

A model to interpret the desorption of H and D from graphite

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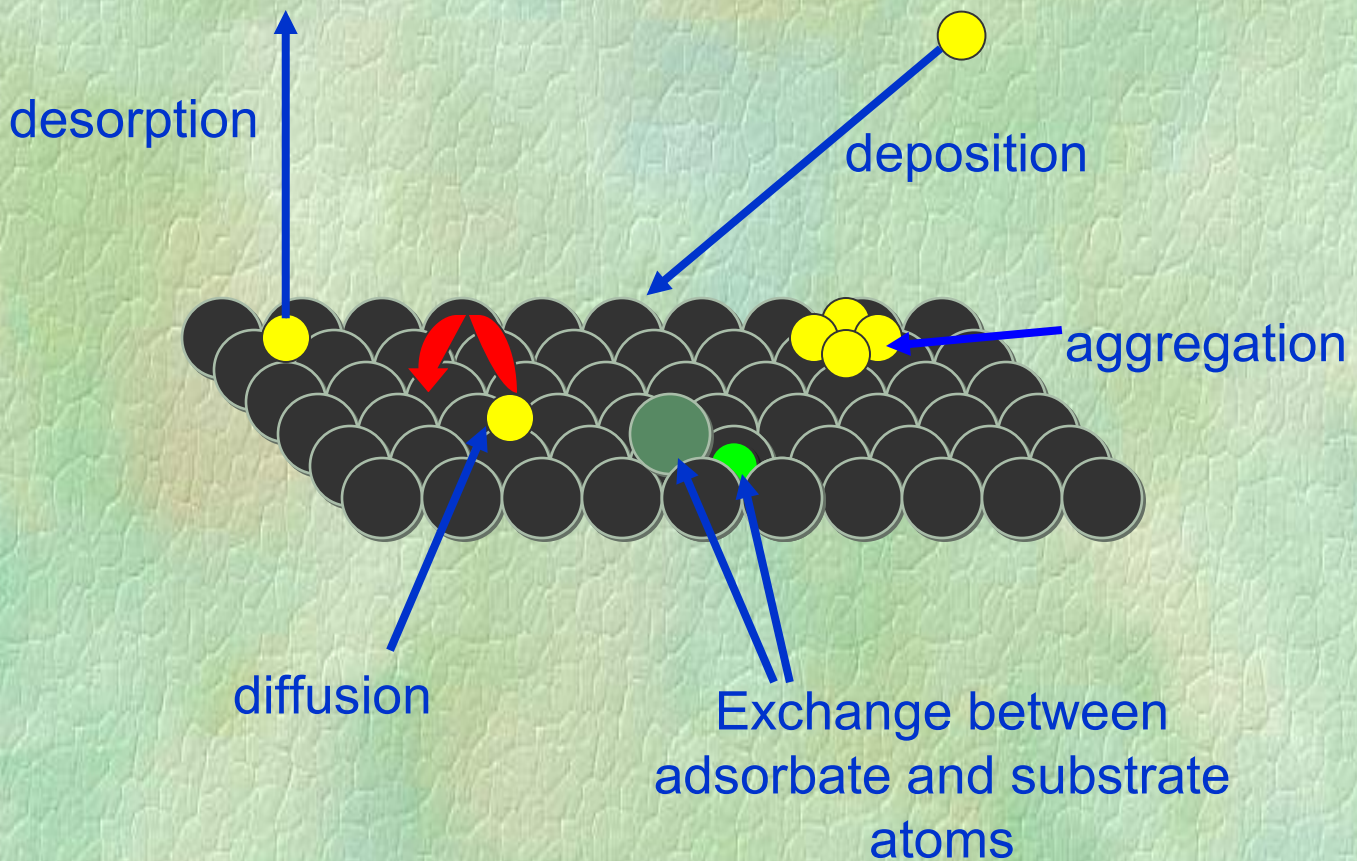
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Simulations of MBE experiments

Growth of atomic species adsorbed on surfaces is mainly governed by random processes.



