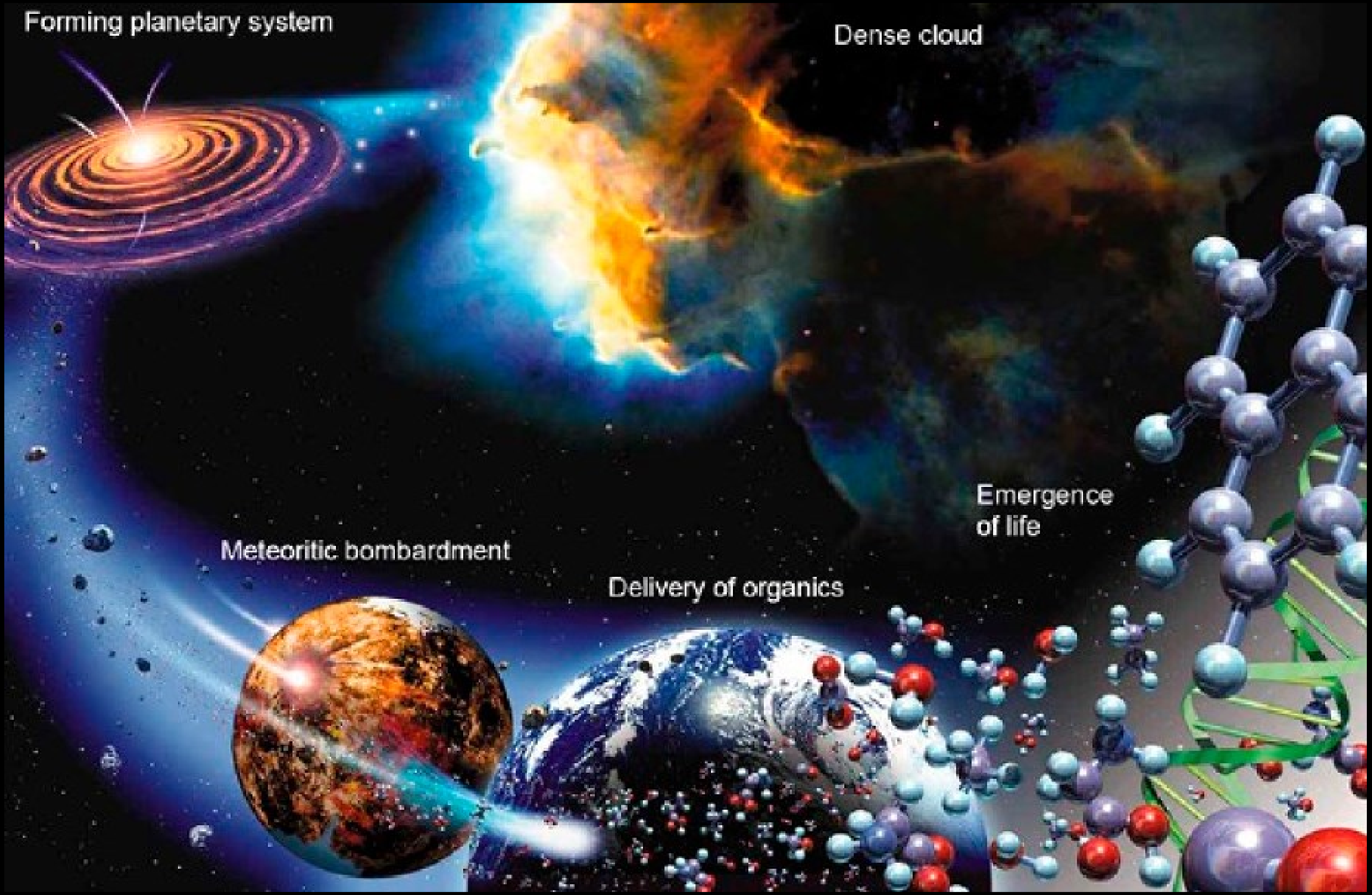
Master course: Astrochemistry I:

Lecture 2: Basic processes (continued)

Reading list:

Tielens chapt. 4.1, 4.2
Water review:
van Dishoeck *et al.* (2013) Chemical Reviews
Section 3

van Dishoeck (1988) Review from Rates in Astrochemistry book

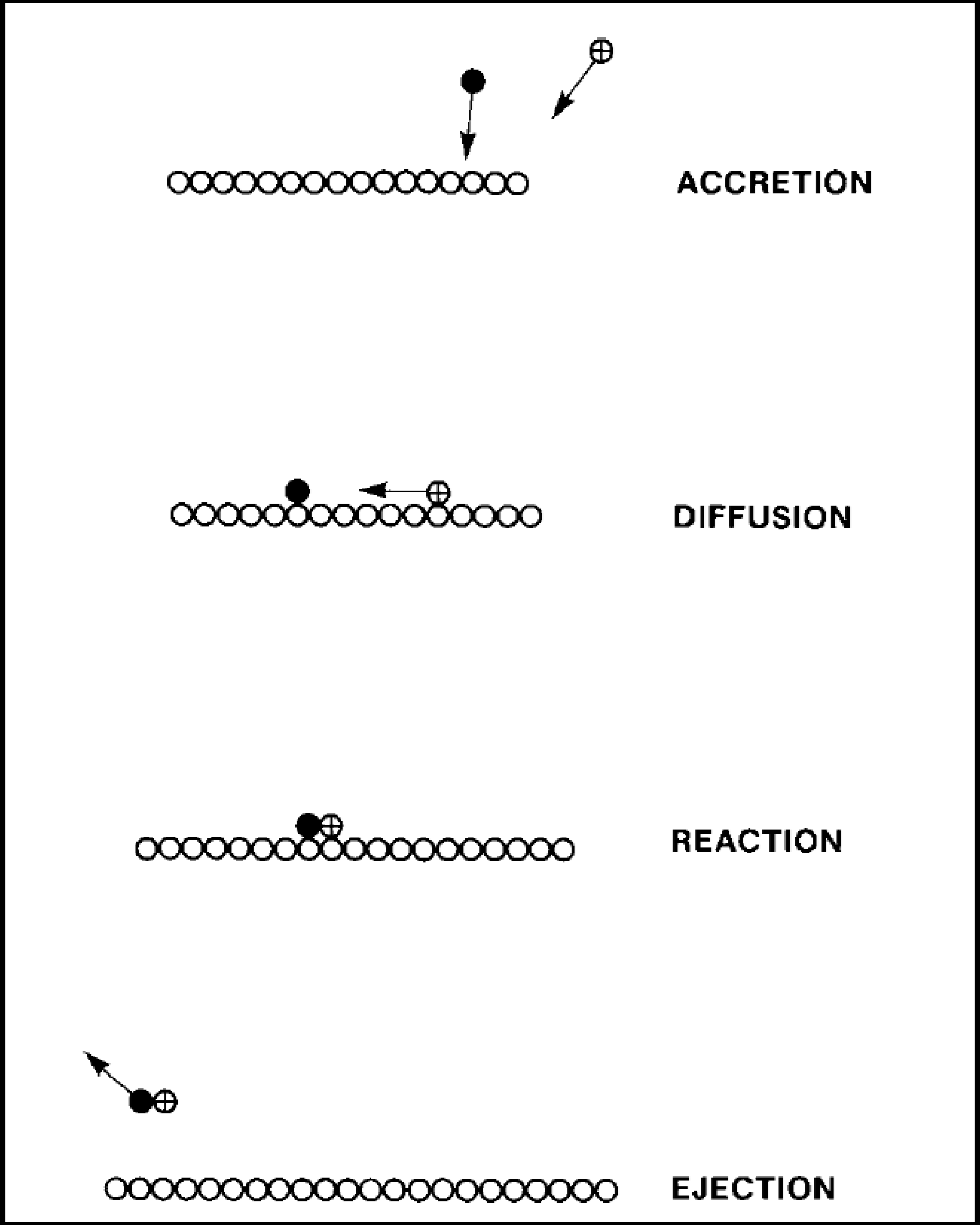


Dr. Helgi Rafn Hrodmarsson – UPEC – 2026-2027

Types of chemical reactions

- Formation of bonds
  - Radiative association: $X^+ + Y \rightarrow XY^+ + h\nu$
  - Associative detachment: $X^- + Y \rightarrow XY + e^-$
  - **Grain surface:** $\mathbf{X + Y{:}g \rightarrow XY + g}$
- Destruction of bonds
  - Photodissociation: $XY + h\nu \rightarrow X + Y$
  - Dissociative recombination: $XY^+ + e^- \rightarrow X + Y$
  - Collisional dissociation: $XY + M \rightarrow X + Y + M$
- Rearrangement of bonds
  - **Ion-molecule reactions:** $\mathbf{X^+ + YZ \rightarrow XY^+ + Z}$
  - **Charge-transfer reactions:** $\mathbf{X^+ + YZ \rightarrow X + YZ^+}$
  - **Neutral-neutral reactions:** $\mathbf{X + YZ \rightarrow XY + Z}$

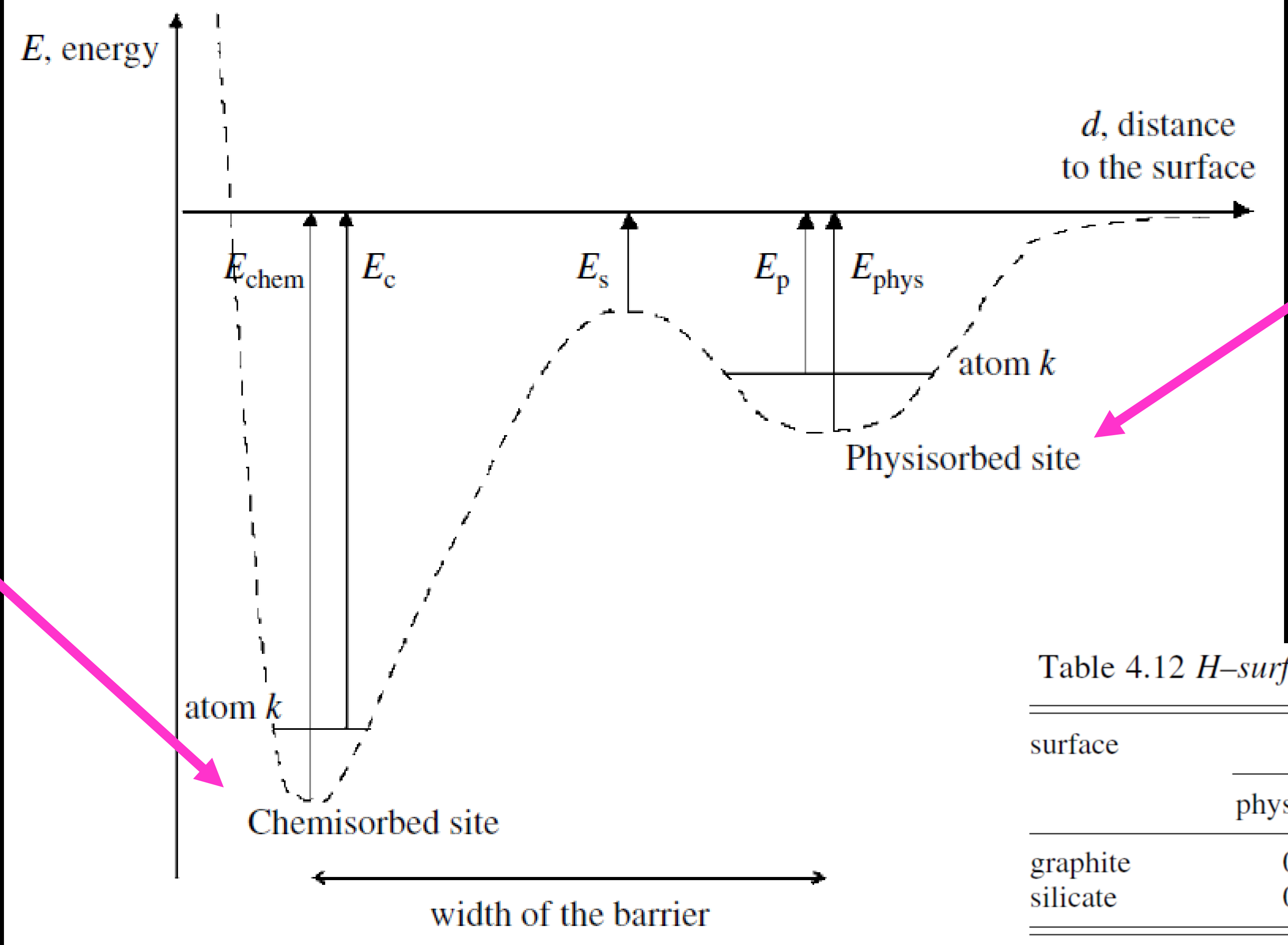
Few technical terms



Also ‘migration’ or ‘surface migration’

Tielens chapt. 4.2

Physisorption & chemisorption



van der Waals complex

Chemical bond with surface

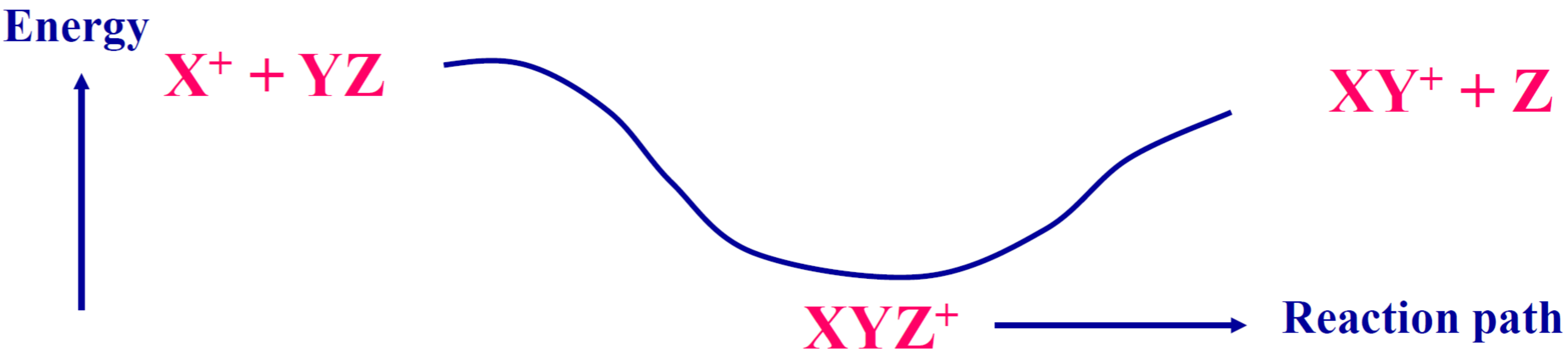
Table 4.12 *H–surface interaction energies*

surface	Energy(eV)	
	physisorbed	chemisorbed
graphite	0.06	∼ 2.5
silicate	0.05	∼ 2.5

Tielens chapt. 4.2

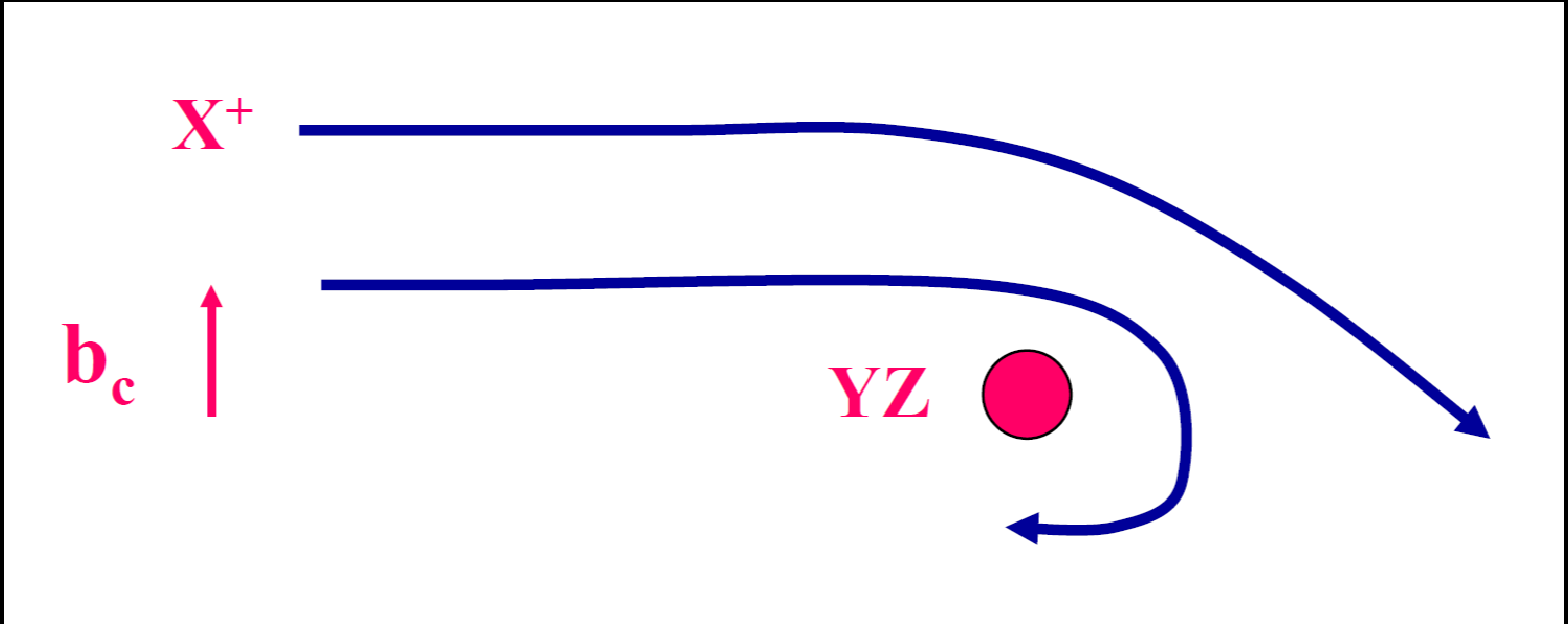
2.1 Ion-molecule reactions

- 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 small enough that X^+ is 'captured', i.e., spends enough time near YZ for reaction to take place.



