MANIPAL
ACADEMY of HIGHER EDUCATION

**DEPARTMENT OF SCIENCES, MIT, MANIPAL**
**III SEMESTER M.Sc. (Chemistry)**
**END SEMESTER EXAMINATIONS, NOVEMBER 2023**
Spectroscopy II [CHM 6101]
**(CHOICE BASED CREDIT SYSTEM - 2021)**

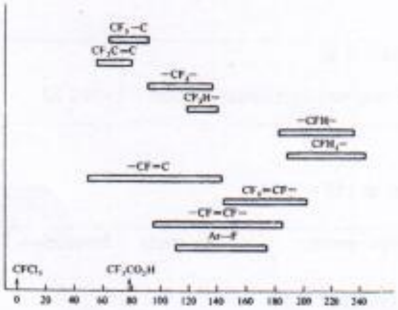
**SCHEME OF EVALUATION**

Time: 3 Hours | Date: 28/11/2023 | MAX. MARKS: 50

Note : (i) Answer **ALL** questions

(ii) Draw diagrams, and write equations wherever necessary

<table>
<tr><th>Q No</th><th>Question</th><th>Marks</th></tr>
<tr><td><b>1A</b></td><td>Illuciation of peaks obtained in $^1H$ NMR and mass spectra of benzene, chlorobenzene and benzyl chloride - 1+1+1 M<br>Differences in each spectra – 1 M</td><td>4</td></tr>
<tr><td><b>1B</b></td><td>Explanation on-first order NMR spectra work – 1 M<br>Explain about the three techniques for resolving non-first-order spectra - 1+1+1 M</td><td>4</td></tr>
<tr><td><b>1C</b></td><td>Method – Distillation – ½ M<br>1725 $cm^{-1}$ – CO peak – ½ M<br>Reason for peaks m/z = 150 and a M+2 peak at 152 – ½ M<br>Structural formula of m/z =57 – ½ M</td><td>2</td></tr>
<tr><td><b>2A</b></td><td>Instrumentation of Secondary ion mass spectrometry – Various Parts – Ionization chamb, analyser – 3 M<br>Hard and soft ionization techniques – 2 differences – 1 M</td><td>4</td></tr>
<tr><td><b>2B</b></td><td>Explanation on the effect of chemical exchange on $^1H$ NMR spectra – 2 M<br>Example – explanation - 2 M</td><td>4</td></tr>
<tr><td><b>2C</b></td><td>i) Reason – 1 M<br>ii) Reason – 1 M</td><td>2</td></tr>
<tr><td><b>3A</b></td><td>Elucidation with proper justification of mass spectra - 2 M<br>Elucidation with proper justification of 1H NMR spectra - 2 M</td><td>4</td></tr>
<tr><td><b>3B</b></td><td>(i)
<table>
<tr><th>ESR</th><th>NMR</th></tr>
<tr><td>• Different energy states are produced due to the alignment of the electronic magnetic moments relative to applied magnetic filed and the transition between these energy states occurs on the application of an appropriate frequency in the microwave region.<br>• ESR absorption positions are expressed in terms of "g" values.</td><td>• Different energy states are produced due to the alignment of the nuclear magnetic moments relative to applied magnetic field and the transition between these energy states occurs on the application of an appropriate frequency in the radio frequency region.<br>• NMR absorption positions are expressed in terms of chemical shifts.</td></tr>
</table></td><td>2</td></tr>
</table>