Ingredients in KMC and assumptions

1. Deposition is governed by **the flux F (ML/s)**.

- Monomers H or D
- Monoenergetic $E_{\text{incident}} = E_i$ (the most probable in M.B. distribution)

2 assumptions

Instantaneous thermalization



Only monomer deposition is allowed at E_i fixed



- on the surface, the impinging H (D) has to jump over the adsorption barrier E_a with a probability described by an Arrhenius law
- E_A is site dependent (monomer or dimers)

KMC ingredients and assumptions

2. Diffusion and Desorption are governed by Arrhenius law

- depend on prefactors fixed by the relation

$$v_{D,E} = \frac{kT_m}{h}$$

- Depend on barriers calculated from DFT

$$P_{D,E} = v_{D,E} e^{-\frac{E_{D,E}}{kT}}$$

3. The detection of evaporated species : We consider only particles which leave the surface

Sump up of KMC

Atomic growth is governed through the competition of different processes :

DEPOSITION



F, T, E_A

DIFFUSION
DESORPTION



T, E_E, E_D

DIMERIZATION



$T, E_A(s)$

Several internal parameters : **potential barriers.**
⇒ Necessary to have improved ab initio calculations

Several hypotheses which have a practical use in KMC to simplify discussion, but which can strongly influence the results when compared to experiments.

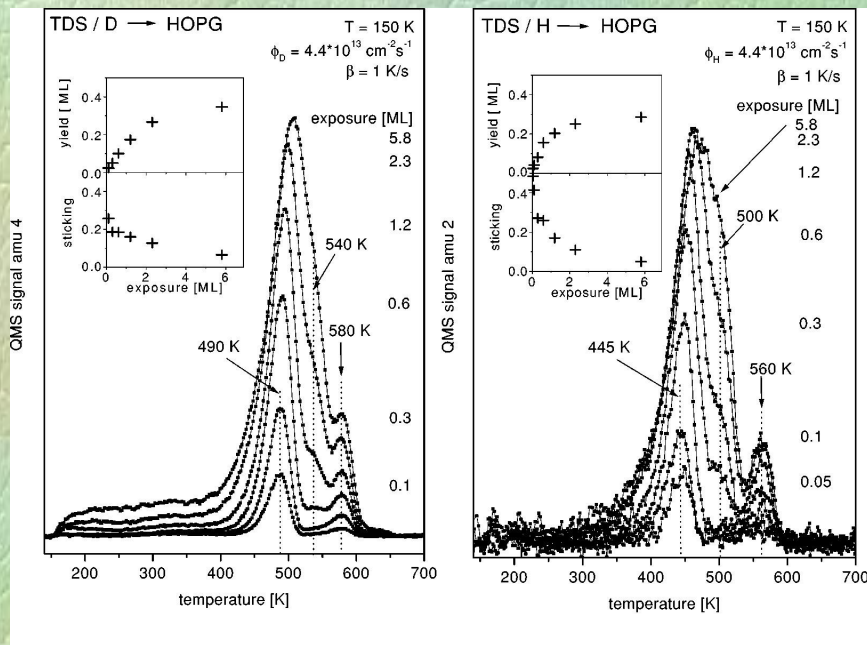
See Cupen and Hornekaer (J. Chem. Phys. 2008)

What is known about this topic

TDS experiments

H or D coverage vs exposure at $T=150\text{K}$ and $F=10^{-2}\text{ MLs}^{-1}$
Sticking $=0.4\pm 0.2$

- The desorption spectrum exhibits two peaks at 500 and 570 K with an isotopic dependence which is different for the two peaks (Zecho et al. , JCP 117, 8486 (2002))



