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RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. Honours in Chemistry
Fourth Year - Semester I Examination – January / February 2021

CHE 4210 – MOLECULAR AND SURFACE SPECTROSCOPY

Time: Two (02) hours

Answer **All** questions.

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

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

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

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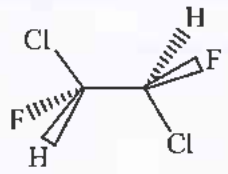
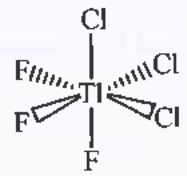
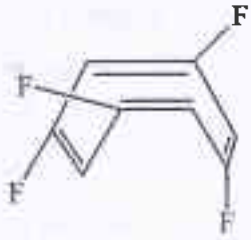
1. a) Show all the symmetry elements for the given molecules.

i. 

ii. 

iii. 

(30 marks)

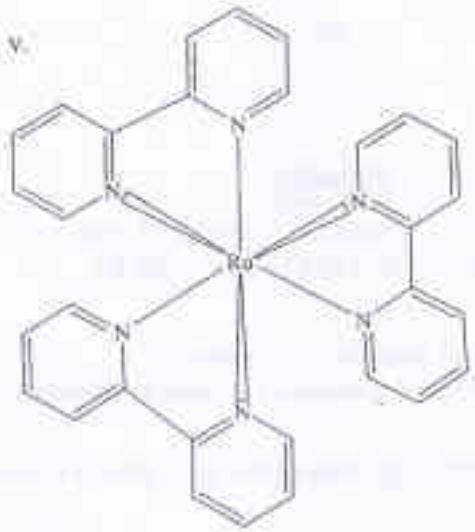
b) Consider the C_3V symmetry group.
   i. Deduce the order of the point group.
   ii. Show that C_3V group is an Abelian group using a proper example.

(30 marks)

c) Find the point group of following molecules. Use the given flow chart to obtain your answers.
   i. SF_4' ii. XeF_4 iii. Sn iv. IF_7

Cont'd

v.



vi.

(25 marks)

b) Give an example for each point group given below.

i. C_s ii. D_{3d} iii. C_3 (15 marks)

2. a) When an atom is replaced by its isotopes, moment of inertia, I is changed and bond length, r remains unchanged. D, E and F are atoms. F and F' are isotopes.

D—E—F

D—E—F'

Moment of inertia can be given by following equation.

$$I_F = I_{F'} - \frac{\Delta m\, M}{(\Delta m + M)}\, r_F^2$$

Where,

M = mass of the molecule

Δm = change in molar mass

r_F = distance from center of the gravity to atom F

In rotational spectroscopy for a harmonic rotor, wavelength $\bar{\nu}$ is given by,

$$\bar{\nu} = 2B\,(J + 1)$$

Where,

$$B = \frac{h}{8\pi^2 Ic}$$

Cont'd

For J = 1→ 2 transition of **OCS** molecule have been obtained in the following frequencies.

Molecule	Frequency (MHz)
$^{16}O^{12}C^{32}S$	24,326
$^{16}O^{12}C^{34}S$	23,731
$^{16}O^{13}C^{32}S$	24,248

Using the values given, calculate

i. the moment of inertia

ii. the bond length r_{CS} (60 marks)

b) Three consecutive lines in the rotational spectrum of $H^{79}Cl$ are observed at 84.544, 101.355, 118.112 (wave numbers in cm^{-1}).

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

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

i. Assign the above lines to J (J+1) → 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. (40 marks)

3. a) Account for the hot bands and overtones in vibrational spectroscopy. (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 where as 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) Energy levels of a vibrational rotor is given by.

$$E = \left(v + \frac{1}{2}\right) h\,\nu_0 + BhJ(J+1)$$

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

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

ii. Calculate the wavenumber, $\tilde{\nu}$ 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)

4 a) Explain the line broadening with respect to electronic spectroscopy (14 marks)

b) Arrange the compounds, CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 in an increasing order of,

i. dipole moment ii. polarizability (16 marks)

c) Determine which of the following molecules may show only pure rotational microwave absorption spectra

PH_3, CS_2, N_2O, H_2O, CCl_4, H_2O_2, NH_3 and CO_2 (15 marks)

d) Determine which of the following molecules may show only pure rotational Raman absorption spectra

CCl_4, CO_2, $CHCl_3$, H_2, HBr, SF_6 (15 marks)

e) 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.

