

Diffusion and reaction on surfaces: crucial aspects

Minissale Marco

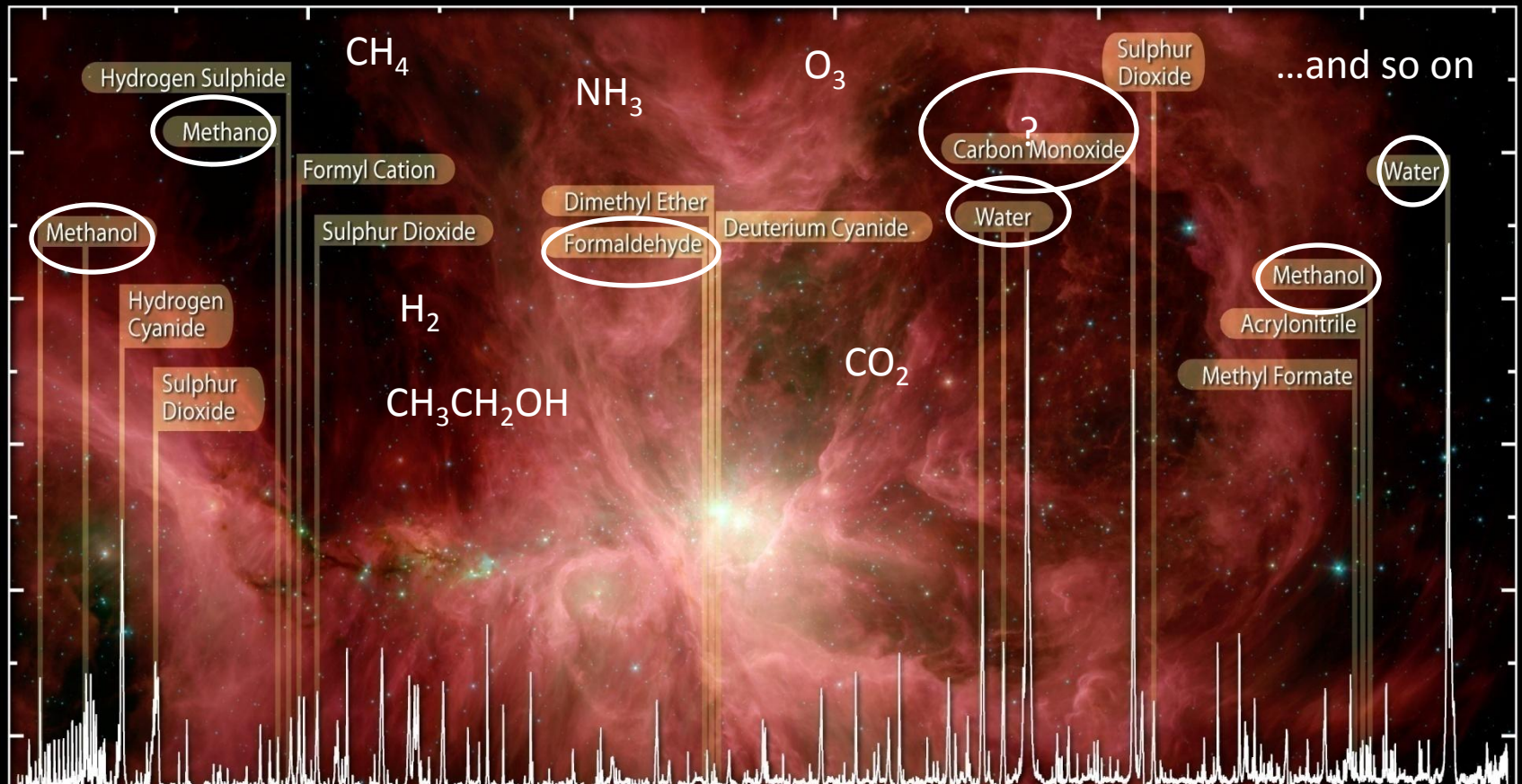


Laboratoire d'Étude du Rayonnement et de la Matière en Astrophysique



Paris, KIDA 7th May 2015

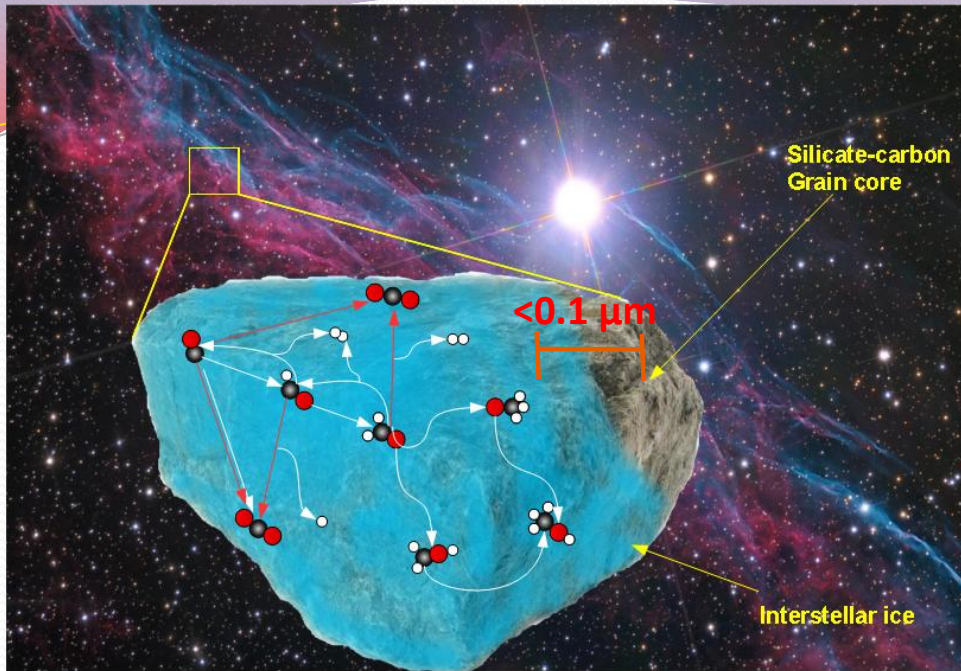
Most of the (molecular) information is carried by gas phase



Gas phase reactions cannot explain observed abundances

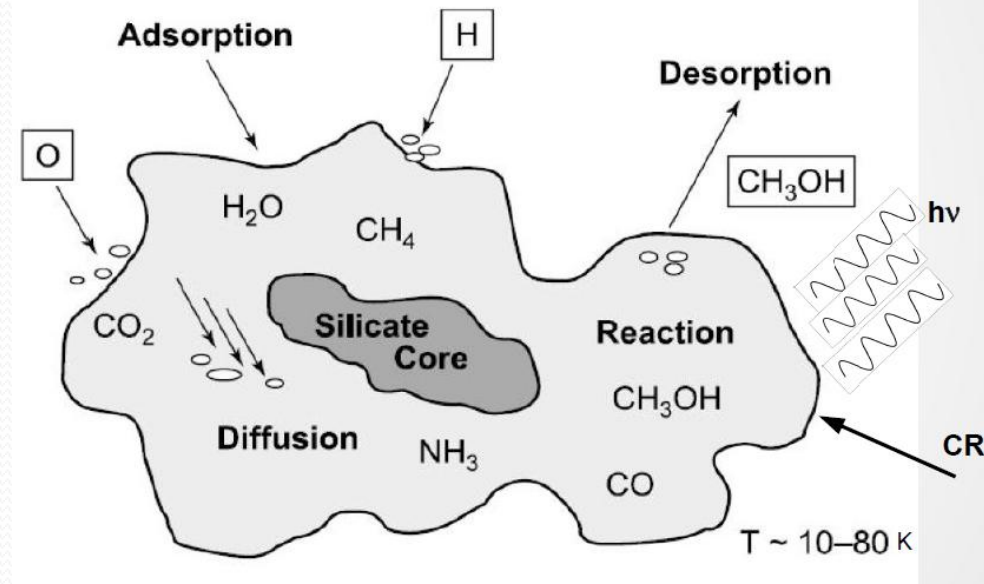
HIFI Spectrum of Water and
Organics in the Orion Nebula

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E. Bergin



Grains act as catalysts

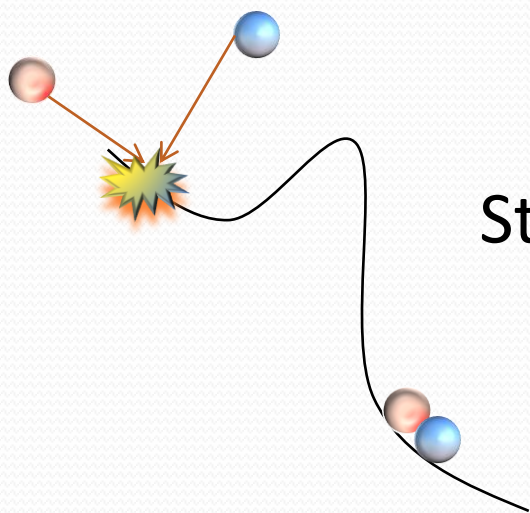
Chemistry on dust grains works when gas phase does not!



