00108

The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc Degree Programme

Department	**: Chemistry**
Level	**: 5**
Name of the Examination	**: Final Examination**
Course Title and Code	**: CYU5301 – Concepts of Spectroscopy**
Academic Year	**: 2024/2025**
Date	**: 04.12.2024**
Time	**: 9.30 a.m. – 11.30 a.m.**
Duration	**: 2 hours**

General Instructions

1. Read all instructions carefully before answering the questions.
2. This question paper consists of **four (04)** questions in **five (05)** pages.
3. Answer **all parts** of **all questions.** Each question carries 100 marks.
4. The answer to each question should be started on a fresh page.
5. Answers to all parts of any question should be written together.
6. Draw fully labeled diagrams where necessary.
7. Any exam-related offense will result in punishment.
8. Use blue or black ink to answer the questions.
9. Clearly state your index number on all pages of your answer script.
10. Use of non-programmable calculators will be allowed.
11. Mobile phones and other electronic equipment are not allowed. Switch off and leave them outside.
12. A list of constants and equations is provided overleaf for reference.
13. Show all your calculations

List of important constants

Gas constant (R) -	8.314 J $K^{-1}mol^{-1}$	The velocity of light (C) -	3.0×10^{8} ms^{-1}
Avogadro constant (N_A)	6.023 $\times10^{23}$ mol^{-1}	Standard atmospheric pressure (atm)	10^{5} Pa N m^{-2}
Faraday constant (F) -	96,500 $Cmol^{-1}$	1 amu	1.66×10^{-27} Kg
Planck constant (h)-	6.63×10^{-34} J s	$\log_e(X)$	2.303 $\log_{10}(X)$

Some equations used in spectroscopy with standard notation

$$\tilde{\upsilon} = \bar{\omega}_e(1-2\bar{X}_e) \qquad \tilde{\upsilon} = 2\bar{\omega}_e(1-3\bar{X}_e) \qquad E = h\omega\{(\upsilon+½) - (\upsilon + ½)^2 X_e \qquad \upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\tilde{\upsilon} = \frac{1}{2\pi C}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 \times m_2}{m_1 + m_2} \qquad \Delta\tilde{\upsilon} = \sqrt{\frac{8kTB}{hC}} \qquad \Delta\tilde{\upsilon} = \tilde{\upsilon}_{in} \pm B(4J+6)$$

$$\frac{\text{Intensity of anti-Stokes line}}{\text{Intensity of Stokes line}} = \frac{(\nu_0 + |\Delta\nu|)^4}{(\nu_0 - |\Delta\nu|)^4} \times \exp\left(-\frac{h|\Delta\nu|}{kT}\right)$$

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Question 1 (Total 100 marks)

Part A **(Total 50 marks)**

The fundamental and first overtone IR bands (peaks) of the $^{14}N^{16}O$ molecule were observed at 1876 cm^{-1} and 3724 cm^{-1} respectively.

(i) Calculate the anharmonicity constant (10 marks)

(ii) Calculate the equilibrium vibrational frequency in wavenumber (10 marks)

(iii) Zero-point energy in wavenumber term (10 marks)

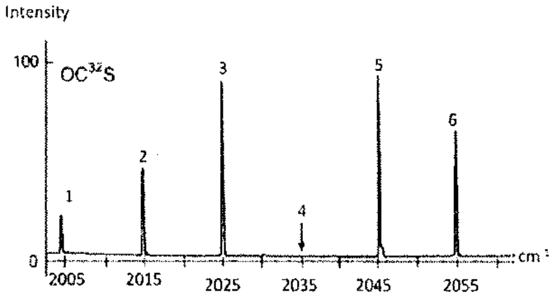
(iv) Force constant at the equilibrium vibrational frequency (20 marks)

Part B **(Total 50 marks)**

(i) Consider the molecule O=C=S. Classify the molecule according to its ellipsoid of inertia then give the relationship among the components of moment of inertia along the three principal axes (04 marks)

(ii) What are the gross and specific selection rules for rotational vibrational spectroscopy for the above molecule? (08 marks)

(iii) The figure below shows the ideal rotational-vibrational spectrum of O=C=S. Identify the branch to which each peak belongs and give the specific rotational selection rule associated with each peak (12 marks)



(iv) How does the real rotational-vibrational spectrum of OCS deviate from the ideal rotational-vibrational spectrum of OCS? Explain why the real spectrum differs from the ideal spectrum (06 marks)

