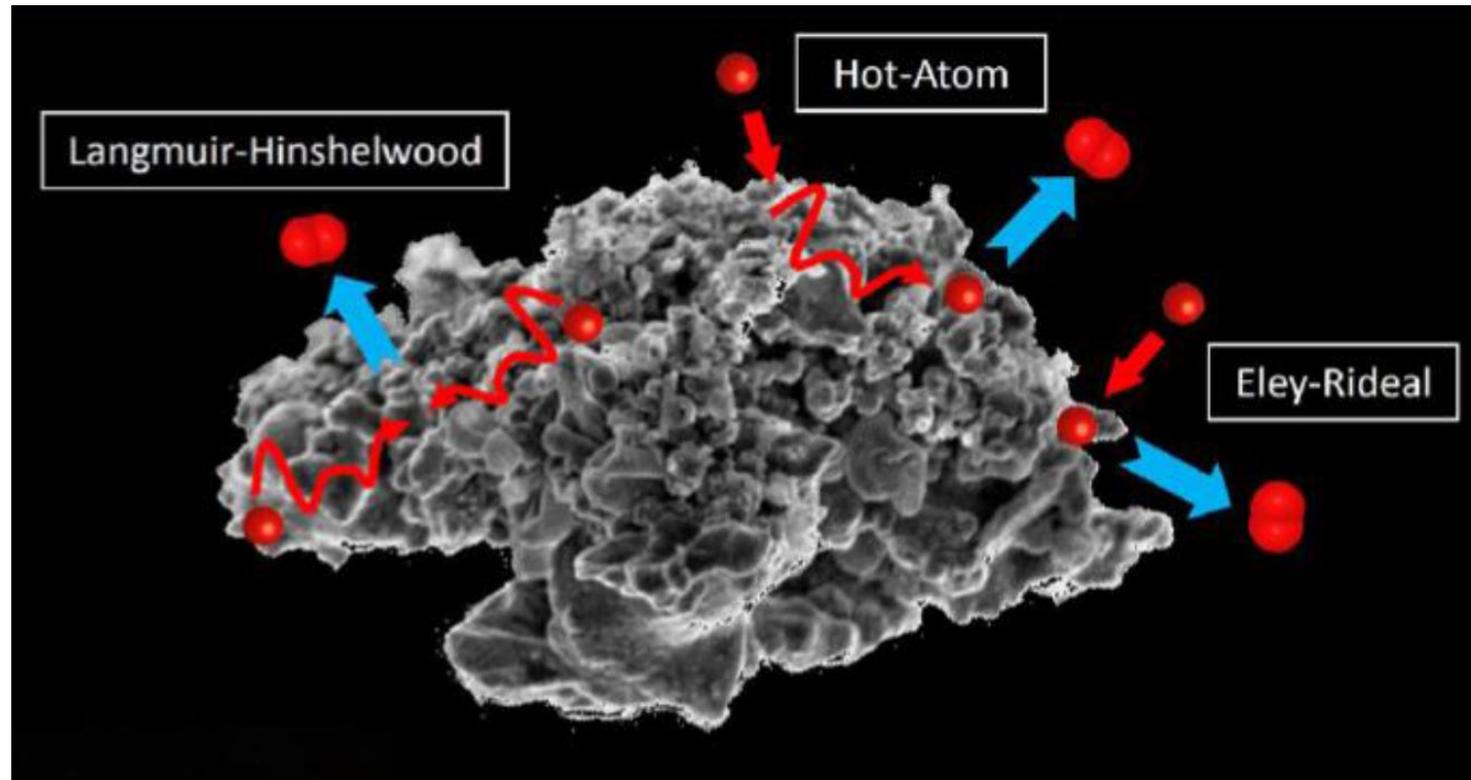
5. Ejection

- Since there are no strong H₂-grain bonds, H₂ is now physically adsorbed and will be rapidly ejected
- From 1-5 it is plausible that $\eta_s \eta_r \eta_d \approx 1$, provided the dust temperature is not too high or strong bonding sites

