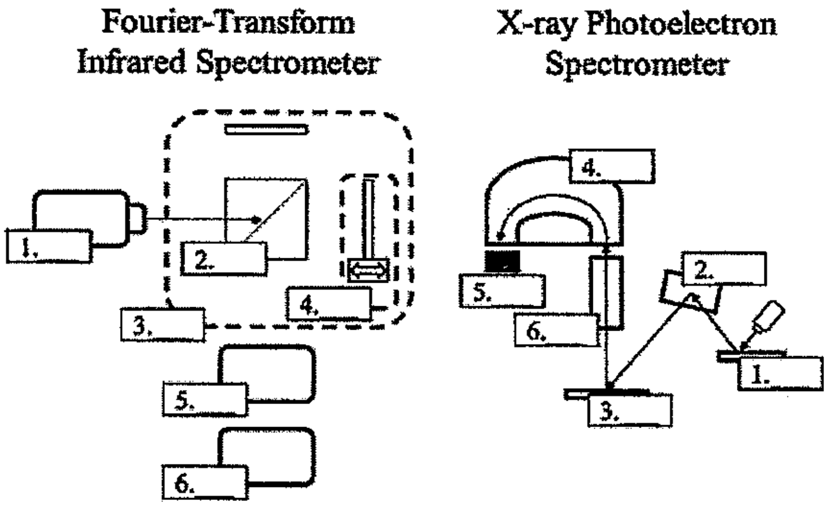
※ 注意：請於試卷內之「非選擇題作答區」依序作答，並應註明作答之大題及小題題號。

#1-3: Basic Concept (20 pts)

The following two schemes illustrate the operational principle and instrumentation design of a Fourier-Transform Infrared Spectrometer (FT-IR) and an X-ray Photoelectron Spectrometer (XPS). **Please choose only one instrument to answer the question.**



A. White LED Light
B. Broad Band Infrared
C. Monochromatic Infrared
D. Infrared Laser
E. Cathode
F. Anode
G. X-ray
H. Mirror
I. Slit
J. Hemispherical Analyzer
K. Michelson Interferometer
L. Grating
M. Moving Stage
N. Photon Multiplier Tube
O. CCD
P. Reference Cell
Q. Beamsplitter
R. Band-Pass Filter
S. Beam stopper
T. Monochromator
U. Focusing Lens
V. Sample Holder
W. Polarizer

1. Please fill the blank from 1 to 6 with using the provided terms from A to S at right hand side. **(6 pts)**
2. Question set for choosing FT-IR: (14 pts)

2.1 What is the correct description between IR and Raman? (A) Raman is a scattering process which is often categorized as an absorption spectroscopy. (B) IR involving vibration mode excitation, leading to electron polarization change. (C) Changing of dipole moment is the selection rule of Raman. (D) IR active mode is not necessary the Raman active mode. (**2 pts**, single choice)

2.2 Which of the following statements of FT-IR is incorrect? (A) The interferogram is generated by changing the distance between the beamsplitter and sample. (B) The Fourier transform is converting the mirror displacement to wavenumber. (C) The light source is a monochromatic IR laser. (D) the spectrum resolution is determined by the accuracy of the mirror displacement. (**4 pts**, multiple choice)

2.3 In absorption spectroscopy, which correlations between the Absorbance (A), Transmittance (T), Incident light intensity(I_0), transmitted light intensity (I), attenuation coefficient (ε), molar concentration (c) and optical path length (b) are correct? (A) $A = \varepsilon bc$, (B) $T = I/I_0$, (C) $T=10^{-A}$ (D) $I_0/I=\exp(-\varepsilon bc)$. (**4 pts**, multiple choice)

2.4 Experimentally, if a sample with very high measured absorbance (nearly out of range), which following statements are correct? (A) Such measurement provides very accurate quantitative information. (B) The sample has no room for further dilution. (C) High absorbance indicate low transmitted light, which provides higher error. (D) One should concentrate the sample to lower the absorbance. (**2 pts**, single choice)

2.5 *In-situ* measuring a reaction converting X to Y where the Y is an IR active species that absorb IR. The reaction rate v (assuming $v = k[X]$, k is the rate constant) can be obtained from the time-dependent absorbance increasing. Which function below can be used to describe the change of absorbance (A) with characteristic time constant τ? Boundary conditions: i) t = 0, [X]= c, [Y] = 0. ii) t = ∞, [X] = 0, [Y] = c. (A) $A(t)= \varepsilon bc*(1-\tau k e^{-t/\tau})$, (B) $A(t)= \varepsilon bc$, (C) $A(t)= \varepsilon bc*(e^{t/\tau}+e^{-it/\tau})$, (D) $A(t) = \varepsilon bc*(1-t)e^{-t/\tau}$. (**2 pts**, single choice)