Langevin rate

- Interaction potential (induced dipole + centrifugal barrier):

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

Centrifugal barrier

α = polarizability
b = impact parameter
v = velocity
μ = reduced mass

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

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

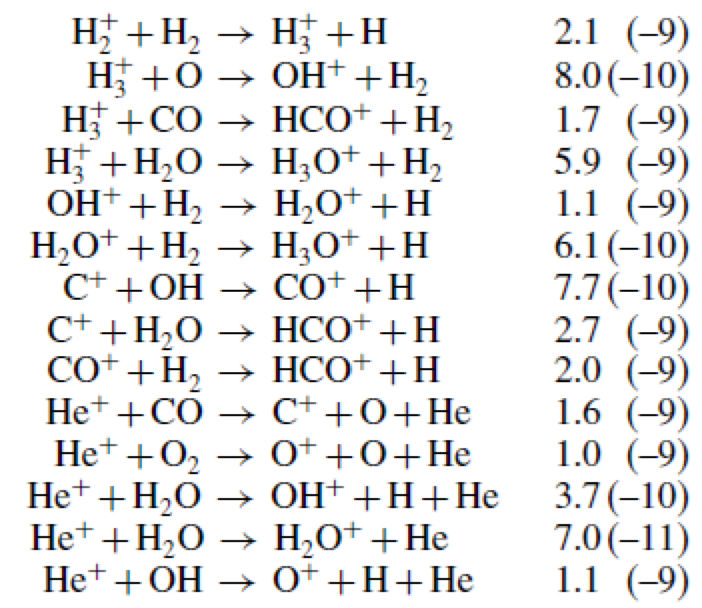
- Rate coefficient is ***<u>independent of T:</u>***

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

Langevin rate

Polarizability - note

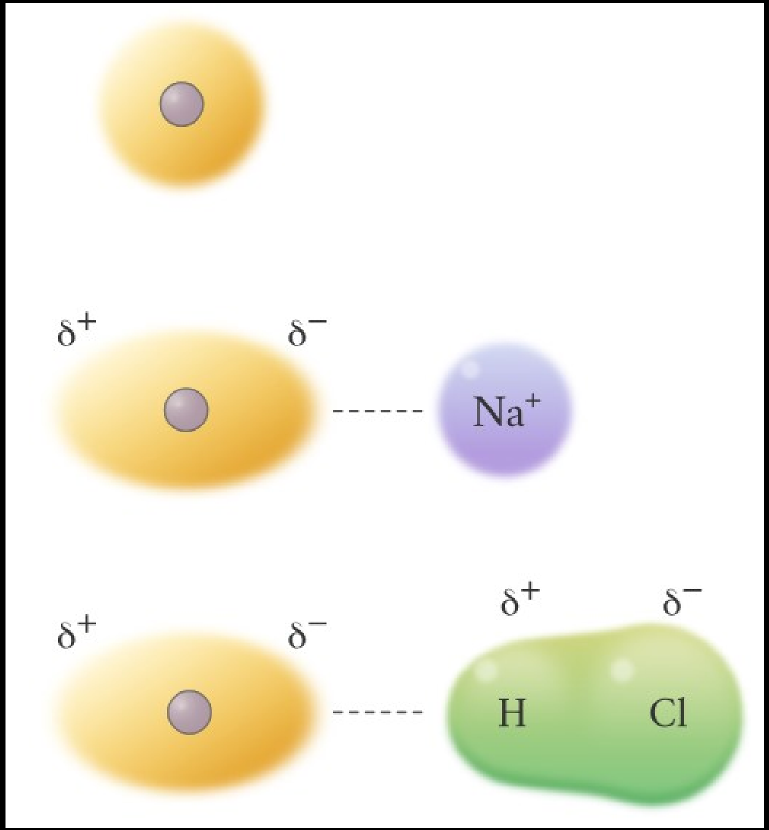
- Polarizability (α): Tendency of molecules to generate induced electric dipole moments when subjected to an electric field.
- Larger molecules = larger electron clouds = more “squishy”
- Typical values, $\alpha \approx 10^{-24}$ cm^3



$H_2^+ + H_2 \rightarrow H_3^+ + H$	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)

Langevin rates

100x faster than neutral-neutral reactions

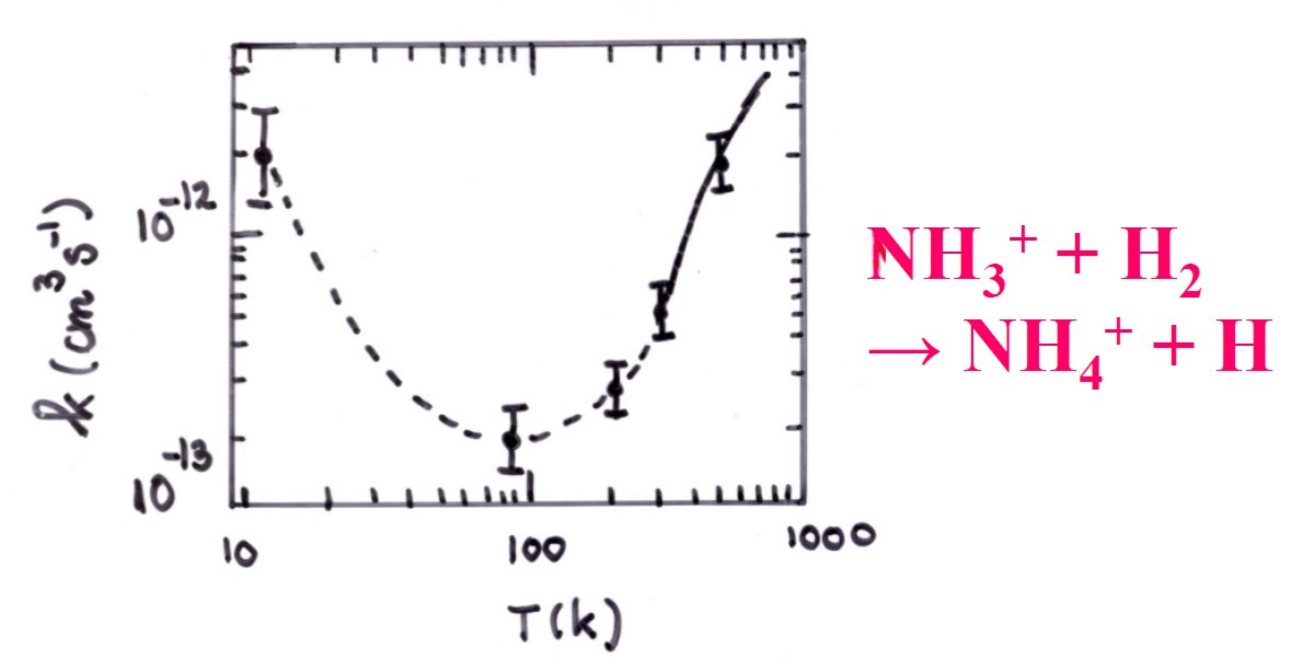


Ion-molecule processes

- Atomic ions: $X^+ + YZ \rightarrow XY^+ + Z$ *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

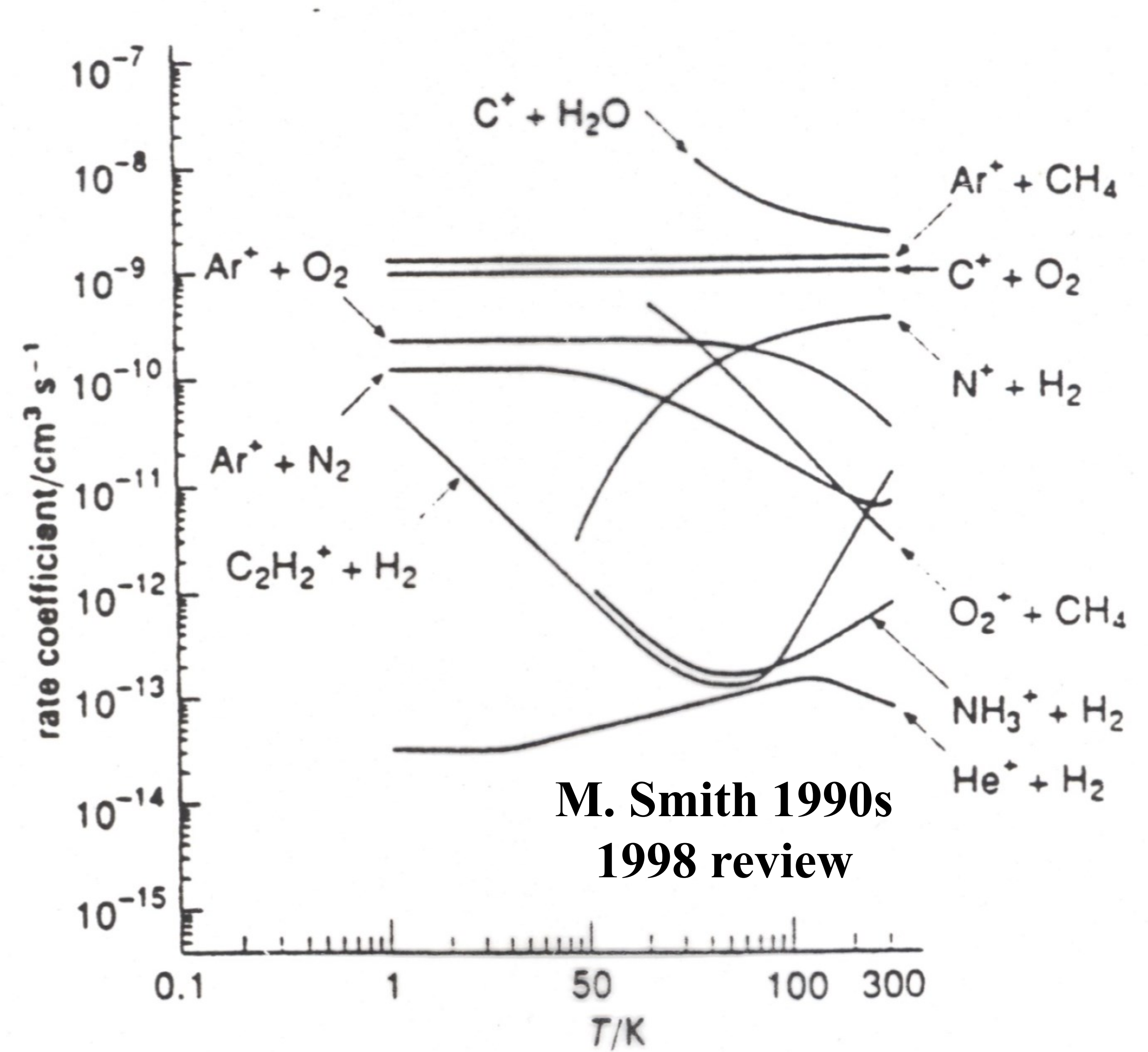


$NH_3^+ + H_2$
$\rightarrow NH_4^+ + H$

Experiments

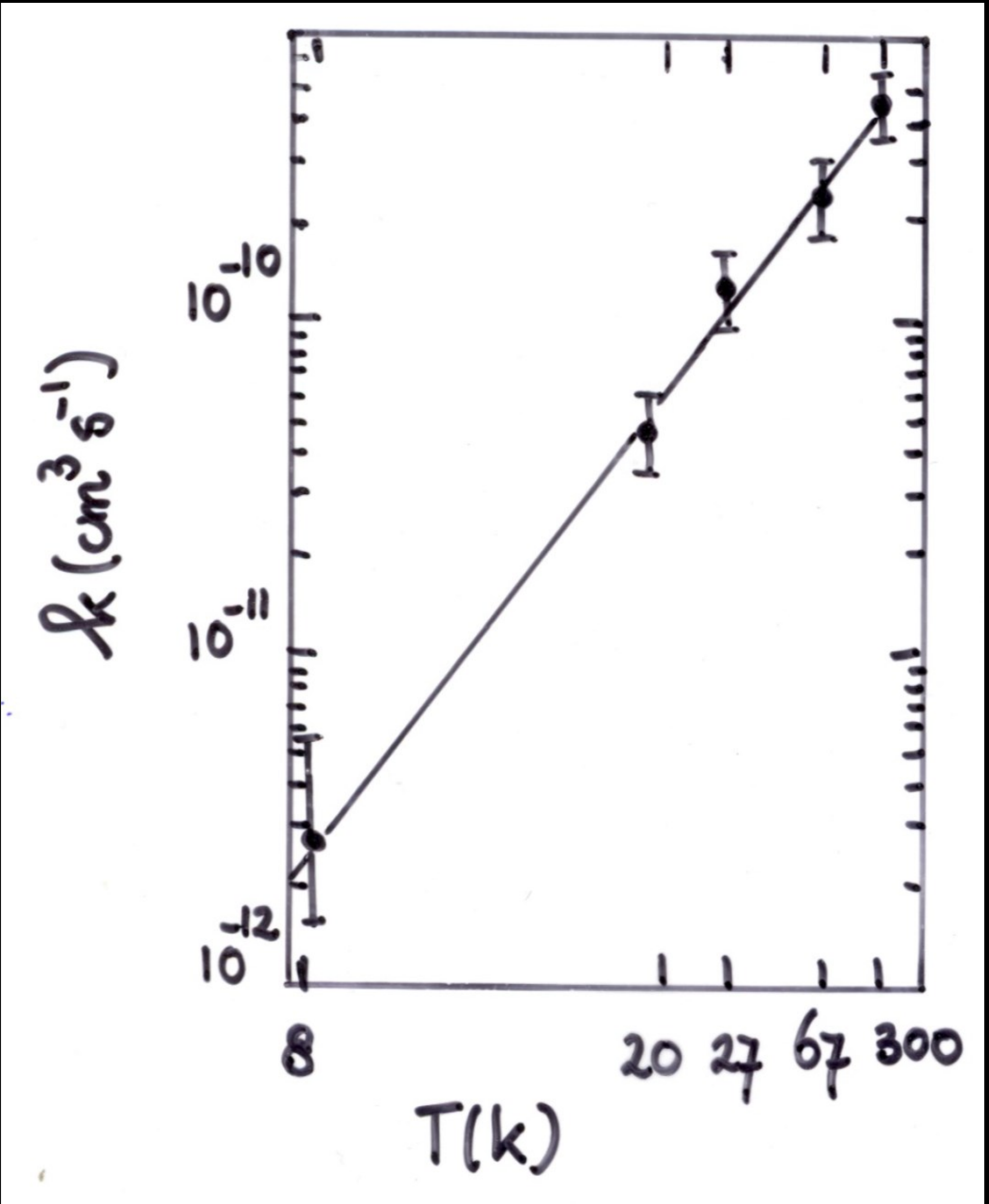
Rate coefficients for ion-polar reactions may be factors of 10-100 larger than Langevin values at low T, because $V(R) \propto R^{-2}$