| | | |
|---|---|---|
| | • Coupling of the electronic spin with nuclear spins (hyperfine coupling) causes the splitting of ESR signals.<br>Nuclear spin-spin coupling causes the splitting of NMR signals | |
| | (ii)<br>$\nu = g\,\beta_e B / h$<br>$g = \nu h / \beta_e B$<br>$= [9590\times10^6\times6.626\times10^{-34}\,Js] / [9.274\times10^{-24}\times0.33]$<br>$= 2.07$ | 2 |
| **3C** | Explanation on the interfaces between HPLC and MS -2 M | 2 |
| **4A** | (i) Prediction of decoupled $^{13}C$ spectrum of 4-propyloxy-ethylbenzoate<br>decoupled $^{13}C$ spectrum of 4-propyloxy-ethylbenzoate - description | 1<br>1 |
| | (ii)<br> <br>Figure 3.51 *Chemical shift ranges (ppm) for $^{19}F$ in common organic environments.* | 2 |
| **4B** | **Quadrupole interactions**:<br>The energy Eigen values $E_{mI}$ of the Hamiltonian are doubly degenerate since plus and minus $m_I$ values give the same energy<br>$E_{m_I} = \frac{e^2qQ}{4I(2I-1)}[3m_I^2 - I(I+1)]\left(1+\frac{\eta^2}{3}\right)^{1/2}$ (12)<br>e.g., consider the case in which the nuclear spin of the ground and first excited states are ½ and 3/2 respectively<br>• Eq. 12 leads to zero energy for the ground state since it will not have a nuclear quadrupole moment<br>• For the excited state, eq. 12 the energies with respect of the energy of the excited state $E_e$ are<br>$E_{\pm 3/2} = \frac{3e^2qQ}{4I(2I-1)}\left(1+\frac{\eta^2}{3}\right)^{1/2}$ (13)<br>$E_{\pm 1/2} = -\frac{3e^2qQ}{4I(2I-1)}\left(1+\frac{\eta^2}{3}\right)^{1/2}$ (14)<br>• Thus the quadrupole interaction results in the splitting of the excited nuclear level into two levels | |

- If the quadrupole moment is +ve, the ±3/2 states will be above that of the ±½ states
- A reverse situation exists when the quadrupole moment is –ve
- The selection rule for transitions $\Delta m_I = 0, \pm 1$ leads to two lines in place of one line
- The energy level scheme of the system is shown in following fig.
- When quadrupole interaction alone is observed, a two line Mössbauer spectrum results with a separation (Δ) which is called as the quadrupole splitting and is given by

$$\Delta = \frac{6e^2qQ}{4I(2I-1)}\left(1+\frac{\eta^2}{3}\right)^{1/2} \qquad (15)$$

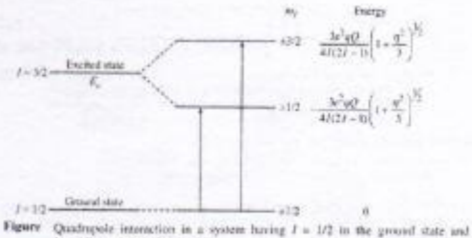


**Figure** Quadrupole interaction in a system having I = 1/2 in the ground state and I = 3/2 in the excited state.

2

**Magnetic Hyperfine Interactions:**

- Mössbauer nuclei will have non-zero spin in the ground and excited states and therefore both the levels will directly interact with a magnetic field of flux density B giving rise the interaction energy

$E_{mI} = - g_N \mu_N B\, m_I$

Where $\mu_N$ is the nuclear magneton

$g_N$ is the nuclear g factor

- The magnetic quantum number $m_I$ takes the values –I, (-I+1),,, +I
- The magnetic field thus splits the ground and excited Mössbauer levels into (2I+1) non-degenerate equally spaced levels

Consider the case where the ground (double prime) and the first excited (single prime) nuclear states have spin $I''_g = ½$ and $I'_e = 3/2$ respectively

For the ground state,

$$E_{\frac{1}{2}} = -\frac{1}{2} g''_N \mu_N B$$
$$E_{-\frac{1}{2}} = \frac{1}{2} g''_N \mu_N B$$

For the excited state,

$$E_{\frac{3}{2}} = -\frac{3}{2} g'_N \mu_N B$$
$$E_{\frac{1}{2}} = -\frac{1}{2} g'_N \mu_N B$$
$$E_{-\frac{1}{2}} = \frac{1}{2} g'_N \mu_N B$$
$$E_{-\frac{3}{2}} = \frac{3}{2} g'_N \mu_N B$$