From gas to solid phase

In collision theory, the rate constant is:

$$k_r = \rho A_r (\mathcal{N}_a, \mathcal{N}_b, \sigma, v_{\text{rel}}) e^{(-E_r/RT)}$$

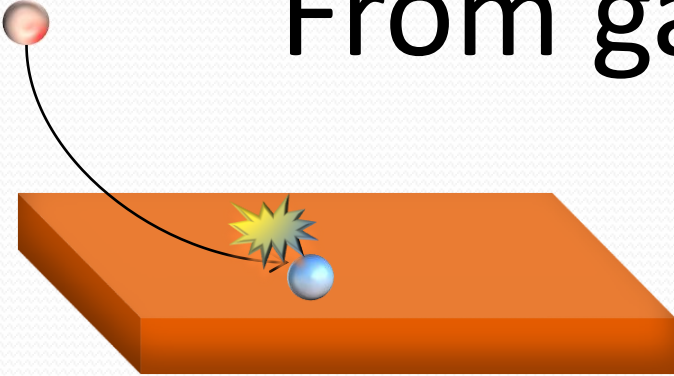


Steric factor

Collision frequency

Energy requirement

From gas to solid phase

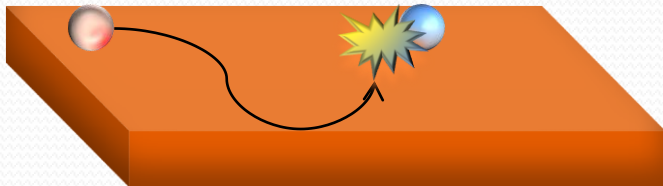


Eley-Rideal

$$k_r = \rho A_r e^{(-E_r/RT_{\text{system}})}$$

$$A_r (f_a, S_b, \sigma)$$

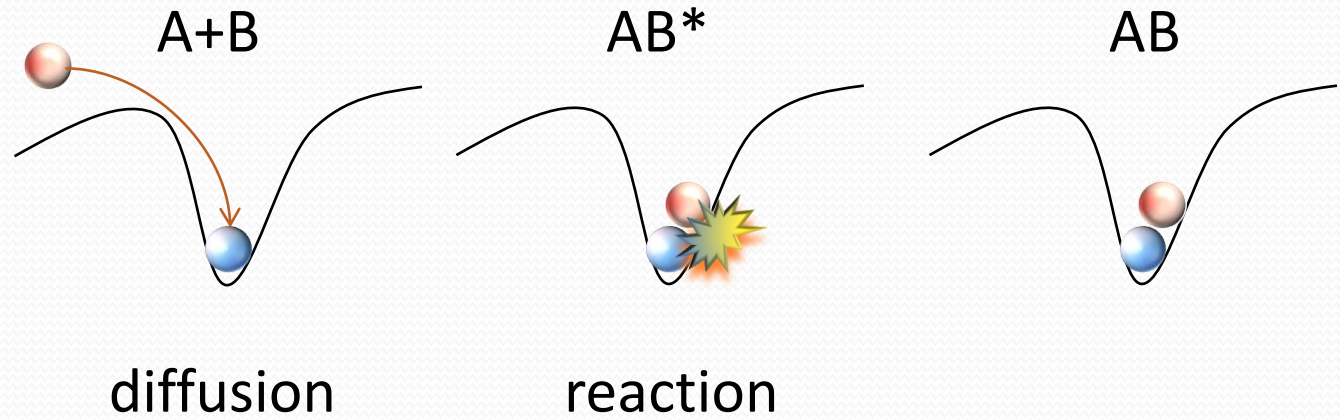
Langmuir-Hinshelwood



$$A_r (S_a, S_b, k_{d_{a,b}}, \sigma)$$

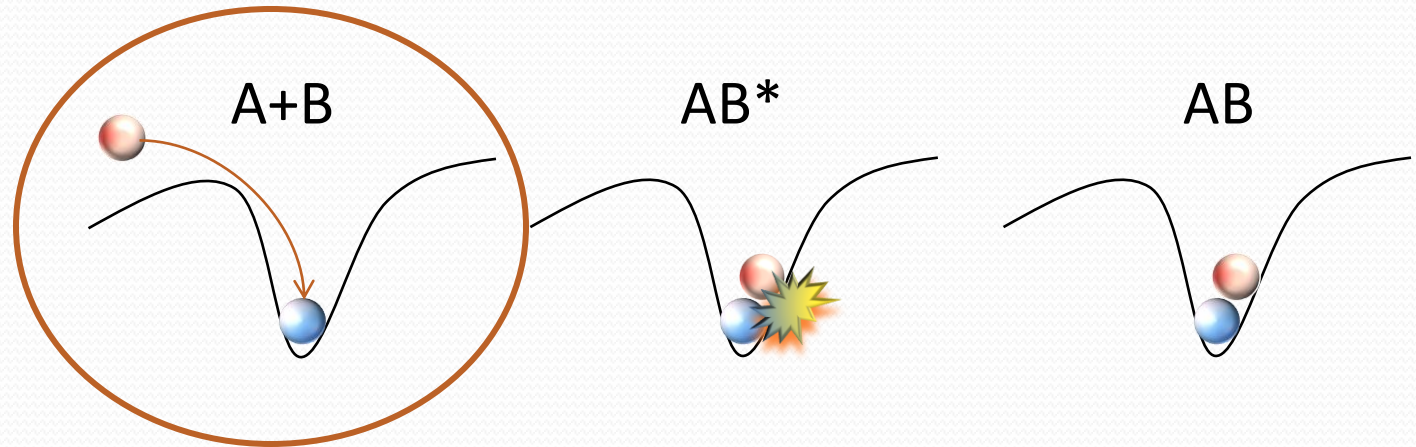
$$k_d = A_d e^{(-E_d/RT_{\text{system}})}$$

Two steps

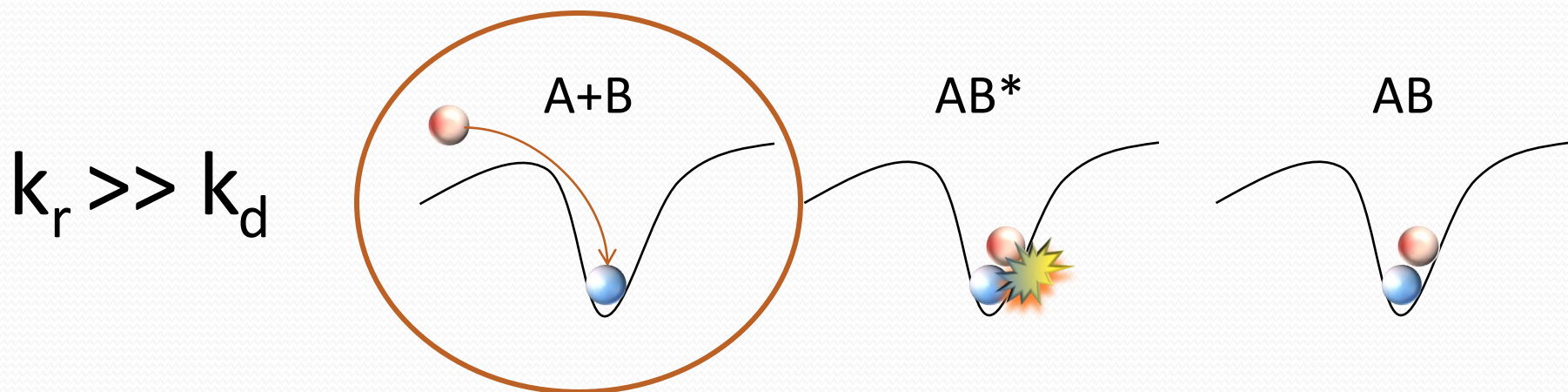


Diffusion-controlled reaction

$$k_r \gg k_d$$



Diffusion-controlled reaction

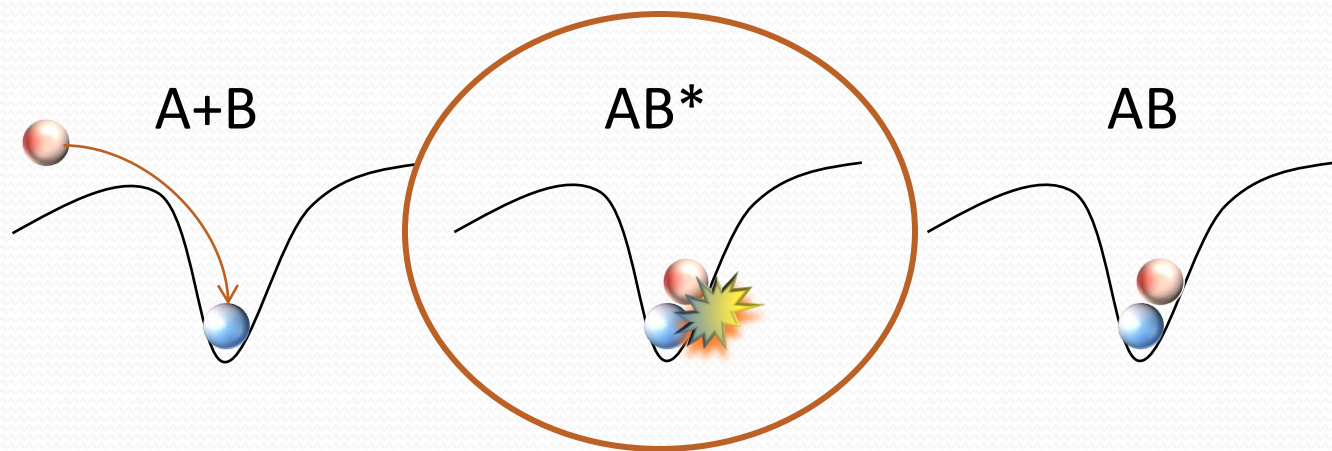


If $E_r \ll E_d$ or if the escape of molecules from the AB cage is difficult

The kinetics are dominated by k_d , and thus by the activation energy of diffusion.

