RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

BSc Honours in Chemistry
Fourth Year - Semester I Examination – July / August 2023

CHE 4210 – MOLECULAR AND SURFACE SPECTROSCOPY

Time: Two (02) hours

Answer **All** questions.

$R = 8.314$ J K^{-1} mol^{-1}, $e = 1.602 \times 10^{-19}$ C, $1D = 3.336 \times 10^{-30}$ C m, $h = 6.63 \times 10^{-34}$ J s,

Boltzmaan constant, $k = 1.381 \times 10^{-23}$ J K^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1}, $c = 3.0 \times 10^8$ m s^{-1}

All the other symbols given are as of their usual meaning. Use of a non-programmable calculator is permitted.

1.

a) Draw three types of molecules with different molecular shapes those fall into each point group given below (Non-real molecules are accepted as answers).

   i. D_{4h} ii. C_{3v} iii. C_2 (30 marks)

b) Consider the molecule CI_2F_2.

   i. Write down the point group.

   ii. Predict whether the point group is an Abelian group or not.

   iii. Find the irreducible representations of the point group.   (30 marks)

c) Find the point group of following molecules. Use the given flow chart to obtain your answers.

   i. SF_5Br ii. *cis*-C_2I_2ClF iii. $P(Ph)_3$ iv. Cyclohexane   (20 marks)

d) Describe the symmetry element, "improper rotation" using CH_4 as an example.   (20 marks)

2. a) Give a comparative account of the principle of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) (30 marks)

b) Discus the effects that produce more than one peak in XPS (30 marks)

c) Given below are the deconvolution results of XPS of Fe 2p electrons. Interpret the two peaks in figure (a) and (b) which correspond to the same oxidation state of Fe and two different oxidation state of Fe respectively.
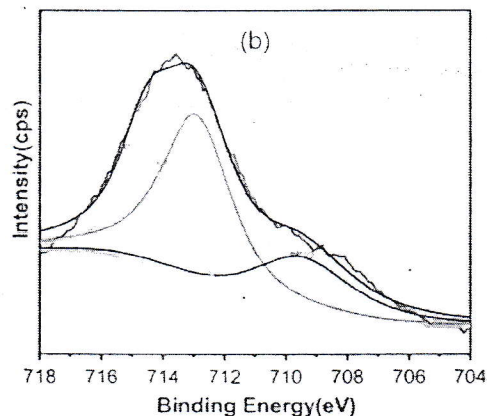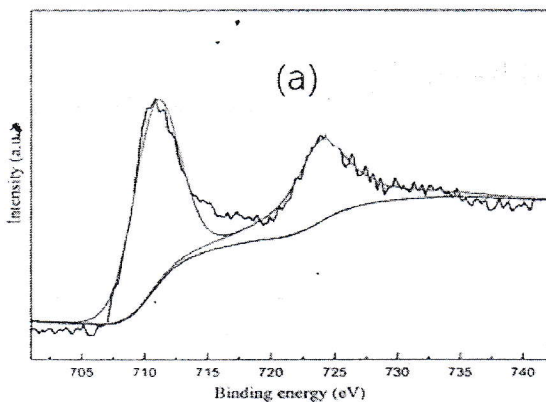
(20 marks)

d) Briefly explain with suitable examples that what additional information could be obtained from XPS. (20 marks)

3. a) Three consecutive lines in the rotational spectrum of $H^{35}Cl$ are observed at 84.544, 101.355, 118.112 (wave numbers in cm^{-1}).

Wavenumber, $\tilde{v}$ for a vibrational rotor is given by the equation,

$$\tilde{v} = 2B\,(J+1) - 4D\,(J+1)^3$$

i. Assign the above lines to $J\,(J+1) \rightarrow$ transitions.

ii. Calculate the value of rotational constant, B and the centrifugal distortion constant, D.

iii. Calculate the force constant for the $H^{37}Cl$ bond. (30 marks)

b) H_2O gas shows three (03) absorptions at $3651.1\ cm^{-1}$, $1595.0\ cm^{-1}$ and $3755.8\ cm^{-1}$ in the IR spectrum whereas the IR spectrum of CO_2 gas consists of only two (02) absorptions which appear at $2349.0\ cm^{-1}$ and $667.3\ cm^{-1}$. Explain the observations. Assign these absorptions to the respective vibrational modes for both. (30 marks)

c) Predict the form of the rotational Raman spectrum of $^{14}NH_3$, for which $B = 9.977\,cm^{-1}$, when it is exposed to monochromatic wavelength of 336.732 nm laser radiation.

Spectral positions for the Strokes lines are given by the equation,

$$\bar{v}_{J \rightarrow J+2} = \bar{v}_i - 2B\,(2J + 3).$$

Spectral positions for the anti-Strokes lines are given by the equation,

$$\bar{v}_{J \rightarrow J-2} = \bar{v}_i + 2B\,(2J - 1). \tag{40 marks}$$

4. a) Given that the fundamental vibrational frequency of $H^{35}Cl$ is 2890 cm^{-1}.

      i. Calculate the force constant of HCl.

      ii. Calculate the fundamental vibrational frequency of $H^{37}Cl$ in cm^{-1}. Write any assumptions you made here.

(30 marks)

b) Energy levels of a vibrational rotor is given by,

$$E = \left(v + \frac{1}{2}\right) h\, v_0 + BhJ(J + 1)$$

    i. Derive an expression to obtain the frequencies of R band, v_R.

