

Molecular Spectroscopy

- Q1. a) Which of the following molecules would you expect to show a microwave (pure rotational) spectrum?
H₂, HCl, CH₃, CH₃Cl, CH₂Cl₂, H₂O, NH₃, benzene, toluene, CO₂
- b) Suggest a structure for XY₃ so that it i) gives a rotational spectrum and ii) does not give a rotational spectrum (give reasons).

- Q2. The molecule H³⁵Cl exhibits rotational absorption lines in the far infrared at the following wavenumbers (cm⁻¹):
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.

- Q3. 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 $J = 0 \rightarrow 1$ and $1 \rightarrow 2$ transitions in the rotational spectrum of OCS.

- Q4. Calculate the energies of the $J = 2$ levels of CF₃I, ignoring centrifugal distortion, given that $A_0 = 0.191 \text{ cm}^{-1}$ and $B_0 = 0.0507 \text{ cm}^{-1}$. What would be the magnitudes of the Stark splittings of these levels in a static electric field of 10 V m^{-1} if the dipole moment of CF₃I is $3.34 \times 10^{-30} \text{ C m}$ (1 Debye). Draw an energy level diagram illustrating the splittings.

- Q5. a) The energy levels of a symmetric top molecule including centrifugal distortion are given (in wavenumber units) by the expression

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

where D_J , D_{JK} and D_K are centrifugal distortion constants. Derive an expression for the wavenumbers of the allowed transitions in the rotational spectrum ($\Delta J = \pm 1$, $\Delta K = 0$).

- b) In the rotational spectrum of CH₃F, 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_J and D_{JK} for CH₃F.

- Q6. What are the numbers of vibrational modes for the following molecules?

NH₃, HCN, SO₂, C₂H₂, C₁₀H₈, C₆₀.

Sketch the normal modes for HCN and SO₂.

Q7. The following lines are observed in the fundamental (infrared) vibration-rotation band of H³⁵Cl:

2998.05, 2981.05, 2963.35, 2944.99, 2925.92, 2906.25,
2865.14, 2843.63, 2821.59, 2799.00, 2775.77 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 .

Q8. a) 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 (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.

Q9. Adjacent vibration-rotation lines near the centre of the ν_3 stretching fundamental band in the infrared spectrum of CO₂ occur at the following wavenumbers:

2351.64, 2350.08, 2347.74, 2346.18 cm⁻¹.

Calculate the band origin of this fundamental vibration and the C–O internuclear distance.

Q10. a) 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 Δ ($= \Delta_1 = \Delta_2$) are given for some J values below.

J	5	10	15	20	25
D / 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?

- Q11. 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 cm^{-1} , 1043 cm^{-1} and 1103 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 ν_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?

- Q12. a) The rotational Raman spectrum of $^{35}Cl_2$ shows a series of lines separated by 0.9752 cm^{-1} in both Stokes and anti-Stokes branches. Determine the bond length of Cl_2 .
- b) Given that the CO and CS bond lengths in CO_2 and CS_2 are 0.1162 nm and 0.1555 nm , respectively, explain why the line spacing in the rotational Raman spectrum of OCS is very close to that for CS_2 .

- Q13. The rotational Raman spectrum of H_2 was recorded at 350 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 / cm^{-1}	Intensity
364.8	1.0
608.0	5.46
851.2	1.12
1094.4	1.05
1337.6	0.06

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

- Q14. 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 cm^{-1}	Infrared	PQR branches
506 cm^{-1}	Raman	PQR branches
848 cm^{-1}	Raman	PR branches only
2149 cm^{-1}	Infrared	PR branches only
2322 cm^{-1}	Raman	PR branches only

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