

6 Other/Miscellaneous Techniques

6.1 Temperature Programmed Desorption (TPD)

also known as thermal desorption spectroscopy (TDS)

Adsorbed molecule bound to surface in potential well of depth E_{des}

Probability that molecule will desorb at any one temperature, to produce an equilibrium vapor pressure, is governed by Boltzmann statistics

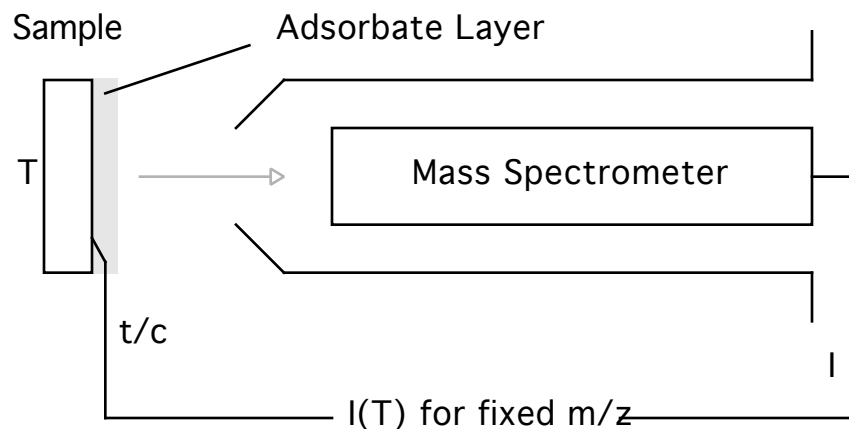
In TPD experiment, gaseous molecule/atom is adsorbed onto surface (sometimes cooled) then desorbed by heating surface

Pressure rise monitored by

- total pressure gauge (e.g. ion gauge)
- mass spectrometer

usually quadrupole (not TOF)

can acquire single or multiple m/z during heating



In principle can get

- Heat of adsorption (if adsorption and desorption are reversible/non-dissociative processes)

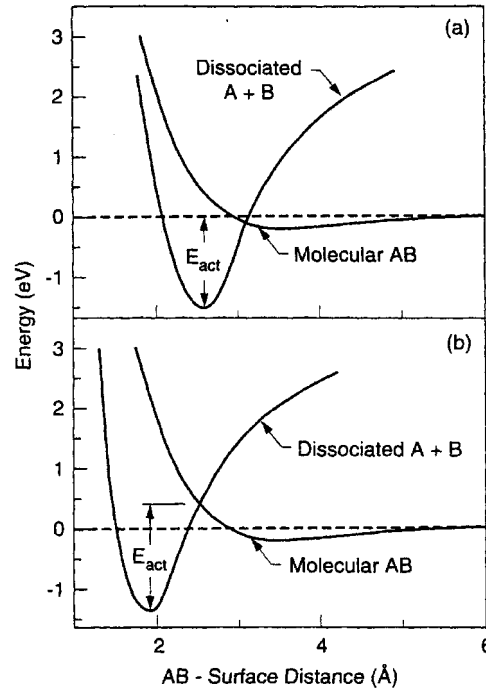


Fig. 3. Conventional Lennard-Jones picture of dissociative adsorption of a diatomic molecule AB on a surface: (a) non-activated; (b) activated.

for (a) $E_{\text{ads}} = E_{\text{des}}$ but for (b) $E_{\text{ads}} < E_{\text{des}}$!

- Quantitative coverage information about dissociative and non-dissociative adsorption
- Energetic information about phases transitions, interadsorbate interactions, multiple adsorption sites
- Kinetic information about desorption process

Two ways to collect data:

(a) thermal desorption (TPD/TDS)

