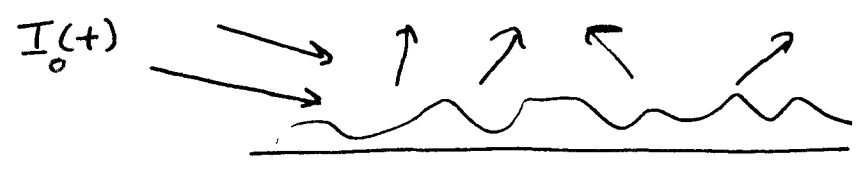


R: reflectivity  $\frac{\Delta R(\nu)}{R_0(\nu)} = \frac{R_0(\nu) - R(\nu)}{R_0(\nu)} \quad (1)$

$\propto \sigma$  (molecules per unit area)

Proportionality only true if there are not strong interactions among adsorbates.

3. Diffuse Reflectance (DRIFTS: diffuse reflectance infrared Fourier transform spectroscopy)

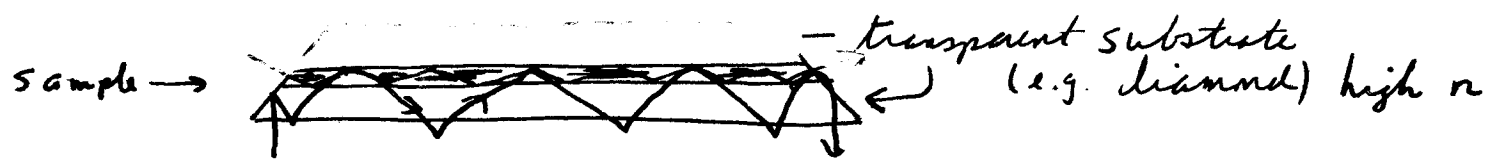


used on rough surfaces or powders that scatter radiation diffusely rather than specularly

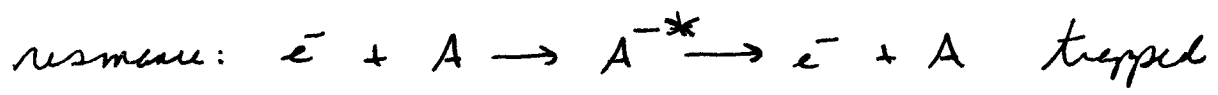
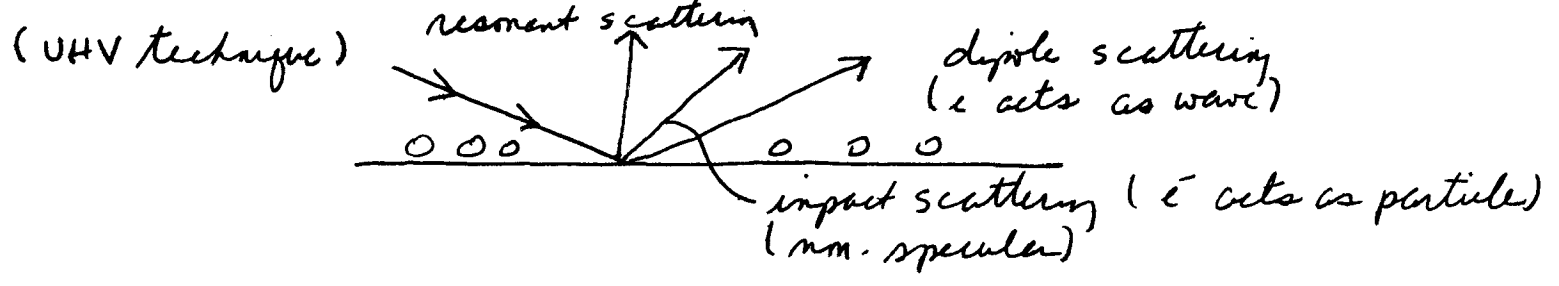
total I(λ) measured & converted to I(ν)

4. Internal Reflection (interface)

- ATR: attenuated total reflection See eq. (1)
- MIR: multiple internal reflection: less used term



(High Resolution) Electron Energy Loss Spectroscopy (EELS)