Example: $C^+ + OH \rightarrow CO^+ + H$



M. Smith 1990s
1998 review

Unusual case: $N^+ + H_2$

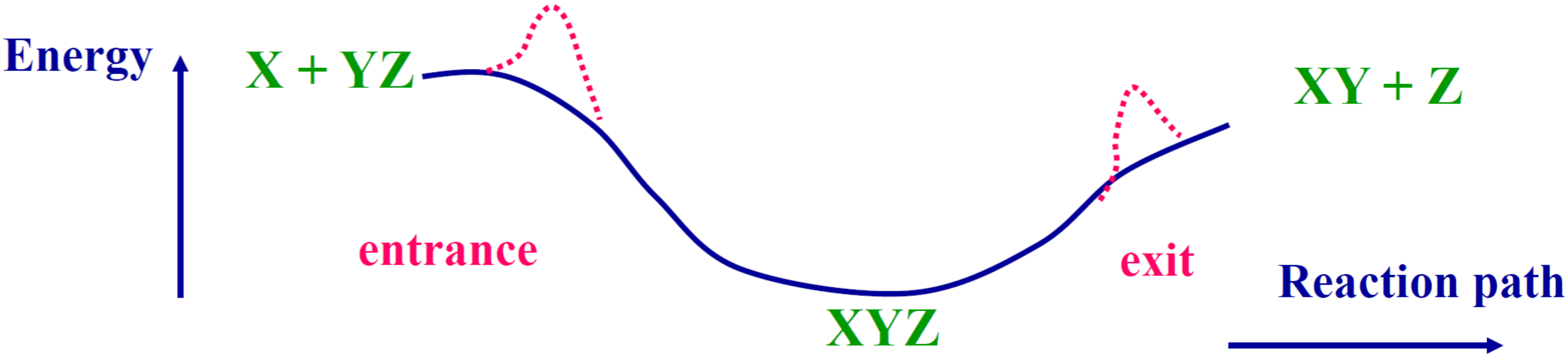


Potentially initiates much of nitrogen chemistry: forms $NH^+ + H$

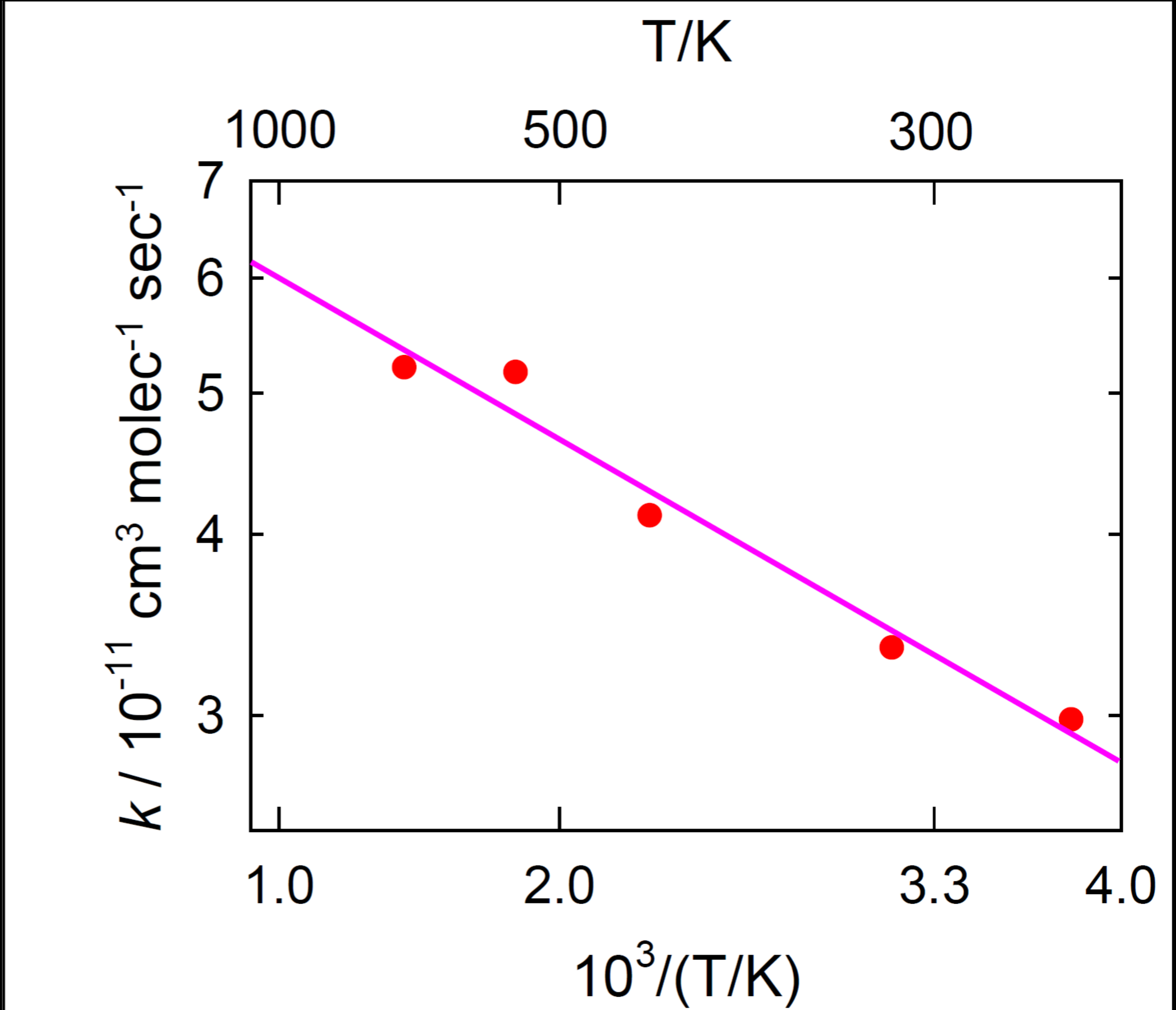
Rate decreases rapidly at low *T*, however, because reaction slightly ***endo***thermic at $T < 100$ K.

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 → reactions thought to be slow at low *T*
- Experiments: reactions can be fast at low *T*!

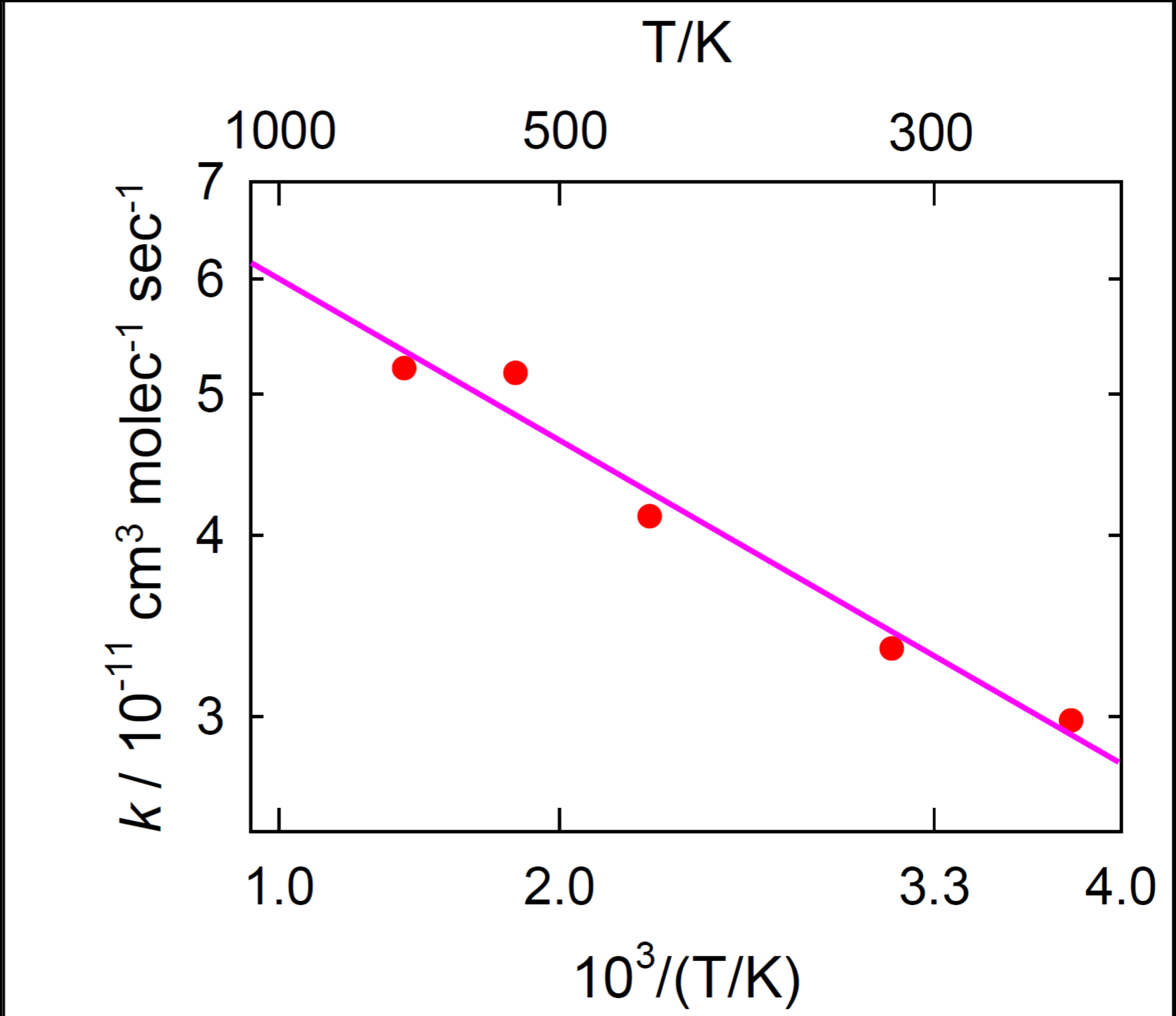


$CN+C_2H_6$: or why extrapolation is unreliable



**I. Sims et al.
Rennes/Birmingham**

Exercise! Extrapolate to 20 K and predict



I. Sims et al.
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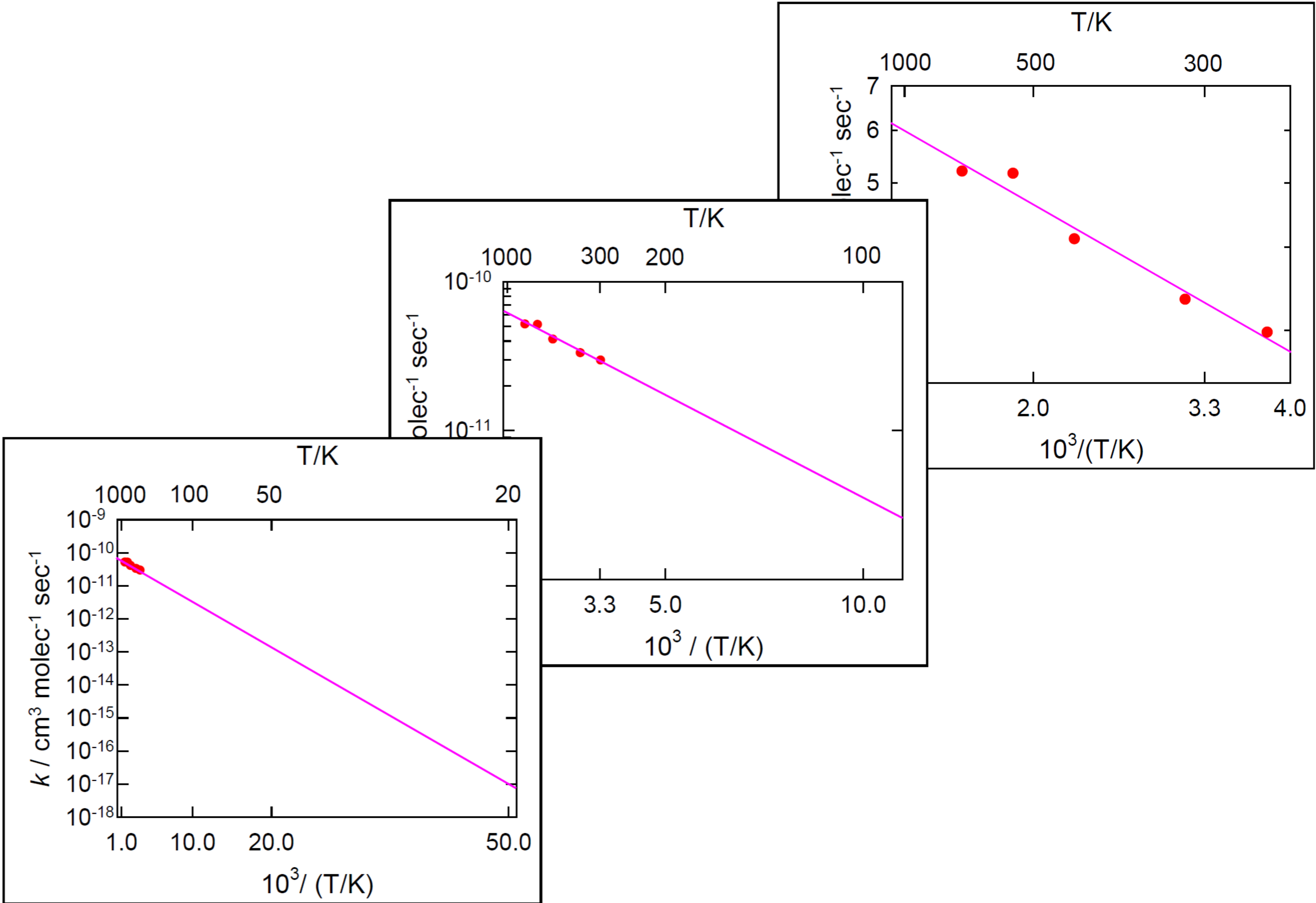
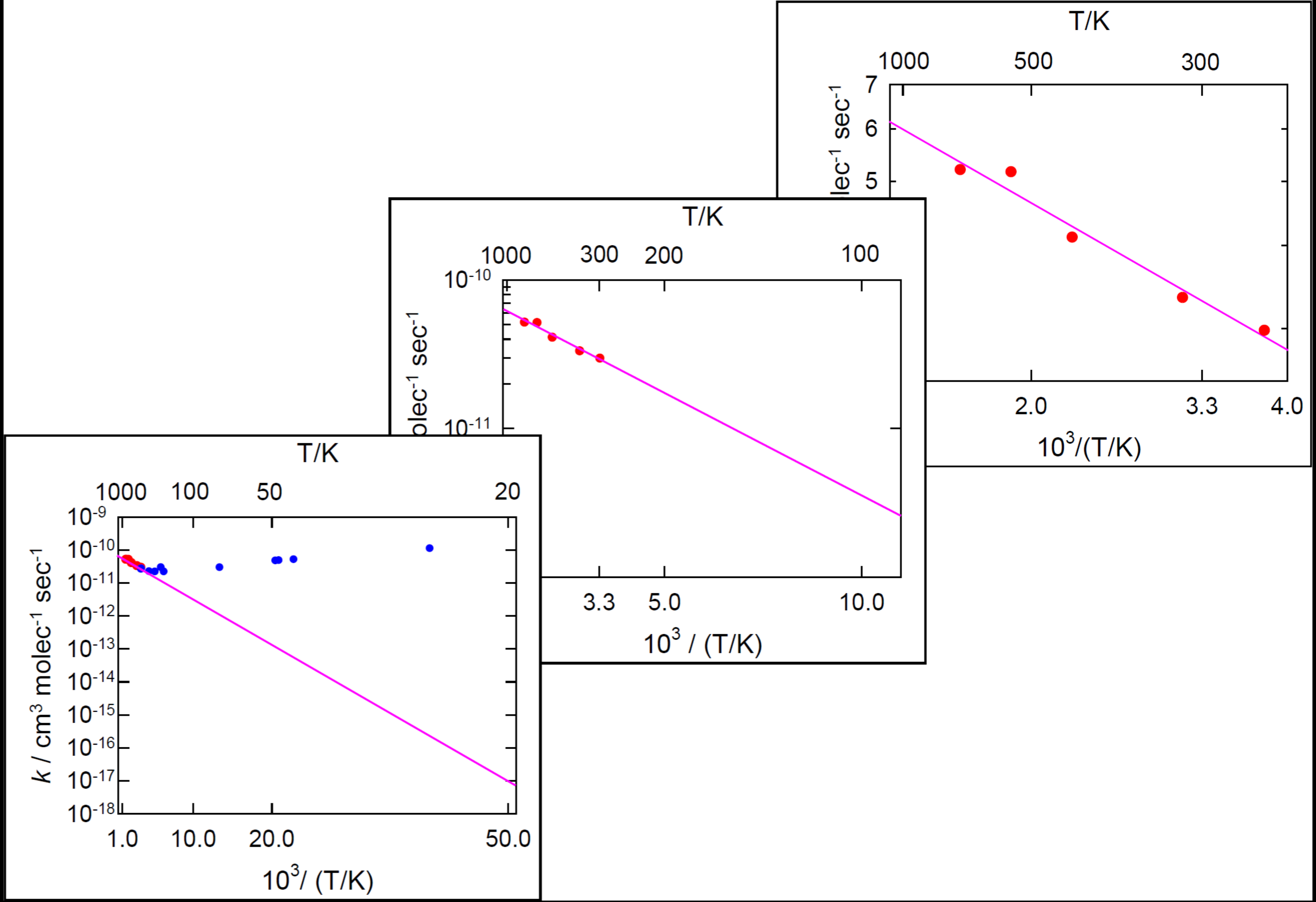
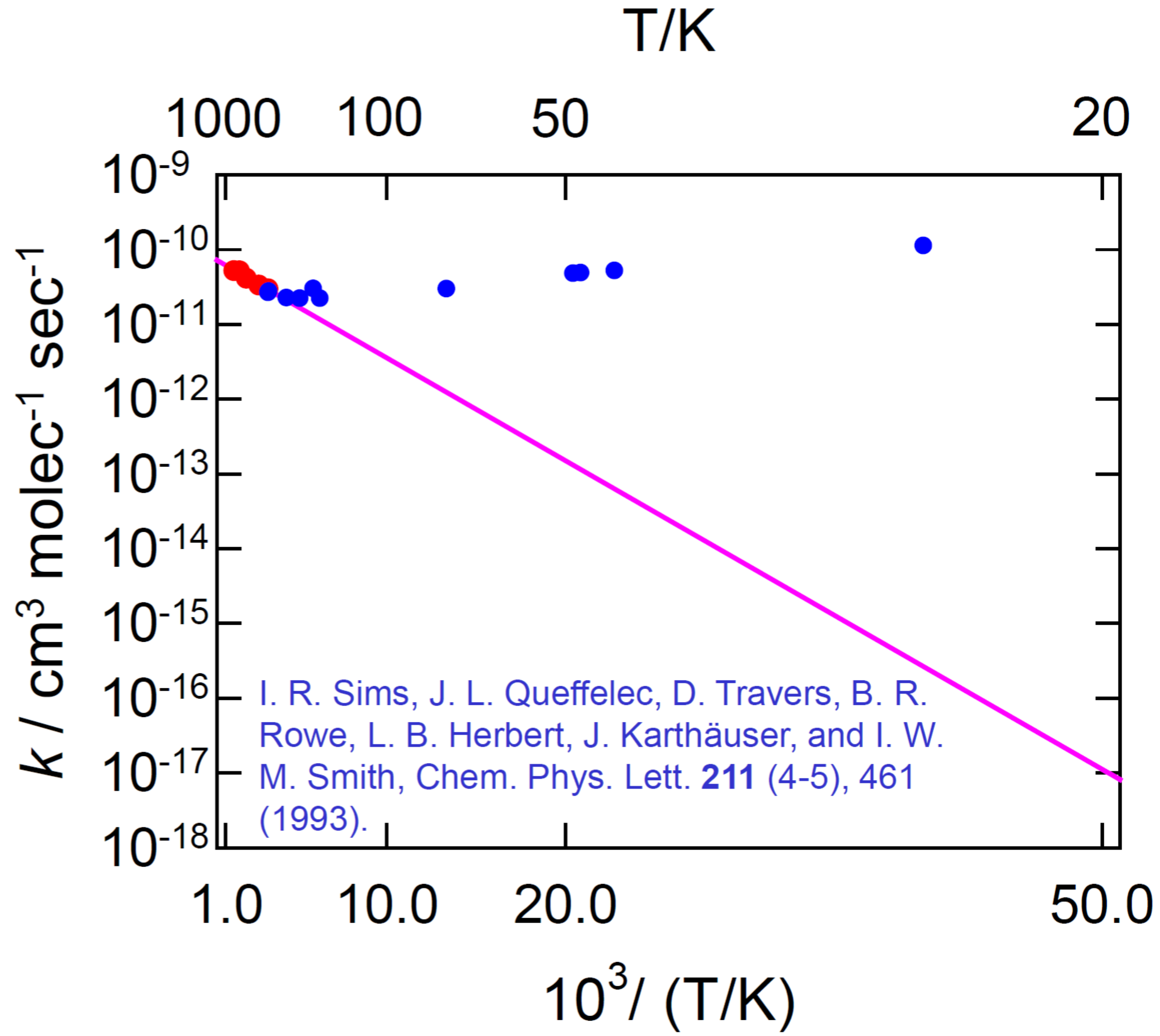
$CN+C_2H_6$: or why extrapolation is unreliable



