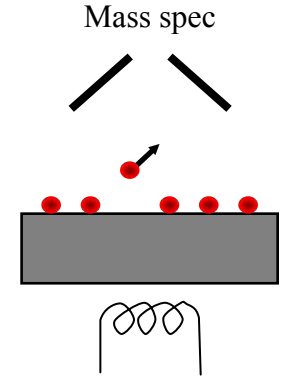


## 6. Desorption techniques

### 6.1 Temperature Programmed Desorption (TPD or TDS)

- 6.1.1. General setup:
- Adsorb fixed amount of molecules at surface
  - Gradually increased heating of surface leads to desorption
  - Desorbed particles analyzed by pressure gauge / mass spectrometer



- Information on:
- Kinetics of desorption process  $\rightarrow$  heat of adsorption
  - Adsorbate interactions, multiple adsorption sites, phase transitions
  - Quantitative coverage (calibration!)
  - Dissociative vs. non-dissociative adsorption (isotope scrambling!)
  - Surface reactions (TPRS)

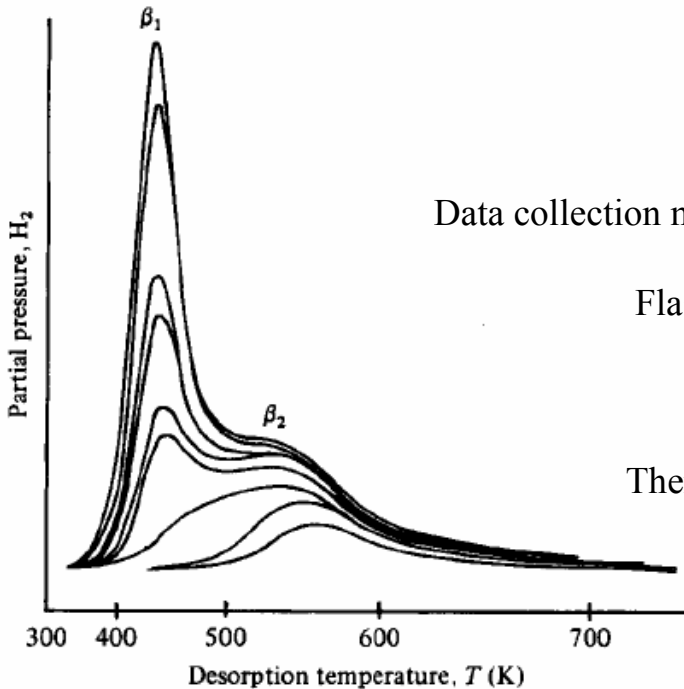
Data collection mode:

Flash desorption

rapid temperature ramp  
rate of desorption  $>$  pumping speed of vacuum system  
primarily used for surface cleaning

