NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, APPLIED SCIENCES AND NATURAL RESOURCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	LEVEL: 7
COURSE NAME: QUANTUM CHEMISTRY AND MOLECULAR SPECTROSCOPY	COURSE CODE: QCM701S
SESSION: JUNE 2022	PAPER: THEORY
DURATION: 3 HOURS	MARKS: 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	Prof Habauka M Kwaambwa
MODERATOR:	Prof Edet F Archibong

INSTRUCTIONS
1. Answer ALL the SIX questions. 2. Write clearly and neatly 3. Number the answers clearly 4. All written work must be done in bule or black ink 5. No books, notes and other additional aids are allowed 6. Mark all answers clearly with their respective question numbers

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENT

List of Useful Constants

THIS QUESTION PAPER CONSISTS OF 6 PAGES (Including this front page and List of Useful Constants an attachment)

QUESTION 1 **[20]**

(a) Define the terms **blackbody radiation** and **UV catastrophe.** Draw a schematic diagram of the energy density, $U(\lambda)$, against wavelength, λ, for the blackbody radiation at temperatures T_1 and T_2 (where $T_1 < T_2$). (5)

(b) Rayleigh-Jeans law of a blackbody radiation as function of frequency is given as:

$$U(\nu) = \frac{8\pi kT\nu^3}{c^3}$$

Under what condition would this theory agree with blackbody radiation experimental results. (2)

(c) The derivation by Bohr of the hydrogen atom given below.

$$\bar{\nu} = R_g\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \text{ where } R_g = 109677.58 \text{ cm}^{-1}$$

(i) State the **three** basic considerations this equation is based on or was derived. (3)

(ii) Calculate the wavelength, λ(in **nm**) and ionisation energy (in **eV**) for the Balmer line of the H emission. (The $n_1 = 2$ for the Balmer series). (3)

(d) Electromagnetic radiation of wavelength 200 nm is used to irradiate gold metal.

(i) Given that the work function of gold is 5.10 eV, determine the kinetic energy (in Joules) and velocity of the electrons ejected. (5)

(ii) State briefly the effect, if any, of increasing the intensity of incident light of wavelength 200 nm? (2)

QUESTION 2 **[14]**

Consider a π-electron which is a part of a conjugated polymethine dye. Use the free-electron molecular orbital (FEMO) method, which assumes that the π electrons are trapped in a 1-D box of length 11.2 Å to answer the following questions:

(a) Calculate the zero-point energy (in eV) of the system. (3)

(b) Why is the zero-point energy equal to zero not feasible? (2)

(c) Assuming the length of the chain to be 11.2 Å, determine the transition caused by excitation using the light of wavelength of 460 nm. (6)

(d) Determine the number of pi electrons. (1)

(e) What is the main weakness of the FEMO model? (2)

QUESTION 3 **[22]**

(a) One of the requirements for useful wave functions in Quantum Mechanics is that they must be well-behaved. State briefly the meaning of **well-behaved wave function.** (2)

(b) The wave function, Ψ, for an electron in the highest occupied molecular orbital of polydiene based on 1-dimensional particle-in-a-box model is given by:

$$\Psi(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{4\pi x}{L}\right) \text{ for } 0 \le x \le L$$

(i) Plot the variation of $\Psi(x)$ and $\Psi^2(x)$ for a particle-in-a-box for $0 \le x \le L$. (3)

(ii) State for which values of **x** in terms of L is the probability of finding the particle, i.e. $\Psi^2(x)$, **maximum** in the range $0 < x < L$. (4)

(c) State using a mathematical expression what is meant in quantum theory for each of the following: (10)

(i) Operator $\hat{A}$ is linear to the wave functions Ψ_i and Ψ_j.

(ii) Wave functions Ψ_1 and Ψ_2 **are not** orthogonal.

(iii) Operators A and B commute of wave function Ψ.

(iv) Hermitian operator $\hat{A}$ of wave functions Ψ_i and Ψ_j.

(v) Expectation value, $\langle a \rangle$, of the observable A derived from a normalised wave function Ψ .

(d) What are the physical meanings of **commuting operators** and **orthogonal wave functions** in Quantum mechanics? (3)

QUESTION 4 **[9]**

(a) Show that the function $\Psi = e^{-ikx}$ of the free particle is also an eigenfunction of the linear operator, $\hat{P}_x = -i\hbar\frac{d}{dx}$. What is the expression for the eigenvalue corresponding to this eigenfunction? (4)

(b) For circular motion in a fixed plane, the operator the Schrodinger equation is of the form

$$-\frac{\hbar^2}{2mr^2}\left(\frac{d^2\Psi}{d\phi^2}\right) = E\Psi$$, where $m_l = 0, \pm1, \pm2, \pm3$, etc.

Show that $\Psi = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}$ is an acceptable solution of the differential equation. What is the eigenvalue expression? (5)

QUESTION 5 **[20]**

(a) Which of the following molecules have a pure rotational spectrum and which ones are IR active?

