

### Question 1

- a) Which of the following molecules would you expect to show a microwave (pure rotational) spectrum?

H<sub>2</sub>, HCl, CH<sub>3</sub>, CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, benzene, toluene, CO<sub>2</sub>

- b) Suggest a structure for XY<sub>3</sub> so that it i) gives a rotational spectrum and ii) does not give a rotational spectrum (give reasons).

### Question 2

The molecule H<sup>35</sup>Cl exhibits rotational absorption lines in the far infrared at the following wavenumbers (cm<sup>-1</sup>): 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60 and 226.86 (note that there may be other lines in the microwave region too).

- a) Identify the transitions and use a graphical procedure to determine the rotational and centrifugal distortion constants. Calculate the bond length of HCl.  
b) Predict the rotational constant for DCl.  
c) Determine the most populated rotational level in HCl at 300 K.

### Question 3

Given that the CO bond length in the molecule OCS is 0.1165 nm and the CS bond length is 0.1158 nm, predict the frequencies (in Hz) of the J = 0 ← 1 and 1 ← 2 transitions in the rotational spectrum of OCS.

### Question 4

Calculate the energies of the J = 2 levels of CF<sub>3</sub>I, ignoring centrifugal distortion, given A<sub>0</sub> = 0.191 cm<sup>-1</sup> and B<sub>0</sub> = 0.0507 cm<sup>-1</sup>. What would be the magnitudes of the Stark splittings of these levels in a static electric field of 10 Vm<sup>-1</sup> if the dipole moment of CF<sub>3</sub>I is 3.34 × 10<sup>-30</sup> Cm (1 Debye). Draw an energy level diagram illustrating the splittings.

### Question 5

- a) The energy levels of a symmetric top molecule including centrifugal distortion are given (in wavenumber units) by the expression

$$F(J,K) = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

where D<sub>J</sub>, D<sub>JK</sub> and D<sub>K</sub> are centrifugal distortion constants. Derive an expression for the wavenumbers of the allowed transitions in the rotational spectrum (ΔJ = +1 or -1, ΔK = 0).

- b) In the rotational spectrum of CH<sub>3</sub>F, lines were observed at the frequencies 51071.8, 102142.6, 102140.8, 153210.3, 153207.6, 153199.6 MHz. Assign quantum numbers to the transitions and determine B, D<sub>J</sub> and D<sub>JK</sub> for CH<sub>3</sub>F.

### Question 6

What are the numbers of vibrational modes for the following molecules? NH<sub>3</sub>, HCN, SO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>10</sub>H<sub>8</sub>, C<sub>60</sub>. Sketch the normal modes for HCN and SO<sub>2</sub>.

### Question 7

The following lines are observed in the fundamental (infrared) vibration-rotation band of  $\text{H}^{35}\text{Cl}$ : 2998.05, 2981.05, 2963.35, 2944.99, 2925.92, 2906.25, 2865.14, 2843.63, 2821.59, 2799.00, 2775.77  $\text{cm}^{-1}$

- Assign the rotational quantum numbers for  $v = 0$  and  $v = 1$  associated with each transition.
- Graphically or otherwise, using the method of combination differences, determine the rotational constants in both levels ( $B_0$  and  $B_1$ ); ignore centrifugal distortion.
- Hence determine the equilibrium internuclear distance  $r_e$ .

### Question 8

- Derive an expression for the separation between adjacent lines in the P branch of the fundamental vibration-rotation band of a diatomic molecule in terms of the rotational constants  $B_1$  and  $B_0$  (ignore centrifugal distortion).
- Lines are observed in the P branch of the fundamental band of carbon monoxide with the following wavenumbers ( $\text{cm}^{-1}$ ).

P(9)	P(10)	P(14)	P(15)
2107.425	2103.271	2086.323	2082.003

Determine the rotational constants  $B_0$  and  $B_1$  and comment on their relative values.

### Question 9

Adjacent vibration-rotation lines near the centre of the  $\nu_3$  stretching fundamental band in the infrared spectrum of  $\text{CO}_2$  occur at the following wavenumbers: 2351.64, 2350.08, 2347.74, 2346.18  $\text{cm}^{-1}$ . Calculate the band origin of this fundamental vibration and the C-O internuclear distance.

### Question 10

- A band in the infrared spectrum of ethyne shows P, Q and R branches. Draw an energy level diagram of the rotational levels in the two vibrational states and use it to explain why you might expect the frequency differences  $\Delta_1 = R(J) - Q(J)$  and  $\Delta_2 = Q(J+1) - P(J+1)$  to be the same.
- The measured values of  $\Delta$  ( $= \Delta_1 = \Delta_2$ ) are given for some J values below.

J	5	10	15	20	25
D / $\text{cm}^{-1}$	14.144	25.919	37.676	49.404	61.096

Extract as many parameters as possible from the data. What information do they provide about the structure of the molecule?

### Question 11

Determine the symmetries of the vibrational modes for a homonuclear triatomic molecule  $X_3$  with an equilateral triangular structure ( $D_{3h}$  symmetry) and hence determine which vibrations are active in a) the infrared and b) the Raman spectrum.

Ozone,  $O_3$ , exhibits fundamental vibrational bands in the infrared spectrum at  $710\text{ cm}^{-1}$ ,  $1043\text{ cm}^{-1}$  and  $1103\text{ cm}^{-1}$ . Is this observation consistent with the hypothesis that ozone has an equilateral triangular structure?

Consider one other possible structure and determine the infrared and Raman rules for it. Is this structure consistent with the experimental evidence given above?

In the infrared spectrum of  $BF_3$ , the  $A_2''$  fundamental  $\nu_2$  and its second overtone  $3\nu_2$  are seen in absorption from the ground state, but not the first overtone  $2\nu_2$ . Why is this?

### Question 12

- The rotational Raman spectrum of  $^{35}Cl_2$  shows a series of lines separated by  $0.9752\text{ cm}^{-1}$  in both Stokes and anti-Stokes branches. Determine the bond length of  $Cl_2$ .
- Given that the CO and CS bond lengths in  $CO_2$  and  $CS_2$  are  $0.1162\text{ nm}$  and  $0.1555\text{ nm}$ , respectively, explain why the line spacing in the rotational Raman spectrum of OCS is very close to that for  $CS_2$ .

### Question 13

The rotational Raman spectrum of  $H_2$  was recorded at  $350\text{ K}$ . The displacements of the first five lines of the Stokes branch from the exciting line are listed below, together with their relative intensities.

Displacement / $\text{cm}^{-1}$	Intensity
364.8	1.0
608.0	5.46
851.2	1.12
1094.4	1.05
1337.6	0.06

- Explain quantitatively the magnitude of both the displacements and intensities.
- Predict what differences in displacements and intensities you would expect for  $D_2$ .

### Question 14

The table below lists the vibrational frequencies and infrared/Raman activities for cyanogen ( $C_2N_2$ ). What does this information tell us about the structure of cyanogen? Suggest an assignment for the bands.

$226\text{ cm}^{-1}$	Infrared	PQR branches
$506\text{ cm}^{-1}$	Raman	PQR branches
$848\text{ cm}^{-1}$	Raman	PR branches only
$2149\text{ cm}^{-1}$	Infrared	PR branches only
$2322\text{ cm}^{-1}$	Raman	PR branches only

The rotational Raman spectrum of the molecule shows a series of anti-Stokes lines separated by  $0.63\text{ cm}^{-1}$ . If the CN bond length is  $0.1165\text{ cm}^{-1}$ , determine the C-C bond length.