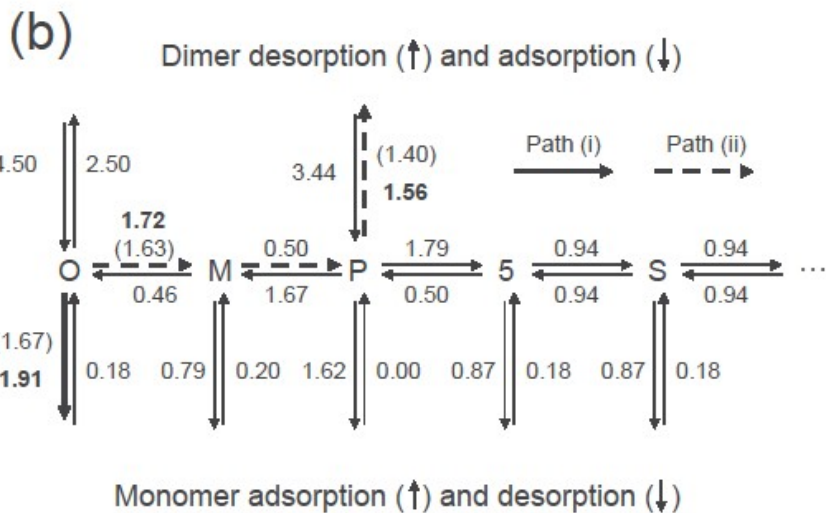
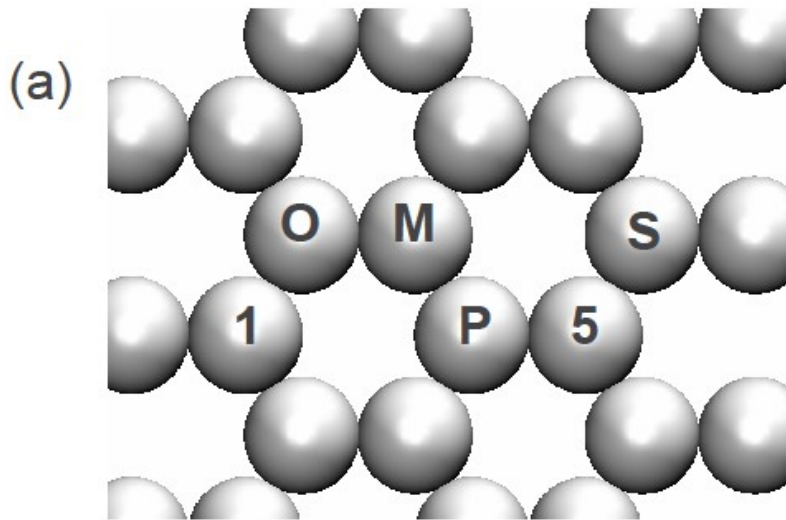
STM data

- para and ortho dimers play a crucial role, their behavior with T can interpret the two peaks occurrence (Hornekaer et al. , PRL 96, 156104; 97 186102 (2006))

DFT

•calculations for the barrier values

(Jeloaica et al CPL 300, 157 (1999) , Rougeau et al; CPL 431, 135 (2006), Ferro et al JCP 116, 8124 (2002), 120, 1182 (2004), Hornekaer et al.)