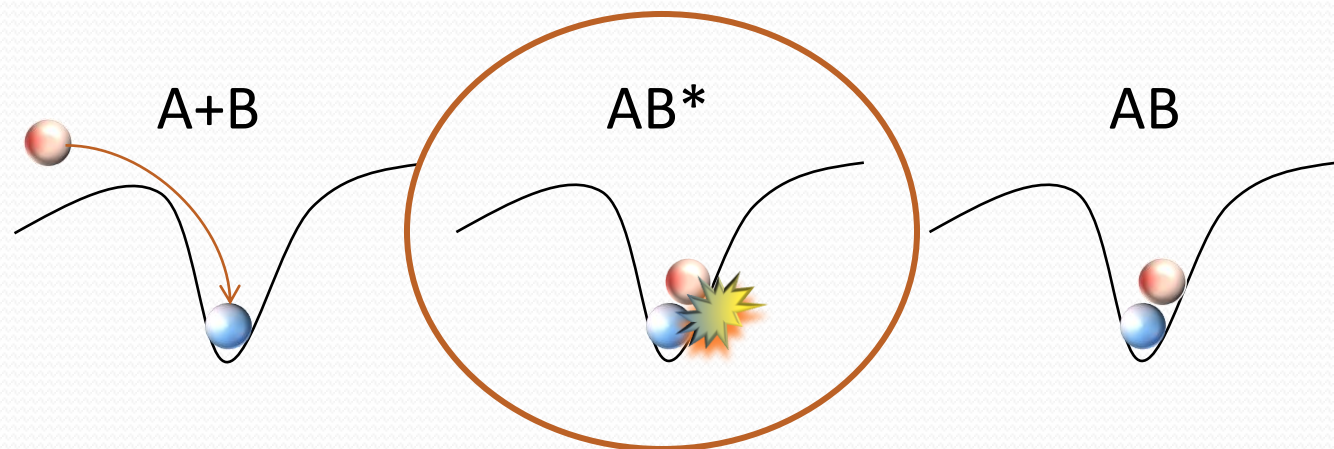
Activation-controlled reaction

$$k_r \ll k_d$$



Activation-controlled reaction

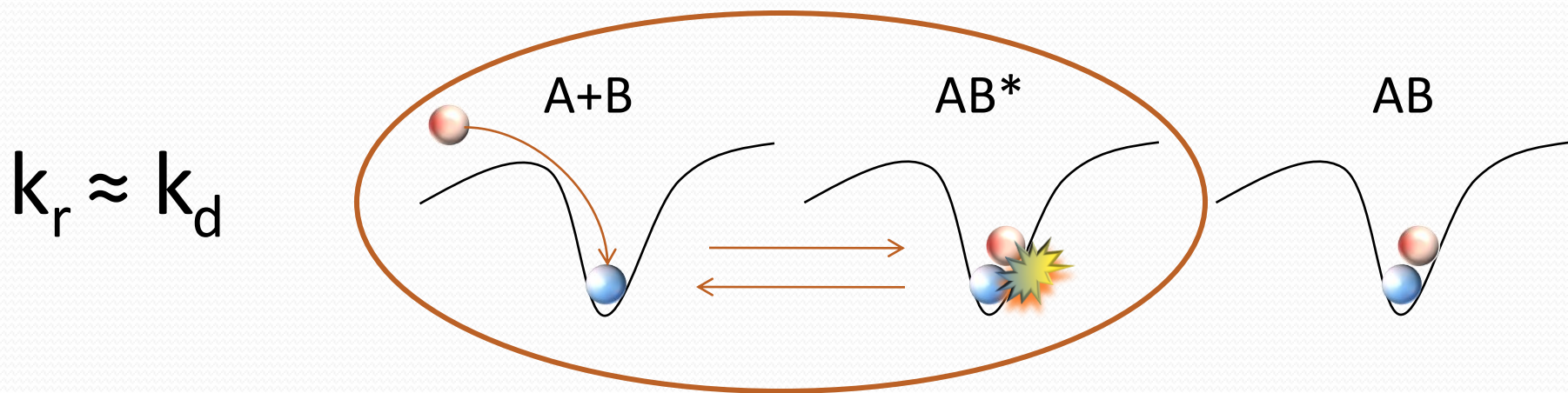
$$k_r \ll k_d$$



$$\text{If } E_r \gg E_d$$

The kinetics are dominated by k_r , and thus by the activation energy of reaction.