$CN+C_2H_6$: or why extrapolation is unreliable



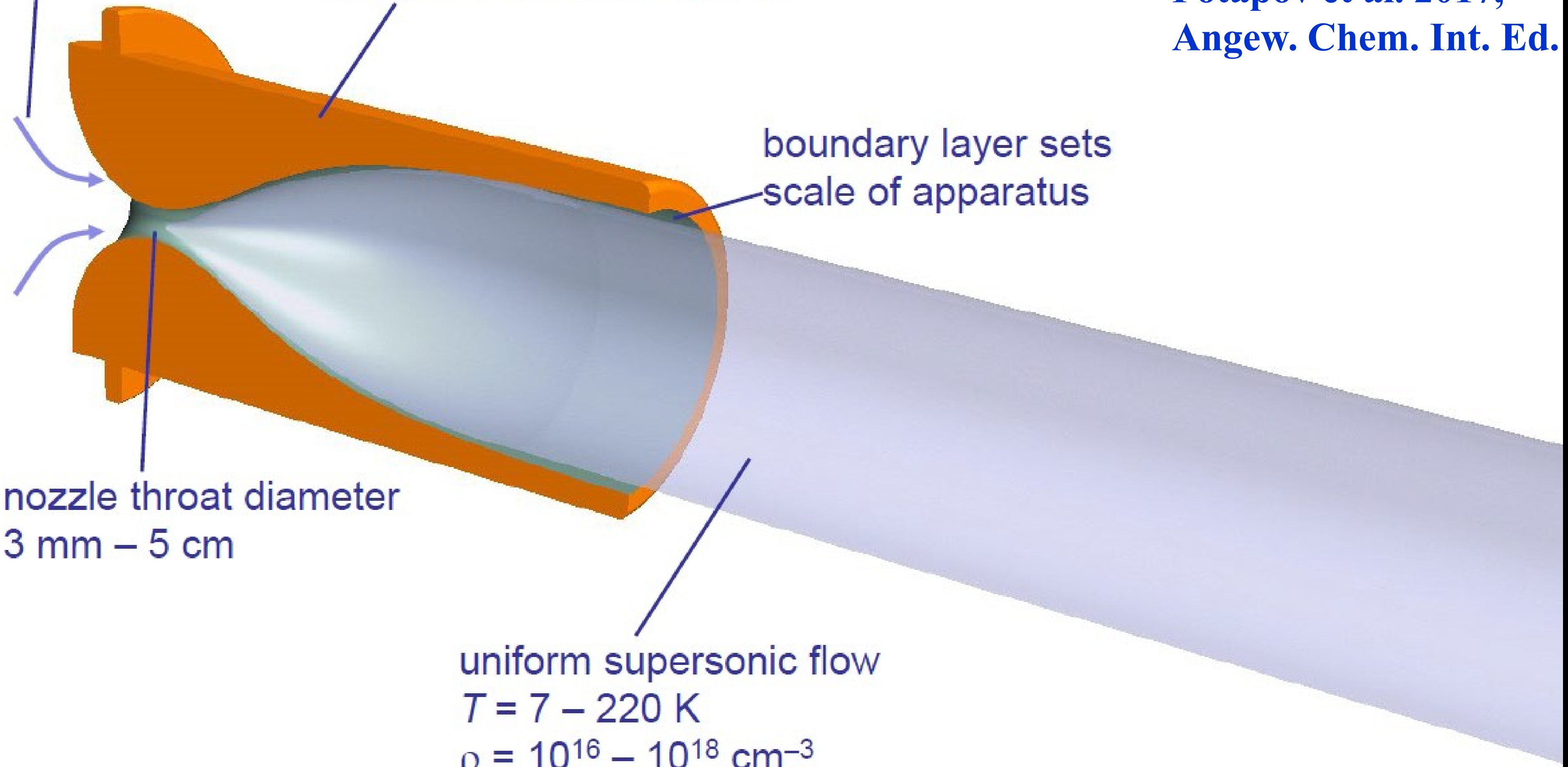
$CN+C_2H_6$: reaction stays rapid at low *T*!



I. R. Sims, J. L. Queffelec, D. Travers, B. R. Rowe, L. B. Herbert, J. Karthäuser, and I. W. M. Smith, Chem. Phys. Lett. **211** (4-5), 461 (1993).

CRESU technique

Review:
Potapov et al. 2017,
Angew. Chem. Int. Ed.



50-100 slm carrier gas (He, Ar or N_2) + precursor + reagent

axisymmetric Laval nozzle

boundary layer sets scale of apparatus

nozzle throat diameter
3 mm – 5 cm

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

chamber pressure 0.1 – 0.25 mbar
pumping speed ~ 30000 m^3 hr^{-1}

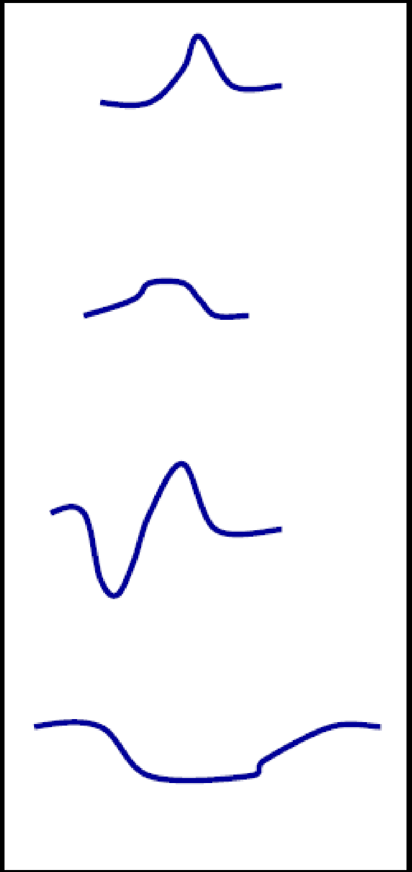
Laval nozzle and isentropic flow


USA

Types of neutral-neutral reactions

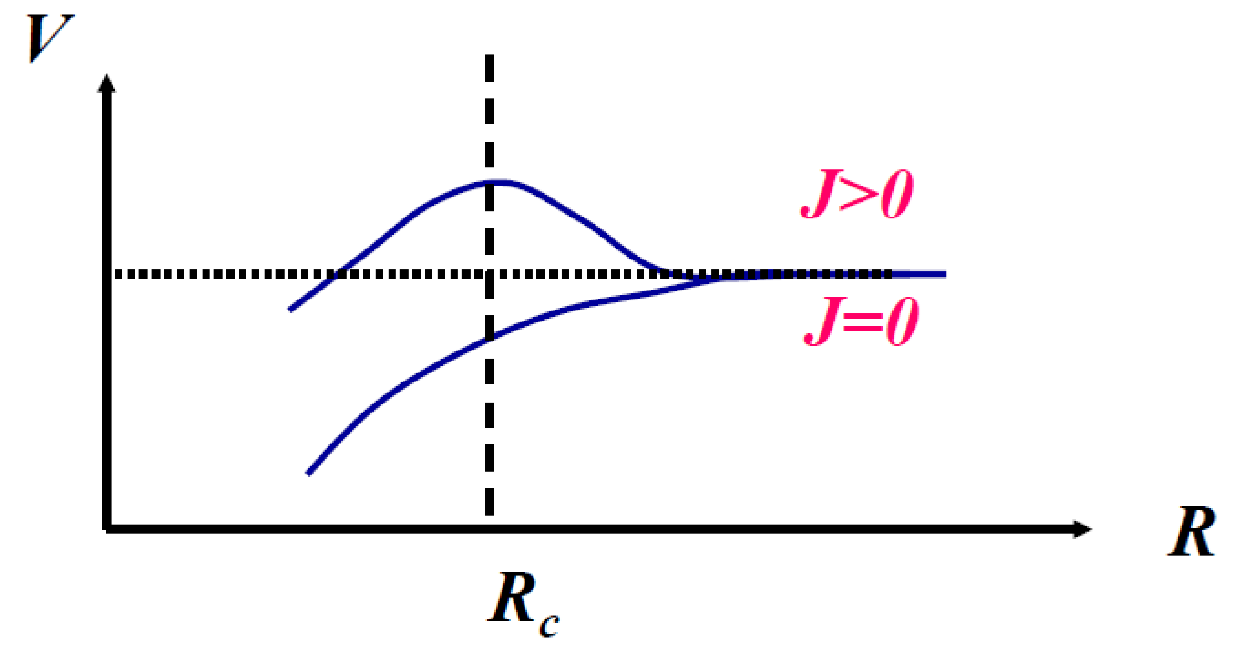
	E_A/k
Molecule-molecule	$>10^4$ K
E.g., $H_2 + D_2 \rightarrow 2HD$	
Radical-saturated molecule	~2000
E.g., $OH + H_2 \rightarrow H_2O + H$	
Radical-unsaturated molecule	~0
E.g., $OH + CO \rightarrow CO_2 + H$	
Radical-radical	–100
E.g., $O + OH \rightarrow O_2 + H$	

$V(R)$



Rate coefficient

Blow-up entrance channel



$$V_{eff} = V_A(R) + \frac{-J^2}{2\mu R^2}$$

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

Adiabatic capture approximation

- If collision energy < $V_{\mathrm{eff}}(R_C)$: reaction probability = 0
- If collision energy > $V_{\mathrm{eff}}(R_C)$: 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

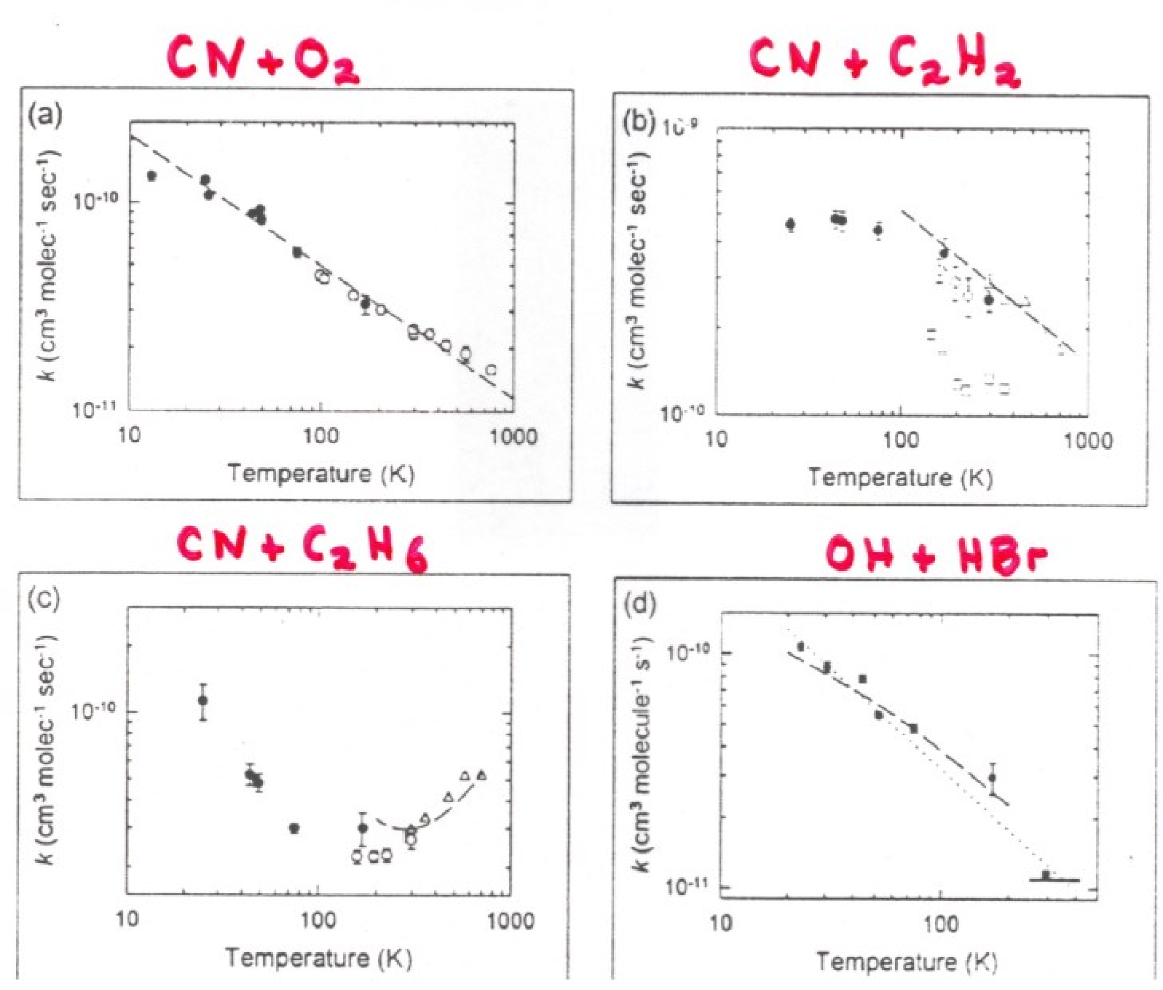
D. Clary (1993), *J. Chem. Soc. Faraday Trans.*