(v) Calculate the rotational constant using the information provided in the spectrum (10 marks)

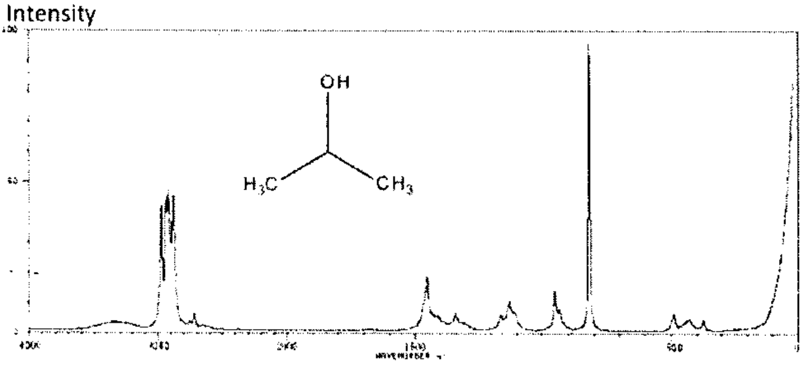
(vi) Estimate the sample temperature using the spectrum provided (10 marks)

Question 2 (Total 100 marks)

Part A **(Total 50 marks)**

(i) What are the gross and specific selection rules for vibrational Raman spectroscopy (10 marks)

(ii) The following spectrum shows the vibrational Raman spectrum of iso-propanol ($CH_3CH_2(OH)CH_3$). If you obtain the IR spectrum of isopropanol, what are the differences you would expect? (Consider normal vibrational modes). (10 marks)



Band position cm^{-1}	Intensity
2972	41
2938	44
2919	46
2881	45
1464	18
1132	10
955	13
820	95

(iii) Calculate the ratio of Anti-Stokes to Stokes scattering intensity when T = 300 K and the vibrational frequency shift 3000 cm^{-1}. The excitation wavelength is 633 nm (10 marks)

(iv) What effect would raising the temperature have on the intensity of Stokes and Anti-Stokes lines in a Raman spectrum? Explain your answer (10 marks)

(v) If you found a water sample heavily contaminated with isopropanol, can you identify the contaminant using vibrational Raman spectroscopy? (Assumption: there are no other contaminants except isopropanol) (10 marks)

Part B **(Total 50 marks)**

(i) What are the gross and specific selection rules for a linear molecule's pure rotational Raman spectrum? Explain the specific selection rules applicable to different types of scattering (10 marks)

(ii) The rotational constant of the $^{14}N^{16}O$ molecule is 2 cm^{-1}. The wavelength of incident radiation is 633 cm^{-1}. What is the wavenumber of the first scattered stoke line (cm^{-1}) of the $^{14}N^{16}O$ Rotational Raman spectrum (10 marks)

(iii) A 20490 cm^{-1} laser line was used to excite the $^{16}O_2$ molecule to acquire the Raman spectrum. In the resulting Raman spectrum, the first stoke line appeared at 20480 cm^{-1}. Calculate the Rotational constant (10 marks)

(iv) Calculate the wavenumber at which the next rotational line would appear at (10 marks)

(v) What type of sample's rotational Raman spectra that the nuclear spin affect and explain the consequence of nuclear spin on the Rotational Raman spectrum (10 marks)

Question 3 Total 100 marks)

Part A (Total 50 marks)

(i) State the gross and specific selection rules for UV-visible spectroscopy (10 marks)

(ii) What do you understand by spin-orbital coupling (10 marks)

(iii) Explain why most of the UV-Vis absorption appears as a band (10 marks)

(iv) A 1 cm cuvette containing iodine crystals was heated until $I_{2(g)}$ was visible. The cuvette was placed in a Cary UV-visible spectrophotometer and $I_{2(g)}$ was scanned from 500-600 nm. The settings on the spectrophotometer included an average time of 1 sec, an average data interval of 0.1 nm, a bandwidth of 0.2 nm, and a double beam mode. The resulting spectrum was analyzed yielding the vibrational and electronic parameters. These parameters were calculated using Equations 1-5 and a Birge-Sponer plot. Calculate the equilibrium vibrational frequency and anharmonicity constant (20 marks)