- rate of desorption < pumping speed of vacuum system
- most common method

(b) flash desorption

- rate of desorption > pumping speed of vacuum system
- rarely used

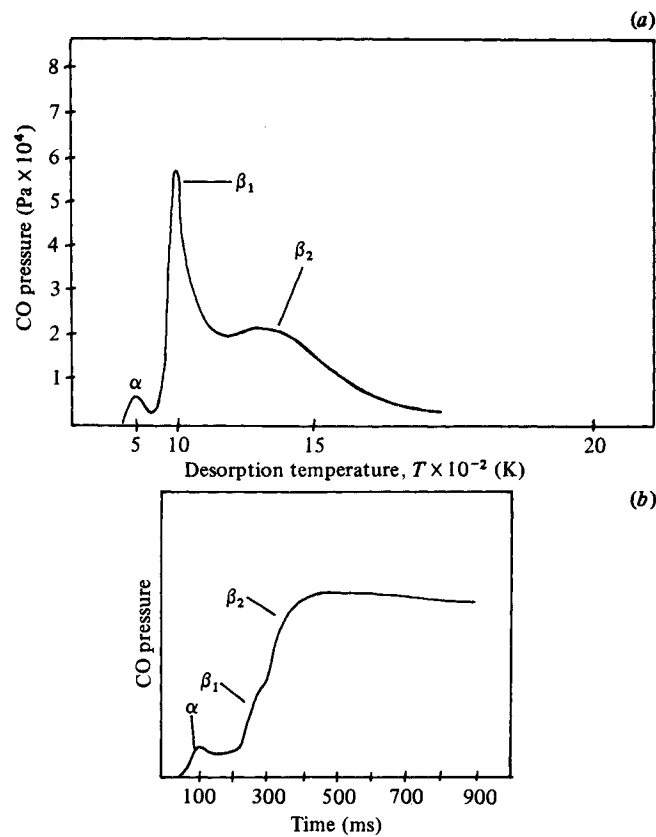


Fig. 5.1 Comparison of (a) thermal desorption and (b) flash desorption curves showing the α , β_1 and β_2 states of CO on W (Goymour & King, 1973; Ehrlich, 1961b).

Partial pressure recorded at one m/z (say, base peak) by mass spectrometer is

- to instantaneous partial pressure of adsorbate p_M

- to rate of desorption of adsorbate $\frac{dM}{dt}$

- $\frac{dM}{dt}$ = rate of loss of coverage $-\frac{d}{dt} \theta$

Several points worth noting:

- $I(T)$ does not rise indefinitely - at some stage, all molecules desorbed

- If the mass spectrometer collected and ionized all adsorbates, area under TPD $I(T)$ curve would *equal* molecular coverage

- Only fraction desorbed molecules collected and ionized - area under TPD $I(T)$ curve is *proportional* to molecular coverage

- Shape of $I(T)$ curve contains information about desorption kinetics

6.1.1 Theoretical Description of TPD Data

The rate of desorption follows Arrhenius-type behavior

$$I(T) \frac{dM}{dt} = -\frac{dM}{dt} = (\nu_M) M^n \exp \frac{-E_{des}(M)}{R T}$$

Polanyi-Wigner equation

where

(ν_M) = frequency factor

M = instantaneous coverage

n = kinetic order or desorption order

$E_{des}(M)$ = activation energy to desorption

R = gas constant

During TPD sample is heated in linear fashion

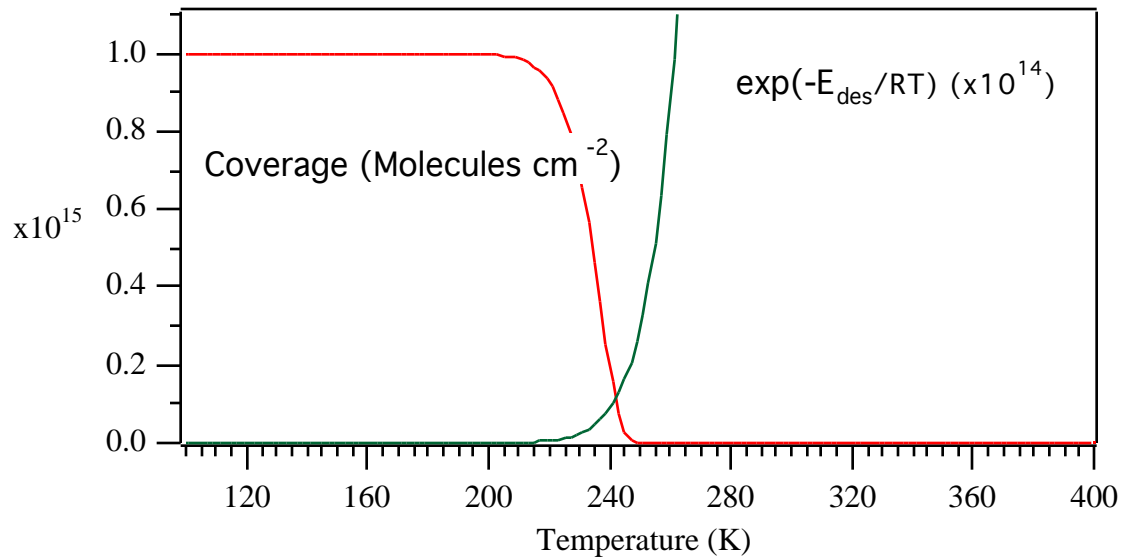
$$\begin{aligned} T(t) &= T_0 + \frac{dT}{dt} t \\ &= T_0 + \beta t \end{aligned}$$

where β is the heating rate ($K \cdot s^{-1}$)

