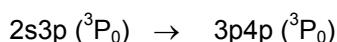
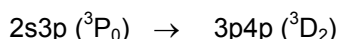
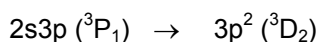
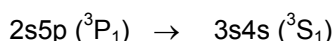
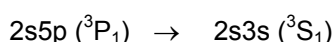
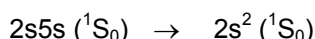
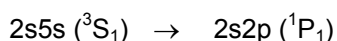
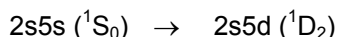


Numerical Problem Set for Atomic and Molecular Spectroscopy

Yr 2 HT SRM

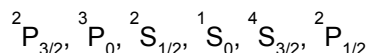
Section 1: Atomic Spectra

- For each of the atomic term symbols 1S , 2P , 3P , 3D , 4D , write down:
 - The associated values of the total spin and orbital angular momentum quantum numbers, S and L ;
 - the possible values of J , the total angular momentum quantum number; and
 - the number of states associated with each value of J .
- How many fine-structure components would be observed in the emission line $n = 4 \rightarrow 3$ of the H-atom if the effects of spin-orbit coupling were fully resolved in the spectrum? Illustrate these transitions on a Grotrian diagram.
 - One of the $n = 5$ terms of hydrogen is split by spin-orbit coupling into two levels with an energy difference of 0.0039 cm^{-1} . Determine the orbital angular momentum quantum number, l , for this state and predict the analogous splitting in Li^{2+} . The fine structure constant, $\alpha = 0.0072973$.
- A line in the *emission* spectrum of potassium arises from the transition $4^2P \leftarrow 3^2D$. Upon closer examination it is found to consist of three lines at energies (in cm^{-1}) 8494.13, 8496.45 and 8554.17.
 - Draw a diagram representing these transitions given that the splitting is regular (*i.e.*, energy increases with J) for the 2P terms and inverted for the 2D terms.
 - Calculate the separation of the individual J components of the states involved.
- A number of possible transitions in the beryllium atom are listed below. Which are "fully allowed"? For those which are not allowed, which selection rule would have to be broken and what mechanisms which might lead to such a break-down? (*n.b.*, one term symbol is invalid, which one and why?)

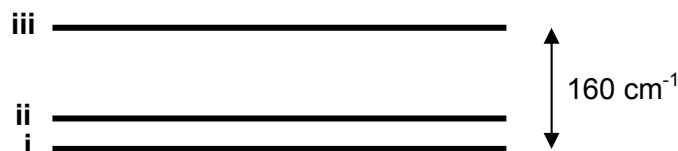


- Sketch the radial distribution function of the $3s$, $3p$ and $3d$ orbitals of sodium and show in your graph where the inner shell electrons lie. Explain why these orbitals have different energies.
 - A transition from the $3s$ to a $3p$ level in Na is at $16\,961 \text{ cm}^{-1}$. Transitions from this $3p$ level to the d levels form a series of lines of which the first three are at $8\,752$, $16\,214$ and $19\,386 \text{ cm}^{-1}$. Sketch the energy level diagram for the transitions involved and deduce the ionisation potential of Na in its ground state. (leave your answer in cm^{-1}).
 - Explain the fact that the $3s \rightarrow 3p$ transition referred to in part (b) is split into a doublet separated by 17 cm^{-1} and under higher resolution the p to d transitions are each seen to consist of three lines. Explain these observations.

6. The following term symbols refer to the ground states of certain first row atoms. Which atoms?



7. The $3s^23p4p$ configuration of an excited state of the Si atom leads to a state with orbital angular momentum $L = 1$ and which is split by spin-orbit coupling into the levels shown below. Deduce possible term symbols for the three levels and indicate the dipole allowed transitions which would arise in absorption from these levels when the $4p$ electron is excited into a $5s$ orbital.