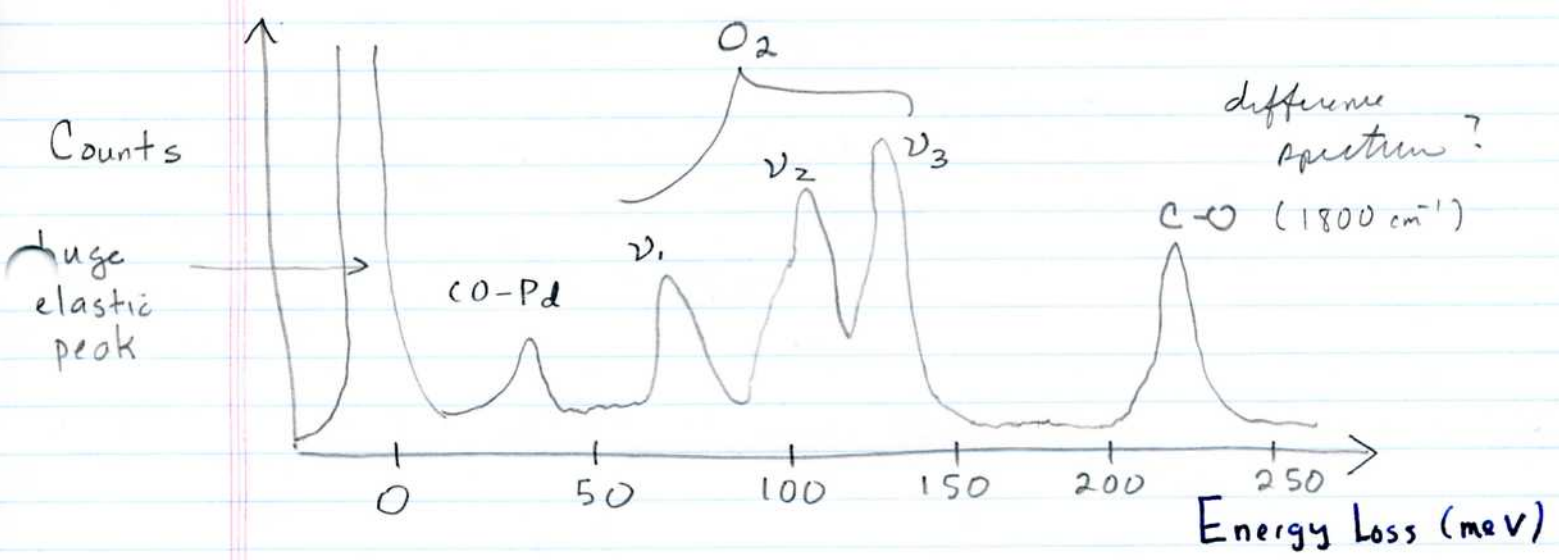


Energy loss measured from beam. Loss in kinetic energy: excitation of vibrational modes near or at surface.  
 Analysis of dipole scattering same as RAIRS.  
 Inelastic scattering follows different selection rules. (non-MSSR)

$$E = E_0 - h\nu = E_0 - hc\tilde{\nu}$$

energy of inelastic peak       $\uparrow$  elastic peak (often set to zero)  
 $E_0 - E = h\nu = hc\tilde{\nu}$       frequency of excited transition

Example:  $O_2 + CO$  adsorbed on Pd (111) 100 K

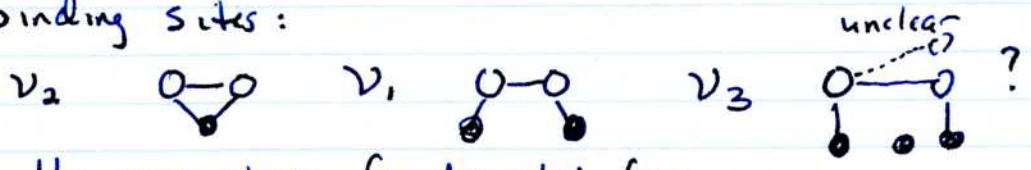


1 meV = 8.065 cm<sup>-1</sup>

Some basic points: a) can study low frequency adsorbate-substrate modes (CO-Pd ~ 300 cm<sup>-1</sup>)  
 b) can study non-polar adsorbates (O<sub>2</sub>).

Here 3 peaks correspond to 3 different binding sites:

can study || dipoles on metal!



Note that the gas phase fundamental for O<sub>2</sub> would occur at 196 meV (1580 cm<sup>-1</sup>) if allowed.