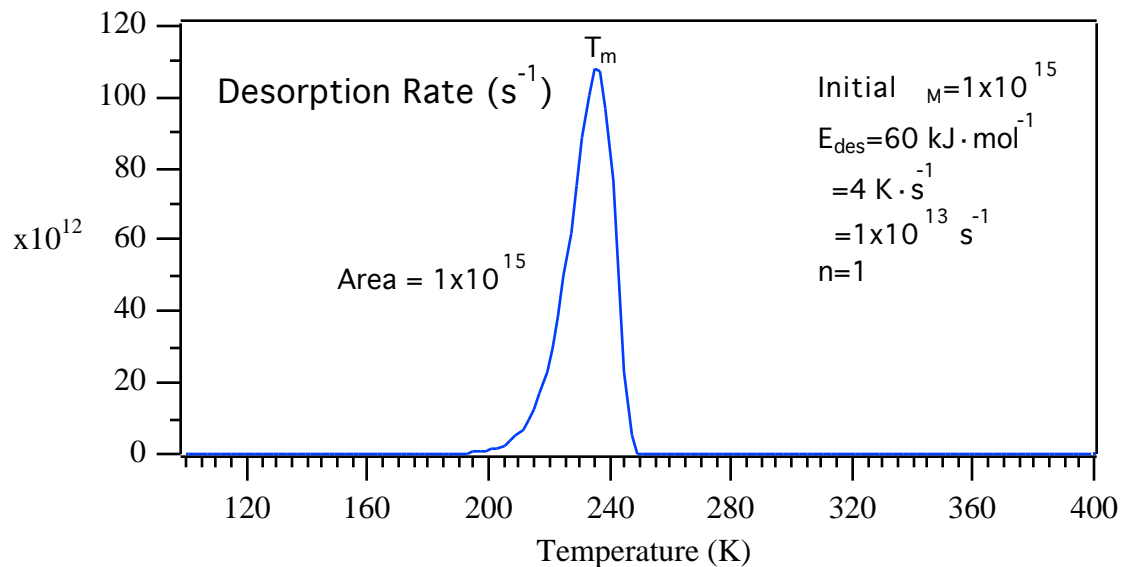
Polanyi-Wigner equation becomes:

$$-\frac{dM}{dT} = \frac{\nu_M^n}{\beta} \exp \frac{-E_{des}}{R T}$$

The rate contains a *coverage* term (M^n) and *energy* term $\frac{-E_{des}}{R T}$



- At low T, $E_{\text{des}} > RT$ and little desorption occurs - $I(T) \sim 0$
- At high T, $\exp \frac{-E_{\text{des}}}{R T}$ rises rapidly - $I(T) > 0$
- As coverage decreases following desorption of fraction of monolayer, $I(T)$ decreases
- At very high T, all molecules desorbed - $I(T) = 0$



6.1.2 Significance of Desorption Order (n)

Most terms in Polanyi-Wigner equation straightforward

Factors affecting peak desorption temperature:

- $E_{\text{des}}, \theta, m (n - 1)$

Factors affecting peak shape:

- θ, n

Factors affecting peak magnitude (area):