Diffusion supporting reaction



No simplification can be made
to determine $k_r \approx k_d$

1) Diffusion-controlled

$$E_r \rightarrow 0 \text{ K}$$
$$E_r/E_d \ll 1$$

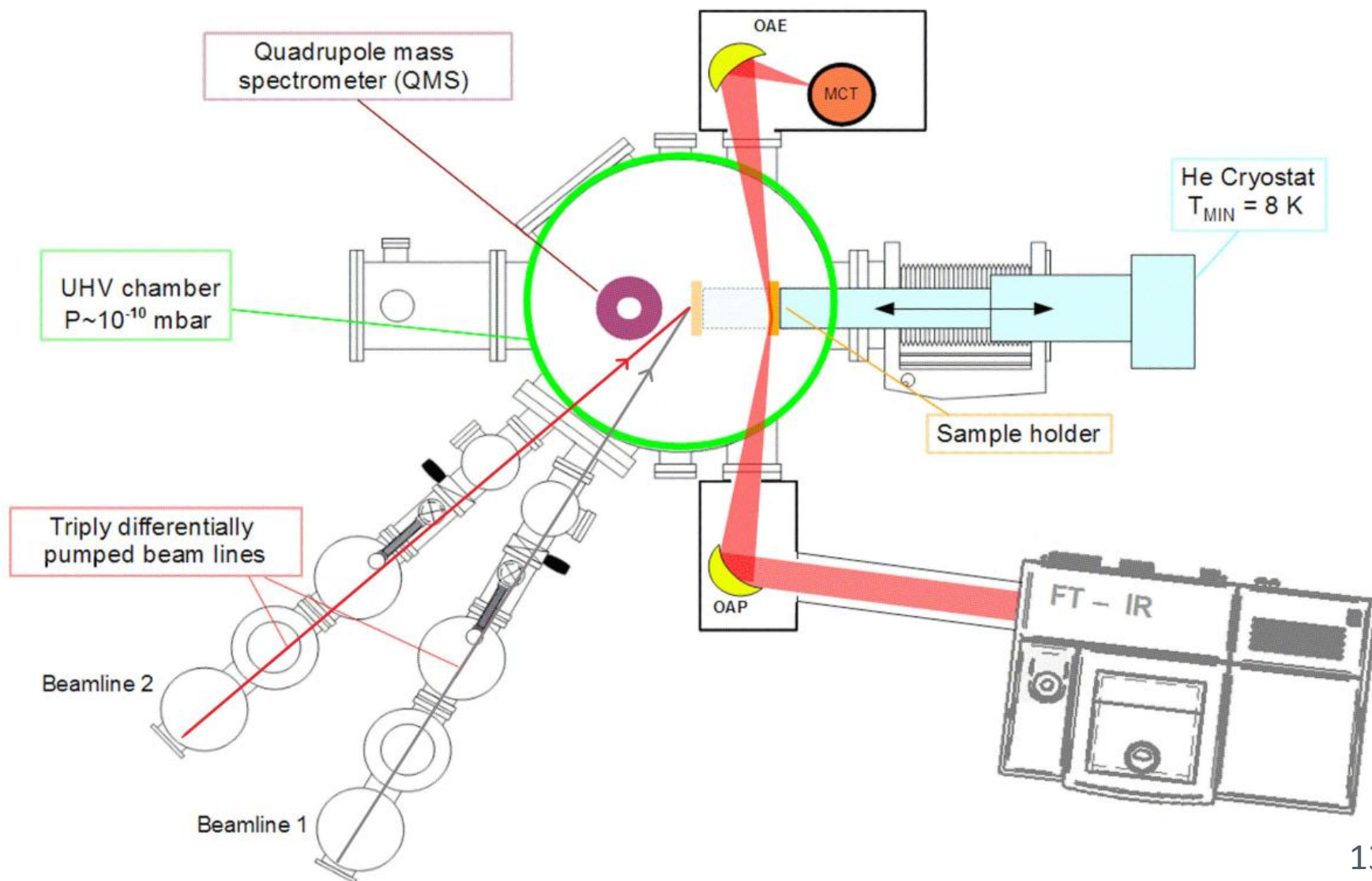
2) Activation-controlled

$$E_d \rightarrow 0 \text{ K}$$
$$E_r/E_d \gg 1$$

3) Diffusion supporting reaction

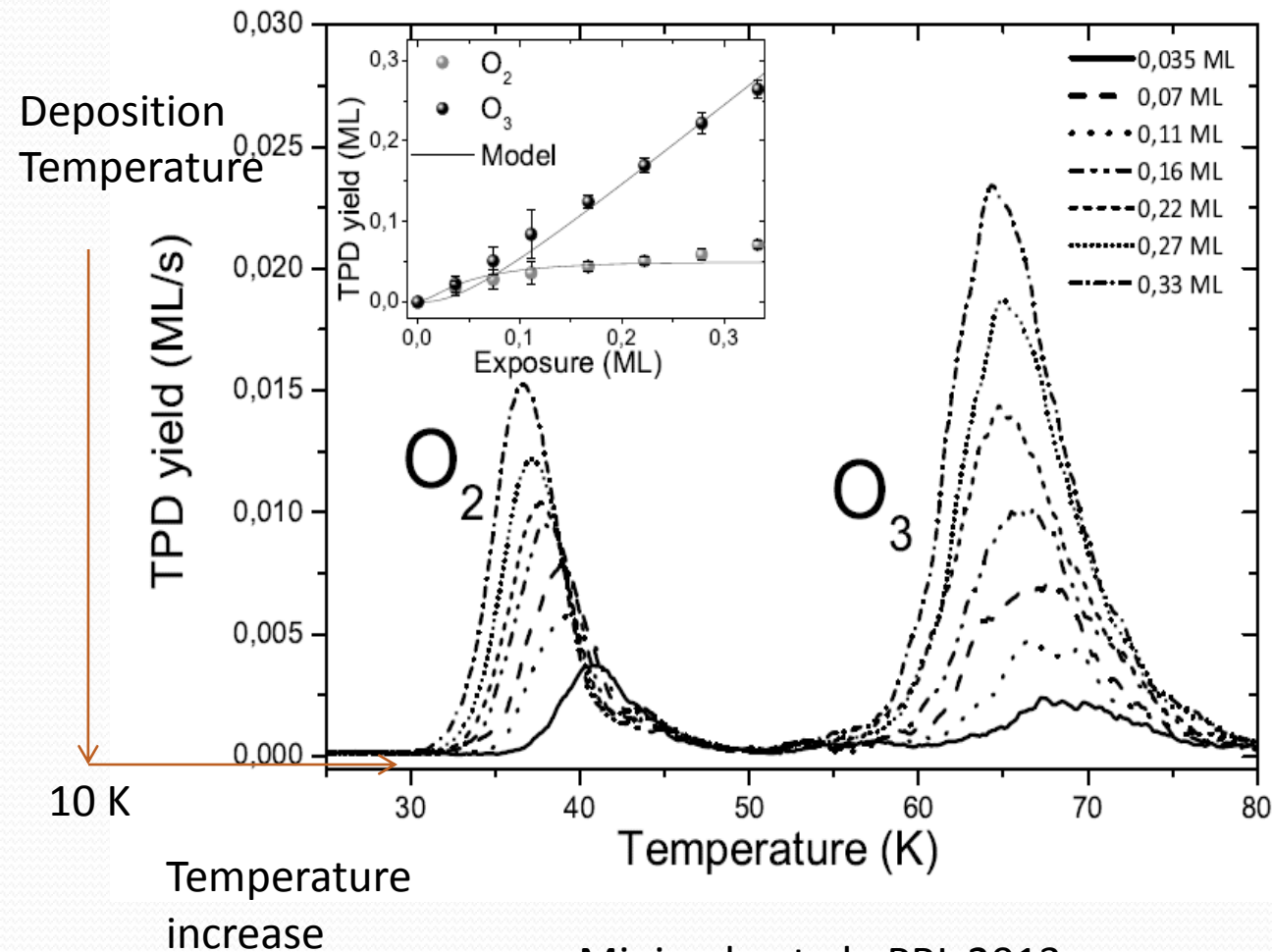
$$E_r/E_d \approx 1$$

FORMOLISM set-up



Diffusion-
controlled
reaction

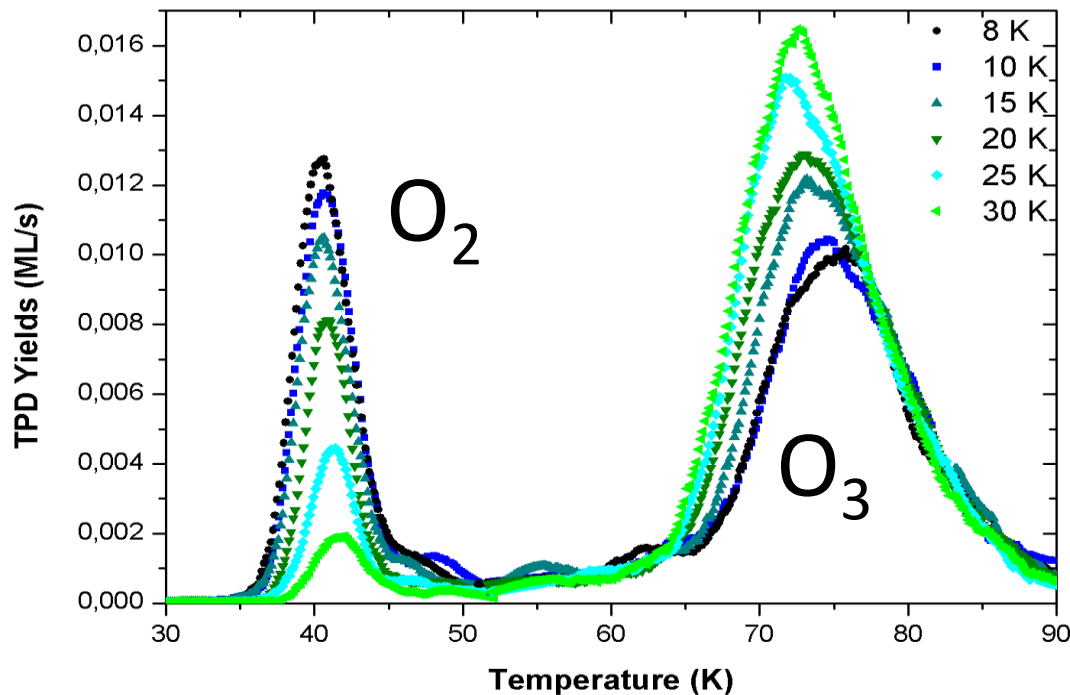
O+O and O+O₂



No O atoms
desorption

O₃ amount
increases, O₂
reaches a
steady state

Oxygen diffusion



O₃/O₂ ratio increases
with surface
temperature



O-diffusion increases
with surface
temperature

Minissale et al., JCP 2014

O+O and O+O₂

$$O'(t) = 2\tau\phi_O(1 - 2O - O_2) - (1 - \tau)\phi_O O$$