Strongest binding to Pd  $\Rightarrow$  lowest  $\nu$

EELS

vs

IR

Advantages

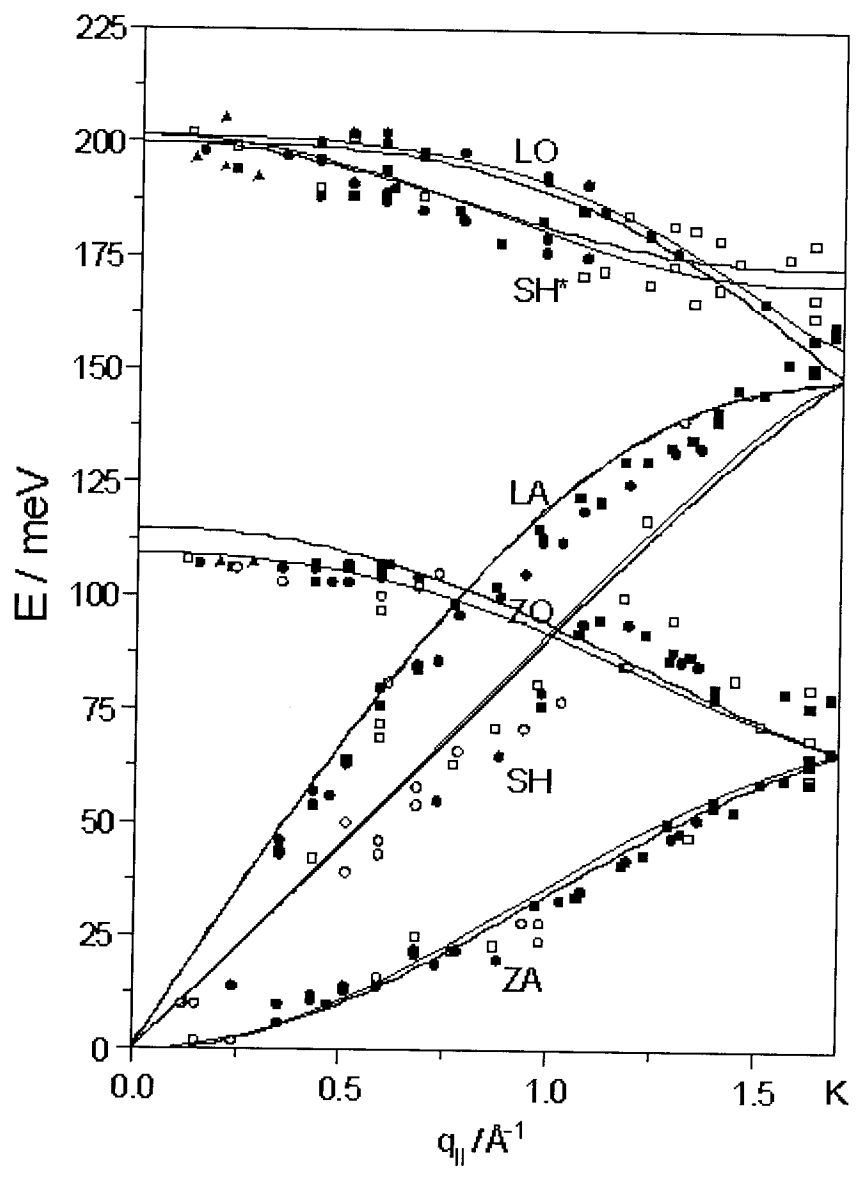
1. weak selection rules  
(can see non-polar species  
& can see dipoles  $\parallel$  to  
metal surface)
2. can probe lower  
frequencies than  
IR & so see  
frustrated modes +  
surface phonons  
(see graphite picture)

Disadvantages

1. low spectral  
resolution  
(1-10 meV; 8-80  $\text{cm}^{-1}$ )  
IR:  $< 0.01 \text{ cm}^{-1}$
2. requires UHV  
whereas IR does not.
- 3.