- m

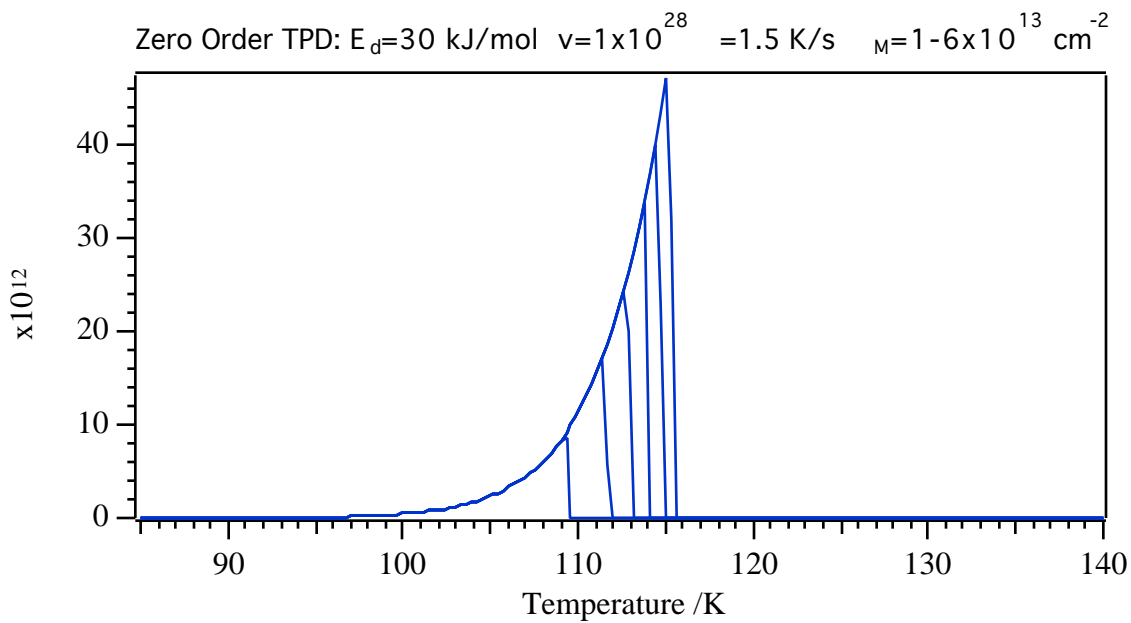
What about desorption order n?

A. *Zero-order desorption kinetics:*

$$-\frac{dM}{dt} = M^{n=0} \exp \frac{-E_{\text{des}}}{R T}$$

$$= \exp \frac{-E_{\text{des}}}{R T}$$

- implies that desorption rate does not depend on coverage
- implies that desorption rate increases exponentially with T



- all coverages have common leading edge
- rapid drop when all molecules have desorbed
- temperature of peak desorption rate, T_m , moves to higher T with θ_m

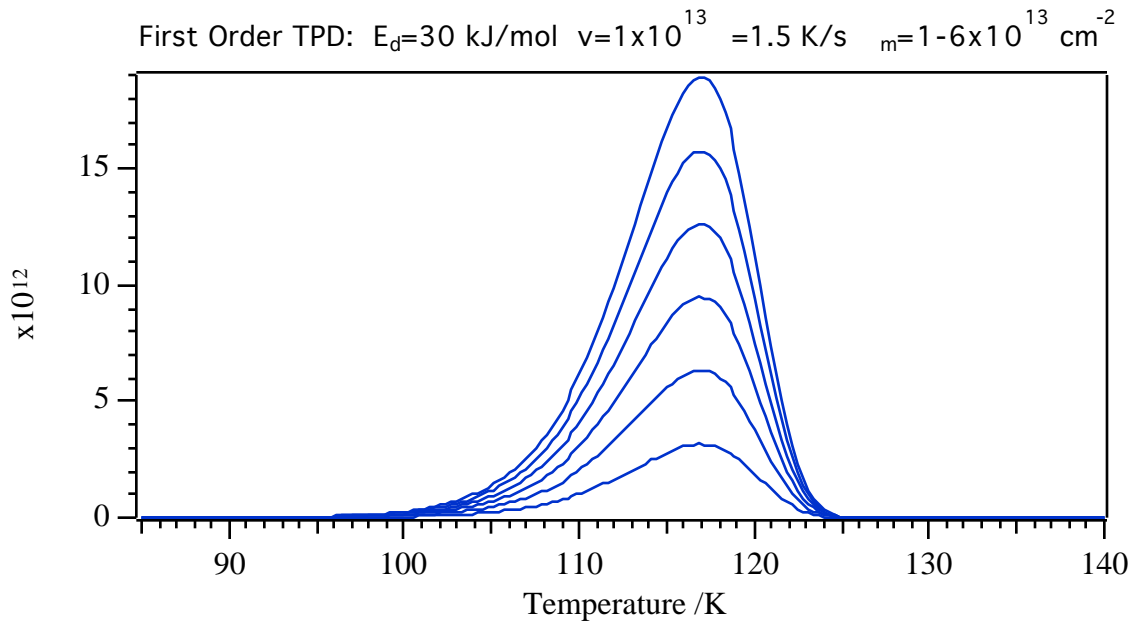
Zero-order kinetics observed in thick layers (multilayers) when supply of molecules is \sim infinite

May also occur if strong attractive interactions between adsorbates (*pseudo* zero-order)

B. First-order desorption kinetics:

$$-\frac{d \theta_M}{dt} = \theta_M \exp \left(\frac{-E_{des}}{R T} \right)$$

- desorption rate proportional to instantaneous coverage
- desorption peak will show balance of θ_M and $\exp(-E_{des}/RT)$ terms