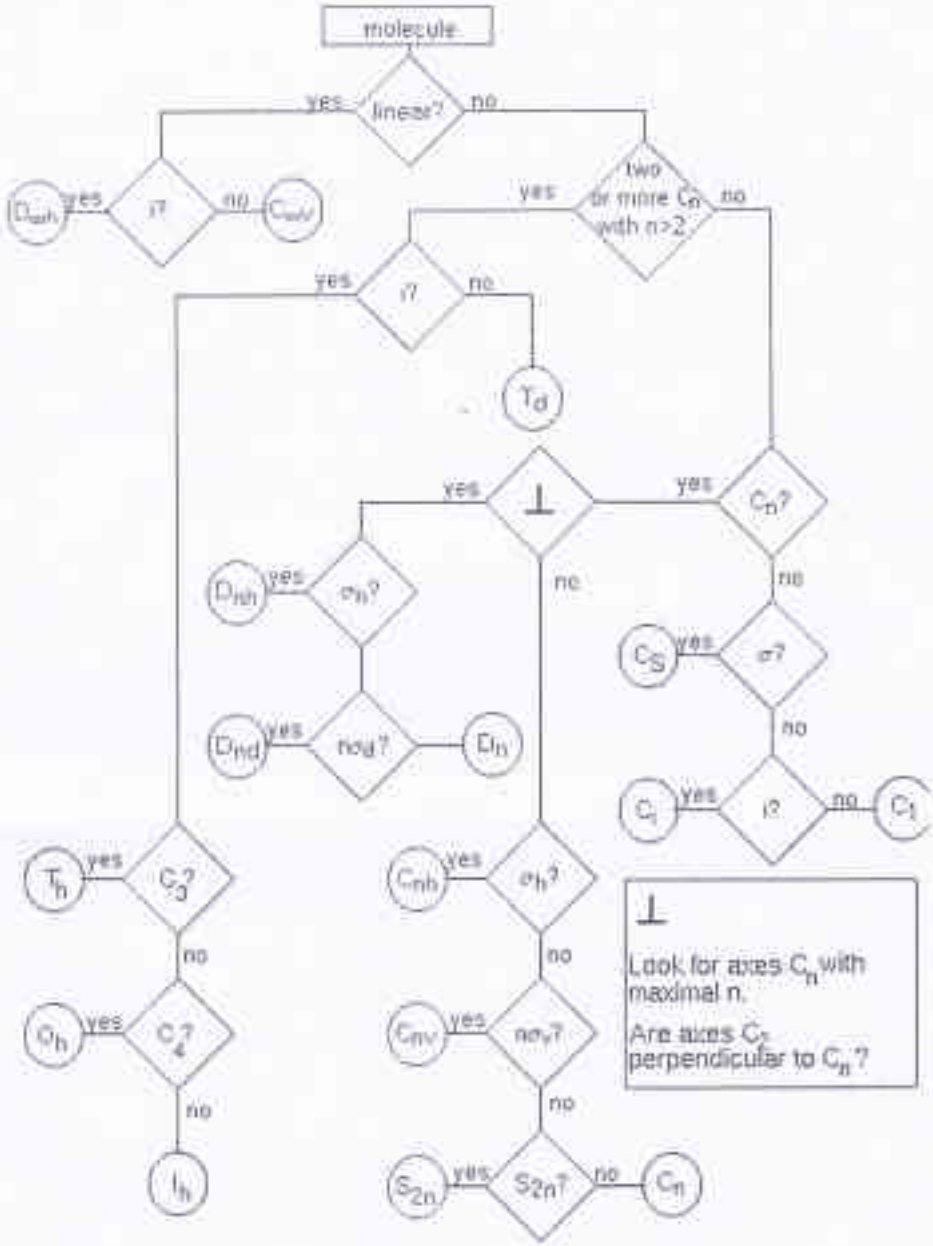
Spectral positions for the Strokes lines are given by the equation,

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

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

$$\bar{\nu}_{J \to J-2} = \bar{\nu}_i + 2\,B\,(2J - 1).$$

(40 marks)


molecule
linear?
yes
no
$D_{\infty h}$
i?
$C_{\infty v}$
two or more C_n with n>2
T_d
$\perp$
C_n?
D_{nh}
σ_h?
D_{nd}
nσ?
D_n
C_s
σ?
C_i
i?
C_1
T_h
C_3?
O_h
C_4?
I_h
C_{nh}
σ_h?
C_{nv}
nσ?
S_{2n}
S2n?
C_n
⊥
Look for axes C_n with maximal n.
Are axes C_2 perpendicular to C_n?

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