

III Match the following:

- | | | |
|-----------------------|---|---------------------------------------------|
| 11. Planck's Constant | - | Orientation of molecule in a magnetic field |
| 12. Polarizability | - | Mass Spectrometry |
| 13. Anisotropy | - | Vibrational Spectrum |
| 14. Meta Stable Peak | - | Frequency |
| 15. Zero point energy | - | Raman effect |
| | - | Joule-Second |

IV Give reasons of the following:

16. Acetylenic protons are more shielded in NMR than ethylenic protons although the former are attached to a more electronegative SP carbon.
17. ESR spectrum shows hyperfine splitting where as NMR spectrum does not
18. The infrared and Raman spectra of methane molecule have no line in common
19. Non-linear molecule has $3N-6$ vibrational degrees of freedom, while linear molecule has $3N-5$
20. Acetone absorbs at 279nm in hexane where as the value of λ_{\max} in water is 264.5nm.

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STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2006-07 & 2007-08)

SUBJECT CODE: CH/PC/MS34

M.Sc. DEGREE EXAMINATION, NOVEMBER 2008
BRANCH IV- CHEMISTRY
THIRD SEMESTER

COURSE : MAJOR CORE

PAPER : MOLECULAR SPECTROSCOPY

TIME : 2½ HOURS

MAX.MARKS : 80

SECTION - B

(5 x 8 = 40)

Answer any five questions:

1. a) The force constant for HF molecule is $9.7 \times 10^2 \text{ Nm}^{-1}$. Calculate the frequency of radiation to excite the molecules from $v = 0$ to $v = 1$. (4)
b) Write notes on (i) Over tones (ii) Spinning side bands (4)
2. a) The observed chemical shift of a proton is 300HZ from TMS and the operative frequency of the spectrometer is 100MHZ. Calculate the chemical shift in terms of δ ($\rho\rho m$). (4)
b) Differentiate between stokes and Antistokes lines. (4)
3. a) Write the structural formulae for the compounds with the following molecular that show ONLY ONE SIGNAL in their PMR spectra
(i) C_5H_{12} (ii) C_3H_6 (iii) C_2H_6O (iv) C_3H_4
(v) C_2H_4Br (vi) C_4H_6 (vii) C_8H_{18} (viii) C_4H_8 (4)
b) Bring out the applications of Raman spectroscopy. (4)
4. The bond length of NO molecule is $1.151 \times 10^{-10} \text{ m}$. Calculate the frequencies in cm^{-1} for the pure rotational lines in the spectrum of NO corresponding to the following changes in the rotational quantum numbers $J = 0 \rightarrow 1$; $J = 1 \rightarrow 2$; $J = 2 \rightarrow 3$.
5. Identify the compound from the following data
Molecular formula C_5H_4
IR ($\bar{\nu} \text{ cm}^{-1}$) : 3300(w), 2900 - 2840(m), 2110(m)
UV (λ, nm) : no absorption above 200nm
PMR($\delta, \rho\rho m$) : 2.0, 3.1 (equal intensity)

6. a) Suggest the structure of a compound with molecular formula $C_{10}H_{12}O$ whose mass spectrum shows peaks at $m/2$ 15, 43, 57, 91, 105 and 148. (4)
- b) Write a note on Mc Lafferty rearrangement. (4)
7. What are Woodward-Fieser rules? How can these be justified?

SECTION – C**(2 x 20 = 40)****Answer any two questions:**

8. a) Discuss the distribution of intensities in first order splitting in NMR. Discuss AMX coupling with an example.
- b) Discuss the Principle of pure rotational spectroscopy and derive the expression for the spacing between lines. (10+10)
9. a) Explain the origin of PQR branches in vibrational-rotational spectra.
- b) Write notes on (i) Nuclear over hauser effect (ii) 2D NMR (10+10)
10. a) Explain the simplification of complex spectra by (i) shift reagents (ii) spin decoupling
- b) Write a short notes on (i) Frank – condon Principle (ii) Nitrogen rule in Mass Spectrum (10+10)
11. a) Discuss the various modes of vibration with water molecule as an example. (6)
- b) An organic compound (Molecular weight 108) is not acid, can be easily oxidized to a crystalline compound (m. pt. 122°C). It gives the following spectral data:
- UV : λ_{max} 255 nm ($\epsilon_{max} = 202$)
- IR : $\nu_{max}^{cm^{-1}}$ 3402 (s, br), 3065 (w), 2888 (m), 1499 (w, sh) 1455 (m);
- | | | | |
|----------------------|------|------|------|
| 1H NMR : δ | 3.90 | 4.60 | 7.26 |
| Multiplicity | s | s | s |
| Integration | 1 | 2 | 5 |
- Deduce the structure of the compound, justify the above observations and predict the principal ions in its mass spectrum. (14)

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