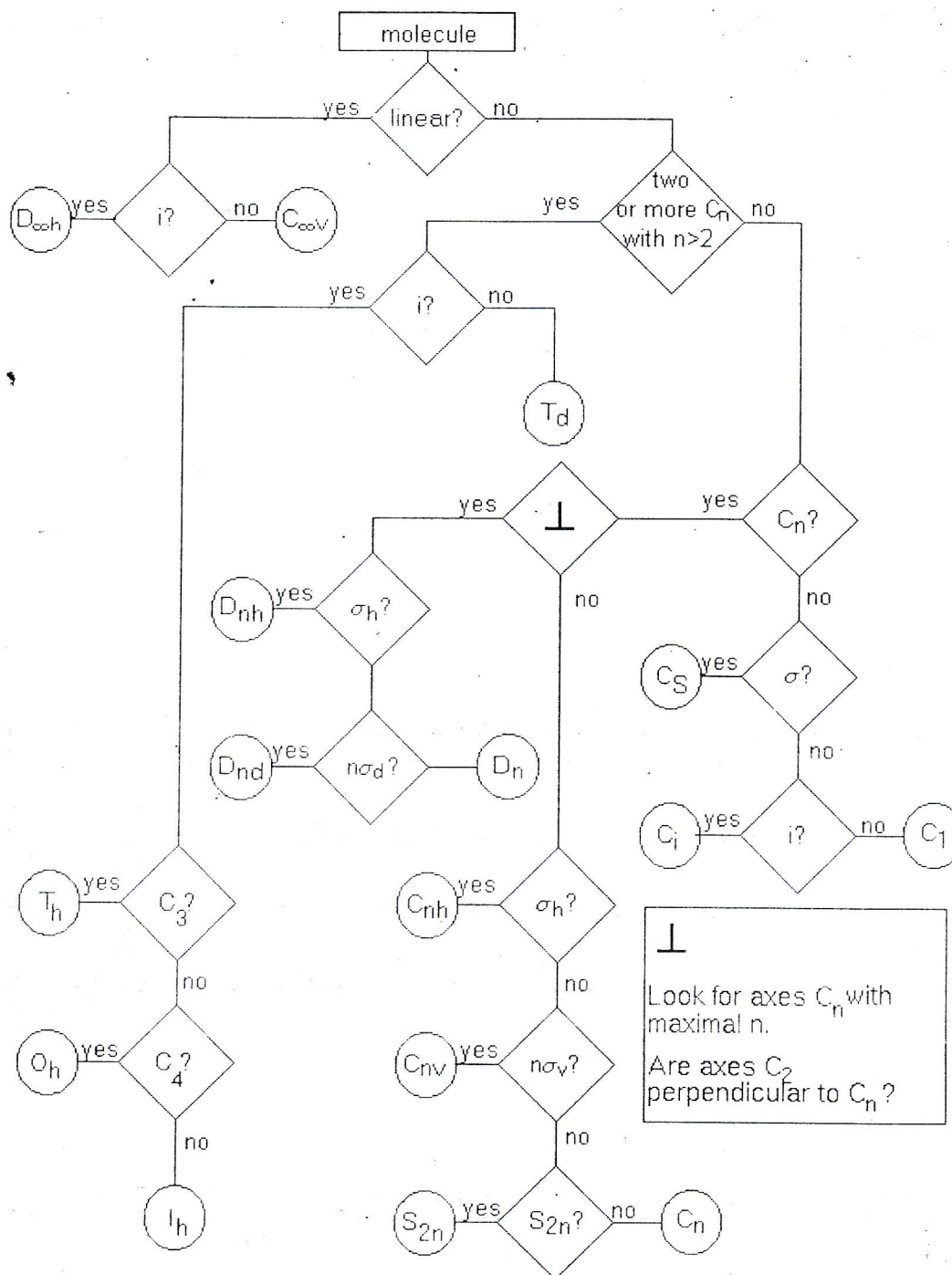   *hint*: Selection rules for the transitions corresponding to R band are $\Delta v = +1$ and $\Delta J = +1$.

    ii. Calculate the wavenumber, $\tilde{v}$ for the line corresponding to $J = 2$ of $^1H^{127}I$ where the R band is observed from $v = 0$. It is given that rotational constant, $B = 6.61$ cm^{-1}.

(40 marks)

c) Account for the hot bands and overtones in vibrational spectroscopy.   (30 marks)

molecule

linear?
— yes → i? — yes → $D_{\infty h}$
              — no → $C_{\infty V}$

— no → two or more C_n with n>2?
    — yes → i?
        — yes → (to left branch)
        — no → T_d

    — no → $\perp$
        — yes → σ_h?
            — yes → D_{nh}
            — no → $n\sigma_d$?
                — yes → D_{nd}
                — no → D_n

Cn?
— yes → $\perp$
— no → σ?
    — yes → C_S
    — no → i?
        — yes → C_i
        — no → C_1

T_h — yes — C_3?
            — no → C_4?
                — yes → O_h
                — no → I_h

C_{nh} — yes — σ_h?
            — no → $n\sigma_v$?
                — yes → C_{nv}
                — no → S_{2n}?
                    — yes → S_{2n}
                    — no → C_n

$\perp$

Look for axes C_n with maximal n.

Are axes C_2 perpendicular to C_n?

— END —