$$O'_2(t) = (1 - \tau)\phi_O(1 - O) - 2\tau\phi_O O_2 + 2\tau\phi_O O$$

$$O'_3(t) = (1 - \tau)\phi_O O + 2\tau\phi_O O_2$$

ER

$$E_r < 150 \text{ K}$$

$$O'(t) = -4kOO - kOO_2$$

$$O'_2(t) = 2kOO - kOO_2$$

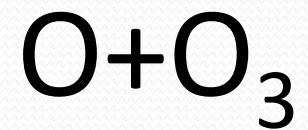
$$O'_3(t) = +kOO_2$$

LH

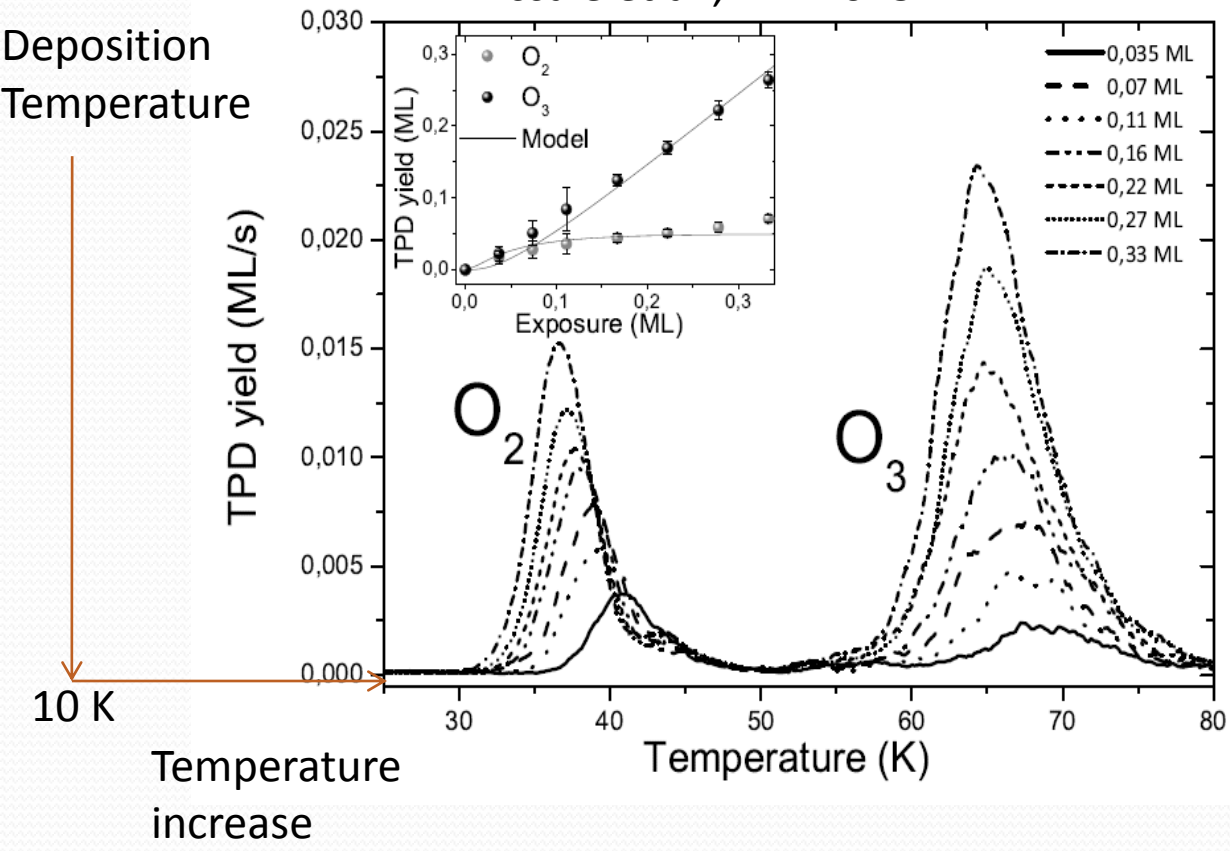
$$800 \text{ K} > E_d > 500 \text{ K}$$

$$E_r/E_d \ll 1$$

Activation-controlled reaction



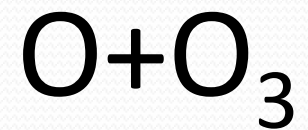
Minissale et al., PRL 2013



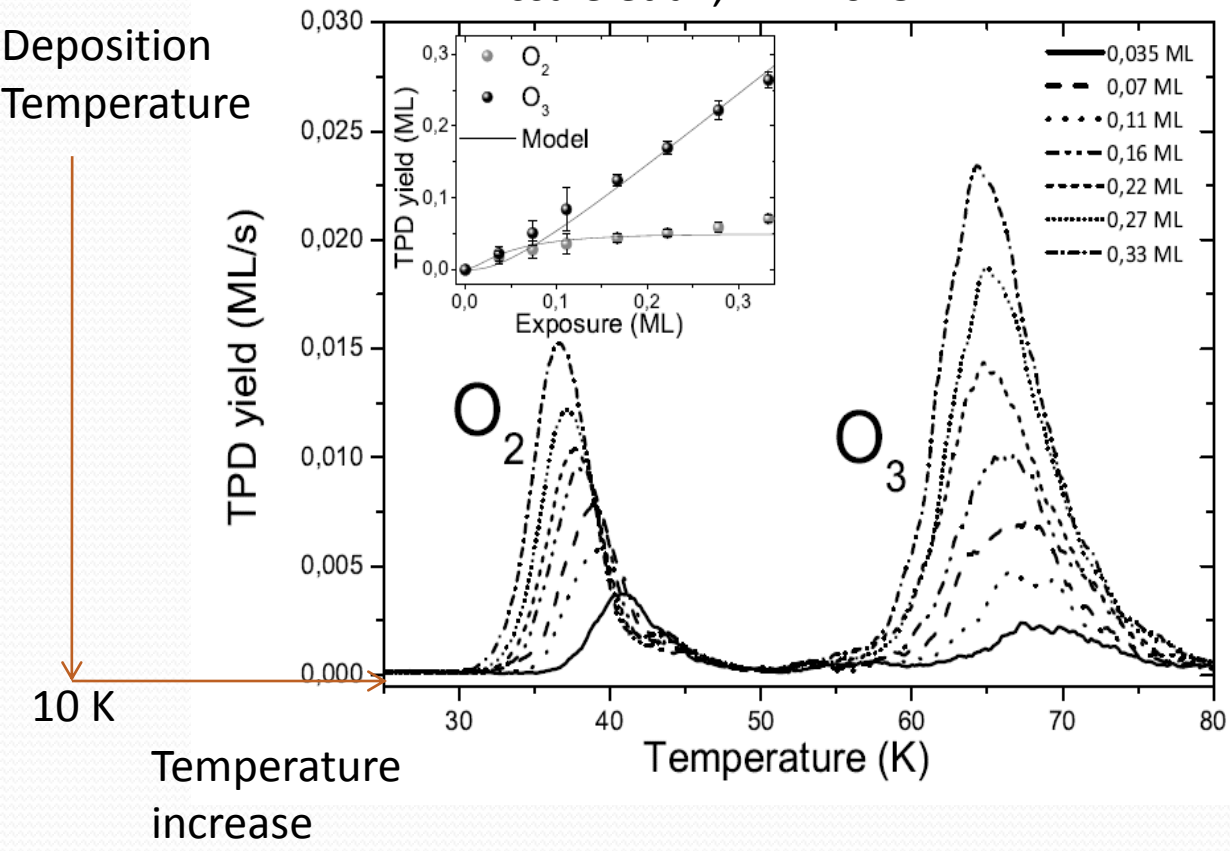
No O atoms desorption

O_3 amount increases, O_2 reaches a steady state

Activation-controlled reaction



Minissale et al., PRL 2013



$\text{O} + \text{O}_3$ barrier more than 2300 K

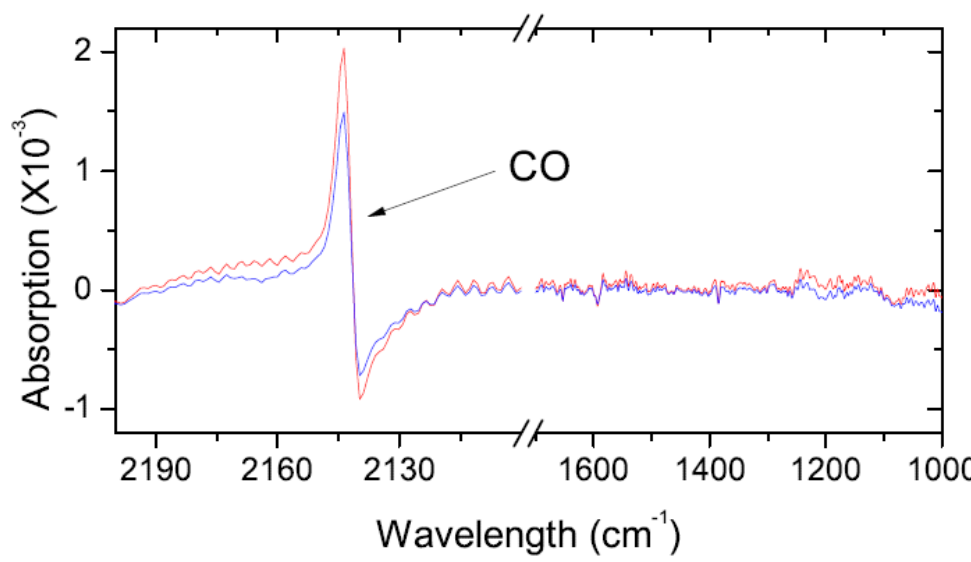
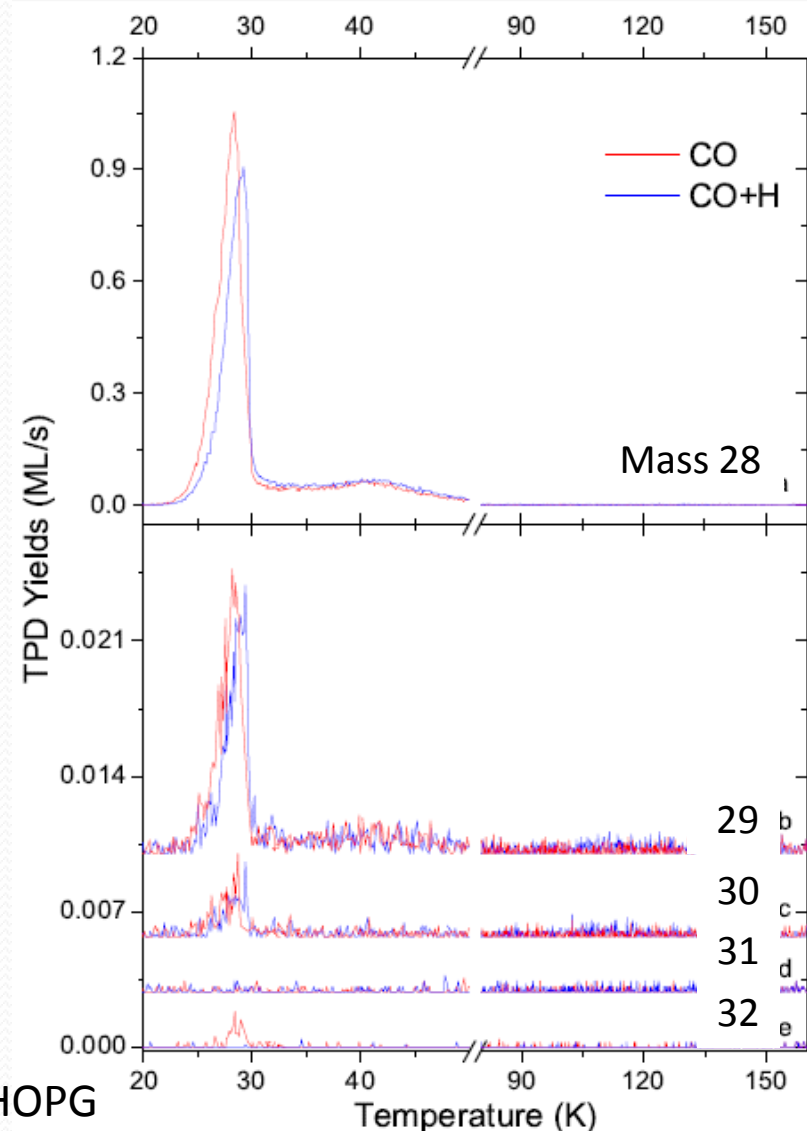
Mallard et al. 1997

