CH448/548 Surface Chemistry 2007

Midterm Exam

Name : Key **Score :** 85 **/ 85**

SHOW WORKING WHERE APPROPRIATE TO ENSURE PARTIAL CREDIT

Possibly useful information :

$k_0 = 2\pi\,[E(eV) / 150]^{1/2}$ Å^{-1} $\lambda = h / mv$

$h = 6.626 \times 10^{-34}$ J s

$k = 1.381 \times 10^{-23}$ J / K

$R = 8.314$ J / mol K

$m_e = 9.109 \times 10^{-31}$ kg

$N_A = 6.022 \times 10^{23}$

1 atm = 760 torr = 101,325 Pa

Molecular masses (amu): H 1.008 C 12.01 O 16.00

0. Circle the most appropriate answer – you might want to answer this after doing the rest of the exam first (circle either answer for 1 pt).

This exam was a Valentine's Day Present / a Valentine's Day Massacre

1. (10 pts) You have finally graduated from OSU (in 2022) with a Ph.D. You go to a job interview with "Surfaces R Us" (President, P.R. Watson, OSU retired). Part of the interview consists in answering the following questions. (2 pts each).

Name a good technique to image the surface of a copolymer. (-1)

AFM (STM needs conducting substrate)

Name a good technique to determine the structure of a reconstructed clean surface.

LEED, LEIS

Name a good technique to determine the adsorption enthalpy of a molecule on a surface.

TDS, adsorption isotherms

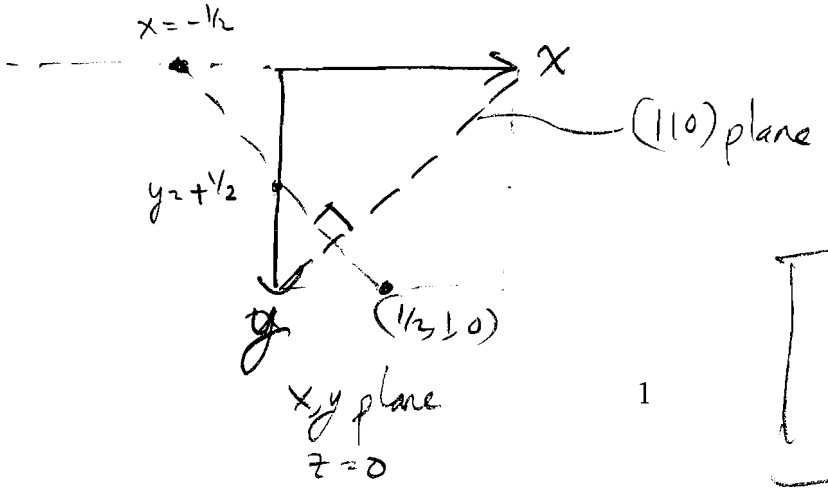
Name a good technique to find the geometry of a molecule adsorbed on a surface.

HREELS, IR (LEED)

Name a good technique to measure the size of atomic-size defects on a Si surface.

STM (AFM (-1) usually does not have resolution)

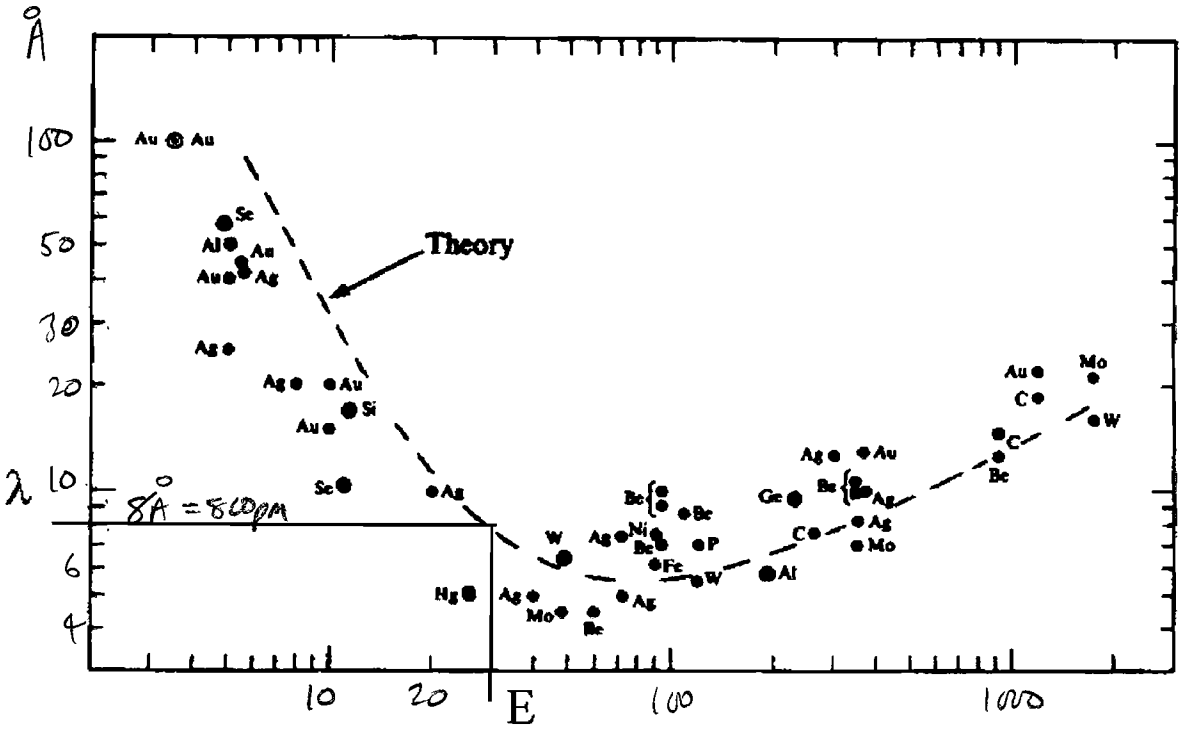
2. (4 pts) A surface is prepared from a single crystal of a bcc metal. The surface is perpendicular to the (110) plane, runs parallel to the z-axis and passes through the point (0.5, 1, 0) in the unit cell. What are the Miller indices of this surface?



