(Important note: Please write your Name and Roll No. on the Q-paper; please return the Q-Paper along with the answer sheet.)

PART A- Subjective type (5 x 1 = 5 Marks):

1. A molecule shows an absorption linewidth of *160 MHz*. Calculate the *overall lifetime*.
2. *NMR and ESR* spectroscopies are normally detected at what *region(s) of the electromagnetic spectrum*?

3. What *NMR spectrum* do you expect for the following molecule:
   $CHCl_2$-$CHCl$-$CHCl_2$
4. How many *ESR hyperfine lines* can be obtained for the following free radical:
   •$C^{13}H_2Cl$
5. Determine the molecular term symbol for He_2^+.

PART B- Subjective type (6 x 2 = 12 Marks):

6. Estimate the approximate value of *Planck constant (in Js)* for a red LED light with λ_{max}=630 nm; at a threshold voltage of *2.2 V*.
7. Which one the following is a *prolate/oblate symmetric top*: CH_3F and BF_3. Justify your answer.
8. Predict all the possible *ro-vibrational line-shapes* (PQR) of CO_2 and N_2O molecules.
9. The first *rotational-Raman lines* of H_2 molecule shows a separation of 6B. Justify your answer with a drawing containing the possible transitions.
10. Write down the *SI units* of: (a)β_N (Bohr magnetron) and (b) g_N (gyromagnetic ratio).
11. Calculate the *chemical shift in parts per million (δ scale)* for a proton that has resonance *128 Hz* downfield from TMS in a spectrometer that operate at *60 MHz*.

PART C- Descriptive type (7 x 3 = 21 Marks):

12. The rotation constant of $^{12}C^{16}O$ is found to be *1.927 cm^{-1}* at *298 K*. Which rotational transition gives rise to maximum population under this condition.
    6.015   17.378
13. The *equilibrium bond-length* and the *force constant* of $^6Li^9F$ are *156 pm* and *250 N/m*. Using rigid rotor simple harmonic approximation, estimate the energies of the P_1 and R_0 ro-vibrational lines.
14. The compound that gives the following *NMR spectrum* has the formula $C_3H_6Br_2$. Draw the structure and justify your answer.

'H NMR
300 MHz $C_3H_6Br_2$

4.12   2.03
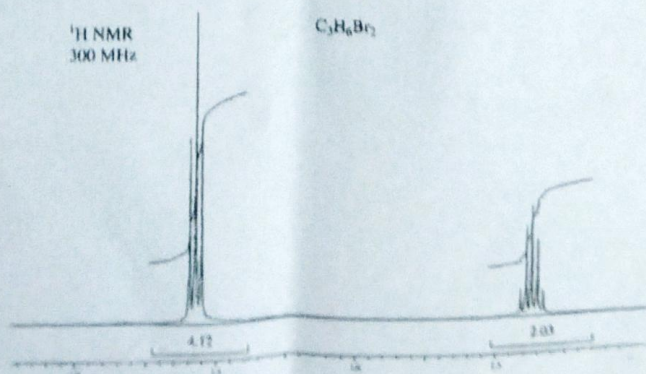
15. Given $D_e = 7.33 \times 10^{-19}$ J/molecule, $\bar{v} = 1580$ cm^{-1} and $r_{eq}=121$ pm for $^{16}O^2$ molecule. Calculate the constant 'a' of the Morse potential.

16. What magnetic field strength must be applied to a free or bare proton for spin resonance to occur at 60 MHz. The gyromagnetic ratio (g_N) of the bare proton is 26.75×10^7.

17. The absorption spectrum of O_2 shows vibrational structure which become a continuum at 56,876 cm^{-1}. The upper electronic state dissociates into one ground state and one excited state atom (the excitation energy of which measured from the atomic spectrum is 15, 875 cm^{-1}). Estimate the ground state dissociation energy (D_0'') of O_2 in kJ/mol.

18. The value of $\bar{v}_e$ and x_e in the ground state ($^3\Pi_u$) and a particular excited state ($^3\Pi_g$) of C_2 are:

State	$\bar{v}_e$	x_e
Ground state	1641 cm^{-1}	7.11×10^{-3}
Excited state	1788 cm^{-1}	9.19×10^{-3}

Use the equation; $v_{max} = \frac{1}{2x_e} - 1$, to find the number of vibrational energy levels below the dissociation limit and hence the ground state dissociation energy (D_0'') of C_2.

PART D- Descriptive type (3 x 4 = 12 Marks):

19. What is the intensity distribution of ro-Raman lines of gas phase $^{14}N_2$ and $^{15}N_2$ molecules? Draw an approximate ro-Raman lines (intensity) based on the above analysis.

20. Two proton NMR signals 'a' and 'b' occurs at 480 Hz and 230 Hz if taken at a 60 MHz spectrometer. Estimate the difference in chemical shift between the hydrogen nuclei 'a' and 'b'. What would be the separation between the signal in Hz if taken on a 270 MHz spectrometer.

21. Draw the electron spin energy diagram for •CH_3 radical and represent the energy of the electron spin states and the hyperfine states.
   (a) What is(are) the possible transition(s) between the hyperfine states?
   (b) What is the intensity distribution?
   (c) Draw a tentative ESR diagram based on the above analysis.

Important Formulae and universal constants:

1. $\varepsilon_J = BJ(J + 1)$; $B = \frac{h}{8\pi^2 Ic}$

2. SHO; $\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

3. Anharmonic; $\bar{v}_v = \left(v + \frac{1}{2}\right)\bar{v}_e - x_e\left(v + \frac{1}{2}\right)^2 \bar{v}_e$

4. Morse Potential: $V(r) = D_e[1 - e^{-a(r-r_{eq})}]^2$; $\left(a = \sqrt{\frac{k}{2D_e}}\right)$

5. Maxwell-Boltzmann distribution;
   Rotational: $J_{max} = \sqrt{\frac{k_B T}{2hcB}} - \frac{1}{2}$
   Ro-vibrational: $\bar{v}_{max} = \bar{v}_0 \pm \left[2B\sqrt{\frac{k_B T}{2hcB}} + \frac{1}{2}\right]$

1. $h = 6.626 * 10^{-34} Js$
2. $k_B = 1.38 * 10^{-23} J/K$
3. $c = 2.998 * 10^8 m/s$
4. $N_A = 6.02 * 10^{23}/mol$
5. $1\ amu = 1.66 \times 10^{-27} kg$

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