8. a) Draw up a table showing the microstates allowed by the Pauli principle for an nd^2 electronic configuration and hence derive the permitted term symbols assuming Russell-Saunders coupling.
 b) Use angular momentum coupling arguments to show that the levels derived in $j-j$ coupling for an $nprf$ configuration are $[\frac{1}{2} \frac{5}{2}]_{3,2}$, $[\frac{1}{2} \frac{7}{2}]_{4,3}$, $[\frac{3}{2} \frac{7}{2}]_{5,4,3,2}$ and $[\frac{3}{2} \frac{5}{2}]_{4,3,2,1}$.
9. a) The lowest energy configuration of the N^+ ion is $2s^22p^2$. The first excited configuration is obtained by promoting an electron from the $2s$ to the $2p$ orbital. Use angular momentum coupling arguments to derive the states that arise from the excited configuration, noting that a p^3 configuration, as in the neutral N atom, gives rise to terms 4S , 2P and 2D .

An allowed transition has been detected in N^+ between one of the levels of its *ground* term and one of the levels associated with the first excited configuration.

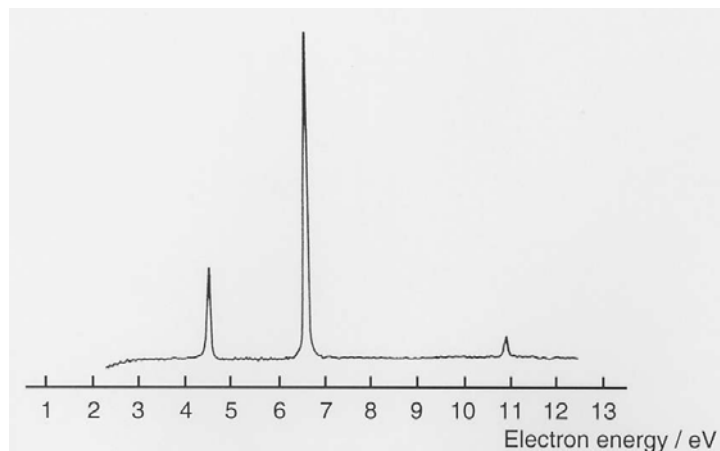
- b) The g -factors of both levels were measured to be 1.50. Assuming the Landé g -factor formula, suggest an assignment for the transition.
10. Explain the following observations:
- a) The four lowest energy electronically excited states of He (at low resolution) lie at 159850 cm^{-1} , 166271 cm^{-1} , 169083 cm^{-1} and 171129 cm^{-1} above the ground state. The absorption spectrum of He, however, displays a strong line at only one of these energies.
- b) He gas shows negligible absorption of radiation in the infra-red, but strong absorption bands are observed at 4858 cm^{-1} and 9233 cm^{-1} when the gas is excited in an electric discharge.
- c) The first two excited electronic states of gaseous carbon and oxygen atoms occur at the following excitation energies:

Species	excitation energies / cm^{-1}
Carbon	16.4, 43.3
Oxygen	158.5, 226.5

However, the first two excited states for gaseous nitrogen atoms lie at more than 19000 cm^{-1} above the ground state.

- d) A ${}^1D_2 \rightarrow {}^1P_1$ transition observed in the emission spectrum of Cd consists of a single line. In the presence of a magnetic field three lines are observed. For the ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ emission line in sodium the single line is observed to split into four lines when a magnetic field is applied.

11. Shown below is the PES spectrum of mercury vapour. The x-axis gives the kinetic energy of the ejected electrons, as determined by the instrument, rather than the more usual ionization energies. The incident photons used to ionize the sample are from a helium resonance lamp and have wavelength 584 Å.



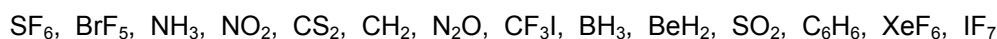
- What is the energy of the incident radiation in eV?
- What are the approximate ionization energies leading to each of the peaks in the spectrum?
- The peaks in the spectrum correspond to removing electrons from the valence shell of the mercury atom, *i.e.* from the 5d shell or the 6s shell. Give the term symbols for the possible ions arising from the ejection of a single electron from either the 5d or 6s shell in Hg.
- By simply considering the degeneracies of each of these ionic levels, what should the expected ratios of the peak intensities in the spectrum be? Assign appropriate term symbols to each of the peaks in the spectrum.