- T_m constant with increasing θ_m
- characteristic asymmetric peak shape
- T_m increases with E_{des}

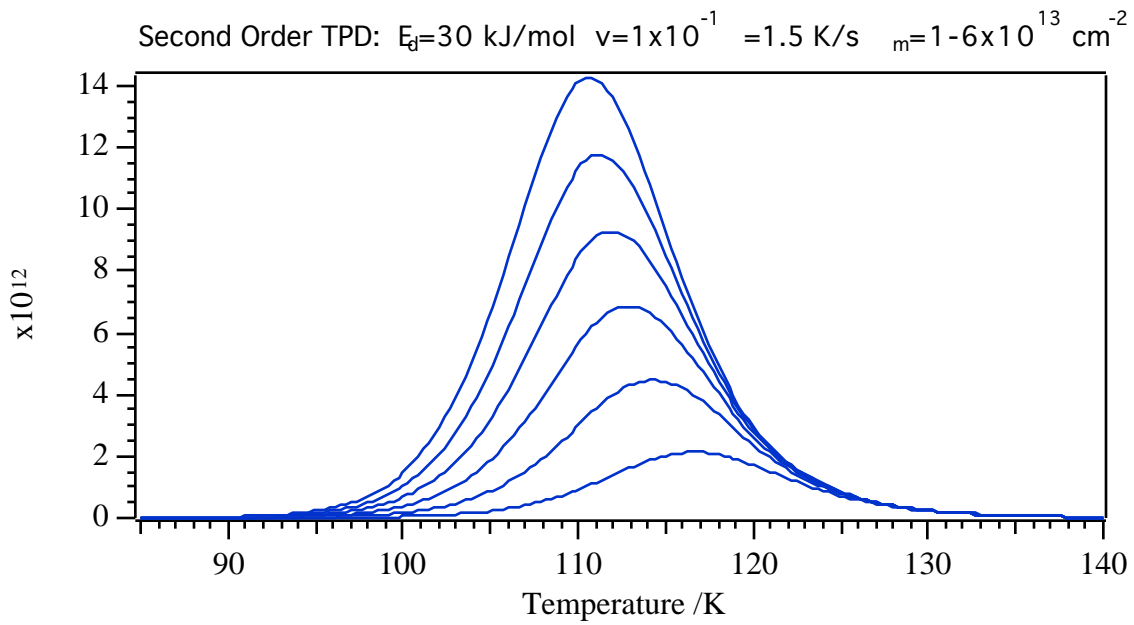
"Normal" desorption order for non-dissociative molecular and atomic adsorption

$$A_{ad} \quad A_g$$

C. *Second-order desorption kinetics:*

$$-\frac{d\theta}{dt} = \theta^2 \exp\left(\frac{-E_{des}}{RT}\right)$$

- desorption rate proportional to instantaneous coverage²
- desorption peak will show balance of θ_m and $\exp(-E_{des}/RT)$ terms



- T_m moves to lower T with m
- Common trailing edges of peaks
- Characteristic nearly symmetric peak shape

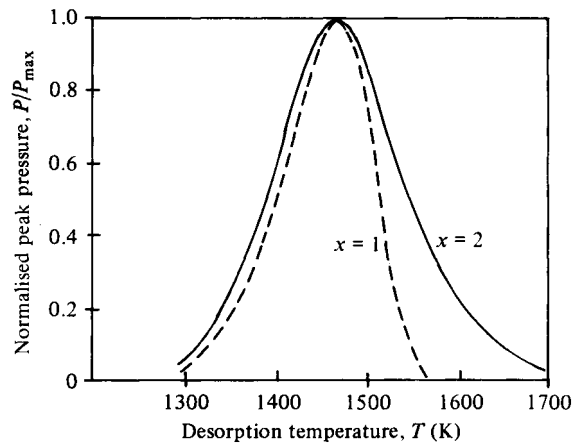


Fig. 5.6 The theoretical shapes of first- and second-order desorption peaks (Redhead, 1962).

