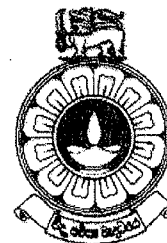


The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc. Degree Programme



Department	: Chemistry
Level	: 5
Name of the Examination	: Final Examination
Course Title and Code	: CYU5301 – Concepts of Spectroscopy
Academic Year	: 2025/2026
Date	: 08.01.2026
Time	: 9.30 a.m. – 11.30 a.m.
Duration	: 2 hours

General Instructions

- Read all instructions carefully before answering the questions.
- This question paper consists of **four (04)** questions in **five (05)** pages.
- **Answer all questions, including all the parts.**
- Each question carries 100 marks.
- The answer to each question should start on a fresh page.
- Question numbers of main and sub sections should be clearly stated.
- Answers to all parts of any question should be written together.
- Draw fully labeled diagrams where necessary.
- Any exam-related offense will result in punishment.
- Use blue or black ink to answer the questions.
- Clearly state your index number on all pages of your answer script.
- Use of non-programmable calculators will be allowed.
- Mobile phones and other electronic equipment are not allowed. Switch off and leave them outside.
- A list of constants and equations is provided.
- Show all your calculations in steps.

List of important constants

Gas constant -	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro constant (N_A) -	$6.023 \times 10^{23} \text{ mol}^{-1}$
Faraday constant (F) -	$96,500 \text{ C mol}^{-1}$
Planck constant (h) -	$6.63 \times 10^{-34} \text{ J s}$
The velocity of light (C) -	$3.0 \times 10^8 \text{ ms}^{-1}$
Standard atmospheric pressure	10^5 Pa
1 cm =	$1 \times 10^{-8} \text{ A}^0$
Boltzmann Constant (k)	$1.38 \times 10^{-23} \text{ J K}^{-1}$
1 amu	$1.66 \times 10^{-27} \text{ Kg}$
$\text{Log}_e (X)$	$2.303 \text{ Log}_{10}(X)$

Some equations used in spectroscopy with standard notation

$$T = \frac{hc(\Delta\bar{\nu})^2}{8k\bar{B}} \quad \bar{\nu}_O = \bar{\nu}_0 + \bar{\nu}_f + \bar{B}(4J+6) \quad \bar{\nu}_S = \bar{\nu}_0 + \bar{\nu}_f - \bar{B}(4J+6) \quad \bar{\nu}_Q = \bar{\nu}_0 + \bar{\nu}_f$$

$$\bar{\nu}_f = (1 - 2x_e)\bar{\omega}_e \quad \tilde{\nu} = 2\bar{\omega}_e(1 - 3x_e) \quad h\nu = 2B(J+1) \quad \bar{\nu} = \bar{\nu}_0 \pm 2\bar{B}(2J+3)$$

$$\Delta\bar{\nu}_{J''}(\text{P}) = -2(\bar{B}'' - \bar{B}')J'' - 2\bar{B}'' \quad \Delta\bar{\nu}_{J''}(\text{R}) = (\bar{B}' - \bar{B}'')(2J''+1) + (3\bar{B}' - \bar{B}'')$$

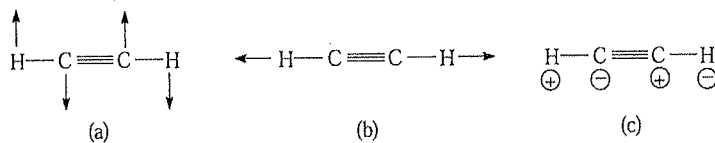
$$\nu = \frac{\gamma(1-\sigma)B_0}{2\pi} \quad |\nu_A - \nu_B| = 0 \quad |\nu_A - \nu_B| \propto B_0$$

$$\Delta\delta = \left| \frac{\nu_1 - \nu_{\text{Reference}}}{\nu_0} - \frac{\nu_2 - \nu_{\text{Reference}}}{\nu_0} \right| \times 10^6$$

Question 01 (100 Marks)

- (i) Using standard notation, sketch all the normal modes of each of the following hypothetical molecules: (a) LiCN, (b) SeO₂, (c) N₂S (22 marks)

- (ii) Three normal modes of acetylene are represented in the following figure.



- (a) Describe the movement of nuclei during vibration in each of these normal modes. (11 marks)

- (b) What is the relationship between the normal modes (a) and (c)? (2 marks)

- (iii) A linear molecule has the formula M₂X. Its microwave spectrum shows a strong series of lines at 10, 20, 30, ... MHz and no other lines. Is the structure of the molecule MMX or MXM? Give reasons. (5 marks)

- (iv) The pure rotational spectrum of ¹⁶O¹²C³²S exhibits two adjacent lines at frequencies 48651.7 MHz and 60814.1 MHz. Calculate the rotational constant, B, for this molecule and assign J values to these transitions. (Example 48651.7 MHz is from J_x to J_y and 60814.1 MHz is from J_a to J_b) (20 marks)

- (v) State the specific selection rules for lines in P and R branches in the IR spectrum of a heteronuclear diatomic molecule (8 marks)

- (vi) Giving reasons, draw the appearance of the 1st overtone bands in the symmetric stretching and bending modes of HCN in an IR spectrum (Hint: Consider a low-resolution spectrum with all the possible branches.) (10 marks)