Which of the species would be: (5)
(i) microwave active?
(ii) infrared (IR) active?
NH_3, HCl, H_2, CO_2, O_2, CH_3Cl, C_2H_4, CH_4, cis-CH_2Cl_2, H_2O_2, trans-CH_2Cl_2, CS_2

(b) The allowed rotational energy levels of a rigid diatomic molecule are given by

$$E_J = BJ(J+1)$$

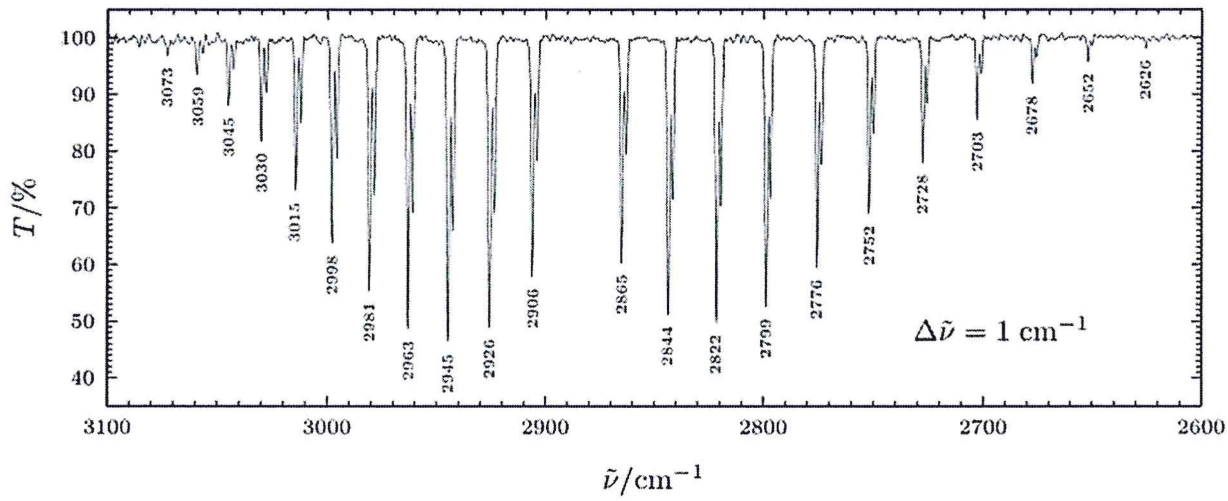
State the selection rule for the rotational energy transitions and derive the separation between the successive spectral absorption lines in terms of the rotation constant, B.

(4)

(c) A particle on the surface of a sphere has quantum number J = 7. What is the degeneracy of the energy level to which this state belongs to? (2)

(d) The ro-vibrational spectrum is divided into three branches, namely, *P*, *Q* and *R*. What is the approximate separation in terms B between the innermost line of the *P* and second innermost line of the *R* branch? (1)

(e) For the rotation-vibration spectrum below, identify the wavenumber and transition for the peak R(2). (2)



(f) The ro-vibrational spectrum of $^{1}H^{127}I$, with peaks at 2296.40, 2322.60 and 2335.70 cm^{-1}, was recovered.

(i) From the recovered data of the spectrum, what is approximate spacing between the peaks? (2)

(ii) Deduce the moment inertia, I, $^{1}H^{127}I$. (2)

(iii) Calculate the reduced of $^{1}H^{127}I$. (2)

(iv) Evaluate the internuclear distance (in Å) of $^{1}H^{127}I$. (2)

Atomic masses (amu): ^{1}H = 1.0079 ^{127}I = 126.90447

QUESTION 6 **[14]**

Two particles of masses 3.32 x 10^{-27} kg and 31.5 x 10^{-27} kg are connected by a Hooke's law spring which requires force of 13.2 x 10^{2} N to stretch it by 1.5 m.

(a) Calculate the force constant (in Nm^{-1}) of the system. (2)

(b) What is the fundmamental vibration frequency (s^{-1}) of the system? (6)

(c) Calculate the potential energy of the system when stretched by 1.5 m from its equilibrium position? (3)

(d) What is the zero point energy (based on quantum theory of simple harmonic oscillator) of the system? (3)

LIST OF USEFUL CONSTANTS:

Universal Gas constant	R	=	8.314 J K^{-1} mol^{-1}
Boltzmann's constant,	k	=	1.381 x 10^{-23} J K^{-1}
Planck's constant	h	=	6.626 x 10^{-34} J s
Debye-Huckel's constant,	A	=	0.509 (mol $dm^{-3})^{1/2}$ or $mol^{-0.5}kg^{0.5}$
Faraday's constant	F	=	96485 C mol^{-1}
Mass of electron	m_e	=	9.109 x 10^{-31} kg
Velocity of light	c	=	2.998 x 10^8 m s^{-1}
Avogadro's constant	N_A	=	6.022 x 10^{23}
1 electron volt (eV)		=	1.602 x 10^{-19} J