x-intercept = -1/2
y-int. = +1/2
z-int = ∞

(-2, 2, 0)
surface

3. (10 pts) Below is the "Universal Curve" of electron escape depth as a function of electron kinetic energy, but it is missing any numerical axis labels.



a) Estimate the values of E and λ . (2 pts each)

E = 30 eV λ = 800 pm

b) Where on this curve is an electron most "surface sensitive"? (2 pts)

At the minimum ~100eV

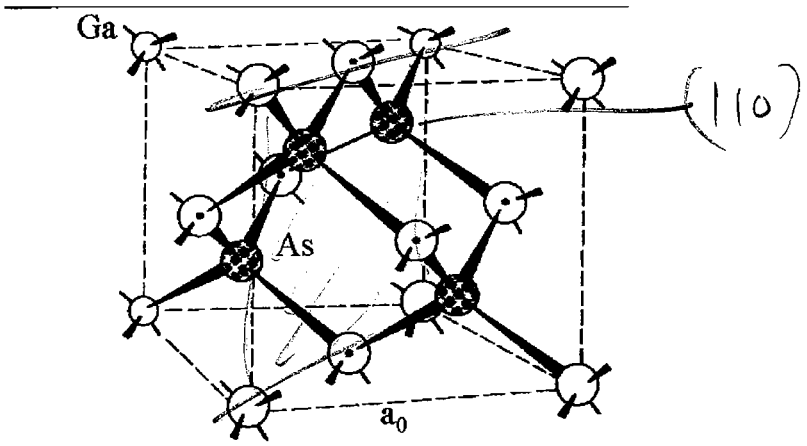
c) What is the meaning of "mean free path"? (4 pts)

i) Average distance an e^- travels in a solid before being scattered

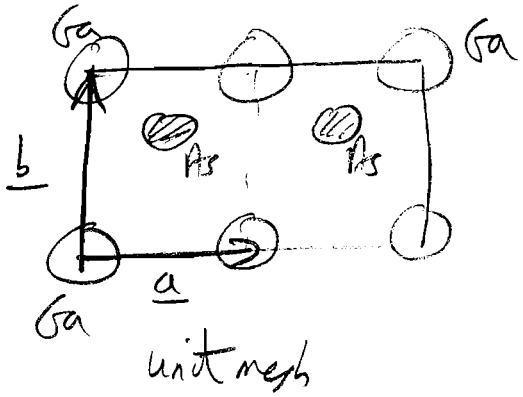
or

ii) Depth at which probability of escape is (1/e)

4. (20 pts) Below is shown the crystal structure of GaAs.



a) Sketch the unit mesh of the GaAs(110) surface and the atoms present in the plane. Only include atoms that lie in the surface plane, not those that lie a little above or below it. The atoms need not be to scale, but identify which are Ga and which are As. Mark the (a, b) vectors that define the unit mesh. (6 pts)



b) What are the lengths of the unit mesh vectors in units of the unit cell parameter a_0? (2 pts)

$|\underline{a}| =$ $\sqrt{2}/2$ a_0 or $1/\sqrt{2}$ $\qquad$ $|\underline{b}| =$ 1 a_0