Eley-Rideal mechanism

- $$X + Y:g \xrightarrow{\text{direct reaction}} X - Y:g \xrightarrow{\text{desorption}} XY + g$$
- If there are enough chemisorption sites so that grain is saturated with H atoms, formation rate of H₂ is controlled by rate of arrival of H atoms at surface
- It is assumed that H₂ is formed at every encounter, and rapidly ejected back into gas phase
- This process is important especially at higher T

Grain surface processes



Linnartz et al. 2015

H₂ formation

- Flurry of experiments and theory
- Experiments provide constraints on mobility of adsorbed H and on binding and diffusion energies on various materials: silicates, carbonaceous material (graphite), ices
- Modeling of experimental data somewhat controversial
 - Roughness/irregularity of surface and temperature fluctuations play a role as well
 - Hot atom reactions considered as well

2.4 Gas-grain chemistry: other species

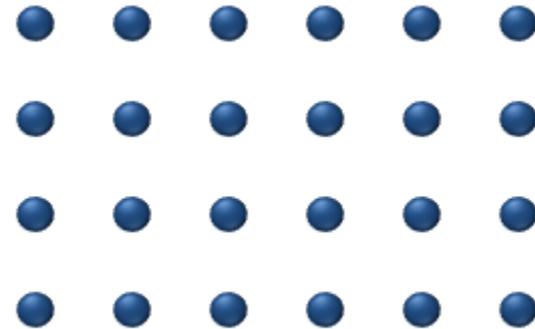
- Usually only diffusive mechanisms considered
- Typical ‘day in the life’ on the surface of a grain in a dense cloud
 - A few molecules or atoms land on the icy surface
 - All species except He, H₂ stick with $\eta_s=1$
 - If sufficiently light, the particle can migrate over the surface by tunneling or thermal hopping
 - Migrating species: H, O, C, N
 - Perhaps: CH, NH, OH, NH₂, CH₂, CH₃
 - Reactions may occur if activation barriers sufficiently low

Surface diffusion

- Site to site hop

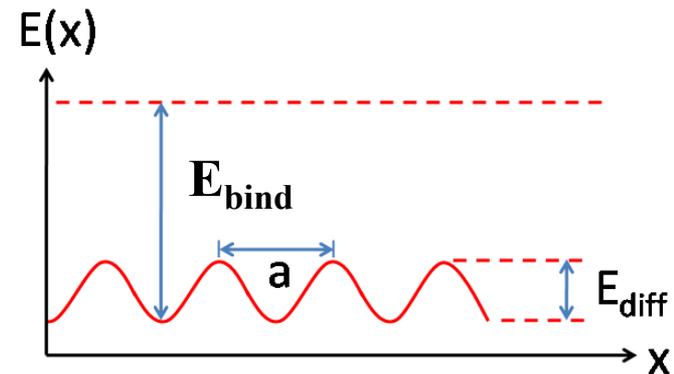
$$K_{\text{hop}} = v \exp(-E_{\text{hop}}/kT_s)$$

- Usually $E_{\text{hop}} = c^{\text{st}} E_{\text{bind}}$
 - c^{st} varies from 0.3-0.7