$$E_r / E_d \gg 1$$

Activation-controlled reaction



Minissale et al, to be submitted



$$E_r = 1200 \text{ K}$$

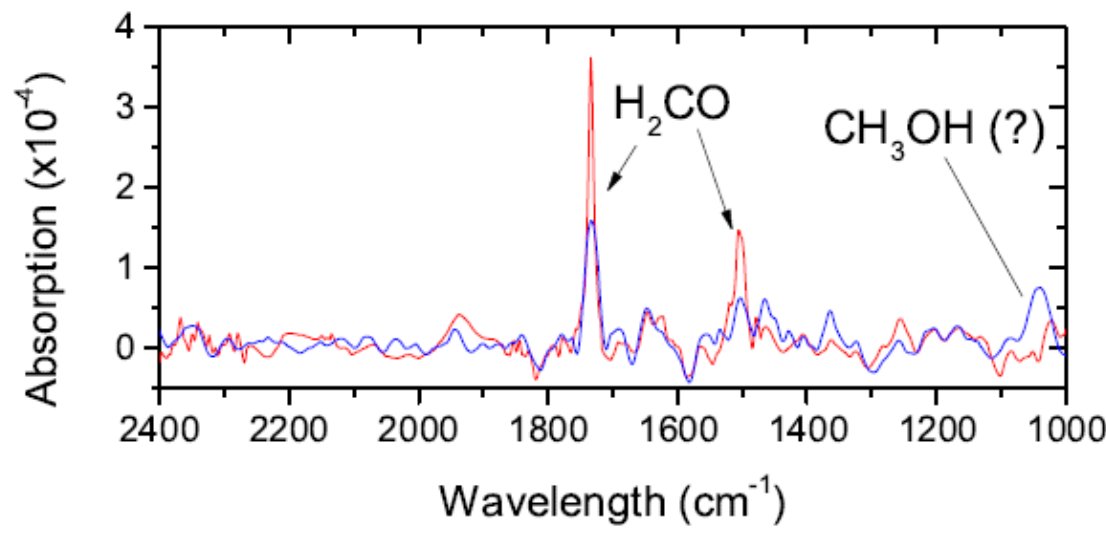
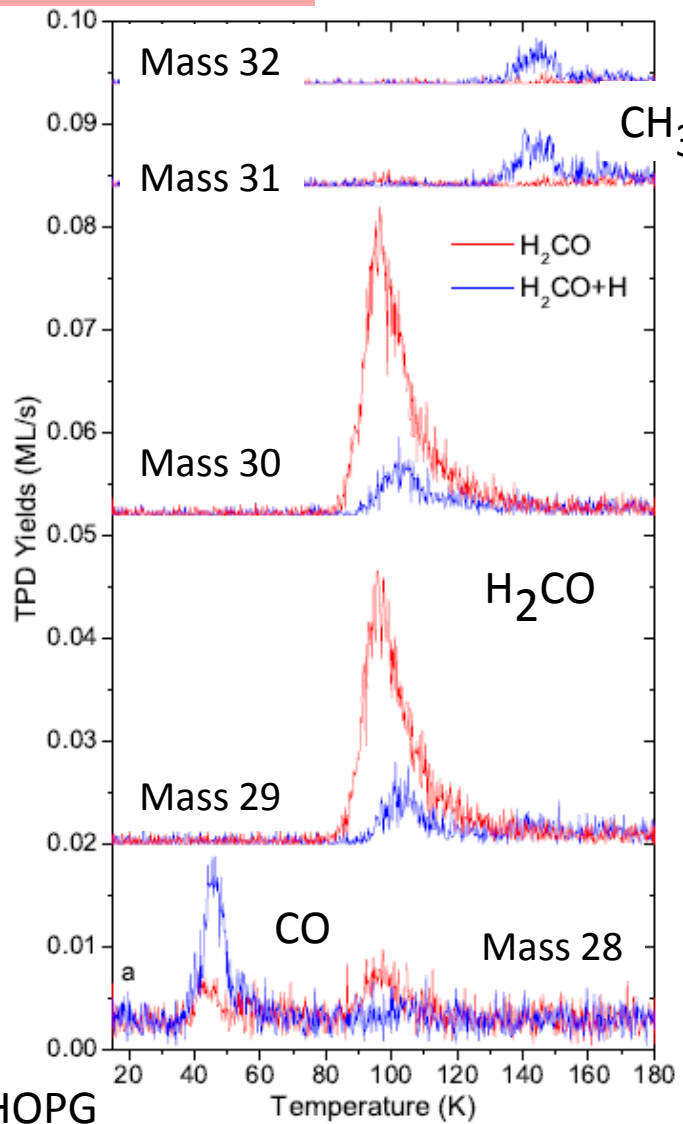
$$E_r / E_d \gg 1$$

On HOPG

Activation-controlled reaction



Minissale et al, to be submitted



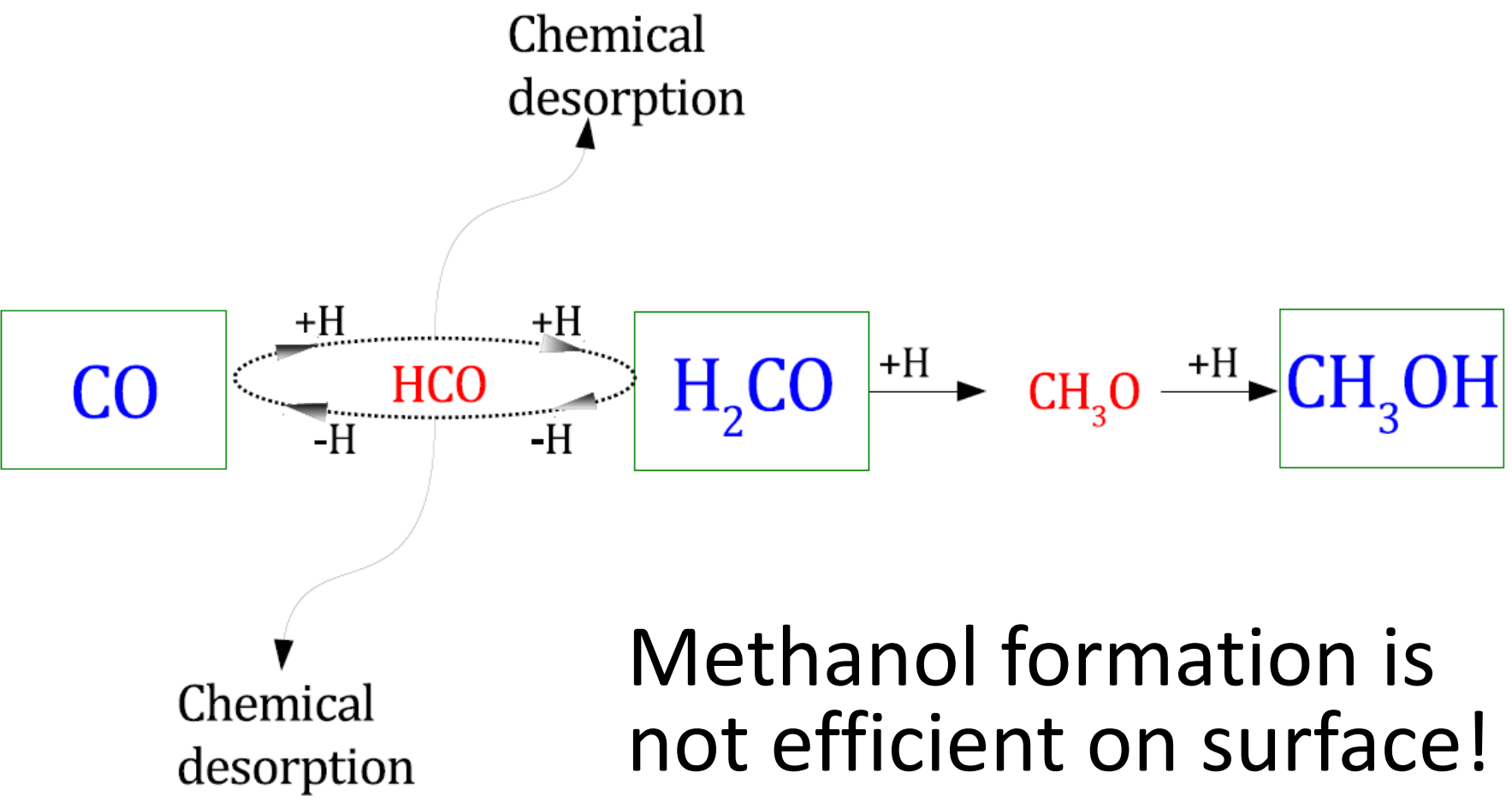
$$E_r = 900 \text{ K}$$

$$E_r / E_d > 1$$

Activation-controlled reaction



Minissale et al, to be submitted

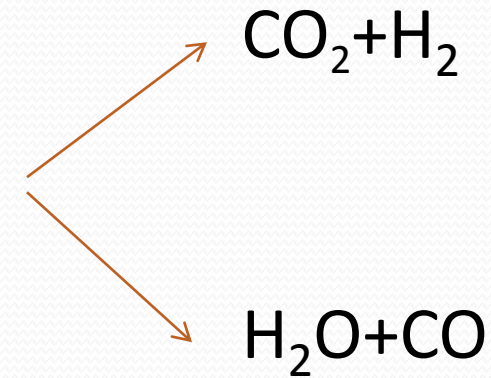


Methanol formation is not efficient on surface!



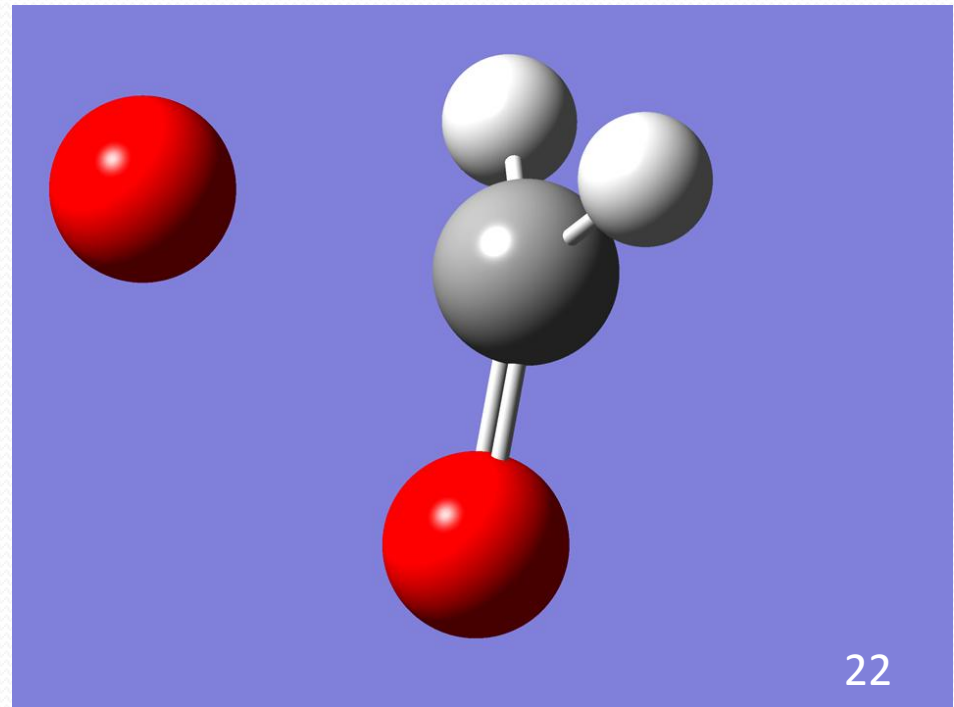
In gas phase $\text{H}_2\text{CO} + \text{O}$