3. Question set for choosing XPS: (14 pts)

   3.1 Sample under which environmental conditions can be measured in XPS? (A) Ultra-high vacuum, (B) Vacuum, (C) Near-ambient, (D) Ambient. (**4 pts**, multiple choice)

   3.2 What is the definition of *one Langmuir*? (A) Time required for a monolayer molecule adsorption on the surface under 1 atm. (B) Entropy gained from a monolayer molecule desorbed from the surface. (C) Pressure to achieve a monolayer molecule adsorption in 1 s. (D) Surface pressure change with a monolayer molecule adsorption. (**2 pts**, single choice)

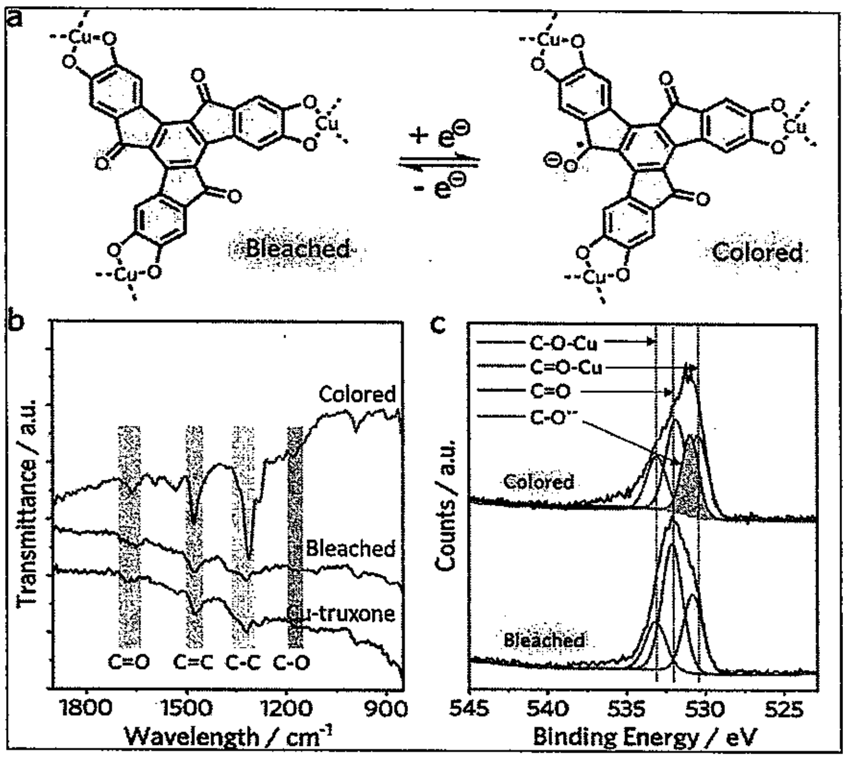
   3.3 Which of the following process can generate X-ray for XPS analysis? (A) Acceleration of a charged particle. (B) Changing the trajectory of an electron. (C) Annihilation/recombination of electron from core level with electron hole from outer level. (D) None of the above. (**2 pts**, single choice)

   3.4 How is the binding energy axis in a XPS spectrum generated? (A) The energy of the collected electron. (B) The energy difference between the Sample bias and the photoelectron energy. (C) The energy difference between the selected kinetic energy and the X-ray energy. (D) The energy difference between the work function and X-ray energy. (**2 pts**, single choice)

   3.5 What is the nature of the Auger electron? (A) It's kinetic energy correlated to the X-ray energy. (B) Generation of an electron hole is necessary for Auger electron emission. (C) By carefully tuning the incident angle of the X-ray, the Auger electron emission can be removed from the spectrum. (D) When the Auger electron emission is overlapped with the photoelectron feature, changing the X-ray energy can resolve the overlapping issue. (**4 pts**, multiple choice)

#4-6: Scientific Skills (30 pts)

A recent publication (*J. Am. Chem. Soc.* 2025, 147, 51, 46806–46811) reporting FTIR and XPS (O 1s) characterization results of the given molecule: Cu-truxone shown below:



4. Please provide a figure caption for the given graph. (**5 pts**)
5. Please provide a comprehensive <u>description</u>, <u>discussion</u> and <u>conclusion</u> from the provided graph within 150 words (**15 pts**)
6. Please provide a concern of why the comparison between FTIR and XPS in this graph is **not ideal**? Please justify your answer. (**10 pts**)