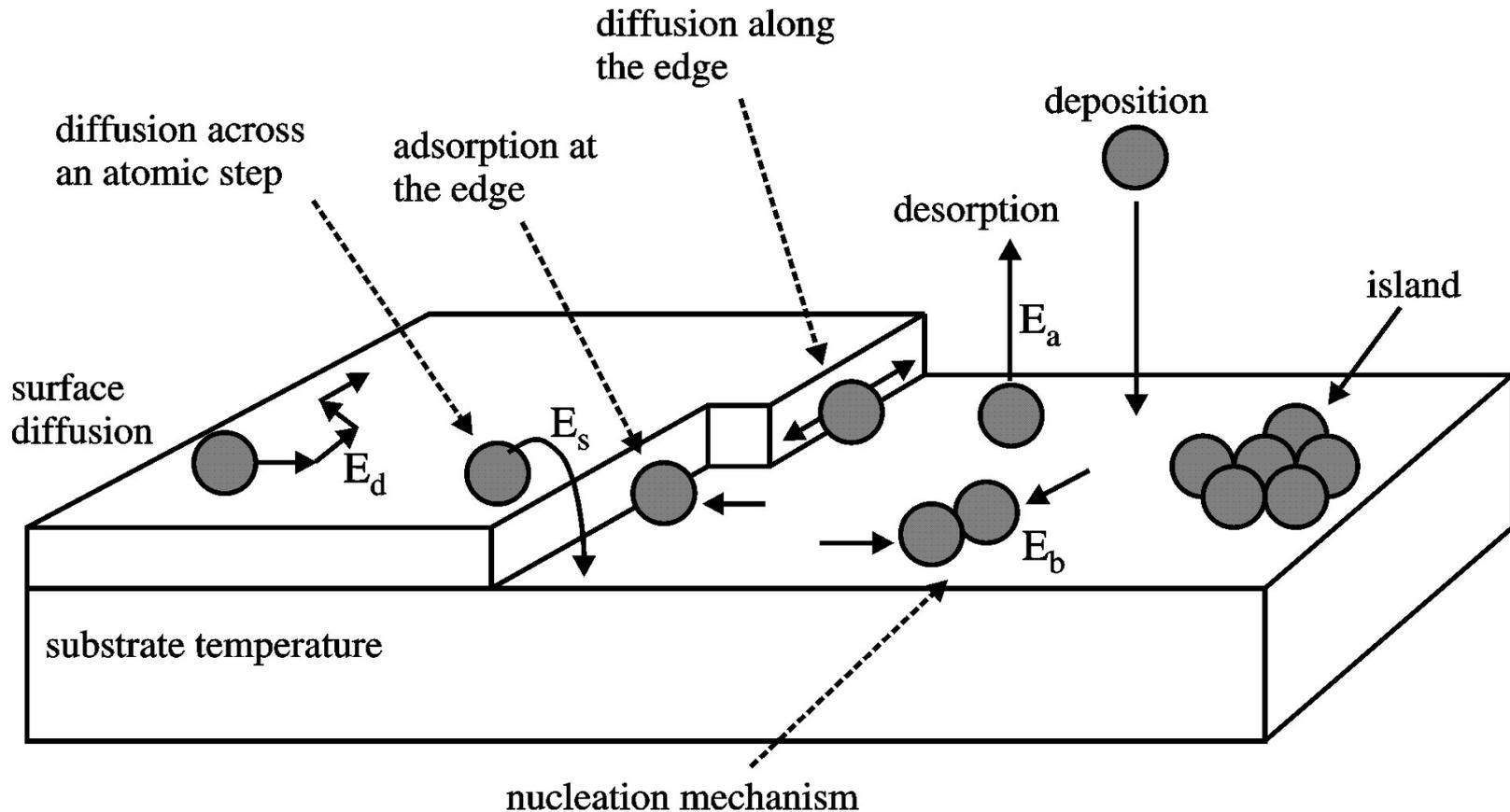
Wikipedia.org

- Diffusion barriers will change from site to site
- Importance of tunneling
- Competition with reaction



Note critical role of surface temperature!

Irregular surfaces



e.g., Cuppen & Herbst 2007

Uni-kl.de

Q: What is a proper formulation in such complex cases?

Relevant time scales

- See Sect. 2.3 for formulae adsorption (=residence) and migration (=thermal hopping) times
- Tunneling only important for H, H₂
- Limiting activation barriers of reactions at $T_d=10$ K
 - H ≤ 3500 K
 - H₂ ≤ 4500 K
 - O,C,N ≤ 450 K