Thermal desorption

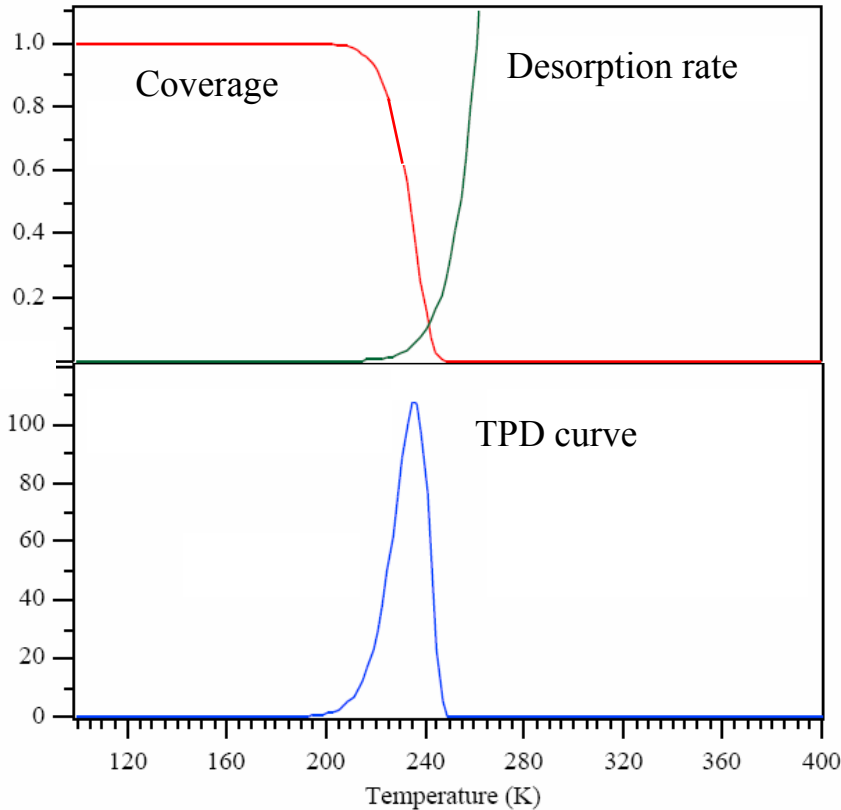
slow (linear) temperature ramp (few K/s)  
rate of desorption  $<$  pumping speed of vacuum system  
(negligible (re)adsorption from gas phase: UHV)



## 6.1.2. Conceptual understanding:

- Number of desorbing particles depends on rate of desorption:  
number of adsorbed particles:

increases monotonously with  $T$   
decreases monotonously with  $T$   
(since more particles are already desorbed)



$$I(T) \sim -\frac{d\theta}{dt} = \nu(\theta, T) \cdot \theta^n \cdot \exp\left(\frac{-E_{des}(\theta, T)}{k_B T}\right)$$

- $\nu$  Frequency factor
- $\theta$  Instantaneous coverage
- $n$  Kinetic desorption order ( $0 \leq n \leq 2$ )
- $E_{des}$  Activation energy to desorption

Polanyi-Wigner Equation

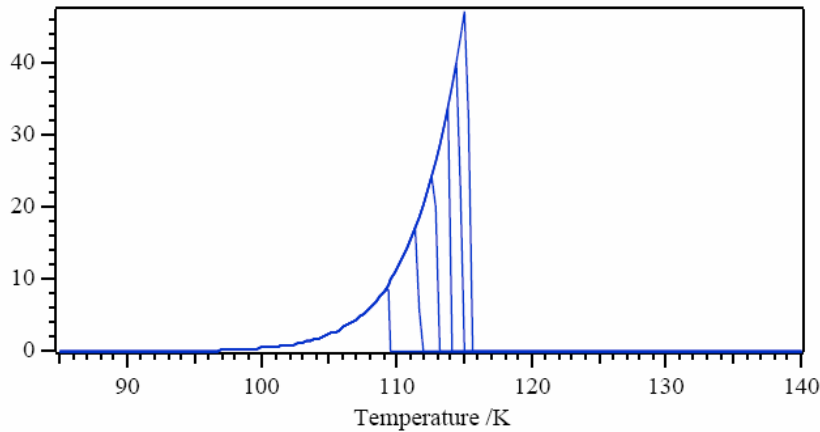
- In general:

$E_{des}$  larger  $\rightarrow$  peak shifts to higher  $T$

$\nu$  smaller  $\rightarrow$  peak shifts to higher  $T$

Faster heating rate  $\rightarrow$  peak shifts slightly to higher  $T$

- Coverage term and desorption order motivated by mean-field theory/no lateral interactions