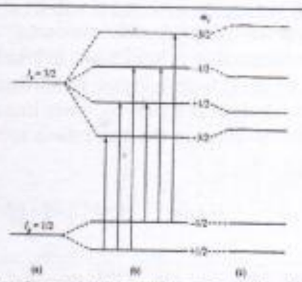


**Figure** (a) The ground and excited energy levels of a $I_g = 1/2$ $I_e = 3/2$ system, (b) the energy levels and transitions illustrating the splitting produced by magnetic field, (c) the energy levels and transitions showing the effect of a simultaneous magnetic and electric field

2

**Table** The Transition Energies when $I''_I = 1/2$ and $I'_I = 3/2$

| *Ground state* $m''_I$ | *Excited state* $m'_I$ | *Transition energy* |
|---|---|---|
| -1/2 | -3/2 | $(1/2)\,\mu_N B\,(3g'_N - g''_N)$ |
| -1/2 | -1/2 | $(1/2)\,\mu_N B\,(g'_N - g''_N)$ |
| -1/2 | 1/2 | $(-1/2)\,\mu_N B\,(g'_N + g''_N)$ |
| 1/2 | -1/2 | $(1/2)\,\mu_N B\,(g'_N + g''_N)$ |
| 1/2 | 1/2 | $(-1/2)\,\mu_N B\,(g'_N - g''_N)$ |
| 1/2 | 3/2 | $(-1/2)\,\mu_N B\,(3g'_N - g''_N)$ |

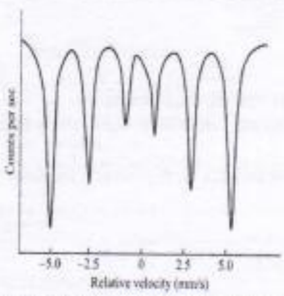


**Figure** Mössbauer spectrum of a thin foil of soft iron with a gamma-ray source of $^{57}$Co in palladium.

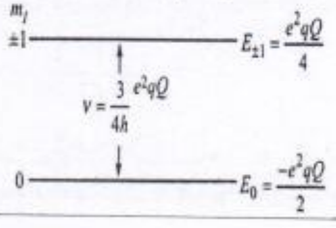
**4C** The eigen values of the system are

$$E_m = \frac{e^2qQ\left[3m_I^2 - I(I+1)\right]}{4I(2I-1)}$$

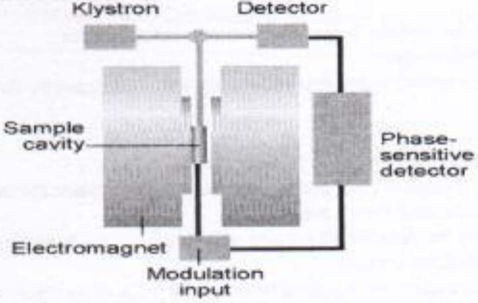
The energy expression leads to (I+1) doubly degenerate and one non-degenerate levels

A single resonance line results for $^{14}$N nucleus (I = 1)

selection rule for magnetic dipole transition is $\Delta m_I = \pm 1$



2

| | | |
|---|---|---|
| | The frequency of absorption, $\nu = \frac{3e^2qQ}{4h}$ | |
| 5A | (i) Chemical shift values of all carbons in n-heptane<br>(ii) Chemical shift values of all carbons in 1,3-dihydroxybenzene | 2<br>2 |
| 5B | • Source<br>• Circulator or Magic -T<br>• Sample Cavity<br>• Magnet System<br>• Crystal Detector<br>• Auto amplifier and Phase sensitive Detector<br>• Oscilloscope and Pen Recorder<br><br> <br>Source:<br>• Klystron<br>• It is a vacuum tube which can produce microwave oscillations centered on a small range of frequency<br>• The frequency of the monochromatic radiation is determined by the voltage applied to Klystron.<br>Wave length is of about 3 cm (generally for free radicals<br>Isolator:<br>• It is a non reciprocal device which minimizes vibrations in the frequency of microwaves produced by Klystron oscillator.<br>• The variations occur in the frequency due to the backward reflections in the region between the Klystron and circulator.<br>• Isolator is a strip of ferrite material.<br>Wave meter:<br>• It is fixed in between the isolator and attenuator to know the frequency of microwaves produced by Klystron oscillator.<br>• Usually it is calibrated in frequency units instead of wavelength.<br>Attenuator:<br>• Attenuator is used to adjust the level of the microwave power incident upon the sample.<br>It possesses an absorption element and corresponds to a neutral filter in light absorption measurement<br>Magic T or Circulator:<br>Microwave radiations finally enter to the circulator through a wave guide by a loop wire which couples with oscillating magnetic field and setting a corresponding field<br>Sample cavity:<br>• This resonant cavity which contains the sample is called the heart of ESR. | ½ |