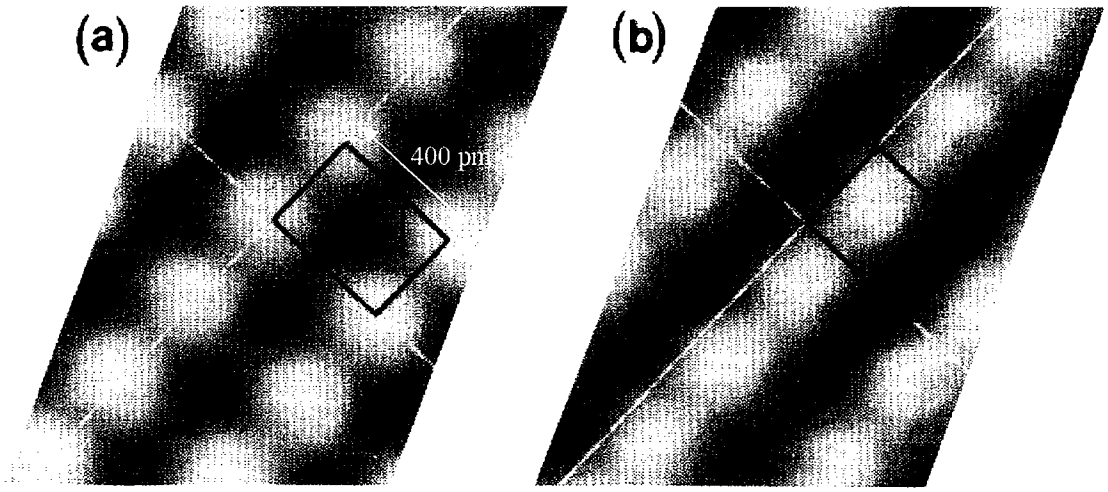
c) What will be the relative lengths of the reciprocal lattice vectors for this surface? (2 pts)

$|\underline{a^*}| / |\underline{b^*}| =$ $1/(\sqrt{2}/2) = \sqrt{2}$

$|a^*| \propto \frac{1}{|a|}$ $\qquad$ $|b^*| \propto \frac{1}{|b|}$

$\frac{|a^*|}{|b^*|} \propto \frac{|b|}{|a|}$

(d) Below are STM images of the GaAs(110) surface taken at two different tip voltages. The white cross-hairs are centered on the same location in each image and the black rectangle is similarly invariant. The lattice constant of GaAs is 400 pm. You can assume that the sample has not physically moved during the measurement or changed chemically in any way.



i) what does the black rectangle represent? Unit mesh of (110) (2 pts)

ii) what are the white features in (a)? One type of atom (Ga say) (2 pts)

iii) what are the white features in (b) Other type of atom (As say) (2 pts)

could be other order

iv) why do one set of white features show up in each image and not both sets in both images? (4 pts)

The tip voltage samples different wavefns in the material. At one voltage, it is sample wavefns that are primarily Ga and the other primarily As.

5) (25 pts total) a) What do the following formulas describe and what is the significance of the parameters? (5 pts each part)

i) $r = \nu_m \theta^m \exp(-\Delta H / RT)$ $\quad m = 1, 2$

Formula describes desorption rate

$m =$ order of desorption

$\nu_m =$ attempt frequency

$\theta^m =$ coverage

$\Delta H =$ Δ H of desorption

ii) $\theta = (bP)^m / (1 + (bP)^m)$ $\quad m = 0.5, 1$

Formula describes (Langmuir) chemisorption

$m =$ order 0.5 = dissoc., 1 = assoc.

$b =$ constant = $K = k_{ads}/k_{des}$

$\theta =$ coverage

At high pressures what is the limiting value of θ? 1

iii) $P / V(P^* - P) = 1/ V_m c + (c-1)P / V_m c P^*$

Formula describes Physisorption

Name associated with formula BET

$V_m =$ volume adsorbed at 1 monolayer

$c =$ const. related to ΔH adsorption

$P^* =$ S.V.P. of liquid adsorbate

b) The activation energy of desorption of an associatively adsorbed molecule X_2 is 108 kJ/mol. If the attempt frequency for desorption is 10^{13} s^{-1} what will be the rate of desorption of X_2 at 500K? Take the coverage to be unity and that desorption is first order (5 pts)

$\text{rate} = \nu \theta e^{-\Delta H/RT}$ $\quad \nu = 10^{13} s^{-1}$

$= 10^{13} e^{-108{,}000/8.314\times500}$ $\quad \theta = 1$

$= 10^{13} e^{-25.98}$ $\quad \Delta H = 108\ kJ/mol$

$= 10^{13} \times 5.21\times10^{-12}$ $\quad R = 8.314\ J/molK$

$\text{rate} = 52.1\ s^{-1}$ $\quad T = 500K$

c) an experiment studies the adsorption of A(g) and B(g) on metal X. Both A and B adsorb associatively on the same site on the surface. Assuming the adsorptions are Langmuirian with b_A = 1 $torr^{-1}$ and b_B = 10 $torr^{-1}$ what will be the coverages of A and B on the surface when $P_A = P_B$ = 100 torr? (5 pts)