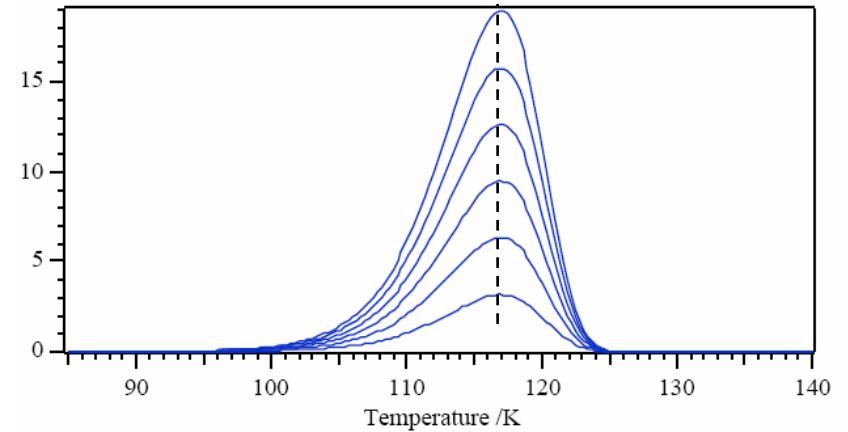


**i) Zero-order kinetics:**

- multilayer desorption
- unlimited supply of particles
- (no coverage dependence)
- common leading edges

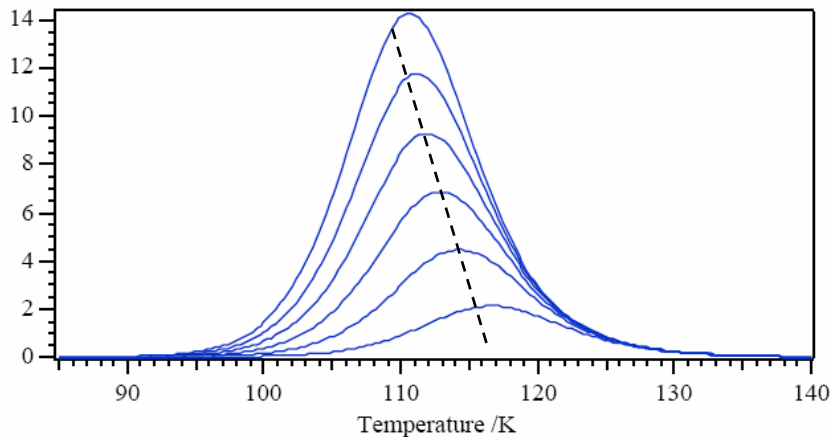
**ii) First-order kinetics:**

- unimolecular desorption
- $I(T) \sim$  no. of particles
- peak position independent of  $\theta$
- asymmetric peak shape



**iii) Second-order kinetics:**

- recombinative desorption
- $I(T) \sim$  no. of particles (no. of particles - 1)  $\sim \theta^2$
- peak position shifts to lower  $T$  with increasing  $\theta$
- symmetric peak shape
- common trailing edges



### 6.1.3. Data analysis

#### a) Redhead analysis

- Assume: desorption follows Polanyi-Wigner equation  
 $\nu$ ,  $E_{\text{des}}$  are independent of coverage and temperature

- Order of magnitude estimate:  $E_{\text{des}} \sim 250 \text{ meV} \cdot T_{\text{peak}}/\text{K}$