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}	$T^{-½}$
Charge-quadrupole	R^{-3}	$T^{-1/6}$
Dipole-dipole	R^{-3}	$T^{-1/6}$
Dipole-quadrupole	R^{-4}	T^{0}
Dispersion	R^{-6}	$T^{-1/6}$

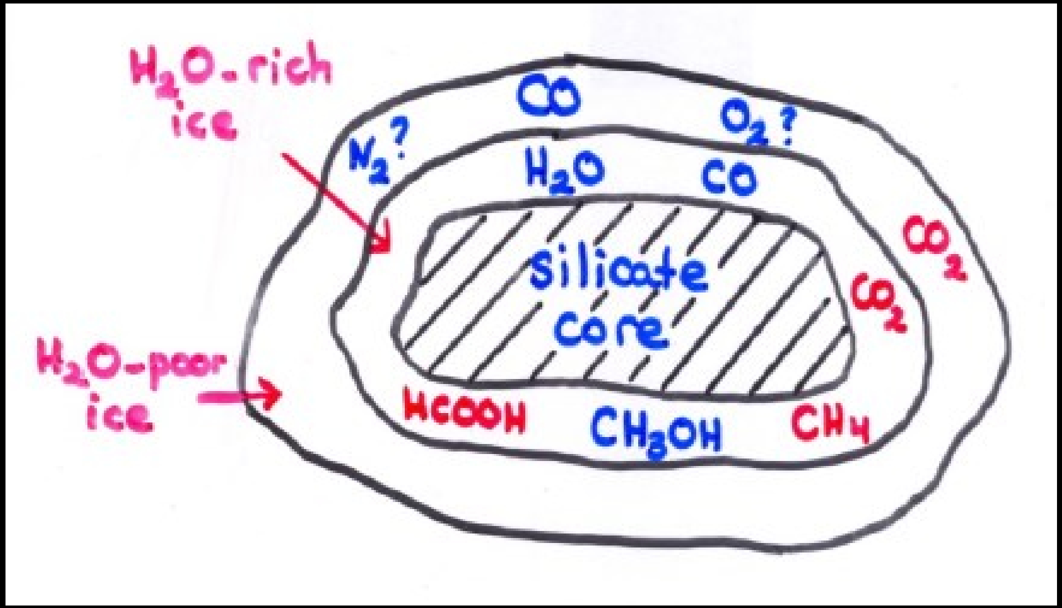
Experiments: examples



- 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: H_2

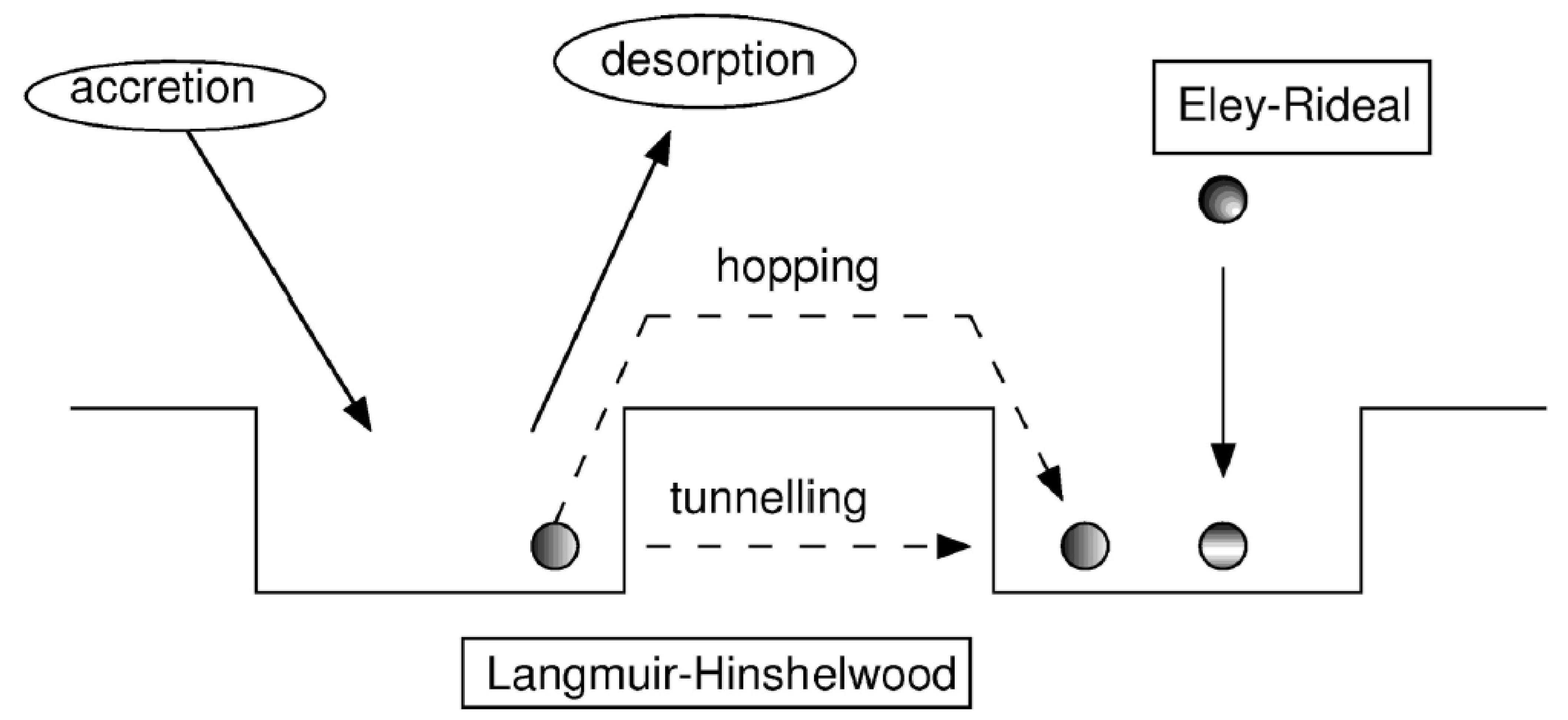
- Evidence for gas-grain chemistry
  - H_2 in interstellar clouds
  - NH in diffuse clouds
  - Abundances of H_2O, CO_2, CH_3OH, … in ices higher than expected from freeze-out of gas phase



Formation mechanisms

- ***Diffusive mechanism*** (Langmuir-Hinshelwood)
- $\mathrm{X} + \mathrm{g{:}Y} \xrightarrow[\text{sticking}]{} \mathrm{X{:}g{:}Y} \xrightarrow[\text{diffusion + molecule formation}]{} \mathrm{X\text{-}Y{:}g} \xrightarrow[\text{desorption}]{} \mathrm{XY} + \mathrm{g}$
- ***Direct mechanism*** (Eley-Rideal)
- $\mathrm{X} + \mathrm{Y{:}g} \xrightarrow[\text{direct reaction}]{} \mathrm{X\text{-}Y{:}g} \xrightarrow[\text{desorption}]{} \mathrm{XY} + \mathrm{g}$
- Surfaces can be silicates, carbonaceous ice, …

Grain surface processes – diffuse vs direct



E. Herbst

Diffusive mechanism

- X + g:Y → X:g:Y → X–Y:g → XY + g

  sticking Diffusion + mol.form desorption

- Process proceeds in several steps (consider case of H_2):

  1. H atom must collide with grain: H + g

  2. Colliding atom must stick to surface: H + g → H : g

  3. H atom must be retained until another atom gets absorbed:

  H : g → H : g : H

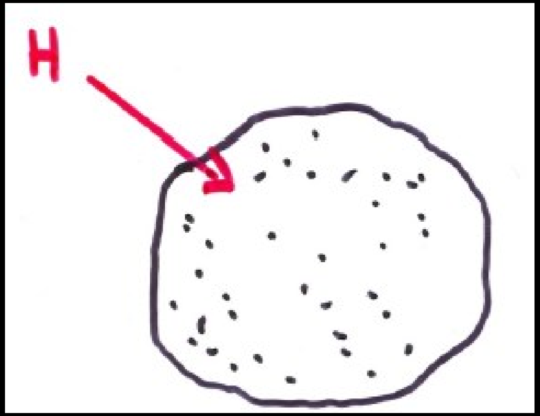
  4. H atoms must be mobile to find each other and form bond:

  H : g : H → H – H : g

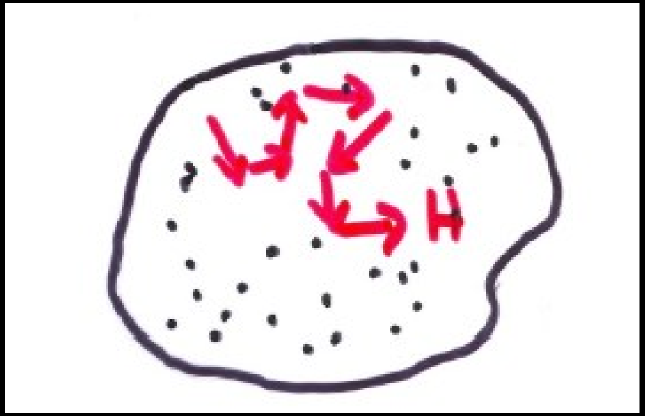
  5. H_2 must be ejected from surface: H – H : g → H_2 + g

- **Probabilities of 2, 3+4, and 5 are η_S, η_r, η_d.**

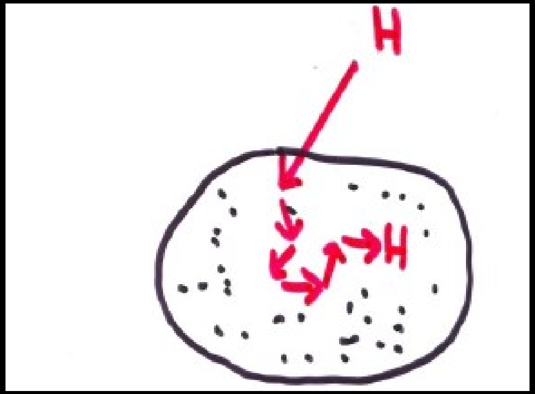
H_2 formation on grains



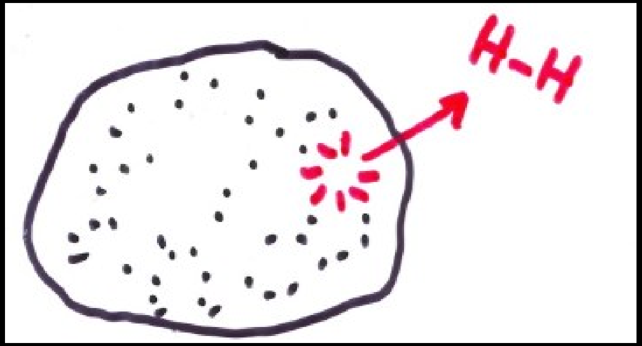
1. H collides with grain



2. H explores grain until either it encounters another H or is immobilized at enhanced binding site



3+4. Second H atom collides with grain: explores surface and encounters first H atom



5. H_2 formation on surface, H_2 ejected from surface.

1. Collision rate with grain

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

  where πa^2= geometrical cross section

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

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

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

- Compare with required H_2 formation rate (from observations)

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

$\Rightarrow$ all probabilities must be nearly unity

2. Adsorption time

- Classical expression: $$t_a = \frac{1}{v}\exp\left(\frac{E_d}{kT}\right)$$
- With E_d = binding energy (also called E_bind)

  $v = E_\mathrm{d}/h \sim 10^{13}\ \mathrm{s}^{-1}$
- Physical adsorption: $E_\mathrm{d} \sim 400$ K =>
  - $t_a = 3\mathrm{x}10^5$ s at $T = 10$ K
  - $t_a = 2\mathrm{x}10^{-8}$ s at $T = 40$ K
- Chemisorption: $E_\mathrm{d} \sim 20000$ K =>
  - $t_a = \infty$ at 100 K
- => 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

$$t_C = \frac{1}{r_C n(H)} \qquad = 3 \times 10^4 \text{ for } n(\mathrm{H}) = 1$$

$$= 3 \times 10^2 \text{ for } n(\mathrm{H}) = 100 \text{ cm}^{-3}$$

=> $t_C < t_a$ if $T < 15$ 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

1000 Å

$$t_M = \frac{4\pi a^2}{r^2} t_h \approx 10^{-2}\ s$$

Same as migration time on a clean silicate surface in the ISM

- Second H atom can find first H atom before evaporation

5. Ejection

- Since there are no strong H_2-grain bonds, H_2 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 and/or there are strong binding sites
- However, H_2 formation will still remain efficient up to 500 K thanks to chemisorption and tunneling.

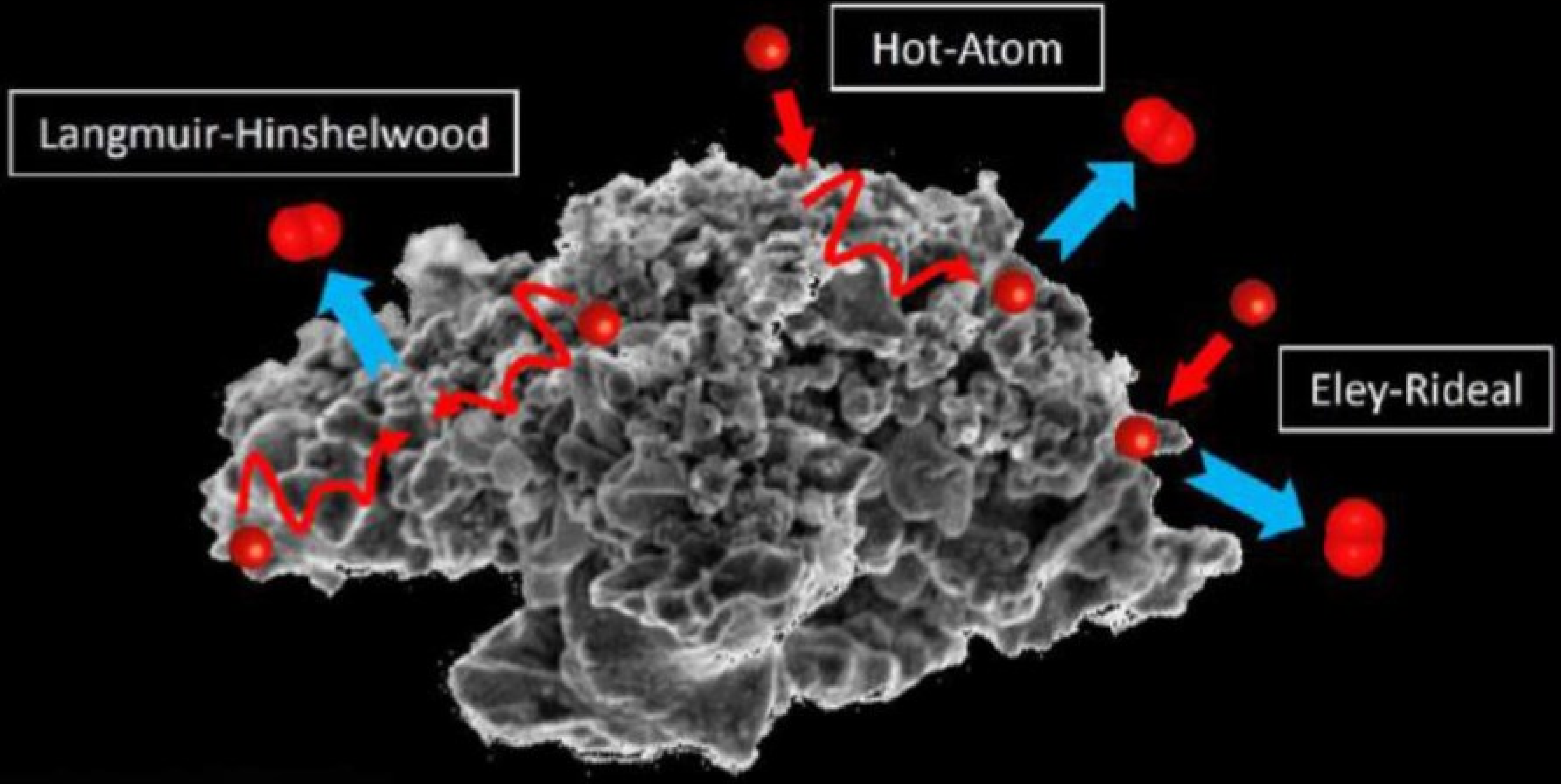
Cazaux & Tielens 2002, 2004, 2010

Eley-Rideal mechanism

- $\mathrm{X} + \mathrm{g{:}Y} \xrightarrow[\text{direct reaction}]{} \mathrm{X{-}Y{:}g} \xrightarrow[\text{desorption}]{} \mathrm{XY} + \mathrm{g}$