Types of surface reactions

1. **Atom-atom reactions**, e.g.,



2. **Radical- atom reactions**, e.g.,



3. **Radical-radical reactions**, e.g.,



4. **Radical-H₂ reactions**, e.g.,



5. **Molecule – atom reactions**, e.g.,



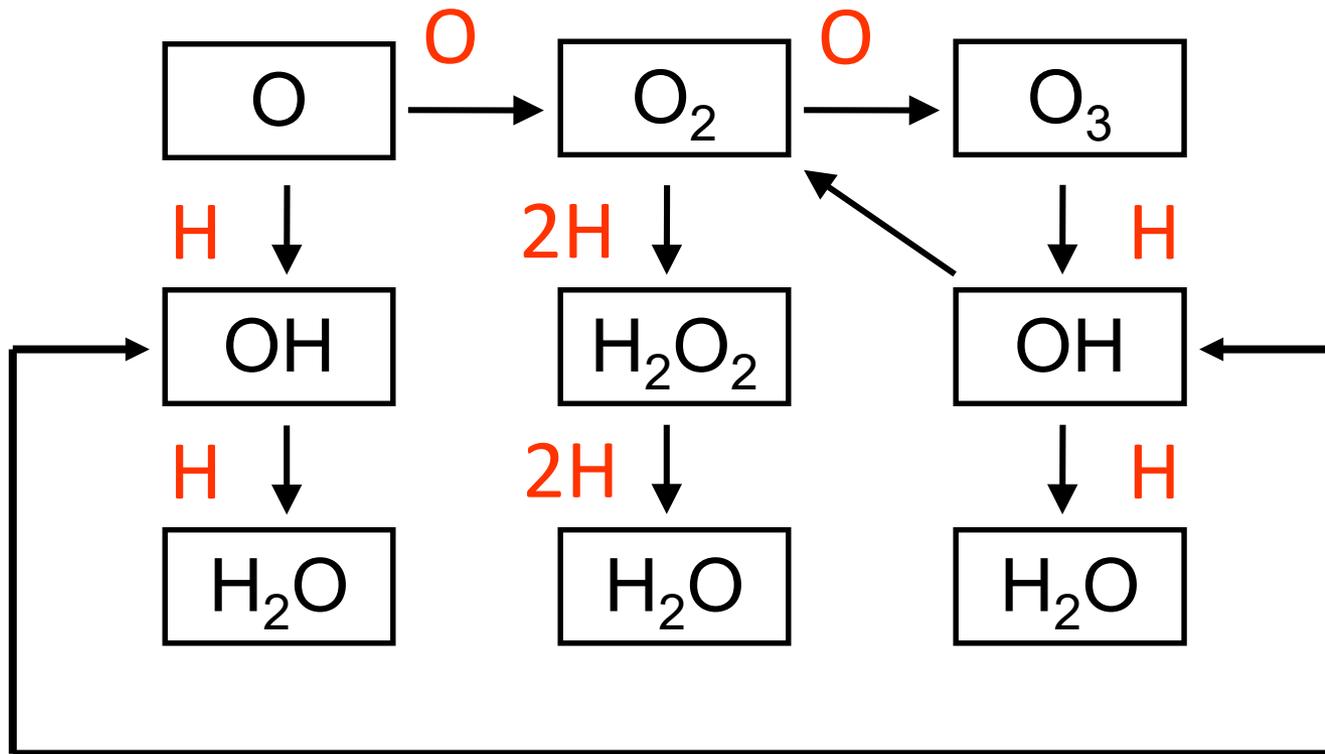
6. **Hydrogen abstraction reactions**, e.g.,



Type 1,2,3: No activation barrier (typically)

Type 4,5,6: Activation barrier (typically)