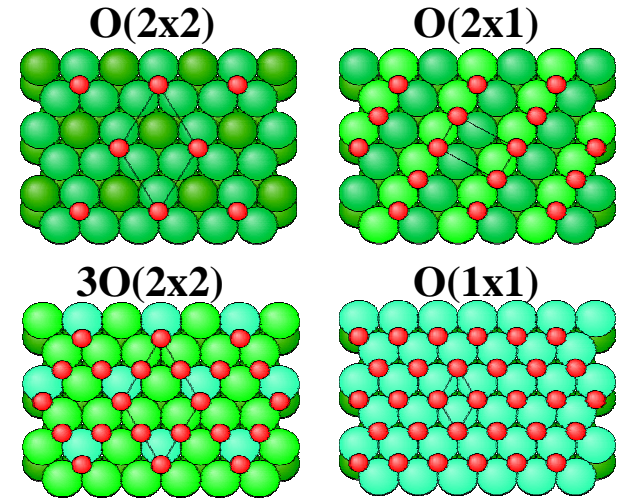
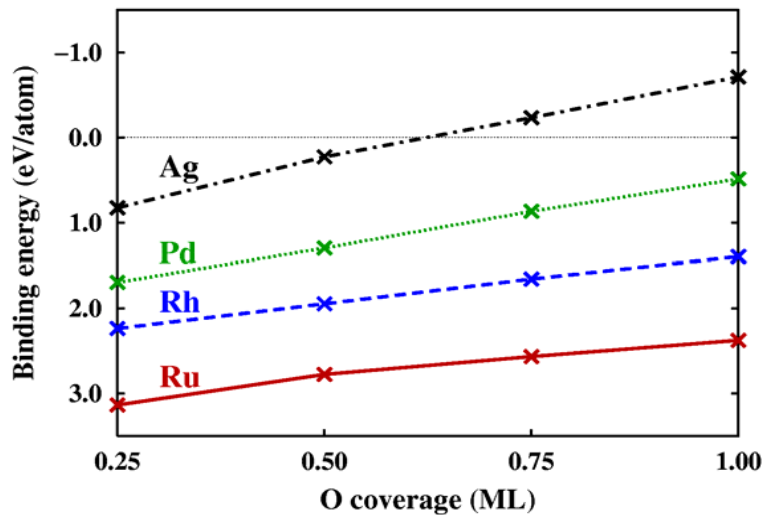
- At fixed initial coverage  $\theta_o$  measure  $T_{\text{peak}}$  for various heating rates  $\beta_H$ :  
 Plot  $(T_{\text{peak}}, \beta_H)$ -data as  $\ln(\beta_H / k_B T_{\text{peak}}^2)$  vs.  $(k_B T_{\text{peak}})^{-1}$   
 Straight line has slope  $-E_{\text{des}}$   
 $\nu$  then given from Polanyi-Wigner equation (for assumed  $n$ )
 
$$\frac{-E_{\text{des}}}{k_B T_{\text{peak}}} = \ln\left(\frac{\beta_H}{k_B T_{\text{peak}}^2}\right) + \ln\left(\frac{E_{\text{des}}}{n \nu \theta_{\text{peak}}^{n-1}}\right)$$

- For 2nd order peak and fixed heating rate  $\beta_H$ ,  
 measure  $T_{\text{peak}}$  for various initial coverages  $\theta_o$ :  
 Plot  $(T_{\text{peak}}, \theta_o)$ -data as  $\ln(1 / \theta_o k_B T_{\text{peak}}^2)$  vs.  $(k_B T_{\text{peak}})^{-1}$   
 Straight line has slope  $-E_{\text{des}}$   
 $\nu$  again given from Polanyi-Wigner equation
 
$$\frac{-E_{\text{des}}}{k_B T_{\text{peak}}} = \ln\left(\frac{1}{\theta_o k_B T_{\text{peak}}^2}\right) + \ln\left(\frac{\beta_H E_{\text{des}}}{\nu}\right)$$