| | | |
|---|---|---|
| | • It is constructed in such a way to maximize the applied magnetic field along the sample dimension.<br>In most ESR spectrometers dual sample cavities are used for simultaneous observation of sample and reference materials<br>Magnet system:<br>• The sample cavity is placed between the pole pieces of an electromagnet<br>• This provides a homogenous magnetic field and can be varied from zero to 500 gauss.<br>The stability of the field is achieved by energizing the magnet with a highly regulated power supply<br>Crystal detectors:<br>• The most commonly used detector is a silicon crystal which acts as a microwave rectifier.<br>• This converts microwave power into a direct current output.<br>Oscilloscope and Pen Recorder<br>The signal from phase sensitive detector and sweep unit is recorded by the oscilloscope or pen recorder<br>Working:<br>• The Klystron oscillator is set to produce microwaves.<br>• After passing though the isolator, wave meter and attenuator the microwaves are entered into the circulator on magic T<br>• Then it reaches the detector which acts as a rectifier, i.e. converting the microwave power into the direct current.<br>• The resonance cavity cell is placed between the poles of an electromagnet<br>• The magnetic field should be stable and uniform over the sample volume<br>• The spacing between the energy levels can be varied with the magnetic field so that the spin transitions can be detected with a monochromatic radiation source by sweeping the magnetic field through the resonance condition<br>• Thus the ESR spectrometer operates at a fixed microwave frequency<br>• The magnetic field is varied<br>• This method is usually adopted in practice, since it is difficult at high frequencies to sweep the frequency of the microwave radiation with a constant magnetic field<br>• One can set the field at any position using the field dial and sweep from that position<br>• The field sweep is assumed to be linear and the g values of the other peaks are calculated relative to the standard.<br>• In order to sweep the magnetic field over a range, provision is made by varying the current in a pair of sweep coils<br>• The magnetic field is varied until resonance occurs<br>• The magnetic dipolar vector of the microwave field, which induces transitions between the energy levels of the unpaired electron is perpendicular to the external applied magnetic field<br>• The sample in the cavity cell is placed at the centre of the gravity, where the magnetic field is maximum<br>The changes in the power level due to the absorption of the microwave radiation are detected, amplified and recorded | 1½<br>2 |
| **5C** | • Hydrogen bonds are also detectable by NQR<br>• The quadrupole coupling constants ($e^2qQ/h$) of nuclei in hydrogen containing molecules is found to be greater in the vapour state (microwave measurements) than in the solid state (NQR measurements) | |

| | | |
|---|---|---|
| | • A reduction in quadrupole coupling constant is noticed while going from the vapour to the solid state.<br>• This is due to the reduction in the field gradient at the nucleus caused by strong intermolecular hydrogen bonding in the solid state<br>• The $^{35}$Cl quadrupole coupling constant in HCl in the solid state is 21% smaller than that in the vapour state<br>• Similarly, the $^{14}$N quadrupole coupling constant in $NH_3$ is smaller by 22.5% in the solid state<br>• The $^{35}$Cl NQR spectrum of sodium tetrachloroaurate dehydrate showed four NQR resonances, one of which is 2.5 MHz lower at 77K.<br>• This is attributed to a $^{35}$Cl atom which is involved in two hydrogen bonds to two adjacent water molecules<br>As the temperature is increased, hydrogen bonding decreased and the frequency of the NQR line starts shifting | 2 |

********