Example: formation routes to water ice



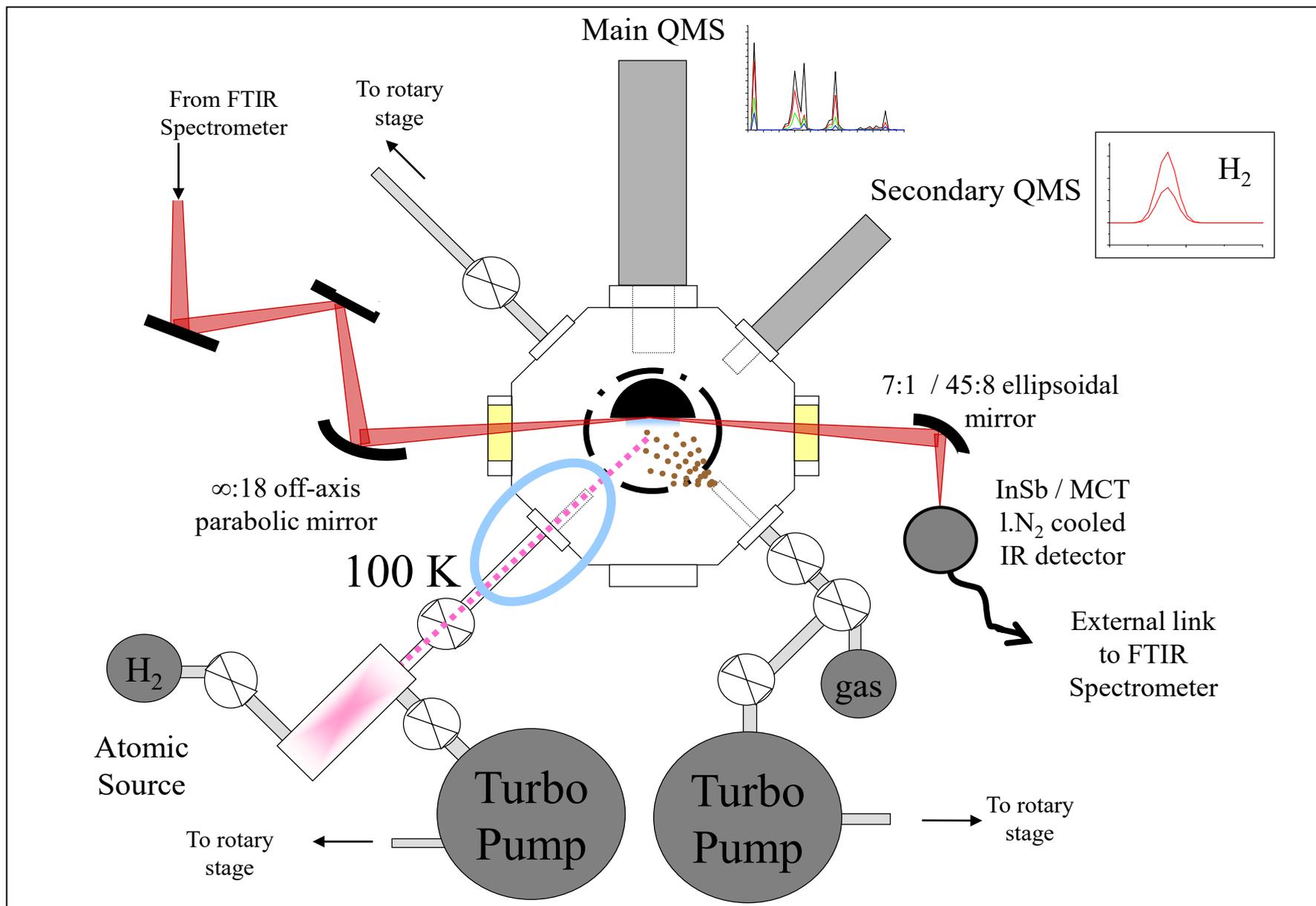
Tielens & Hagen 1982

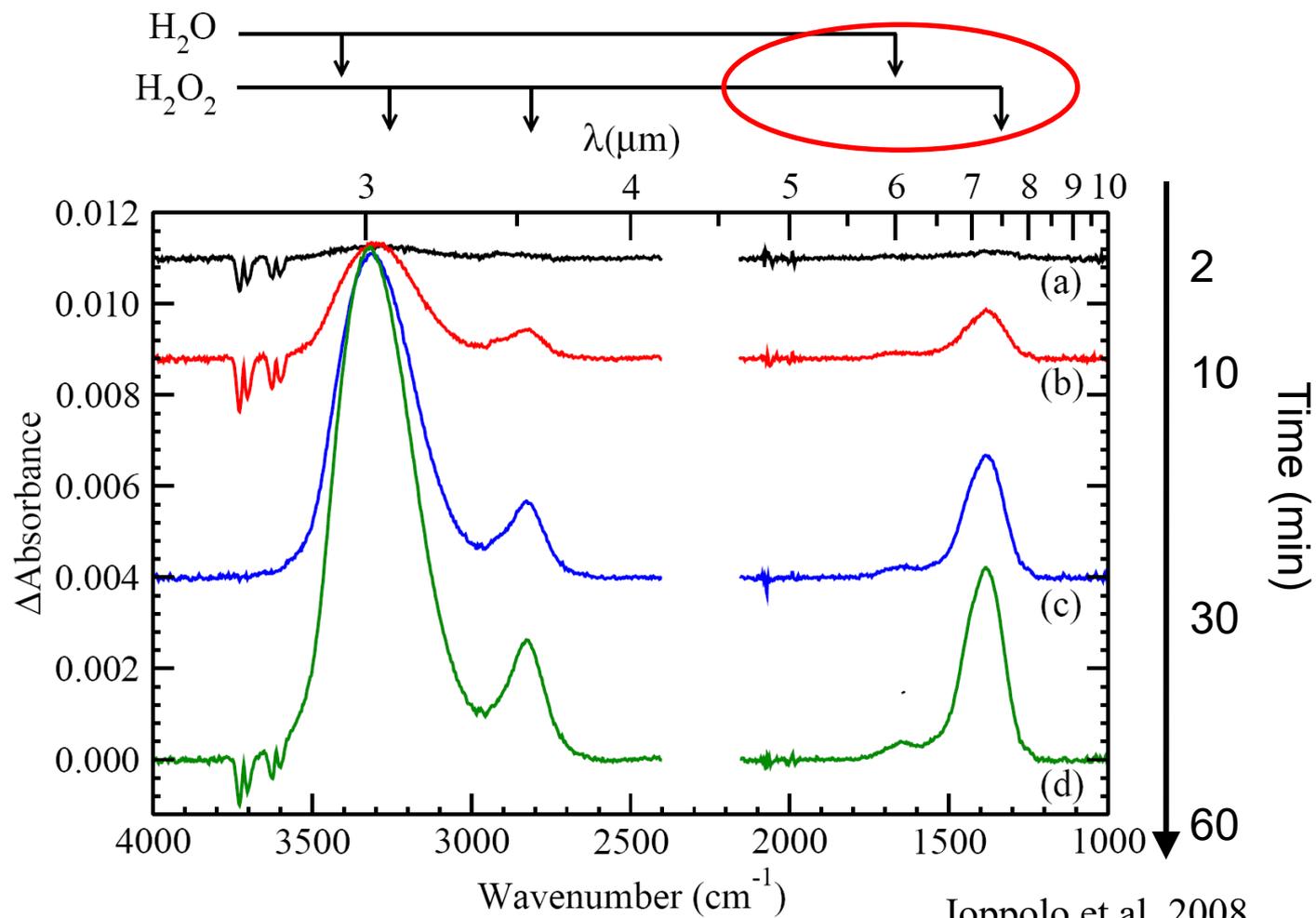
These reactions have now finally been tested in the laboratory 2008-2011

See Cuppen et al. 2010, Lamberts et al. 2013 and below for updated scheme

Experimental simulation

- Condensation of ice (CO, O₂, N₂, ...) in UHV chamber
- Bombardment by cooled atomic beam (H,O) produced in microwave or DC discharge
- Analysis of products by Reflection Absorption InfraRed Spectroscopy (RAIRS) and Mass Spectrometry
- Few groups around the world capable of these experiments, including Leiden laboratory for Astrophysics