- If there are enough chemisorption sites so that grain is saturated with H atoms, formation rate of H_2 is controlled by rate of arrival of H atoms at surface
- It is assumed that H_2 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

H_2 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

Cazaux & Tielens 2004, 2010
Vidali *et al.* 2007
Cuppen & Herbst 2007
Lemaire *et al.* 2010

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, H_2, 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, NH_2, CH_2, CH_3
  - Reactions may occur if activation barriers sufficiently low

Surface diffusion

- Site to site hop

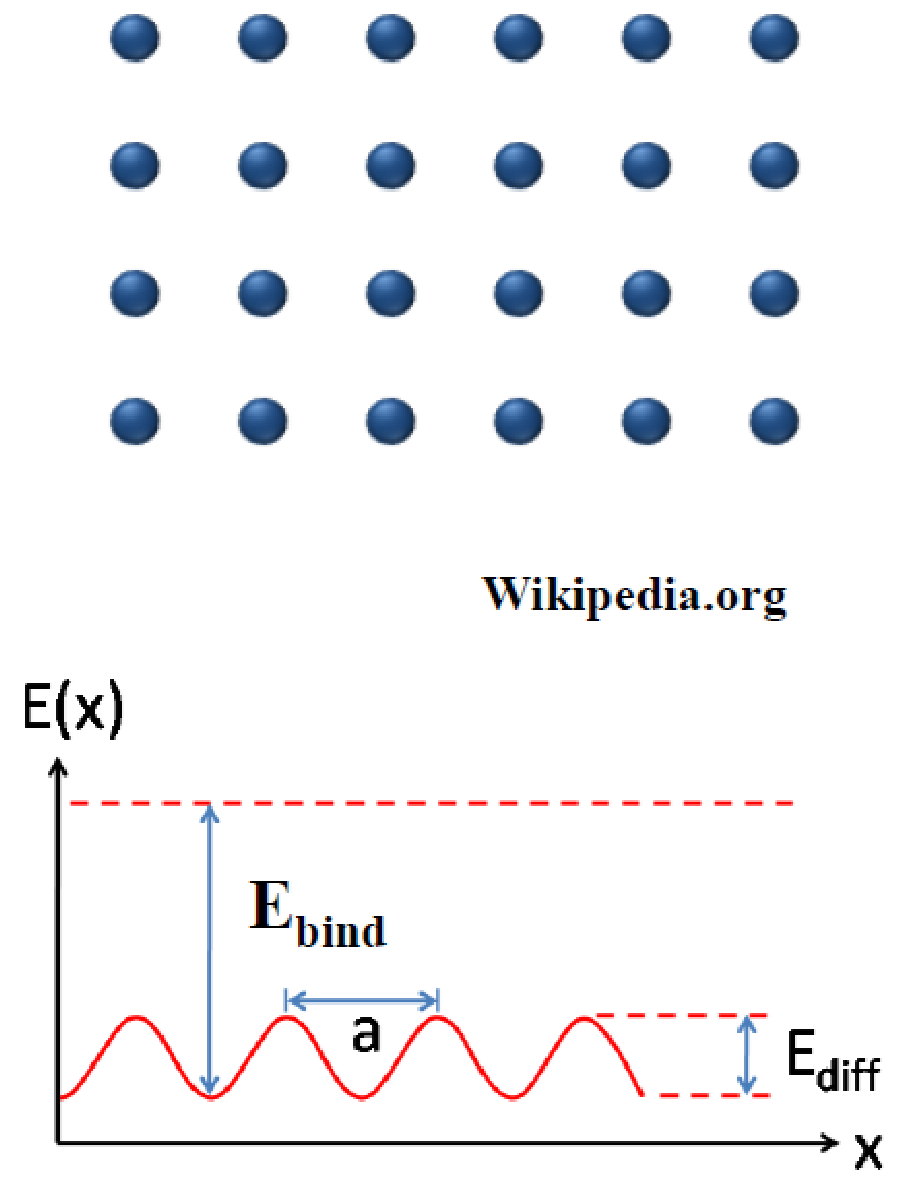
  $k_{\mathrm{hop}} = v \exp(-E_{\mathrm{hop}}/kT_{\mathrm{S}})$

- Usually, $E_{\mathrm{hop}} = \mathrm{c}^{\mathrm{st}}\, E_{\mathrm{bind}}$

  c^{st} varies from 0.3-0.7

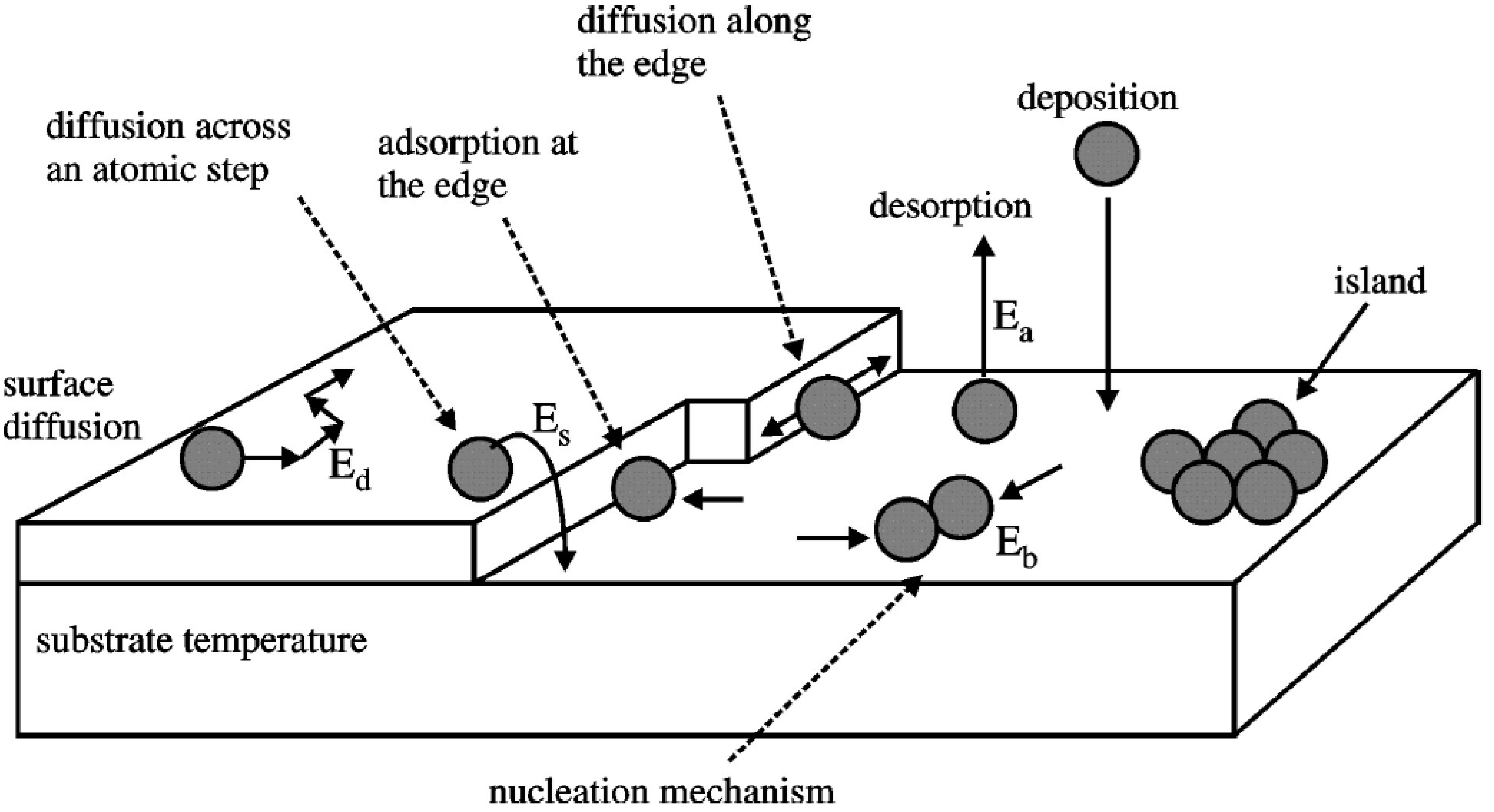
- Diffusion barriers will change from site to site
- Importance of tunneling
- Competition with reaction

Note critical role of surface temperature!



Wikipedia.org

Irregular surfaces



e.g., Cuppen & Herbst 2007

Uni-kl.de

Relevant time scales

- See Sect. 2.3 for formulae adsorption (= residence) and migration (= thermal hopping) times
- Tunneling only important for H, H_2
- Limiting activation barriers of reactions at T_d=10 K
  - H ≤ 3500 K
  - H_2 ≤ 4500 K
  - O,C,N ≤ 450 K

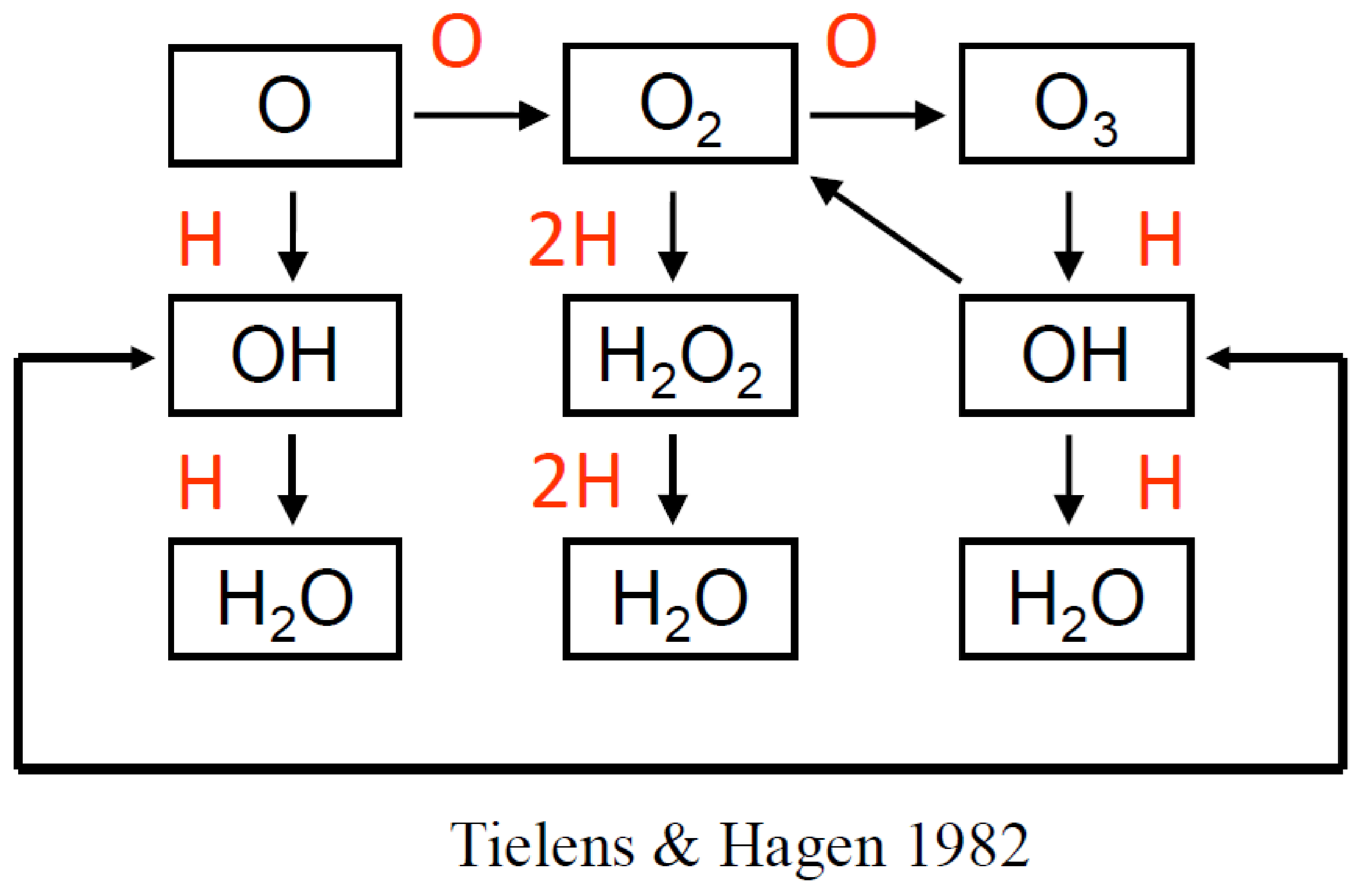
Types of surface reactions

1. **Atom-atom reactions**, e.g., $N + O \rightarrow NO$
2. **Radical-atom reactions**, e.g., $H + NO \rightarrow HNO$
3. **Radical-radical reactions**, e.g., $CH_3 + OH \rightarrow CH_3OH$
4. **Radical-H$_2$ reactions**, e.g., $OH + H_2 \rightarrow H_2O + H$
5. **Molecule–atom reactions**, e.g., $CO + O \rightarrow CO_2$
6. **Hydrogen abstraction reactions**, e.g., $H_2CO + H \rightarrow HCO + H_2$

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

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

Example: formation routes to water ice



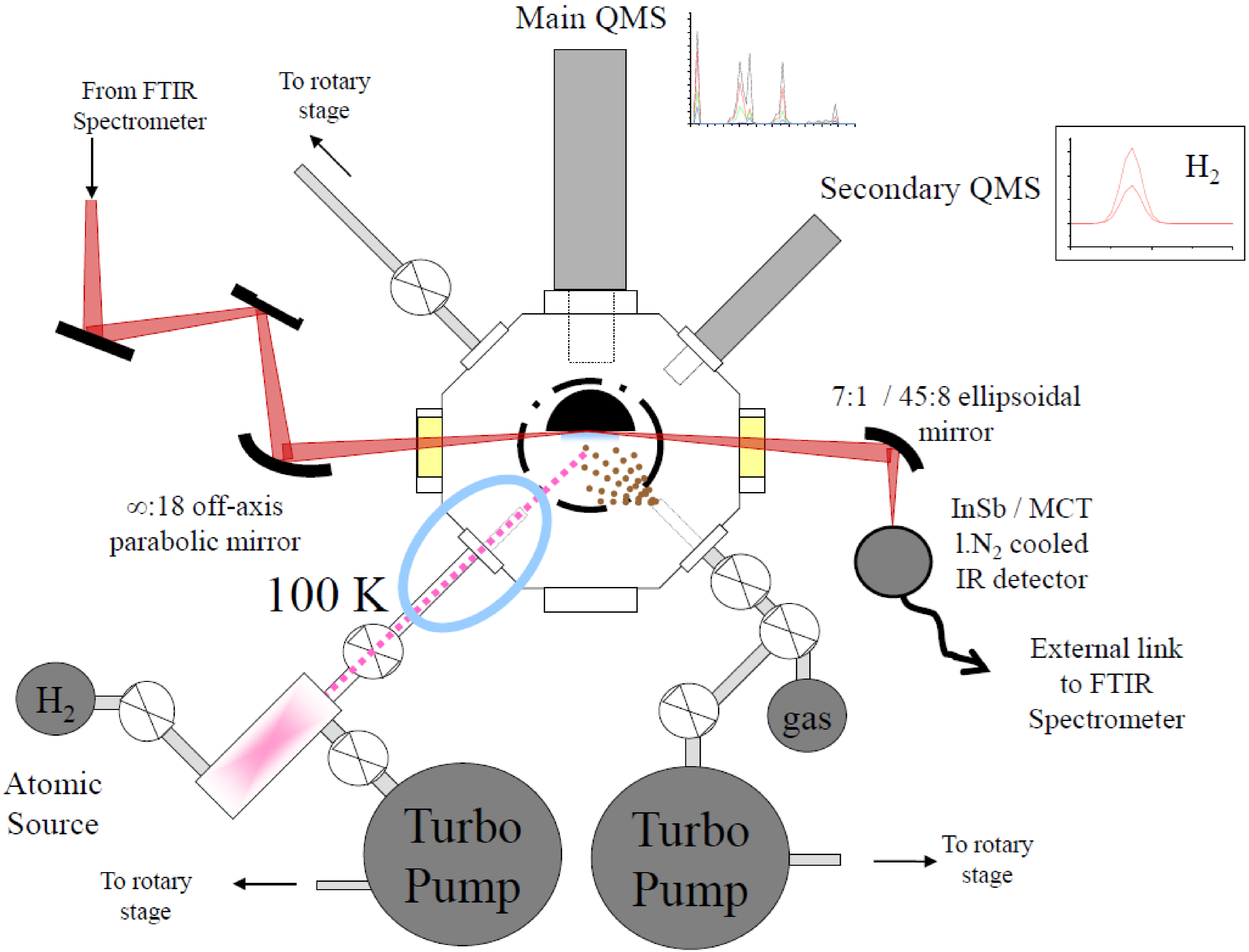
Tielens & Hagen 1982

These reactions were tested in the laboratory 2008-2011

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

Experimental simulation

- Condensation of ice (CO, O_2, N_2, ...) in UHV chamber
- Bombardment by cooled atomic beam (H, O, C, N) produced in microwave or DC discharge
- Analysis of products by Reflection Absorption InfraRed Spectroscopy (RAIRS) and Mass Spectrometry.
- Several notable groups around the world