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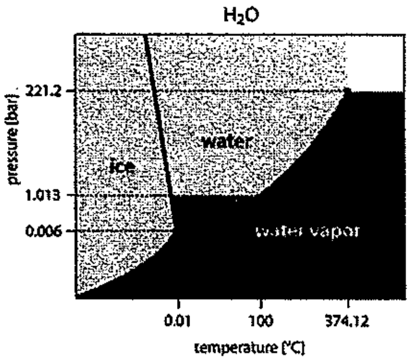
#7-16: Multiple-Choice Questions (20 pts, 2 pts each)



7. The phase diagram to the right shows the stable phases of H_2O as a function of pressure and temperature. Which expression correctly represents the Clapeyron equation describing the slope of a phase boundary?

(A) $\frac{dP}{dT} = -\frac{\Delta V}{\Delta S}$ (B) $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ (C) $\frac{dP}{dT} = -\frac{\Delta H}{T\Delta V}$

(D) $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$ (E) $\frac{dT}{dP} = \frac{\Delta H}{\Delta V}$

8. For a rigid diatomic molecule, the canonical partition function is approximated by:

$$q(T) \approx q_{trans} \times q_{rot} \times q_{vib} \times q_{elec}$$

At moderate temperatures, the translational and rotational modes are fully excited, but the vibrational modes are only partially populated. Which of the following predictions is consistent with statistical thermodynamics?

(A) The molar heat capacity approaches $3R$ at low temperatures.

(B) The molar heat capacity approaches $\frac{5}{2}R$ at intermediate temperatures.

(C) The vibrational contribution to entropy decreases with increasing temperature.

(D) The rotational partition function shows strong temperature dependence below 300 K due to the large rotational energy spacing.

(E) The total internal energy is independent of temperature in the classical limit.

9. Which function is an eigenfunction of the linear kinetic energy operator $\hat{T}_x$ with the eigenvalue $\frac{2\hbar^2 k^2}{m}$?

(A) $\sqrt{2}\sin(2kx)$ (B) $\cos(kx)$ (C) $\cos(4kx)$

(D) e^{2kx} (E) e^{-4ikx}

10. Consider the following four spin wavefunctions of a two-electron system:

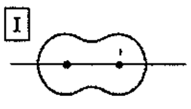
$$\phi_1 = \alpha(1)\alpha(2),\ \phi_2 = \beta(1)\beta(2),\ \phi_3 = \frac{\alpha(1)\beta(2)+\alpha(2)\beta(1)}{\sqrt{2}},\ \phi_4 = \frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}$$

Given that $\hat{S}_1$ and $\hat{S}_2$ are the spin angular momentum operators for electron 1 and 2, respectively, and assume electrons are distinguishable only by labels 1 and 2. Which wavefunctions are the eigenfunctions of $\hat{S}^2_{total} = (\hat{S}_1 + \hat{S}_2)^2$ with the eigenvalue being $2\hbar^2$?

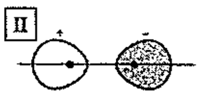
(A) ϕ_1 and ϕ_2 (B) ϕ_3 and ϕ_4 (C) ϕ_1, ϕ_2, and ϕ_3

(D) Only ϕ_4 (E) None of the above

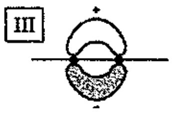
I



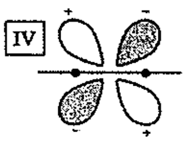
II



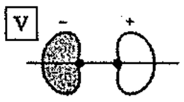
III



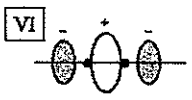
IV



V



VI



11. Among the molecular orbitals of H_2^+ shown to the right, which have the quantum number $m_l = 0$?

(A) I, II (B) III, IV (C) II, III, V

(D) I, III, VI (E) I, II, V, VI

12. Which of the following statements best reflects Bohr's correspondence principle?

(A) The position and momentum of a quantum particle cannot both be known precisely at the same time.

(B) Electromagnetic waves also exhibit particle-like behavior.

(C) Electrons orbit the nucleus in circular paths with fixed radii.

(D) In the limit of large quantum numbers, quantum mechanics converges with classical physics.

(E) The total entropy of an isolated system never decreases.

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13. What statement is *false* about the *stimulated emission* process from state $|2\rangle$ to state $|1\rangle$?