Only strictly observed for recombinative desorption



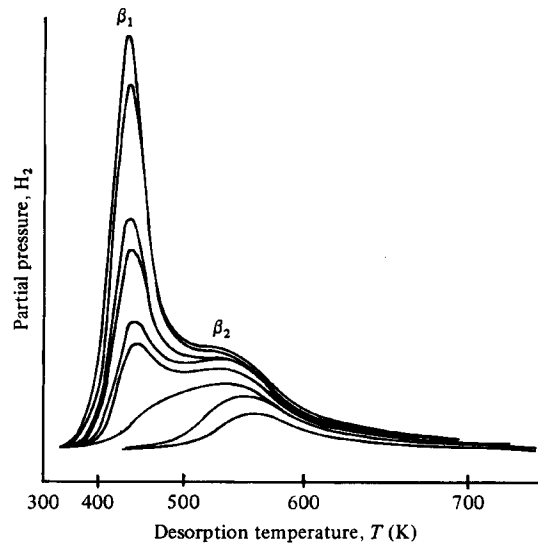


Fig. 5.3 Thermal desorption curves for H on W{100} showing the β_1 and β_2 states. Each curve corresponds to a different initial coverage (Madey & Yates, 1970).

For hydrogen on W, β_2 peak shows second-order desorption kinetics



Pseudo second-order desorption observed for strong *repulsive* interadsorbate interactions

- repulsion increases with coverage and so lowers average desorption temperature

$$-\frac{dM}{dt} = M^2 \exp \frac{-E_{des} + (a M E_{repulsion})}{R T}$$

D. *Fractional-order desorption kinetics:*

Occasionally *fractional order* ($0 < n < 1$) desorption is observed

- believed to indicate cluster formation on surface
- desorption from edges of cluster (2-D or 3-D)

6.1.3 Analysis of TPD Data

Polanyi-Wigner equation can be rewritten

$$-\frac{dM}{dt} = M^n \exp\left(\frac{-E_{des}}{RT}\right)$$

$$\ln \frac{dM}{dt} = \ln M^n + n \ln M + \frac{-E_{des}}{RT}$$

A graph of $\ln \frac{dM}{dt}$ versus $\frac{1}{T}$ will produce a straight line of slope $-\frac{E_{des}}{R}$ and intercept $\ln M^n + n \ln M$

- if the correct value of n (order) is chosen
- if E_{des} and M are coverage independent
- Arrhenius plot

Usually, first part of desorption trace used (<5 % desorption) where M doesn't change appreciably ("leading edge" analysis)

6.1.4 Example of TPD Data: CO₂ on NaCl(100)

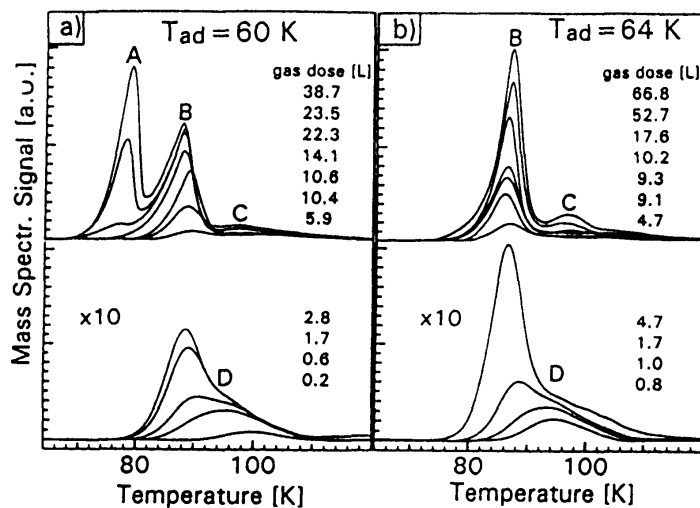


Fig. 3a, left: TPD spectra of CO₂ after adsorption on NaCl(100) at 60 K. Fig. 3b, right: TPD spectra of CO₂ after adsorption at 64 K. The relative quantities are given as exposures (in Langmuir, 15 L correspond approximately to a monolayer).

Even for simple adsorbates, often complex desorption behavior. Four peaks visible

- A - multilayer ($E_{\text{des}} \sim 21 \text{ kJ}\cdot\text{mol}^{-1}$)
- B - monolayer ($E_{\text{des}} \sim 26 \text{ kJ}\cdot\text{mol}^{-1}$)
- C - artifact (desorption from sample holder)
- D - defects and step-edges

Different layer morphology when adsorbed at 60 K or 64 K

- 60 K - separate monolayer/multilayer
- 64 K - one peak that does not saturate (islanding?)
-