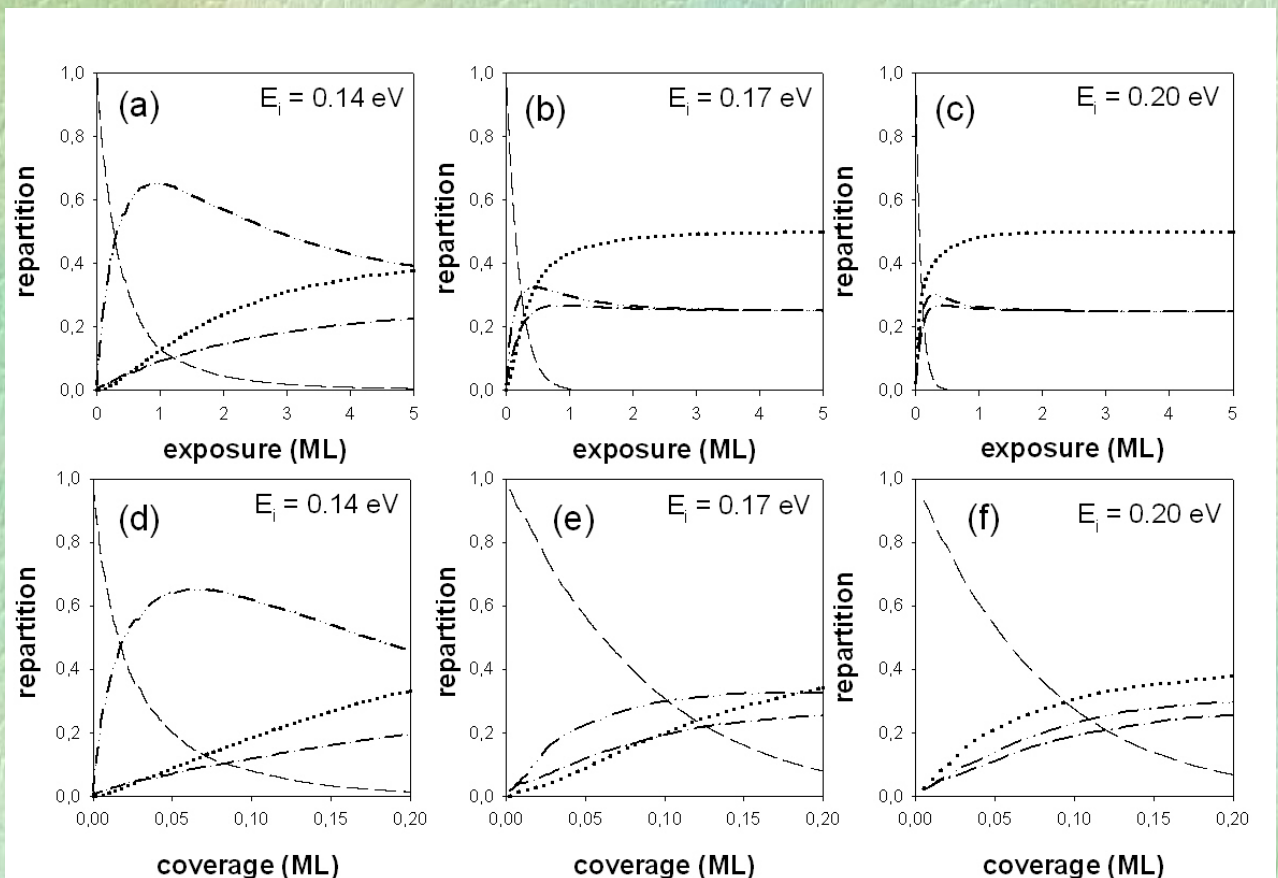


The adsorption process in our KMC

$\forall \Delta E = E_A - E_i$ governs the adsorption at low coverage ($\theta < 0.2$ ML)

- $E_A = 0.18$ eV for the monomer and orthodimer, $E_A = 0$ for the paradimer and $E_A = 0.2$ eV for the metapair $\rightarrow E_i = 0.17$ eV to be consistent with sticking experiments.

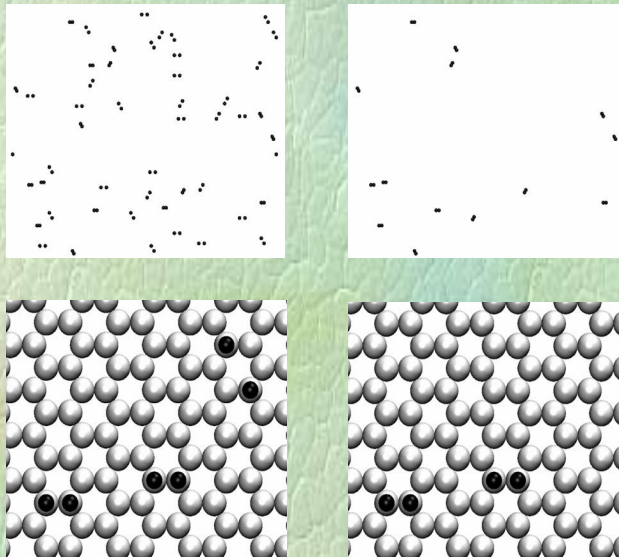
- The proportion of monomers and dimers on the surface is sensitive to the various ΔE (adsorption of a monomer atom, adsorption in dimer configurations)



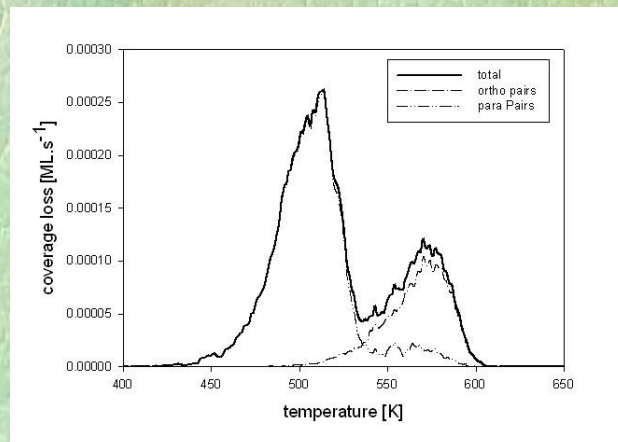
Diffusion and desorption : Competitive processes ?