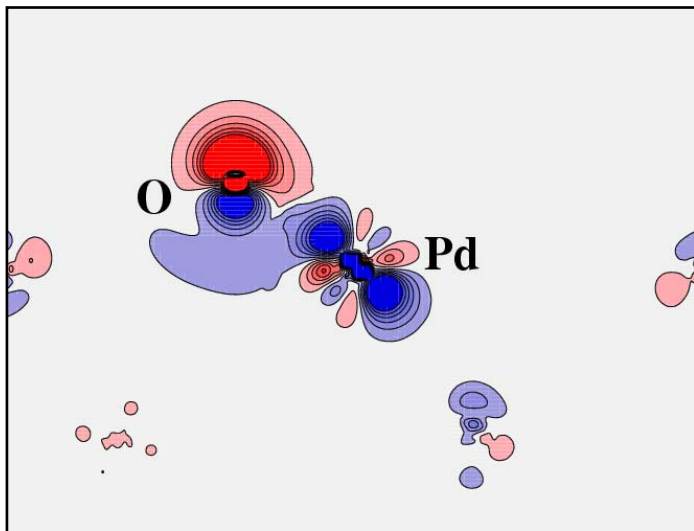
- Assessment:
  - Straightforward and routinely applied
  - Gives good estimates of  $E_{\text{des}}$  by  $\pm 30\%$ , BUT NOT MORE THAN THAT!!
  - Technical problem:  $T_{\text{peak}}$  difficult to determine for multiple peak structure
  - Fundamental problem:
    - Assumed order of desorption process  $n$
    - $E_{\text{des}}$  and  $\nu$  constant

→ At least, include variations of  $E_{\text{des}}$  with coverage: lateral interactions

Short intermission: lateral interactions

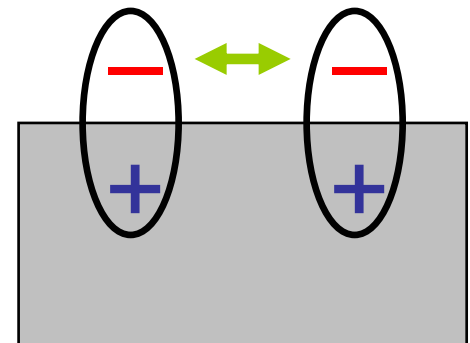


**Direct „through space“ interactions vs. Indirect „substrate mediated“ interactions**



Overall attractive: clustering/islanding  
 Overall repulsive: ~ dilute overlayers

Ordering tendency counteracted by configurational entropy  
 (phase diagram)



## b) Improved Polanyi-Wigner based analyses

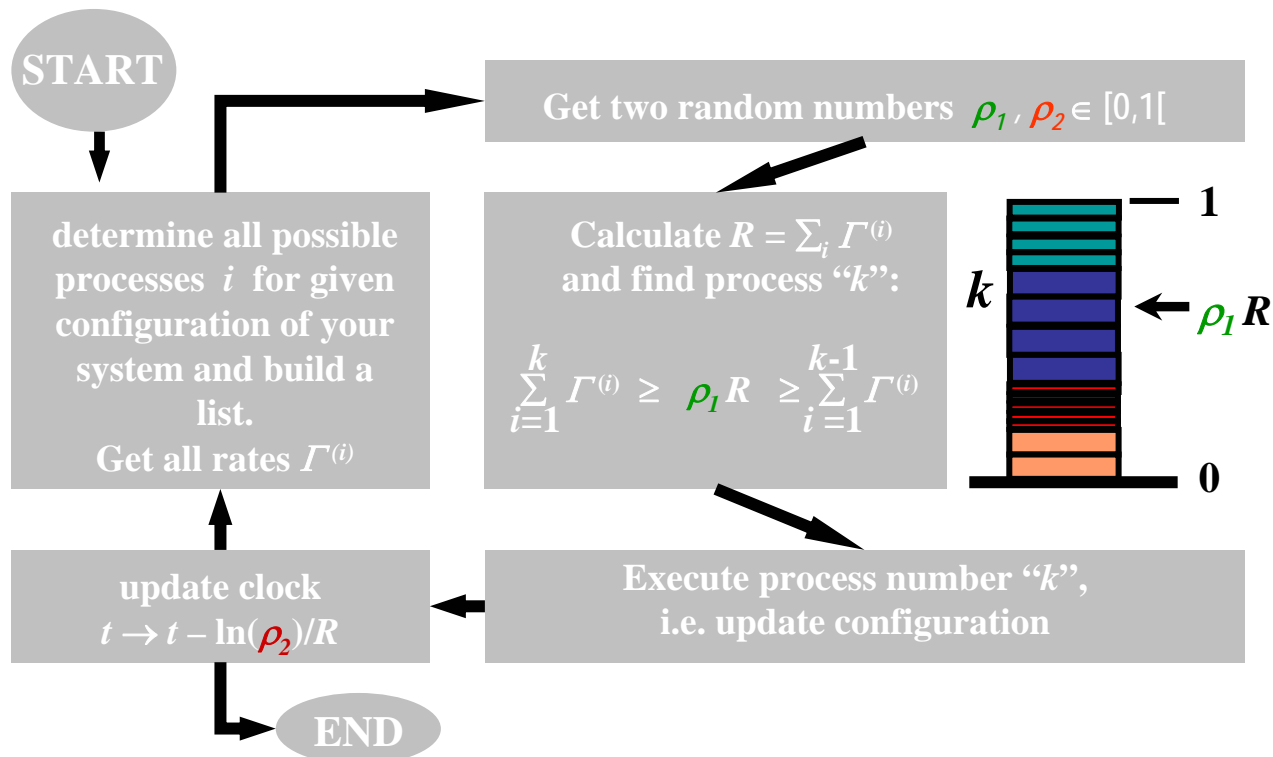
- Assume: desorption follows Polanyi-Wigner equation  
 $\nu$  is independent of coverage and temperature  
 $E_{\text{des}} = E_{\text{des}}(\theta)$ , but not of  $T$