6.1.5 Example of TPD Data: Alkyl Iodides on $\text{TiO}_2(110)$ and $\text{Au}(100)$

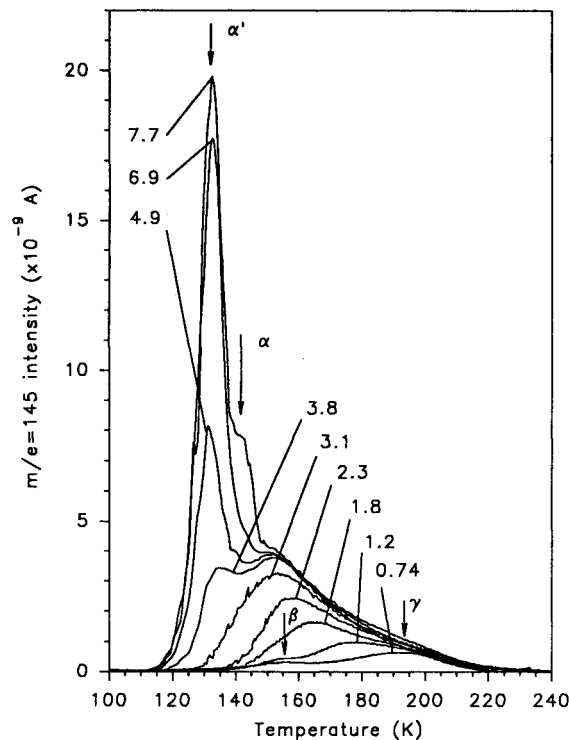


FIG. 4. Desorption profiles for CD_3I ($m/e=145$) adsorbed on the $103 \pm 3 \text{ K}$ $\text{TiO}_2(110)$ surface for exposures between 0.74 and 7.7 L.

- + peak exhibiting second-order desorption behavior
 - first layer/monolayer (+ defects?)
 - repulsive interactions between adsorbates
- ' peak exhibiting first-order desorption behavior
 - second layer?

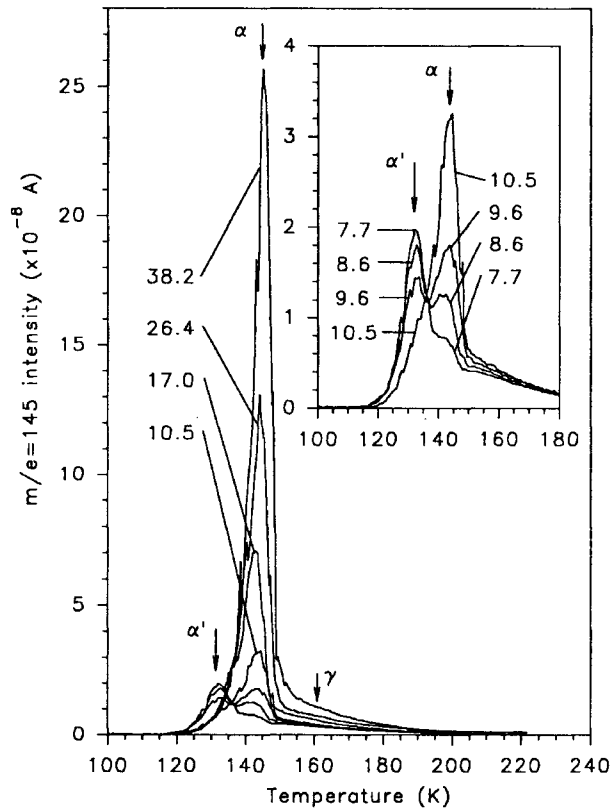


FIG. 5. Desorption profiles for CD_3I ($m/e=145$) adsorbed on the 103 ± 3 K $\text{TiO}_2(110)$ surface for exposures between 7.7 and 38.2 L. The inset shows in detail, the desorption profiles between 7.7 and 10.5 L showing the conversion of the α' phase to the α phase.