(A) It is an incoherent process.
(B) Its rate constant is proportional to $|\vec{\mu}_{12}|^2$, where $\vec{\mu}_{12}$ is the transition dipole moment.
(C) The state $|2\rangle$ must have higher energy than the state $|1\rangle$.
(D) It requires interaction with an electromagnetic wave.
(E) The energy difference between $|2\rangle$ and $|1\rangle$ is converted to a photon.

14. A reaction follows the Arrhenius form:

$$k(T) = Ae^{-E_a/RT}$$

over a temperature range of 300-350 K.
Experimentally, the following observations are made:

- A plot of $ln\ k$ vs. T^{-1} is linear with a slope corresponding to E_a = 62 kJ mol^{-1}.
- The experimentally determined pre-exponential factor A is two orders of magnitude smaller than predicted by collision theory.
- Upon adding a catalyst that stabilizes the transition state by 6 kJ mol^{-1}, the observed activation energy decreases to 56 kJ mol^{-1}, but A increases by a factor of 20.

Which of the following statements is best supported without invoking new assumptions?

(A) The uncatalyzed reaction does not involve a transition state and proceeds barrierlessly.
(B) The small A in the uncatalyzed reaction indicates a strongly negative activation entropy.
(C) The linear Arrhenius plot proves that tunneling contributes significantly to the reaction rate.
(D) The catalyst lowers the activation barrier but does not change the entropy of activation.
(E) The change in both E_a and A upon catalyst addition implies that the reaction mechanism changes in terms of transition-state reorganization.

15. An enzyme catalyzes the transfer of a hydride from a substrate to NAD+, resulting in the formation of NADH. Isotopic substitution gives the following data:

- Replacing the transferring hydrogen with deuterium yields $k_H/k_D = 6.11$
- The kinetic isotope effect remains nearly constant between 5°C and 45°C.
- Replacing a β-C–H with C-D gives $k_H/k_D \approx 1.03$

What of the following statements is *false*?

(A) β-Hydrogen atoms do not participate directly in the transition state.
(B) Cleavage of the transferring C-H bond contributes to the rate-determining step.
(C) The magnitude and temperature independence of primary K.I.E. are consistent with quantum tunneling.
(D) Hydride transfer likely occurs along the reaction coordinate that determines the overall reaction rate.
(E) The identical values of k_H and k_D at different temperatures prove that the reaction mechanism changes upon isotopic substitution.

16. Consider the reaction mechanism:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{I}$$
$$\mathrm{I+B} \xrightarrow{k_2} \mathrm{P}$$
$$\mathrm{I} \xrightarrow{k_3} \mathrm{Q}$$

where I is a reactive intermediate present at low concentration.
Assume [A] and [B] remain essentially constant over the time scale of interest. Using the steady-state approximation, what is the rate law for the formation of product P?

(A) $\frac{d[P]}{dt} = k_2[I][B]$
(B) $\frac{d[P]}{dt} = k_1[A]$
(C) $\frac{d[P]}{dt} = \frac{k_1k_2[A][B]}{k_2[B]+k_3}$
(D) $\frac{d[P]}{dt} = \frac{k_1k_2[A][B]}{k_1+k_3}$
(E) $\frac{d[P]}{dt} = \frac{k_1[A]}{k_2[B]+k_3}$

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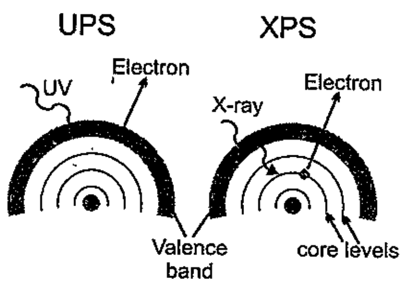
#17-18: Short-Answer Questions (30 pts)

17. **(16 pts)** Ultraviolet photoelectron spectroscopy (UPS) measures the kinetic energies of photoelectrons emitted when a sample is irradiated with ultraviolet photons, allowing the energies of occupied molecular orbitals to be determined (see the graph to the right).



In a typical UPS light source, helium gas is excited in a hollow-cathode discharge, producing two strong resonance emission lines:

- He I (21.22 eV) – produced by relaxation of the neutral helium $1s2p$ excited state back to the $1s^2$ ground state.
- He II (40.81 eV) – produced by electronic relaxation in singly ionized helium (He^+).

Answer the following:

(a) **(2 pts)** The He II line is emitted by He^+. From which hydrogen-like orbital does the electron transition, and to which orbital does it relax?