# GRAPHITE PHONONS

EELS



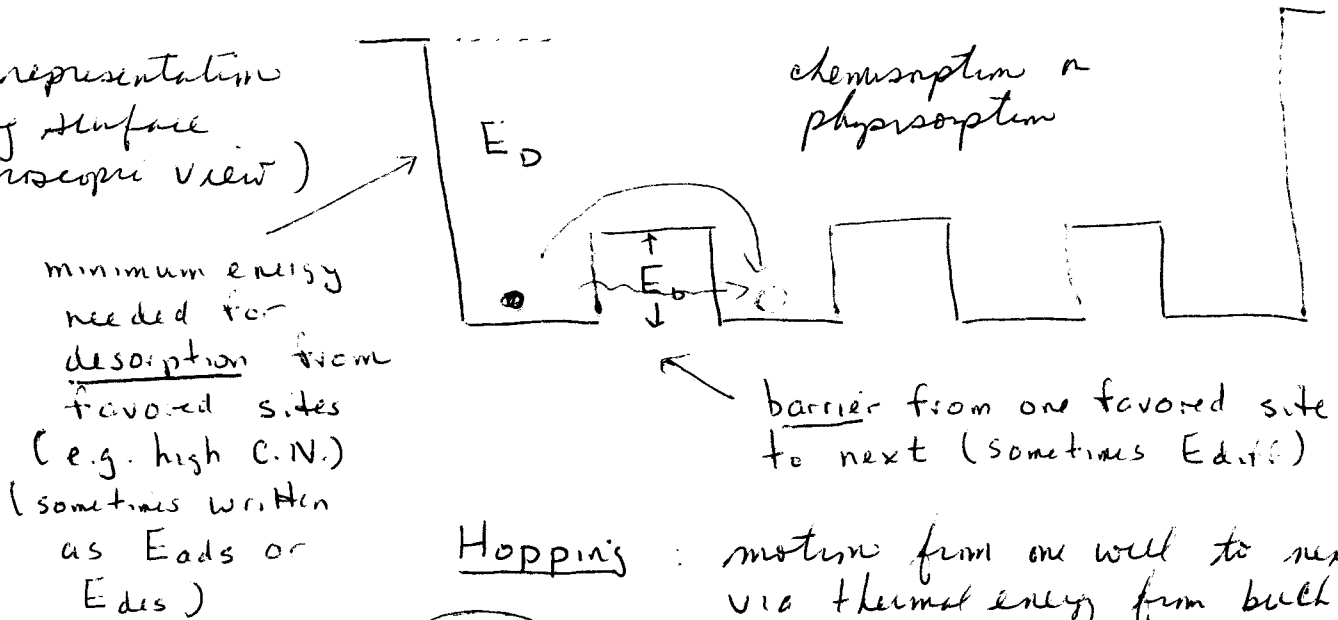
# III. Dynamics + Reactions

## Diffusion

SBS  
thermal

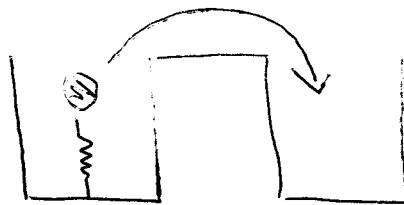
An adsorbate can move on a corrugated surface via thermal hopping or quantum tunneling:

1-D representation along surface (microscopic view)



### Hopping

motion from one well to next via thermal energy from bulk.



### Simplest Model

$\nu$  ( $s^{-1}$ ): adsorbate-substrate vibrational frequency (like frustrated mode)

$\nu$  isotropic  
 $\sim 10^{12} s^{-1}$   
(300  $cm^{-1}$ ) physi.  
 $\approx 10^{13} s^{-1}$  chem.  
(300  $cm^{-1}$ )

Rate of hopping ( $s^{-1}$ ) =  $k_{hop}$  or  $\nu_{hop}$

$$\nu \exp\left[-E_b/k_B T\right]$$

Boltzmann factor

Arrhenius-type expression crudely: BF expression fraction of adsorbates with  $E \geq E_b$ .

Tunneling:  $k_{tunn} = \nu P_{tunn}$

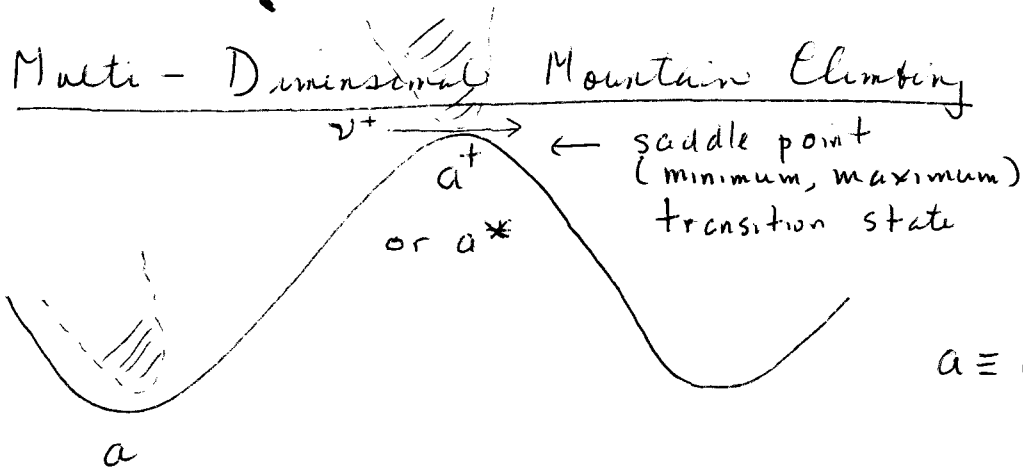
$$P_{tunn} = e^{-2Kd}$$



$$K^2 \approx \frac{2m}{\hbar^2} E_b$$

rule

med light adsorbate such as H and small width d



The process is not a 1-D one. The adiabate  $a$  has other degrees of freedom (diffusion in another direction, internal vibrational modes) which may change as hopping proceeds.