Section 2: Molecular Rotational (microwave) Spectroscopy

12. Which of the following molecules exhibit pure rotational (microwave) spectra?
 HF, NH₃, CH₄, CH₃F, BF₃, H₂O, C₂F₂H₂, O₃, CO₂, toluene, Argon---HCl
13. The rotational constant of H³⁵Cl is 10.5909 cm⁻¹. Calculate the rotational constants of H³⁷Cl and ²H³⁵Cl.
14. Without calculating the specific values, arrange the following molecules in order of increasing value of their rotational constants, B :
 HF, DF, H-C≡C-C≡C-N, HD, ¹²C¹⁶O, ¹³C¹⁶O, ¹²C¹⁸O, ClCN.

15. Given that the CO bond length in the molecule OCS is 0.1165 nm and the CS bond length is 0.1558 nm, determine its moment of inertia. At which frequencies (units Hz or GHz) do the $J = 1 \leftarrow 0$ and $2 \leftarrow 1$ transitions occur in the rotational spectrum of OCS?

16. Classify the following molecules as spherical, symmetric or asymmetric tops, and state which will give pure rotational spectra. For the symmetric tops, sketch the principal axes and indicate the unique axis.



17. The rotational terms of a diatomic molecule (the energy levels expressed as wavenumbers) are given to a good approximation by $F_J = BJ(J+1) - DJ^2(J+1)^2$.

- Explain the meaning of J , B and D in this expression.
- What selection rules apply to pure rotational spectroscopy?
- Derive an expression for the energy of *transitions* observed in a high resolution rotational spectrum.
- In a high resolution microwave study of ²H¹⁹F, the *first* four lines in the spectrum were observed at

22.0180 cm⁻¹
44.0218 cm⁻¹
65.9970 cm⁻¹
87.9295 cm⁻¹

By drawing a suitable straight-line graph, deduce the values of B and D for ²H¹⁹F.

- Hence determine the ²H¹⁹F bond length

18. Ammonia, NH₃, is an oblate symmetric top.

- State the selection rules which apply to this molecule undergoing changes in rotational energy. The origin of these rules. Hence determine an expression for the frequencies of the allowed transitions (ignore centrifugal distortion); draw a labelled sketch of the spectrum you expect.
- The idealized microwave spectrum of ammonia shows absorptions at the following frequencies, in GHz

1798.9 2398.6 2998.2

Assign the transitions (giving your reasons), and determine all you can about the molecule.

19. The molecule H³⁵Cl exhibits rotational absorption lines in the far infrared at the following wavenumbers (in cm⁻¹): 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.6, 226.86.

(Note that there may be other lines in the microwave region, too.)

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

20. Show that the quantum number of the most highly populated rotational level of a rigid diatomic molecule is given by

$$J_{max} = \sqrt{\frac{kT}{2h\tilde{B}c}} - \frac{1}{2}$$

- a) Which state in HCl ($B = 10.6 \text{ cm}^{-1}$) would be the most populated at 700, 800, 900, 1000, 1100 and 1200 K?
- b) If it could be determined experimentally, would J_{max} be a good way to determine the temperature of a sample? Why?
- c) How could one better determine the temperature spectroscopically?
- d) How is the intensity of the transition $J+1 \leftarrow J$ related to the population of state J .
21. The energy levels of a symmetric top molecule including centrifugal distortion are given (in cm^{-1}) by

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

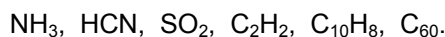
where D_J , D_{JK} and D_K are centrifugal distortion constants.

- a) Derive an expression for the wavenumbers of the allowed transitions in the rotational spectrum ($\Delta J = \pm 1$, $\Delta K = 0$)
- In the rotational spectrum of CH_3F , absorption maxima were found at *wavelengths* of 1.958 mm and 2.937 mm. At higher resolution, these peaks split into three and two components, respectively.
- b) Explain the origin of these observations, assign the transitions and determine as many rotational and centrifugal distortion constants of CH_3F as you can. Give your constants in cm^{-1} and in MHz.
22. Show that for a homonuclear diatomic molecule composed of atoms with nuclear spin quantum numbers I , that the ratio of the number of symmetric nuclear spin functions to antisymmetric nuclear spin wavefunctions is $(I+1/I)$. Comment on the value of this quantity for $I=0$ atoms.
23. a) Draw a diagram showing the effect of an electric field on the energy levels ($J=2, K=1$) and ($J=3, K=1$) of a prolate symmetric top. Indicate the splittings (in terms of μ and E field) of the M_J levels. Identify the allowed transitions and hence predict the expected form of the spectrum.
- b) For CH_3I the rotational constant, B , is 1523 MHz and the dipole moment is 1.0 Debye. Using your results from part i), predict the frequencies (in MHz) of the lines you would expect to see from the ($J=2, K=1$) \rightarrow ($J=3, K=1$) transition when:
- (a) no electric field is applied;
- (b) when an electric field of 10^4 Vm^{-1} is applied parallel to the electric field vector of the radiation.
24. When an electric field, of magnitude $2 \times 10^4 \text{ V}$, is applied parallel to the electric-field vector of the microwave radiation, the rotational transition ($J=2, K=1$) \leftarrow ($J=1, K=1$) of CH_3Cl at 1.67360 cm^{-1} is split into three components, with lines at 1.67569 , 1.67360 and 1.67151 cm^{-1} . Determine the rotational constant, B , of CH_3Cl and its dipole moment, in Debye.