Ioppolo et al. 2008

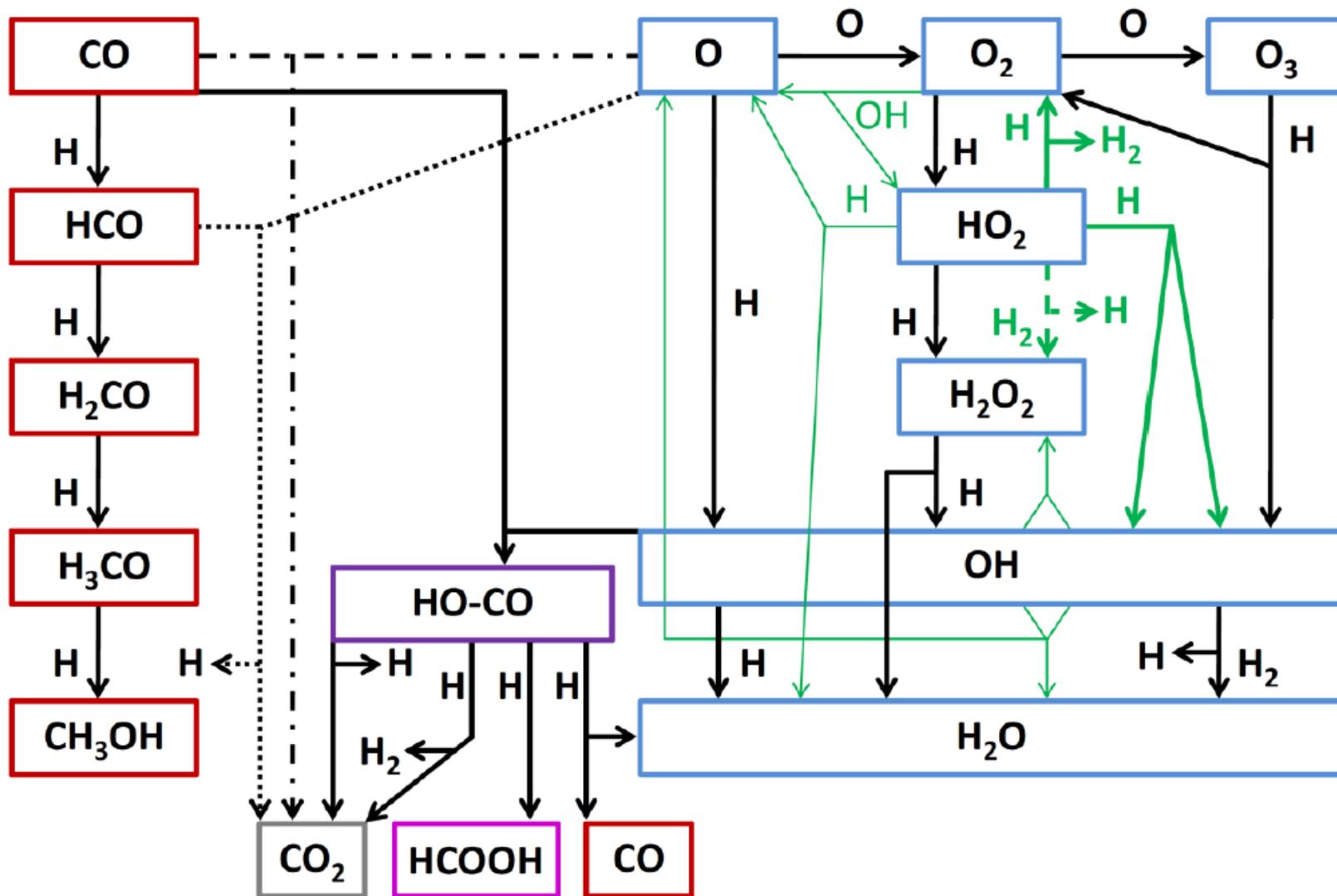
Both H_2O_2 and H_2O indeed formed at low T ! Now observed with APEX

Formation of water on grains



Based on
Cuppen et al. 2010

Starts in clouds with $A_V > 3$ mag



2.5 Photochemistry in ices

- Ices in dark clouds can be irradiated by UV due to
 - Penetration interstellar radiation: up to $A_V=5$ mag
 - Cosmic ray photons
 - Internal sources (young stellar objects)
=> ~ 10 UV photons per molecule in 10^5 yr
- Many experiments in laboratories on different ice mixtures
=> rapid formation of CO_2 , H_2CO , ... in $\text{H}_2\text{O}:\text{CO}$ irradiated ices
 - Experiments with UV and high-energy particle bombardment => large data base
- Interstellar applications need to take competition with reactions with H into account
- Reaction can occur both *on* and *inside* ices
- Observational evidence for UV photolysis of ices controversial