- (vii) Using the value, $\bar{B} = 1.48 \text{ cm}^{-1}$, estimate the separation between the P and R branch maxima in the fundamental band of the bending mode of $^1\text{H}^{12}\text{C}^{14}\text{N}$ (in Born–Oppenheimer approximation) at 300 K. (20 marks)

Question 2 (100 Marks)

- (i) Describe the effect of nuclear spin on the pure rotational Raman spectrum of a linear molecule with a centre of symmetry? Give examples of molecules. (10 marks)
- (ii) Giving reasons, briefly explain how the intensity of Stokes or anti-Stokes lines in the spectrum of a typical pure rotational Raman spectrum of a linear molecule varies. (10 marks)
- (iii) Giving reasons, calculate the following in the pure rotational Raman spectrum of AB_2 linear molecule. $\bar{B} = 2.0 \text{ cm}^{-1}$
- The separation between the 1st Stokes line and the 1st anti-Stokes line. (10 marks)
 - Separation between two adjacent Stokes or anti-Stokes lines. (10 marks)
- (iv) Giving reasons, calculate the following in the pure rotational Raman spectrum of X_2 molecule. $\bar{B} = 61.08 \text{ cm}^{-1}$
- The separation between the 1st Stokes line and the 1st anti-Stokes line. (10 marks)
 - Separation between two adjacent Stokes or anti-Stokes lines. (10 marks)
- (v) The spectroscopic constants for the $\text{Y}^{12}_6\text{X}^{127}_{53}\text{Y}$ linear molecule, are as follows.
- $$\bar{\omega}_e = 384.293 \text{ cm}^{-1} \quad x_e \bar{\omega}_e = 1.501 \text{ cm}^{-1} \quad \bar{B} = 0.114158 \text{ cm}^{-1}$$
- Calculate the Raman shift of the two lines closest to the Rayleigh line in the pure rotational Raman spectrum of YXY ? (10 marks)
 - Calculate the positions of the first line closest to the band origin in the O and S branches in the fundamental anti-Stokes band of the $\text{Y}^{12}_6\text{X}^{127}_{53}\text{Y}$ molecule when the wavelength of the exciting laser line is $5145 \text{ \AA}$. (30 marks)

Question 3 (100 Marks)

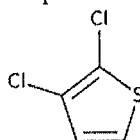
- (i) In general, different electronic states have different rotational constants, leading to the formation of band heads in the rotational structure. What will happen to the band head if both the electronic states have the same rotational constant? Explain your answer using the appropriate equations given above. (30 marks)
- (ii) The following table gives the line positions in a portion of the rotational fine structure of a vibrational band in the electronic spectrum of a diatomic molecule.

J''	$\bar{\nu} / \text{cm}^{-1}$	J''	$\bar{\nu} / \text{cm}^{-1}$	J''	$\bar{\nu} / \text{cm}^{-1}$
1	5900	8	5802	15	5808
2	5880	9	5796	16	5820
3	5862	10	5792	17	5835
4	5848	11	5790	18	5853
5	5832	12	5790	19	5874
6	5820	13	5793	20	5898
7	5810	14	5799	21	5925

- (a) Giving reasons, state whether the lines given in the table belong to a P branch or a R branch. (15 marks)
- (b) At what frequency is the band head formed? (5 marks)
- (c) What can you say about the relative magnitude of B' and B'' of the two electronic states involved in the transition by inspection (without calculations) of the data in the above table? (10 marks)
- (d) The plot $\Delta\bar{\nu}_{J''}(\text{P})$ of versus J'' is a straight line, of the form $y = 2.46x - 24.60$. calculate $\bar{B}'$ and $\bar{B}''$ (15 marks)
- (e) Describe the usefulness of the Fortrat diagram. (5 marks)
- (iii) Explain why the vibrational-rotational structure of electronic spectra of molecules becomes diffused at
- (a) The dissociation limit (10 marks)
- (b) in the solution phase. (10 marks)

Question 4 (100 Marks)

- (i) Show that the high-resolution NMR spectrum of chemically equivalent but magnetically non-equivalent A and B nuclei in a molecule is of A_2 type. (5 marks)
- (ii) Show that an AB spin system can be converted into an AX spin system by recording the NMR spectrum of the AB system at a higher magnetic field. (10 marks)
- (iii) Please see the structure 2,3-dichlorothiophene below



- (a) Spin-spin coupling between the two protons of 2,3-dichlorothiophene is 3.4 Hz at 60 MHz spectrometer. The resonance frequencies of the two protons differ by 18 Hz. Explain what type of spin system the compound 2,3-dichlorothiophene shows in ^1H NMR spectroscopy. (10 marks)
- (b) Sketch the ^1H NMR spectrum of 2,3-dichlorothiophene that would be obtained

using a 60 MHz spectrometer.

(10 marks)

(iv) The chemical shifts, δ , in ppm, of the CH_3 and CHClF protons are 2.30 and 10.5, respectively in the CH_3CHFCl compound. The coupling between the two types of protons is 3.00 Hz. The spectrometer is operating at 300 MHz

(a) Predict the separation between the two peaks in cm^{-1} in ^1H NMR spectroscopy
(10 marks)

(b) Giving reasons, predict the ^1H NMR spectrum of these two types of protons in a spectrometer operating at 300 MHz.
(45 marks)

(v) Explain the importance of studying scalar coupling in NMR spectroscopy. (10 marks)

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