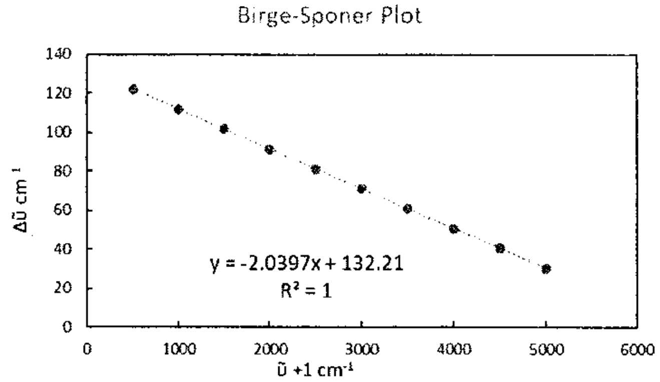
$$\Delta\tilde{\nu}(v') = \tilde{\nu}_e - 2\tilde{x}_e'\tilde{\nu}_e'(v'+1) \qquad \text{Equation 1}$$

$$D_0' = \Delta\tilde{\nu}(v'=0) + \Delta\tilde{\nu}(v'=1) + \Delta\tilde{\nu}(v'=2) + \ldots = A \qquad \text{Equation 2}$$

$$D_e' = D_0' + E_{vib}(v'=0) = D_0' + \frac{1}{2}\tilde{\nu}_e' - \frac{1}{4}\tilde{\nu}_e'\tilde{x}_e \qquad \text{Equation 3}$$

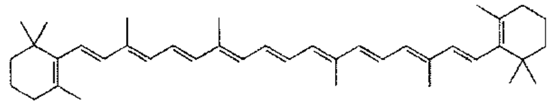
$$E^* = \tilde{\nu}(v'=b) + A' = D_o' + E(I^*) \qquad \text{Equation 4}$$

$$\tilde{T}_e' = D_e'' + E(I^*) - D_e' \qquad \text{Equation 5}$$



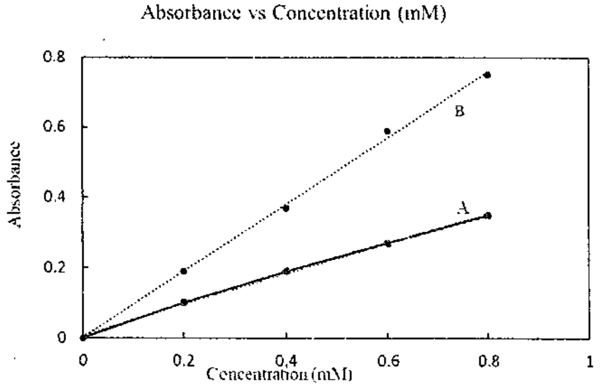
Part B **(Total 50 marks)**

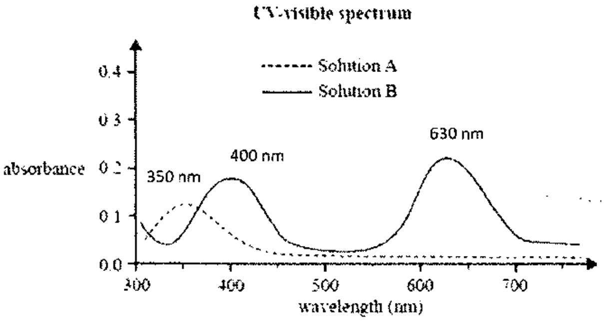
(i) Beta-carotene has the following structure and has strong absorptions in the visible region. The peak appears at 475 nm. Explain why you observe a strong absorption maximum for beta-carotene at 475 nm. (10 marks)



(ii) UV-visible spectra of the solutions A and B were obtained. Solution A was red, while solution B was green. The analyst recorded the absorbance of each solution over a range of wavelengths on the same axes. The resultant absorbance spectra for individual solutions of A and B are shown below. If 10.00 mL of 1 M A solution was mixed with 10.00 mL of 1 M B solution, which wavelength should be used to measure the absorbance of Solution B in this mixture? Justify your answer. (10 marks)

(iii) The analyst used two sets of separate standard solutions for A and B and blanks to determine the calibration curves for the two solutions. The absorbances were plotted on the same axes. The graph is shown below. The analyst found that, when measured at the appropriate wavelength with the path length of 1cm, solution B had an absorbance of 0.2 for the unknown concentration of B in the A and B mixture. Solution B was $NiSO_4$ and the concentration was determined using the Beer-Lambert law. State the Beer-Lambert law and define the terms. Then calculate the concentration (30 marks)