KMC snapshots of 0.1 ML of H atoms deposited with $E_i=0.17$ eV show :

- At 400 K, no monomer, mainly para and ortho dimers coexist in the ratio $\frac{1}{2}$
- At 540 K, only ortho dimers are observed



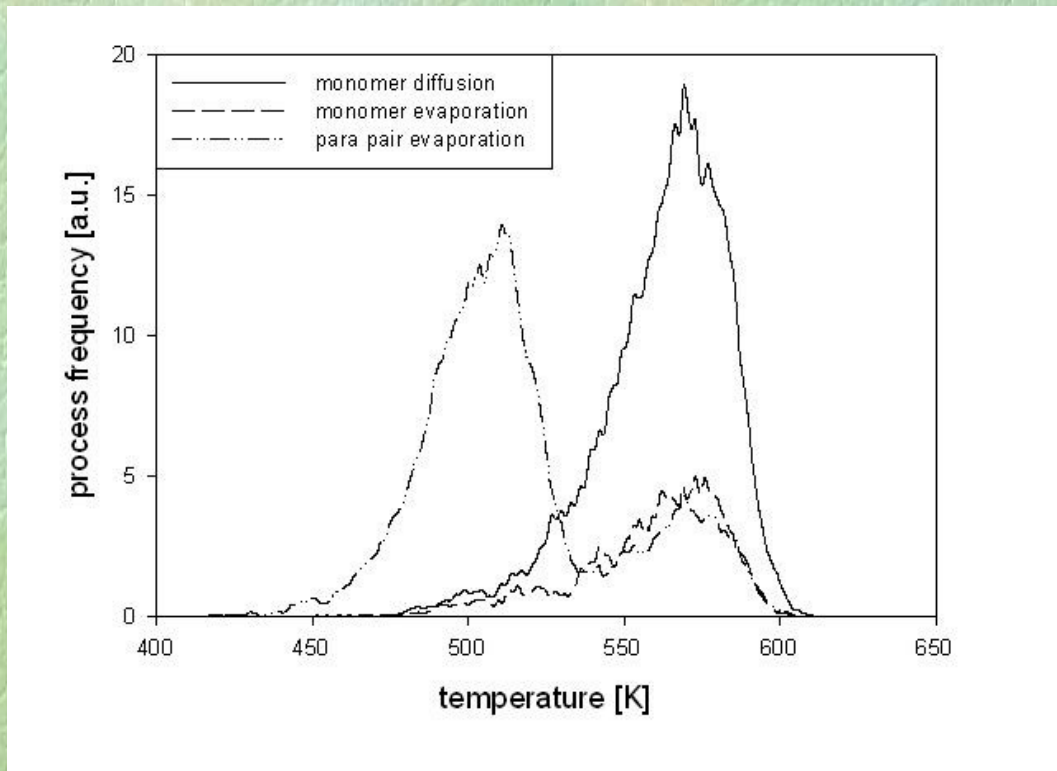
- Two peaks occur in the coverage loss (ML s^{-1}) for $400 < T < 600$ K



Diffusion and desorption : Competitive processes ?

- For $450 < T < 530$ K, orthodimers are stable while paradimer desorption proceeds according to 3 paths
 - Evaporation of one H in the pair ($E_{EE}=1.62$ eV)
 - Diffusion of one H toward meta or 5 ($E_D=1.67$ or 1.79 eV)
 - Direct evaporation ($E_E=1.40$ eV) : the main efficient path !
- For $T > 530$ K, competition between reaction paths leading to the occurrence of the second peak around 570 K
 - Direct evaporation of one H in the orthopair ($E_E=1.67$ eV) followed by the evaporation of the remaining monomer ($E_E=0.87$ eV)
 - ii) Diffusion of one H toward meta ($E_E=1.63$ eV) followed by diffusion toward para (0.46 eV) and evaporation of the newly formed parapair
 - iii) Diffusion of one H toward meta ($E_D=1.63$ eV), followed by evaporation of one H of the metapair ($E_E=0.79$ eV) and evaporation of the remaining monomer
 - iv) Diffusion of one H toward meta ($E_D=1.63$ eV) followed by diffusion from meta to ortho ($E_D=0.46$ eV) to recover the initial situation

Diffusion and desorption : Competitive processes ?