Chang & Barker (1979)
Wellman et al. (1991)

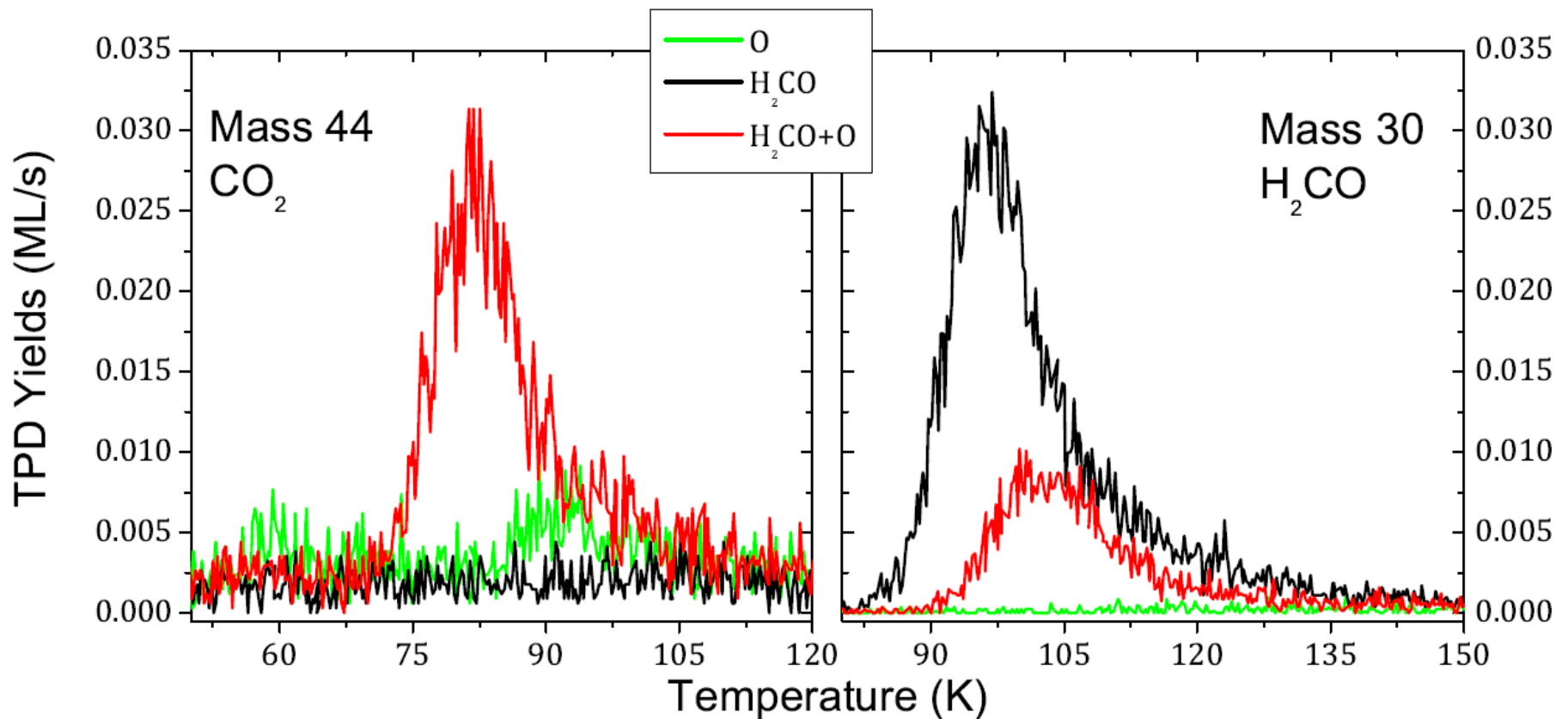


Barrier = 1560 K

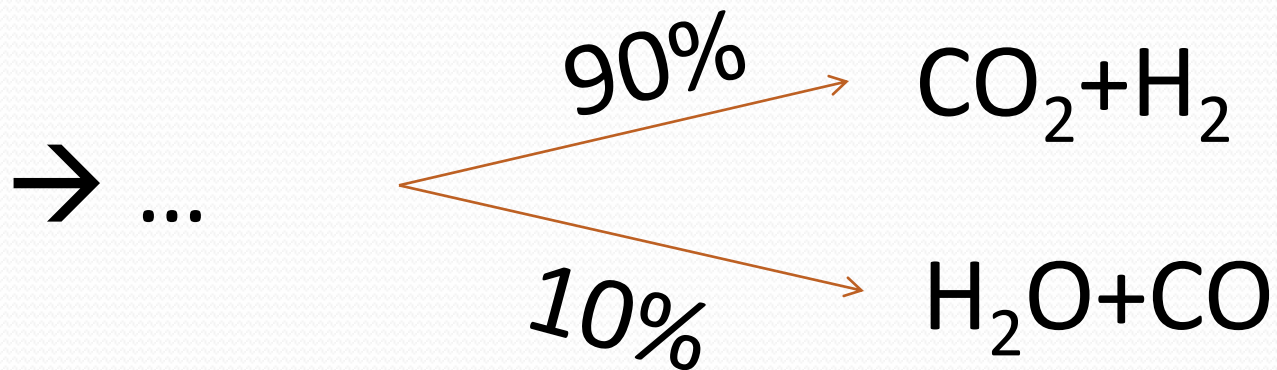
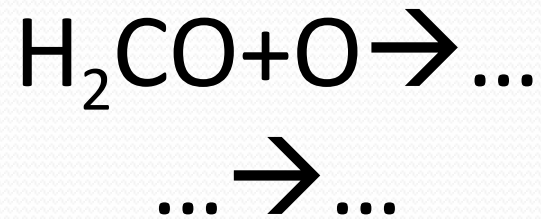
We present the first
experimental study
on solid phase for
 $\text{H}_2\text{CO} + \text{O}$



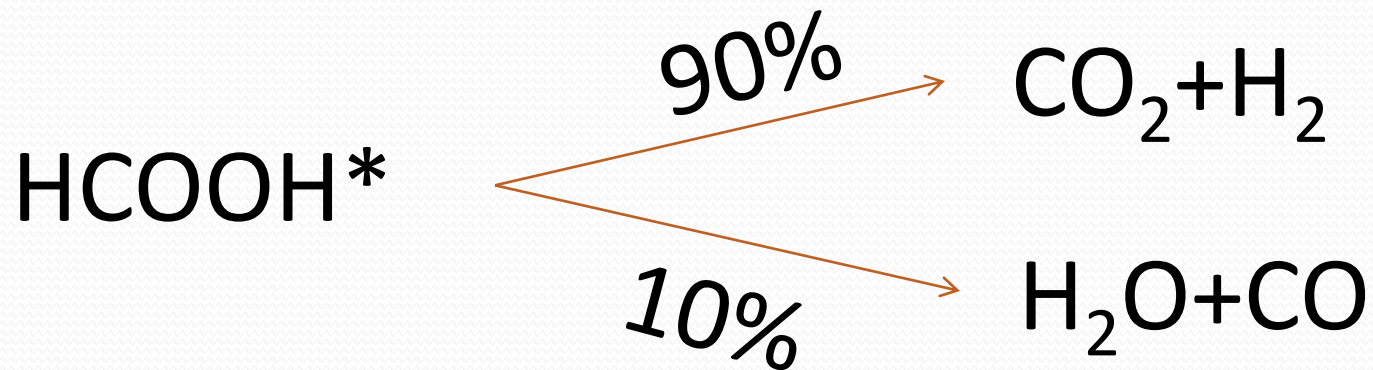
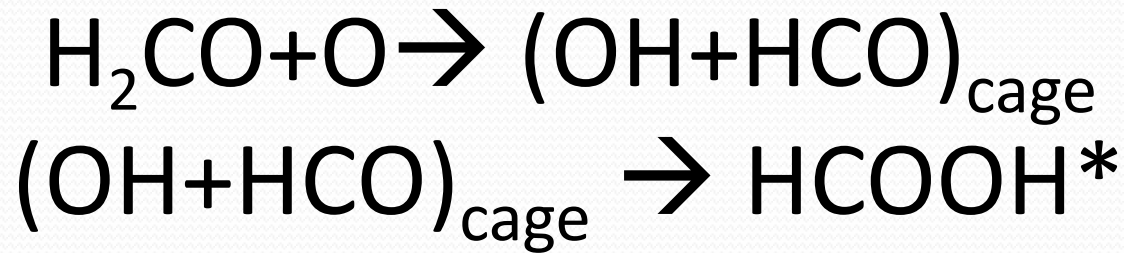
$\text{H}_2\text{CO} + \text{O}$ TPD results