$$\ln(I(T)) = \frac{-E_{\text{des}}(\theta)}{k_B T} + (\ln \nu + n \ln \theta)$$

- If  $\theta$  is either known or at least constant for all used  $I(T)$ -data points, one could plot  $\ln(I(T))$  vs.  $(k_B T)^{-1}$  and get  $E_{\text{des}}(\theta)$  for the particular  $\theta$  as slope (Arrhenius plot)
- Habershaden-Küpers/Leading edge method:
  - Measure  $I(T)$  for various (calibrated)  $\theta_0$
  - Evaluate only leading edge of peak, where  $\theta \approx \theta_0$
- Taylor-Weinberg-King method/Complete analysis:
  - Recognize  $\theta(T) = \frac{c}{\beta_H} \int_T^\infty I(T) dT$
  - Determine  $c$  from one known coverage (and assume  $c$  is independent of  $T, \theta$ )
  - Measure  $I(T)$  for many initial  $\theta_0$  and  $\beta_H$
  - Assign a  $\theta$  to each data point
  - Do Arrhenius plot for all data subsets with equal  $\theta$
- Assessment:
  - Already much better than Redhead
  - Fundamental problem:
    - $E_{\text{des}}$  independent of  $T$ : phase transitions can affect analysis
    - Still assumes  $\nu$  constant and validity of Polanyi-Wigner equation
- Further improvement:
  - Assume more complex form of Polanyi-Wigner equation by including lateral interactions in generic (simplified) form.  
Most prominent: Bragg-Williams (mean-field), Bethe-Peierls (quasichemical) approx.