Concentration (mM)	Absorbance A	Absorbance B
0	0	0
0.2	0.1	0.19
0.4	0.19	0.37
0.6	0.27	0.59
0.8	0.35	0.75

Question 4 (Total 100 marks)

Part A (Total 30 marks)

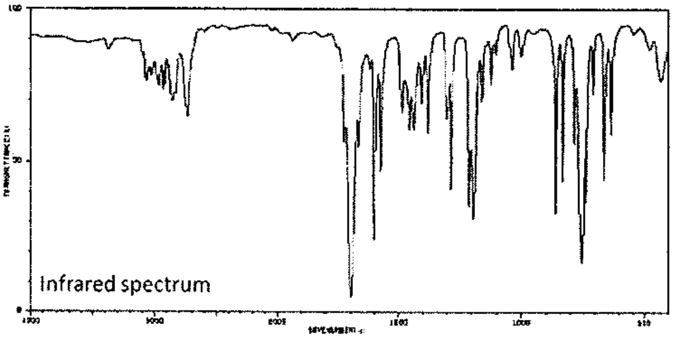
(i) Define the chemical shift scale using an appropriate mathematical equation. Define each term in the equation (10 marks)

(ii) State two important characteristics of a reference compound in NMR spectroscopy. (10 marks)

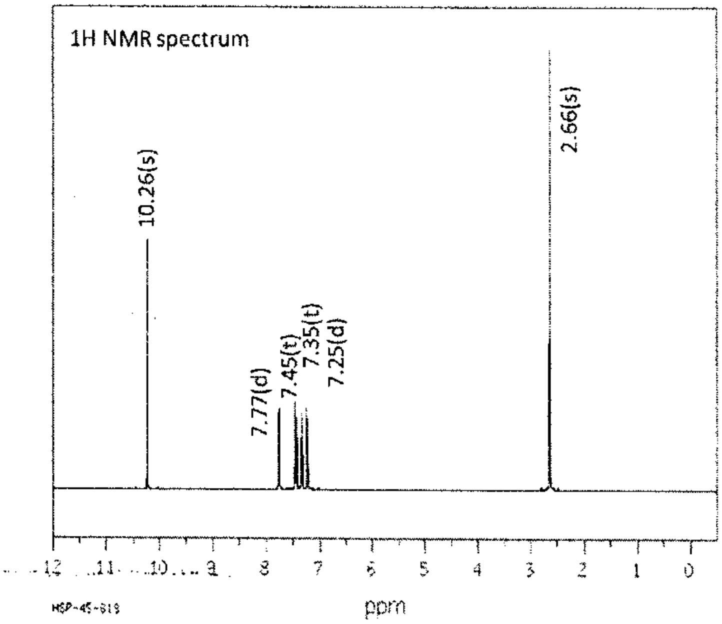
(iii) A solution that contains a mixture of compounds A and B. The compound A produces a line at 10.0 ppm and compound B produces the line at 2.5 ppm in the high-resolution spectrum. B is used as the reference. Calculate the chemical shift (in scale) of the proton NMR line of A (10 marks)

Part B (Total 70 marks)

The following NMR and IR, spectra correspond to the compound X (C_8H_8O). The NMR spectrum was obtained with 400 MHz in $CDCl_3$ as the solvent. An Intense IR band was seen at 1724 cm^{-1}. Deduce the possible structure.



Peak	Int	Peak	Int	Peak	Int	Peak	Int	Peak	Int
3068	74	1724	53	1456	68	1211	34	785	53
3041	77	1697	4	1438	62	1194	29	754	16
3029	74	1664	62	1405	86	1160	68	738	36
2963	72	1619	77	1381	57	1122	72	709	70
2926	70	1601	23	1304	62	1037	77	663	42
2866	86	1573	44	1298	84	862	31	637	57
2733	82	1487	64	1265	39	834	42	434	74



1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.66 (s, 3H), 7.25 (d, J = 8.0Hz, 1H), 7.35 (t, J = 8.0Hz, 1H), 7.45 (t, J = 8.0Hz, 1H), 7.77 (d, J = 8.0Hz, 1H), 10.26 (s, 1H).

-------------------------- End of examination paper --------------------------

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