Large monomer diffusion in the three paths ii), iii), iv)

Presence of parapairs due to the diffusion, though they disappear below 530 K

Resulting scenario : 18% of path i)) ; 41% to each of paths ii) and iv) contributions to the orthodimer disappearance on the surface

Diffusion and desorption processes : influence of isotopic change

TDS experiments :

- H : two peaks at 445 and 560 K
- D : two peaks at 490 and 580 K

$$\Delta T_1 = 45 \text{ K} , \Delta T_2 = 20 \text{ K}$$

Simulations:

- Initial barriers $E_{E,D}$ become effective barriers

$$E_{D,E}^* = E_{D,E} - \frac{1}{2} \sum_s \hbar \omega_s$$

- frequencies are issued from EELS (Zecho et al) and from lattice dynamics calculations (Morisset et al, J. Chem. Phys. 2008)

Barrier to	Initial	H	D
Para pair desorption	1.4	1.08	1.20
Ortho monomer desorption	1.67	1.34	1.47
Diffusion ortho to meta	1.63	1.52	1.55

- The new barriers are too low !
- ΔT is the same for the 2 peaks

Diffusion and desorption processes : influence of isotopic change

A solution to this discrepancy with experiments

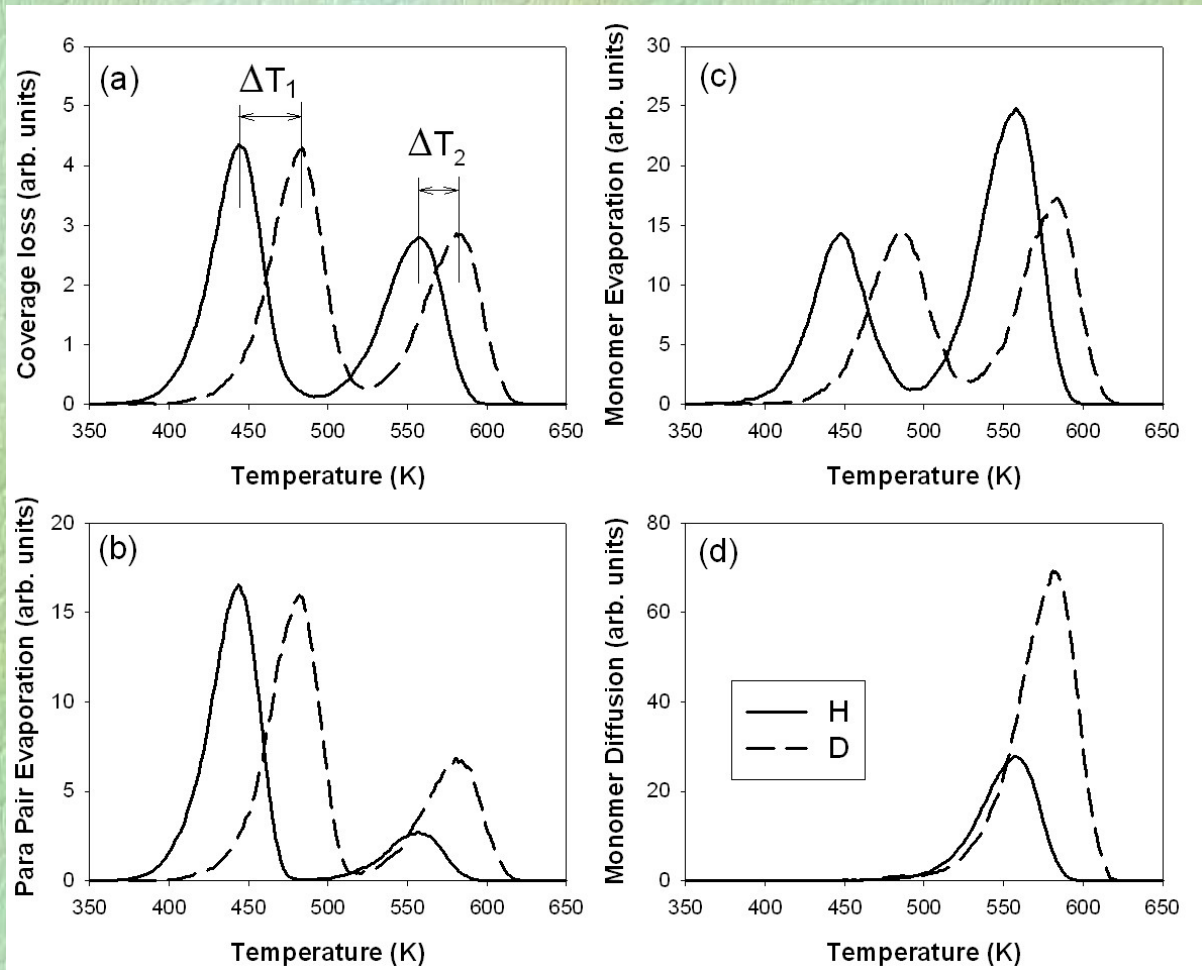
The first peak is well interpreted for both H and D