### c) kinetic Monte-Carlo simulations

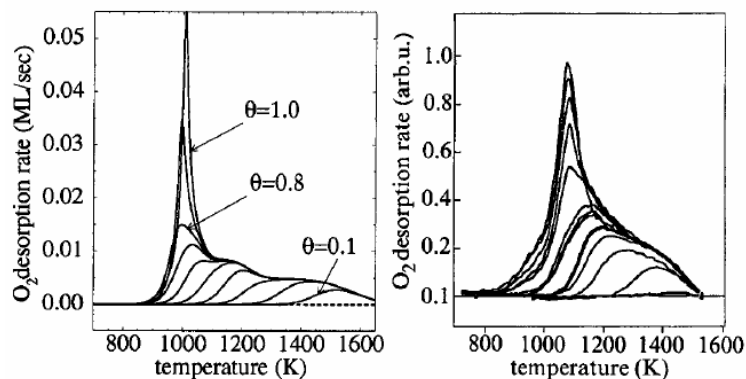
- Indirect method: do not invert exp. spectra, but simulate TPD spectra for given model and compare
- Assume: adsorbate configuration can be described by a lattice with fixed sites
- Start simulation with given equilibrated adsorbate configuration at surface (coverage  $\theta_0$ ), progress time by considering all process rates (e.g. diffusion and desorption) and increase temperature progressively according to heating ramp
- Record number of desorption events as function of  $T$
- Alternatively: mix kMC for desorption with MC simulations for intermediate equilibration steps  
 Advantage: faster and does not require diffusion barriers  
 Disadvantage: assumes heating ramp is slow enough to maintain equilibrium at surface during run



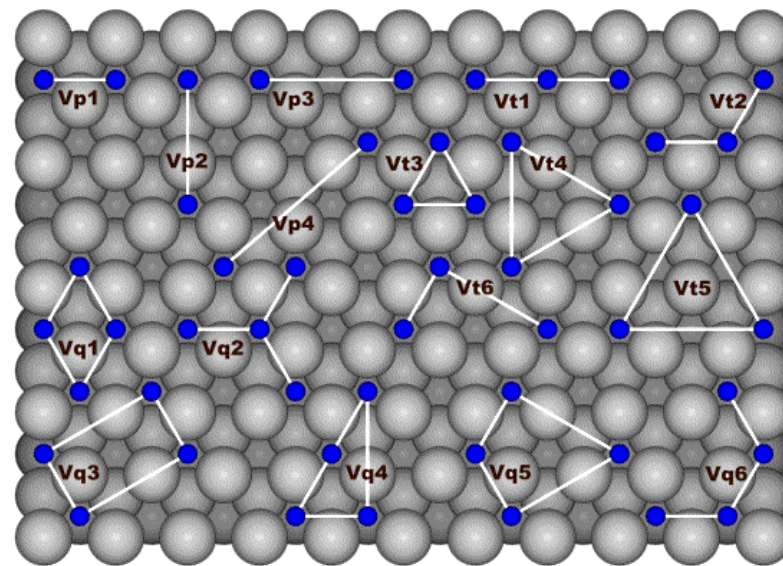
- TPD-kMC in principle trivial. Problem is: need binding energies for any local configuration (i.e. in dependence of lateral interactions)

→ Lattice gas expansion:

$$E = V_0 \sum_{i=1}^N n_i + \sum_{i \neq j} V_p(i, j) n_i n_j + \sum_{i \neq j \neq k} V_t(i, j, k) n_i n_j n_k + \dots$$



C. Stampfl *et al.*,  
Phys. Rev. Lett. 83, 2993 (1999)



- Two approaches to determine lateral interactions in TPD-kMC approach:

Empirical    assume certain forms of lateral interactions (e.g. only nearest-neighbor pairwise repulsion) and show generic effect on TPD spectra

→ conceptual understanding (peak shifts, peak splits)

Weinberg, Kreuzer...

try to fit set of lateral interactions and binding energies to given experimental spectra

→ done, but very questionable (multiparameter fit problem)

*Ab initio*    compute lateral interactions from first-principles via LGH expansion of ordered structures

→ quantitative modelling



## 6.1.4. Pros and cons

- +
- Conceptually simple and rapid
- (Quantitative) coverage information
- Information about ad/desorption enthalpies („fingerprinting of adsorbate states“)  
fragmentation/dissociation & reaction
- 
- Exp. technicalities: desorption from sample holder/chamber walls (snouts!)  
temperature inhomogeneities over sample  
sensitivity at low heating ramps
- Intrinsically destructive
- Probed adlayer properties may be afflicted by temperature rise  
(change of binding site, dissociation, phase transitions)
- „Phenomenological“ data analyses can be easily misapplied