Main QMS

From FTIR Spectrometer

To rotary stage

Secondary QMS

H_2

7:1 / 45:8 ellipsoidal mirror

∞:18 off-axis parabolic mirror

InSb / MCT l.N_2 cooled IR detector

100 K

External link to FTIR Spectrometer

H_2

gas

Atomic Source

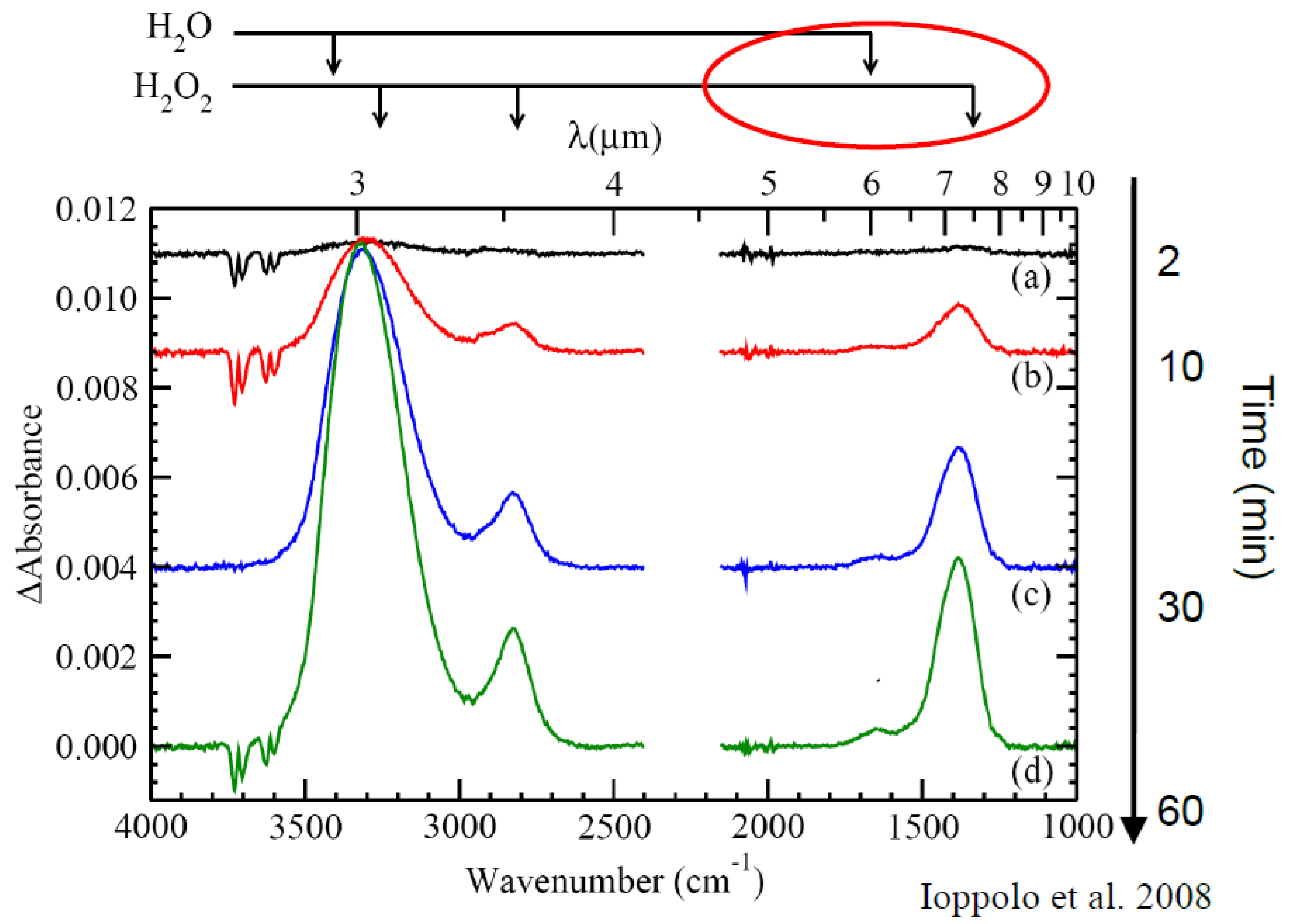
Turbo Pump

Turbo Pump

To rotary stage

To rotary stage

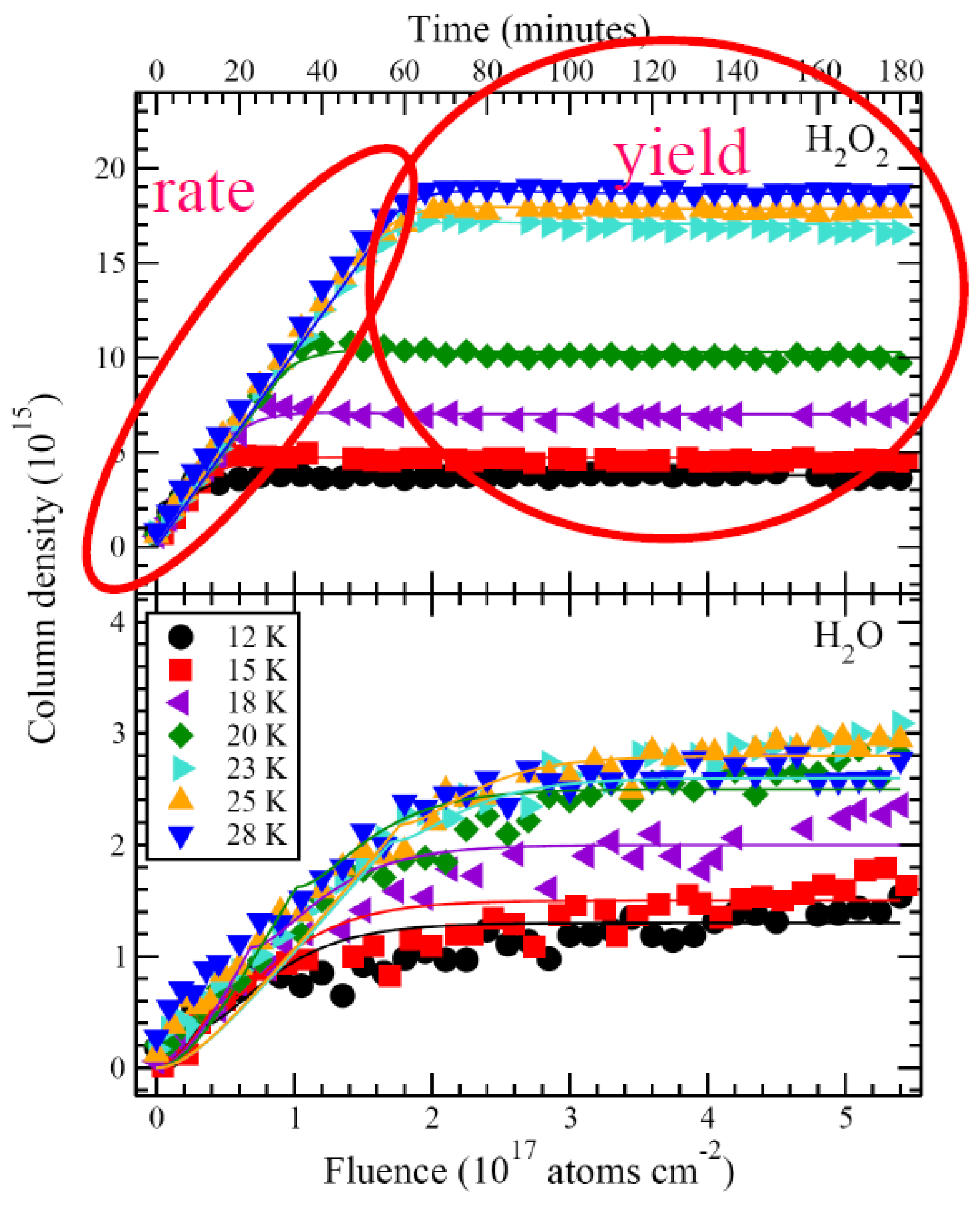
$$O_2 \xrightarrow{2\,H} H_2O_2 \xrightarrow{2\,H} 2\,H_2O$$



Ioppolo et al. 2008

Both H_2O_2 and H_2O indeed at low T! Observed with APEX

Reaction yields at low T



- Rate of reaction is temperature independent
- Yield increases with temperature
- More efficient than estimated