The second peak is due to different desorption processes for H and D

Barrier to	Initial	H	D
Para pair desorption	1.56	1.23	1.36
Ortho monomer desorption	1.91	1.58	1.71
Diffusion ortho to meta	1.72	1.61	1.64

- With these new barriers, the second peak is due to
- for H, a competition between desorption of H orthodimer and its diffusion to meta dimer. Two likely probable processes
 - For D, the diffusion from ortho to meta dimer is largely favored

Diffusion and desorption processes : influence of isotopic change



We find a nice agreement with experiments

$$\Delta T_1 = 38 \text{ K}$$

$$\Delta T_2 = 25 \text{ K}$$

Rate equations approach

More flexible than KMC

Allows to study larger coverage (trimers) to interpret high temperature shoulder of the main peak

System of coupled equations

-densities of species $n_X, X=1,5,P,M,O,T$

-efficiency of processes A_X, D_{XY}, E_X, E_{XX}

-number of equivalent configurations

-number of trimers formed from a dimer $g_Y (Y=P,M,O)$

-coverage $\theta = n_1 + 2(n_5 + n_P + n_M + n_O) + 3n_T$

$$\frac{dn_1}{dt} = A_1(1 - \alpha\theta) - (6A_5 - 3A_P - 6A_M - 3A_O)n_1 + 2\left(\sum_{X \neq 1,T} n_X E_X - n_1 E_1\right) - 18D_{15}n_1^2 + 6D_{51}n_5$$

$$\frac{dn_5}{dt} = (6A_5 - 3D_{51} - D_{5P})n_5 - 2n_1 E_5 + 9D_{15}n_1^2 + 2D_{P5}n_P$$

$$\frac{dn_P}{dt} = (3A_P n_1 + D_{5P} n_5 + 2D_{MP} n_M) - (2E_P + E_{PP} + 2D_{P5} + 4D_{PM})n_P + g_P(3n_T E_T / \sum_Y g_Y - n_P A_T)$$

$$\frac{dn_M}{dt} = (6A_M n_1 + 4D_{PM} n_P + 4D_{OM} n_O) - 2(E_M n_M + D_{MP} n_M + D_{MO} n_P)$$

$$+ g_M(3n_T E_T / \sum_Y g_Y - n_M A_T)$$

$$\frac{dn_O}{dt} = (3A_O n_1 + 2D_{MO} n_M) - (2E_O - E_{PO} - 4D_{OM})n_O$$

$$+ g_O(3n_T E_T / \sum_Y g_Y - n_O A_T)$$

$$\frac{dn_T}{dt} = (g_O A_T - 3E_T)n_T + g_M A_T n_M + g_P A_T n_P$$

Rate equations approach

The corresponding coverage loss for H and D, including the presence of trimers

Nice agreement with experiments

No picture here.....please believe us or try to find our stolen notebook !

Conclusion :

- We are aware that our approach is oversimplified and that some hypotheses should be removed
- This problem is still largely opened (more accurate experiments and DFT informations)