peak exhibiting zero-order desorption kinetics

- multilayer

In fact, ' peak is metastable and rearranges to true multilayer structure

All adsorption is reversible - non-dissociative

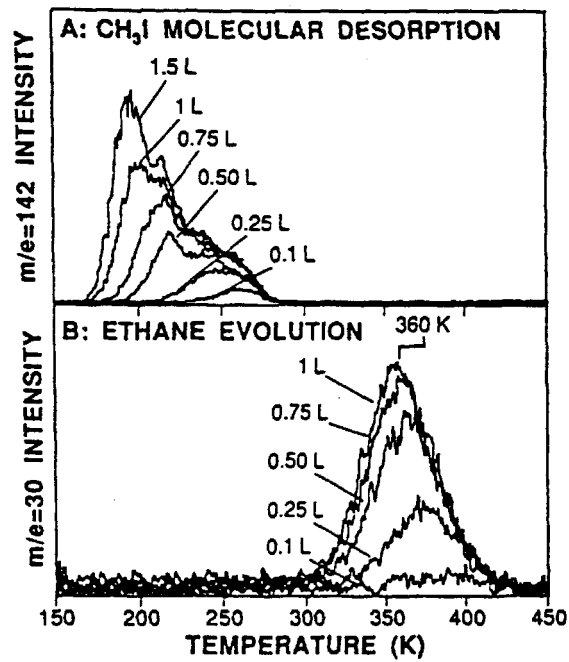
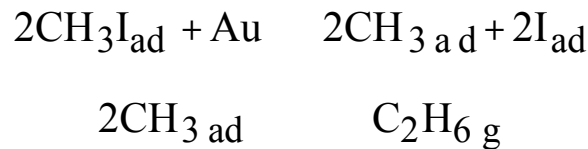


Fig. 1. Temperature-programmed reaction/desorption spectra of CH_3I from $\text{Au}(100)$. (A) $m/e = 142$ (CH_3I molecular desorption) evolution; (B) $m/e = 30$ (C_2H_6) evolution.

Observe monolayer/multilayer behavior

At higher temperatures observe ethane production



Dissociation probably on defects (4 % ethane)

Higher analogs produce range of products:

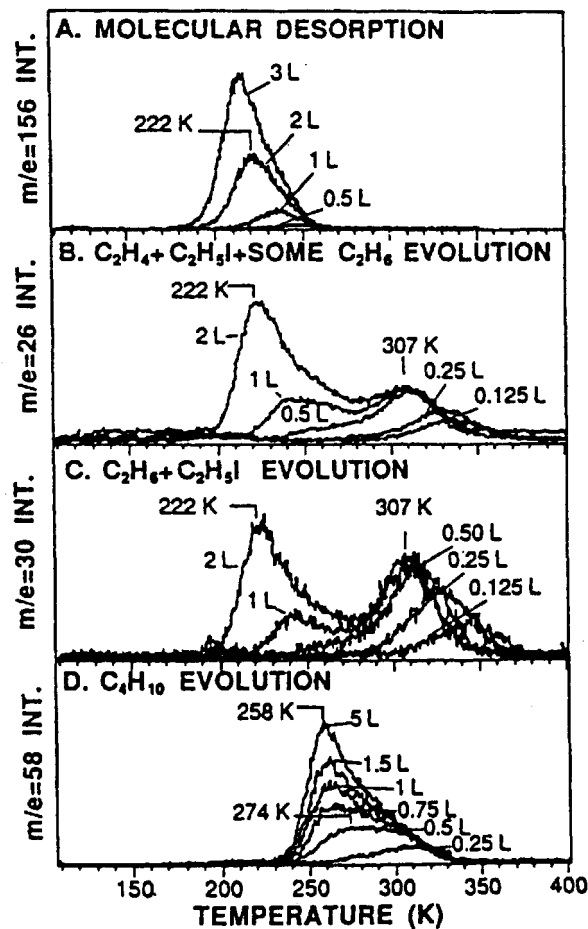


Fig. 2. Temperature-programmed reaction/desorption spectra of C_2H_5I from $Au(100)$. (A) $m/e = 156$ (C_2H_5I) evolution; (B) $m/e = 26$ (C_2H_4 + some C_2H_6 and C_2H_5I) evolution; (C) $m/e = 30$ (C_2H_6 + some C_2H_5I) evolution; (D) $m/e = 58$ (C_4H_{10}) evolution.

Monitoring of several masses during heating to probe for reaction sometimes called *temperature programmed reaction (TPR)* or *temperature programmed reaction spectroscopy (TPRS)*

- *multiplexed* mass spectrometer (quadrupole)

But, based on TPD/TPR alone, difficult to determine if reaction occurs at low temperatures or during heating

Summary

Simple, rapid

Quantitative coverage information (simplest case)

Can accurately determine exposure required for 1 ML coverage (in layer-by-layer systems)

Provides information about adsorption/desorption enthalpies (simplest non-dissociative case)

Provides information about layer stability

Provides information about fragmentation and reaction in dissociative adsorption (TPR)

BUT

Destructive

Binding sites occupied at low temperature not necessarily those from which molecule desorbs during TPD

Mathematical treatment of data useful but can be easily misapplied

Often very complex desorption kinetics observed even for simple systems

- E_{des} , n are temperature dependant

Difficult to determine temperature of reaction

Fragments with coincident m/z peaks can complicate interpretation