$\text{H}_2\text{CO} + \text{O}$ Chemical network

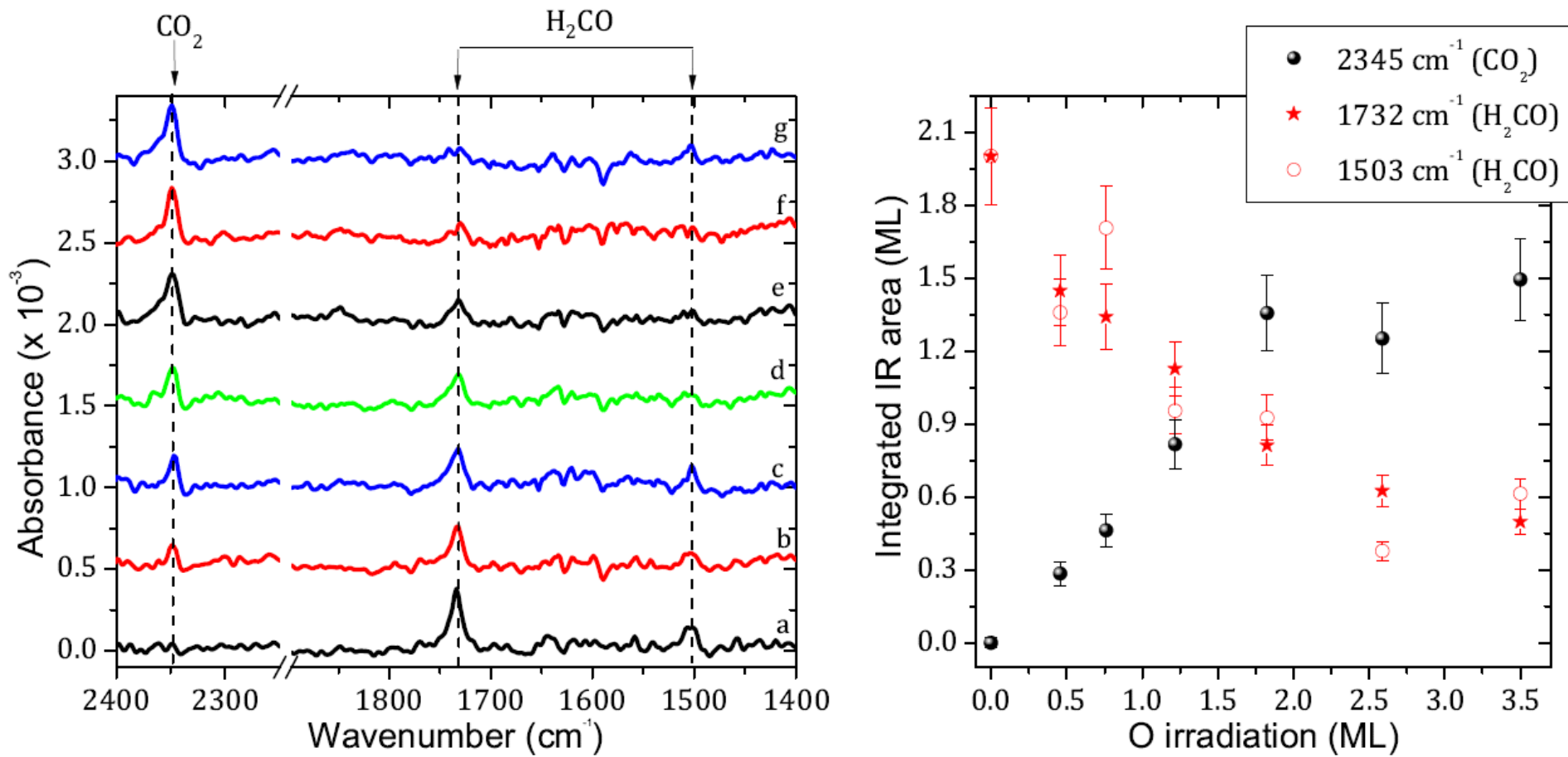


H_2CO+O Chemical network



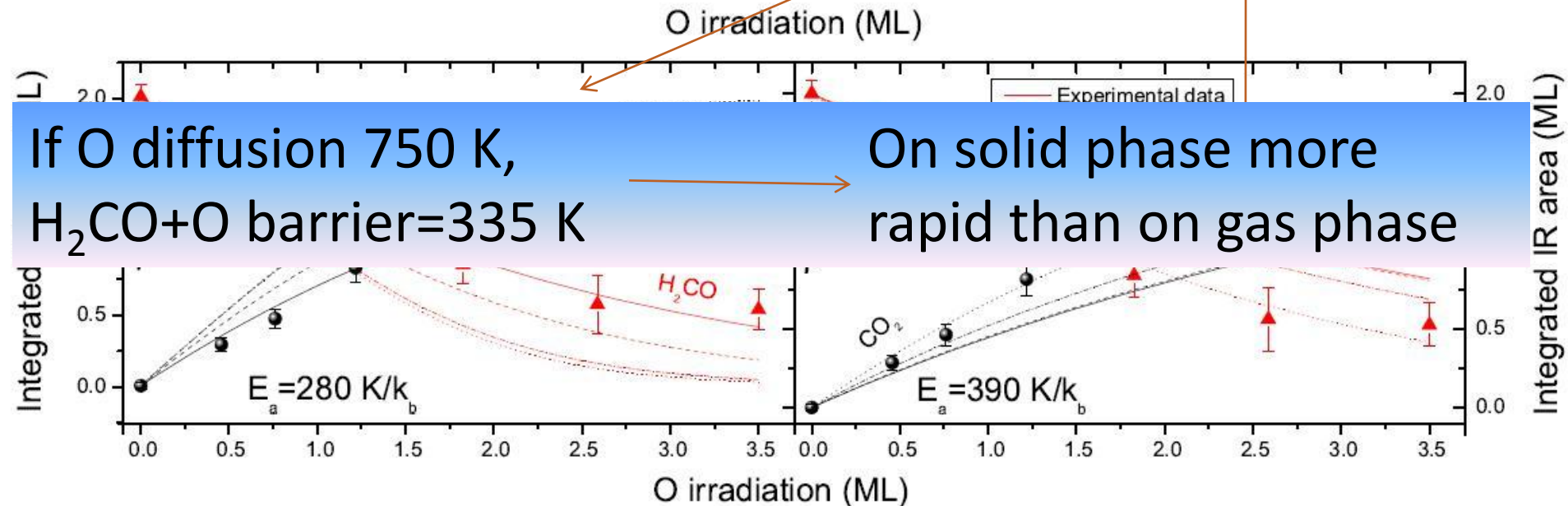
H₂CO+O

IR results @55K



Rate equations: barrier evaluation

- Two parameters: $\text{H}_2\text{CO}+\text{O}$ barrier and O diffusion
- O diffusion estimated to be between 900 and 600 K



Surface chemistry studies

Experimentally

- Kinetics of different reactions
- Products



- Disentangle Langmuir-Hinshelwood & Eley-Rideal mechanisms
- Estimate of diffusion and reaction barriers (model dependent)

Surface chemistry on KIDA

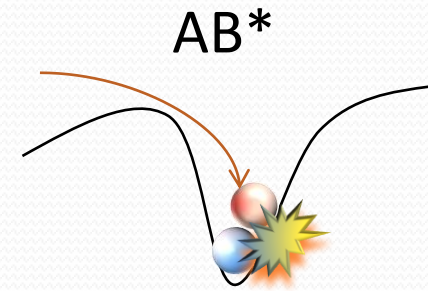
Reaction	Barrier	Surface
O+O O+O ₂ O+O ₃	0 K 0 K >2000 K	Water ice, Oxidized HOPG, Silicate
CO+O H ₂ CO+O	700 K 335 K	Water ice, oxidized HOPG
CO+H H ₂ CO+H CH ₃ OH+H	1200 K 700-800 K >2000 K	oxidized HOPG
O _x +H	...	Water ice, oxidized HOPG Silicate
NO _x +O _x NO _x +H NO _x +N	...	

Rescale barrier to your model

$$\text{Rate} = S_a S_b A_r \exp(-E_{d-a}/T) * P_{\text{reac}}$$

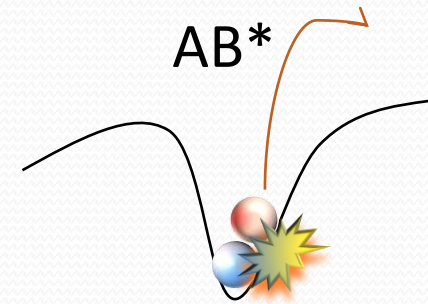
- $P_{\text{reac}} = \exp(-E_{r2}/T)$

Supporting

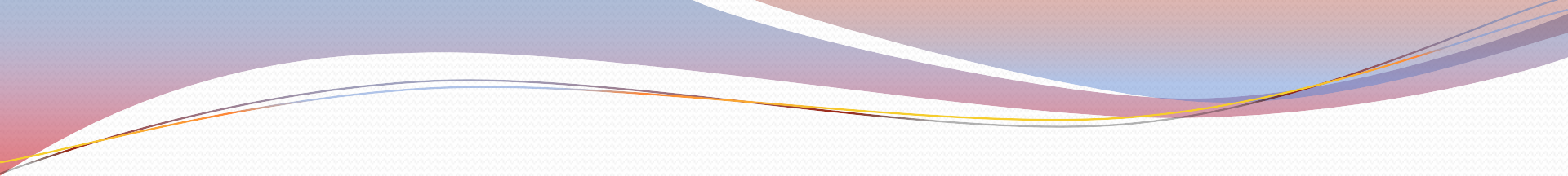


Competition

- $P_{\text{reac}} = \exp(-E_{r1}/T) / (\exp(-E_{r1}/T) + \exp(-E_{d-a}/T))$



So $\exp(-E_{r1}/T) / (\exp(-E_{r1}/T) + \exp(-E_{d-a}/T)) = \exp(-E_{r2}/T)$



I want to thank my colleagues: F.
Dulieu, S. Cazaux,
E. Congiu, S. Baoche, H. Chaabouni, V.
Pirronello, G. Manicò, A. Moudens and so on

Thank you for your attention