Simpliest thing to handle many degrees of freedom is known as absolute rate theory, activated complex theory, transition state theory. Based on statistical mechanics, it was first worked out in the 1930's by Wigner, Eyring, & Polanyi.

The TST, a saddle point, has one fewer degree of internal freedom because one vibration of a normal molecule is replaced in the hopping (reaction) direction by an inverted potential.

Rate of hopping per TST = rate of species on the transition state into the next valley. ( $v^+$ ,  $s^-$ )

$N_a$ : number of adiabates in minima (can also use area)  
 $N_{a^+}$ : number of adiabates in TST (concentrations)

$$\text{Rate of hopping} = v^+ N_{a^+} = v^+ \frac{N_{a^+}}{N_a} N_a$$

It is assumed that thermal equilibrium pertains between  $N_a$  and  $N_{a^+}$ :



--- 3 ---

$$\frac{Na^+}{Na} = K^+ (T) = \frac{\Theta_a^+}{\Theta_a} = \frac{\sigma_a^+}{\sigma_a} \leftarrow \text{surface concentration}$$

$$\text{Rate of hopping} = v^+ K^+ Na = k_{\text{hop}} Na \quad (s^{-1})$$

$$\left( -\frac{dNa}{dt} \right)$$

Sometimes an additional factor  $K$  is used ( $0 \leq K \leq 1$ ) since we don't really know which direction the TST will slide down. But, more typically, we just set  $K=1$  since the theory is approximate anyway.

$$K^+ = \frac{q(a^+)}{q(a)} e^{-E_b/kT} \quad q's: \text{referred to zero-point levels}$$

Reaction Coordinate = adiabatic - substrate vibrations that, when broken, leads to motion over the saddle point.

We determine  $v^+$  using classical statistical mechanics.

$t^+$  : time spent by system when crossing saddle point.

$$v^+ = \int_{q^+=0}^{q^+} \int_{p^+=0}^{\infty} \frac{1}{t^+} \frac{e^{-E^+/kT} dq^+ dp^+}{h}$$

ensemble average

$$E^+ = \frac{1}{2} m \dot{q}^{+2} \quad (\approx \text{pure translation})$$

$$dq^+ dp^+ = dq^+ m d\dot{q}^+ = \frac{dE^+}{\dot{q}^+} dq^+ = dE^+ dt$$

$$dE^+ = m \dot{q}^+ d\dot{q}^+$$

$$v^+ = \frac{1}{h} \int_{t=0}^{t^+} \int_{E^+=0}^{\infty} \frac{1}{t^+} e^{-E^+/kT} dE^+ dt$$

$$\nu^\ddagger = \frac{t^\ddagger}{h t^\ddagger} kT = \frac{kT}{h}$$

$$K^\ddagger = \frac{q(a^\ddagger)}{q(a)} e^{-E_b/kT} = \frac{1}{q_v(a)} e^{-E_b/kT}$$

Assume  $a^\ddagger$  is the same as  $a$  except for one missing vibration

$$q_v(a) = \sum_{v=0}^{\infty} e^{-hv/kT} = \frac{1}{1 - e^{-hv/kT}}$$

$$\therefore K^\ddagger = (1 - e^{-hv/kT}) e^{-E_b/kT}$$

$$\therefore k_{\text{hop}} (s^{-1}) = \frac{kT}{h} (1 - e^{-hv/kT}) e^{-E_b/kT}$$

$A(T)$  "pre-exponential factor"

Limits

$$hv \ll kT \quad \nu \ll \frac{k}{h} T = 2.08 \times 10^{10} T(K)$$

$$e^{-hv/kT} \approx 1 - hv/kT \quad A(T) = \frac{kT}{h} \left[ 1 - 1 + \frac{hv}{kT} \right]$$

$$A(T) = \nu$$

$$k_{\text{hop}} (s^{-1}) = \nu e^{-E_b/kT} \quad \text{but not general}$$

$$T = 300K \quad \nu < 6 \times 10^{12} s^{-1} \quad (200 \text{ cm}^{-1})$$

$$hv \gg kT \quad k_{\text{hop}} = \frac{kT}{h} e^{-E_b/kT}$$

BUT, normally the transition state is more loosely bound to the substrate so its internal energy levels lie close together. In this case, our expression for  $k_{\text{hop}}$  is a lower limit.