For coadsorption of A + B

$\theta_A = b_A P_A / (1 + b_A P_A + b_B P_B)$

$\theta_B = b_B P_B (1 + b_A P_A + b_B P_B)$

$P_A = P_B = 100$ torr $\quad b_A = 1\ torr^{-1}$, $b_B = 10\ torr^{-1}$

$\theta_A = 1\times100 / (1 + 1\times100 + 10\times100) = \frac{100}{1101} = 9.1\%$ $\quad (0.091)$

$\theta_B = 100 - 9.1\% = 90.9\%$ $\quad (0.909)$

5. (15 pts) A 50:50 mixture of $^{12}C^{16}O$ and $^{14}C^{18}O$ is exposed to the surface of a metal. The following are experimental observations.

a) TDS data has asymmetric peaks with equal areas for masses 28 and 32, no peak at mass 30 or any other mass.

Asymmetric peaks means 1st order desorption (intact molecules) (1 pt)

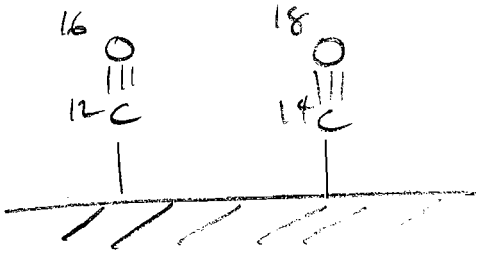
Specie(s) desorbing are $^{12}C^{16}O$ (28); $^{14}C^{18}O$ (32) (2 pts)

Equal areas and no peak at mass 30 means Equal area = 50/50 as adsorbed

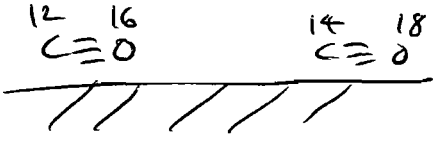
Mass 30 = $^{12}C^{18}O$ or $^{14}C^{16}O$ ∴ no isotopic mixing (2 pts)

The type of adsorption is associative (1 pt)

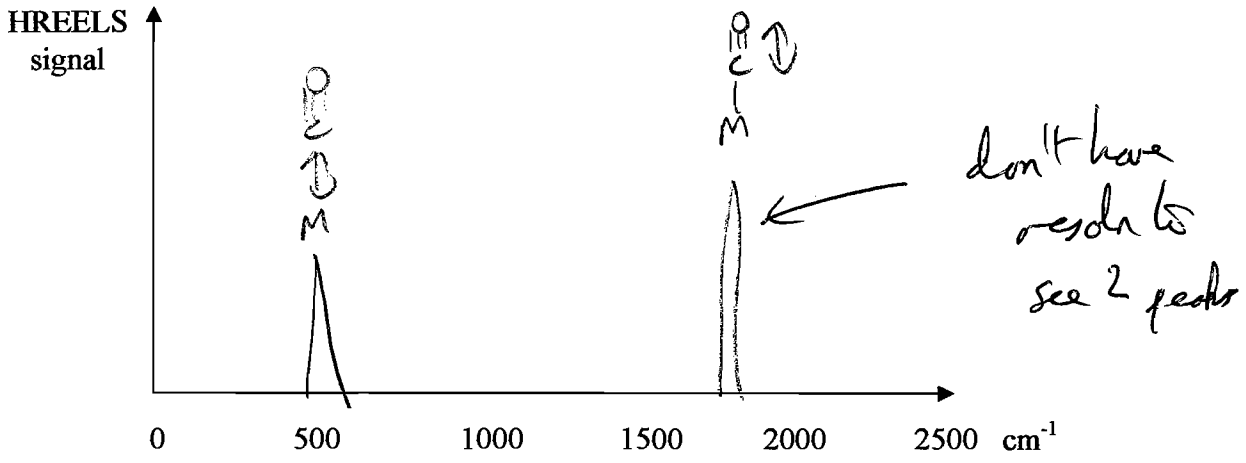
Draw a sketch of the adsorbate(s) on the surface: (4 pts)



could also be



b) Predict the approximate HREELS spectrum for adsorption on the surface. Label peaks with the type of vibration involved. (5 pts)



Intact CO on surface ∴ have C≡O str ~ 1800 cm⁻¹

Also have M⟷C≡O str ~ 500 cm⁻¹ or less

As long as CO is perpendicular, will see both in HREELS