⇒ ***Formation path can be quantified and included in chemical models***

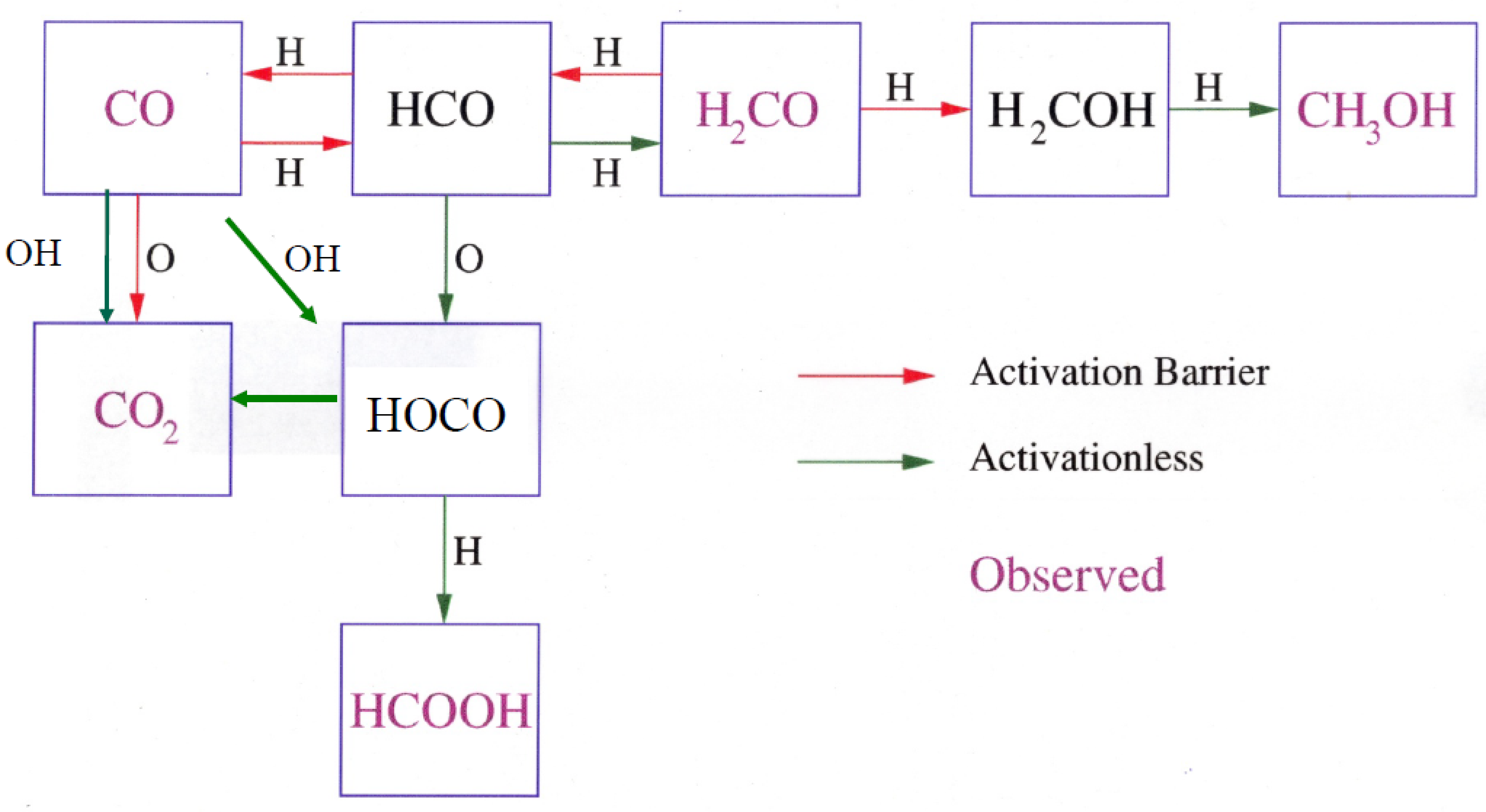
Formation of water on grains

Starts in clouds with $A_V > 3$ mag

Based on
Cuppen *et al.* 2010


ICMS Animation Studio

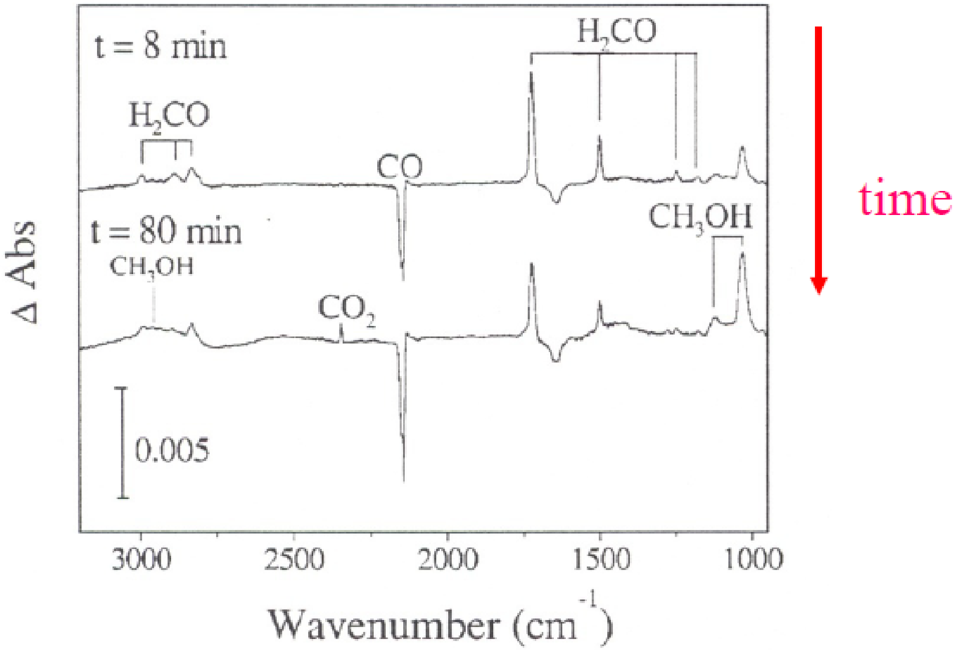
Example: CH_3OH and CO_2

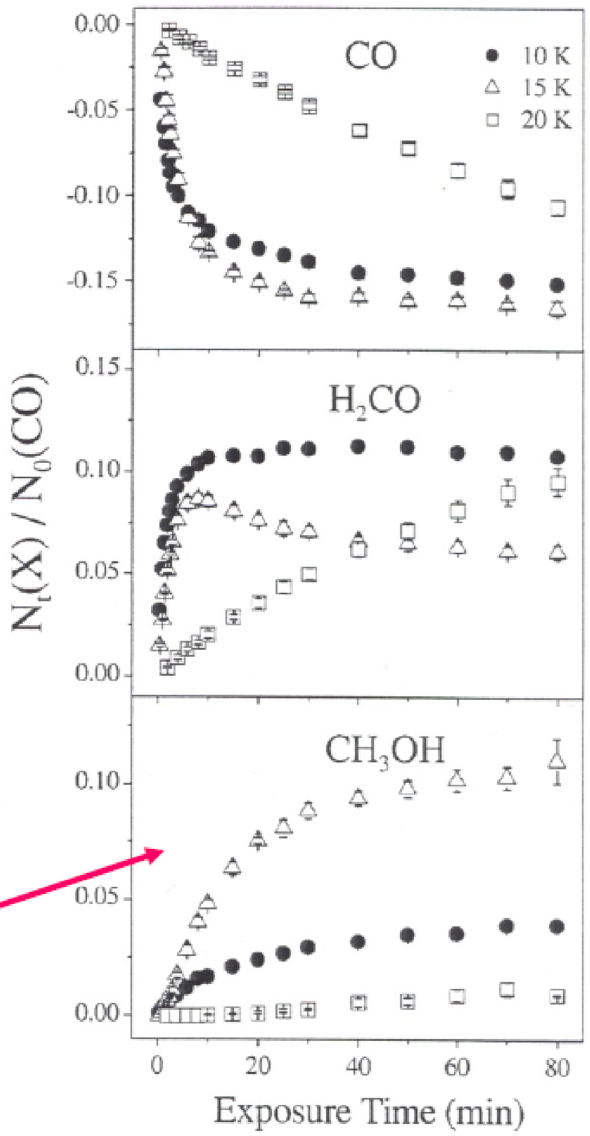


See Fuchs *et al.* 2009
Ioppolo *et al.* 2011a,b

CH_3OH experiment

IR spectroscopy to monitor products





Max. CH_3OH yield at 15 K

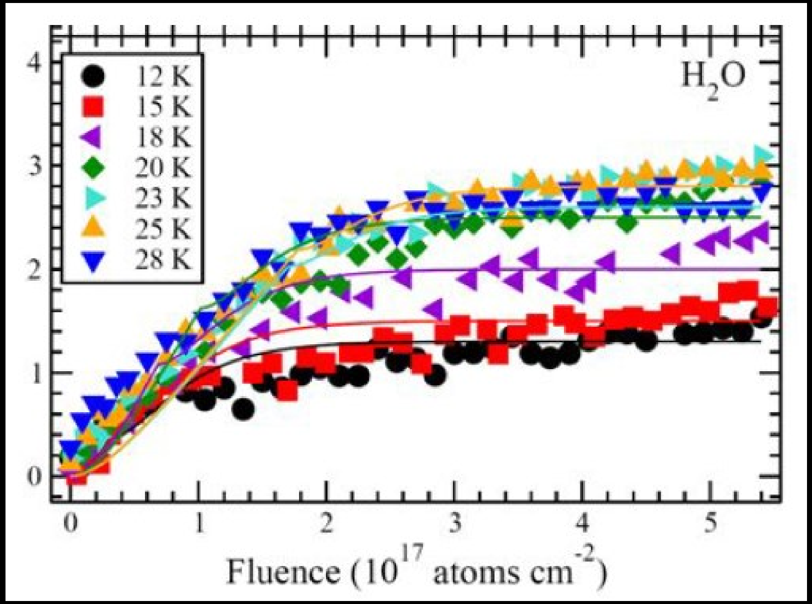
Higher *T* => less sticking of H

Watanabe *et al.* 2003

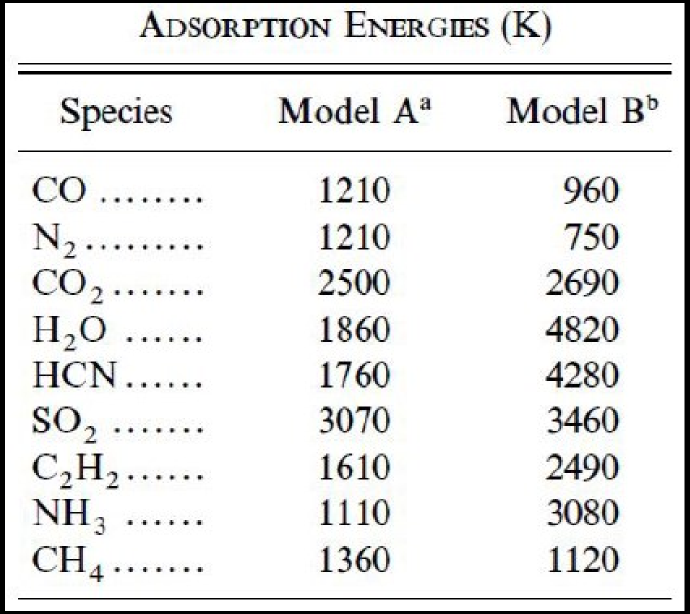
Fuchs *et al.* 2009

CH_3OH can be formed at temperatures as low as 10 K!

From lab experiments to model parameters



Ioppolo *et al.* (2008)



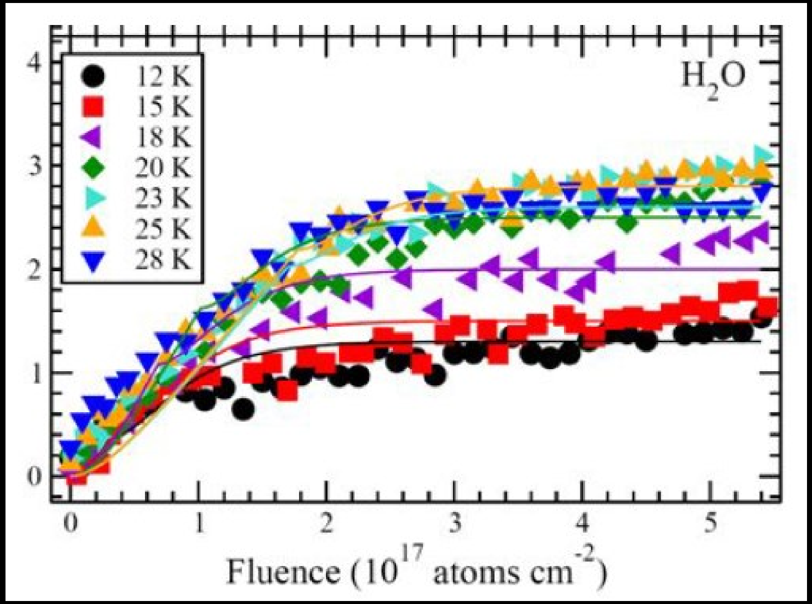
Adsorption Energies (K)

Species	Model A[a]	Model B[b]
CO	1210	960
N_2	1210	750
CO_2	2500	2690
H_2O	1860	4820
HCN	1760	4280
SO_2	3070	3460
C_2H_2	1610	2490
NH_3	1110	3080
CH_4	1360	1120

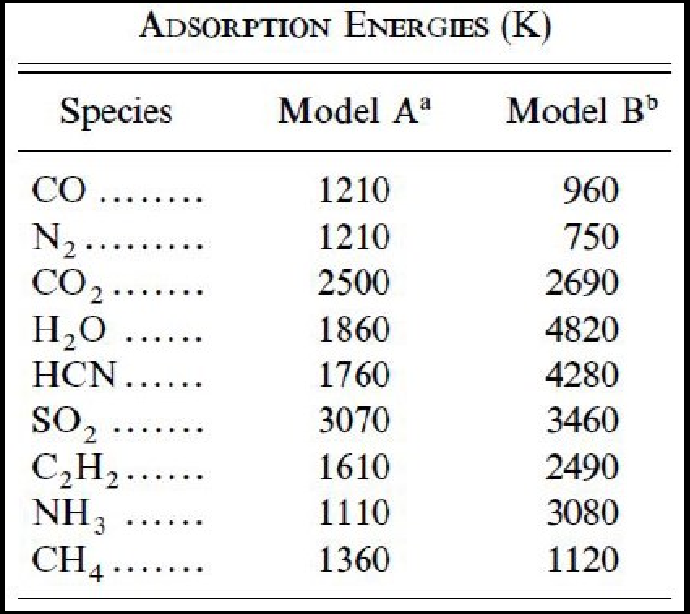
Aikawa *et al.* (2001), Cuppen *et al.* (2009), Lamberts *et al.* (2013)

Q: How to translate lab data to model parameters?

From lab experiments to model parameters



Ioppolo *et al.* (2008)



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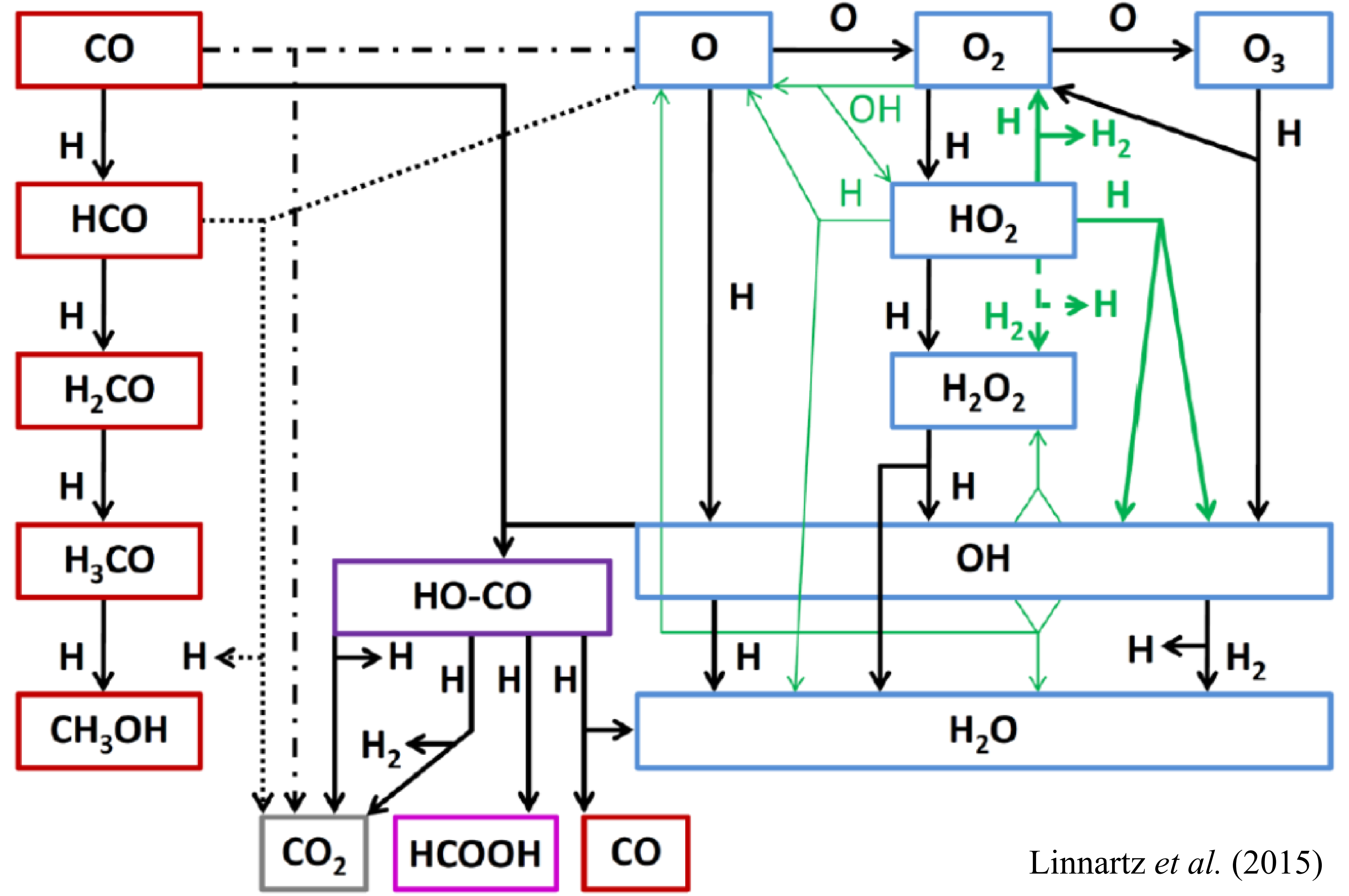
Aikawa *et al.* (2001), Cuppen *et al.* (2009), Lamberts *et al.* (2013)

- Lab provides rates as function of H or UV fluence or some other parameter over timescales of hours
- Astronomical applications involve timescales of $>10^5$ yr
- Models need barriers for desorption, diffusion, etc.

Building up the detailed network



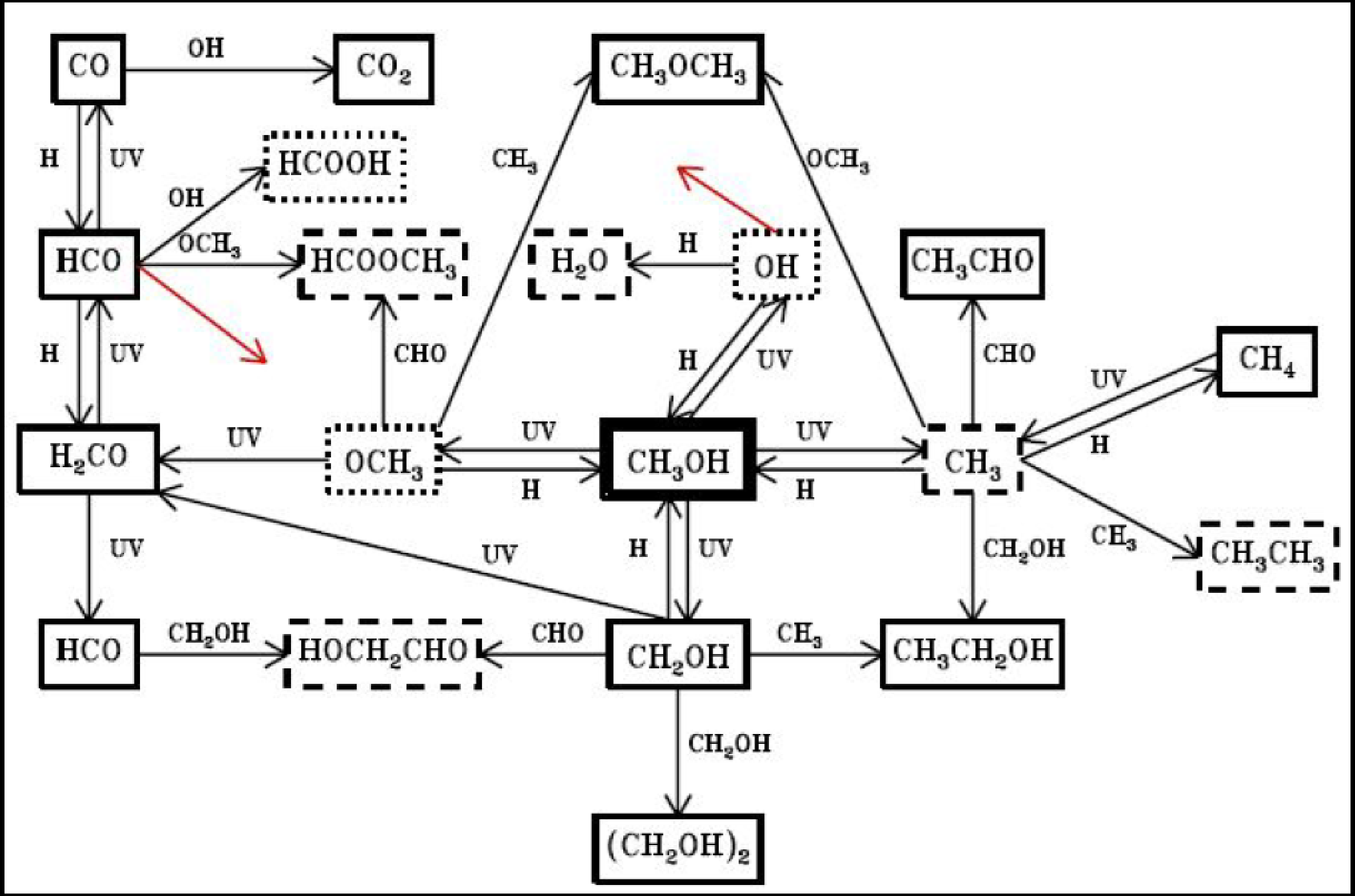
Linnartz *et al.* (2015)

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 H_2O:CO
    - Experiments with UV and high-energy particle bombardment => large database
- Interstellar applications need to take competition with reactions with H into account
- Reactions can occur both *on* and *inside* ices
- Observational evidence for UV photolysis of ices controversial

Photochemistry starting from methanol



Öberg *et al.* 2009

Is UV needed to make complex molecules?

More in lectures 6 & 7

Summary lectures 1+2

- Large variety of molecules observed in ISM
- Basic processes for formation and destruction identified
- Networks built for explaining abundances (Lectures 3 and 4)
- Results depend on thousands of input rates
    - Many not known under astrophysical conditions (but for many accurate rates not needed)
    - Key: identify those reactions which are important to study well
- Many experiments and theory on basic processes over last 30 years
    - Good, new chemical physics questions!
    - Significant progress in neutral-neutral reactions, surface reactions
- Some processes now well understood, others take decades of hard work to make just a little progress
    - Funding of lab astrophysics groups issue
    - Note: Photoionization codes like CLOUDY got atomic input data thanks to a century of efforts in atomic and plasma physics