(b) **(2 pts)** Write the atomic term symbols $^{2S+1}L_J$ for the ground and excited states of He^+ that give rise to the He II line.

(c) **(5 pts)** Write the atomic term symbols $^{2S+1}L_J$ associated with the $1s^2$ ground state and the $1s2p$ configuration of neutral He.

(d) **(3 pts)** Draw a qualitative energy-level diagram showing all of the term symbols in (c). Indicate spin-orbit splitting where appropriate, and use electric dipole selection rules to identify the allowed transition that produces the He I line at 21.22 eV.

(e) **(4 pts)** Using first-order time-independent perturbation theory, estimate the energy of the He I emission line. You may assume the Coulomb and exchange integrals listed below fully determine the relative energies of the $1s^2$ and $1s2p$ configurations:

$$J_{1s1s} = 34.0 \text{ eV}, \qquad J_{1s2p} = 13.2 \text{ eV}, \qquad K_{1s2p} = 0.9 \text{ eV}$$

Compare your calculated photon energy with the experimental value.

18. **(14 pts)** The standard molar entropies S_m^0(25°C), constant-pressure molar heat capacities $C_{P,m}^0$, and standard molar enthalpies of formation $\Delta_f H_m^0$ (25°C) for N_2O_4(g) and NO_2(g) are listed in the table on the next page. Assuming that $C_{P,m}^0$ is independent of temperature in the range of 25-200°C, and that the standard-state pressure is 1 bar.

Consider the equilibrium:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

(a) **(2 pts)** Calculate the molar entropy S_m^0(200°C) of N_2O_4(g).

(b) **(2 pts)** Calculate the standard reaction enthalpy $\Delta_r H^0$(25°C) and standard reaction entropy $\Delta_r S^0$(25°C).

(c) **(4 pts)** Using Kirchhoff's law to calculate $\Delta_r H^0$(200°C) and $\Delta_r S^0$(200°C) for the same reaction.

(d) **(3 pts)** Calculate the equilibrium constant K for this reaction at 25°C and 200°C, respectively.

(e) **(3 pts)** Using the integrated Van't Hoff equation and assuming $\Delta_r H^0$ is independent of temperature, estimate K at 200°C. Briefly explain the source of any discrepancy between this estimate and your result from part (d).

	S_m^0(25°C) (J mol^{-1} K^{-1})	$C_{P,m}^0$ (J mol^{-1} K^{-1})	$\Delta_f H_m^0$ (25°C) (kJ mol^{-1})
N_2O_4(g)	304.3	79.2	9.16
NO_2(g)	240.5	27.2	33.18

$c = 2.99792 \times 10^{8}$ m s^{-1}
$h = 6.62608 \times 10^{-34}$ J s
$N_a = 6.02214 \times 10^{23}$ mol^{-1}
1 eV = 1.60218×10^{-19} J
$m_e = 9.10939 \times 10^{-31}$ kg
a.m.u. = 1.66×10^{-27} kg
$k_B = 1.380649 \times 10^{-23}$ J K^{-1}
$e = 1.60218 \times 10^{-19}$ C
$R_H = 3.290 \times 10^{15}$ Hz
= 13.60 eV
= 2.180×10^{-18} J
$E = h\nu$
$c = \lambda\nu$

Ideal gas constant:
$R = 0.08206$ L atm mol^{-1} K^{-1}
= 0.08314 L bar mol^{-1} K^{-1}
= 62.36 L torr mol^{-1} K^{-1}
= 8.314 J mol^{-1} K^{-1}

1D TISE:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\Psi(x) = E\Psi(x)$$

1D Particle-in-a-box:

$$E_n = \frac{n^2h^2}{8mL^2}$$

Bohr radius:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 5.29 \times 10^{-11}\ \text{m}$$

One-electron atom:

$$E_n = -\frac{Z^2R_H}{n^2}$$

Many-electron atom:

$$E_n = -\frac{Z_{eff}^2R_H}{n^2}$$

Electron's orbital angular momentum:

$$|\vec{L}| = \sqrt{l(l+1)}\hbar$$
$$L_z = m_l\hbar$$

Third law of thermodynamics:

$$S = k_B \ln W$$
$$dS = \frac{dq_{rev}}{T}$$

Kirchhoff's law:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \Delta_r C_P^0(T_2 - T_1)$$
$$\Delta_r S(T_2) = \Delta_r S(T_1) + \Delta_r C_P^0 \ln\frac{T_2}{T_1}$$

Van't Hoff equation:

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$G = H - TS$$
$$\Delta G^0 = -RT\ln K$$

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