Section 3: Molecular vibrational (infrared) and vibration-rotation spectroscopy

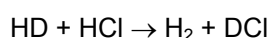
25. The force constant of $^{79}\text{Br}_2$ is 240 Nm^{-1} . Calculate the fundamental vibrational frequency and the zero-point energy of $^{79}\text{Br}_2$.

26. What is meant by a normal mode of vibration? How many normal modes of vibration do the following molecules have?



Sketch the normal modes for HCN and SO_2

27. What is meant by zero-point energy? Calculate the energy change for the reaction



assuming that each molecule is in its ground vibrational state. Ignore anharmonicity effects.

$$[\omega_e(\text{H}_2) = 4395 \text{ cm}^{-1}, \omega_e(\text{HD}) = 3817 \text{ cm}^{-1}, \omega_e(\text{HCl}) = 2990 \text{ cm}^{-1}, \omega_e(\text{DCI}) = 2091 \text{ cm}^{-1}.]$$

28. a) The Morse potential can be written $V(r) = D_e [1 - \exp(-\beta x)]^2$, where x , the displacement, is $(R - R_e)$.

Expand the exponential to first order in x (i.e., $e^x \approx 1 + x$) and show that, in this limit, the potential is harmonic with force constant, k_{Morse} , given by $k_{\text{Morse}} = 2D_e\beta^2$.

The vibrational frequency, ω , is defined in terms of this force constant, ω (in rad s^{-1}) = $\sqrt{\frac{k_{\text{Morse}}}{\mu}}$,

where μ is the reduced mass. Use this definition of ω , together with the expression above for k_{Morse} to find an expression for β in terms of μ , D_e and ω .

Given the anharmonicity parameter for a Morse oscillator is $x_e = \frac{\hbar\beta^2}{2\mu\omega}$ show that D_e (in J) = $\frac{\hbar\omega}{4x_e}$

- b) Using the Morse energy levels, show that the wavenumber of a transition from the ground state ($v = 0$) to the v th vibrational level is given by

$$\tilde{\nu}(0 \rightarrow v) = v\omega_e - v(v+1)\omega_e x_e,$$

where ω_e is the vibrational constant (a wavenumber given by $\omega_e = \omega / 2\pi c$).

In the low resolution IR spectrum of $^1\text{H}^{79}\text{Br}$ a strong absorption is observed at 2558.5 cm^{-1} and a weaker absorption at 5026.5 cm^{-1} . Use the Morse oscillator energy levels to account for these observations; determine the parameters ω_e , x_e , D_e and β , clearly stating the units of your answers.

[Note that all of the formulae given in part (a) are in SI, so to use them to compute β you will need to make sure that ω is in rad s^{-1} and D_e in J. Use integer atomic masses.]

29. Vibrational absorption lines for H^{35}Cl lie at the following wavenumbers:

$$2885.9, 5668.0, 8347.0, 10922.9 \text{ cm}^{-1}$$

Show that these values are in agreement with those expected for a Morse oscillator. Derive values for the force constant, zero-point energy and dissociation energy of the molecule.

30. Adjacent vibration-rotation lines near the centre of the ν_3 stretching fundamental band in the infrared spectrum of 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 bond length.

31. The four central lines in the high resolution $\nu=1 \leftarrow \nu=0$ infra-red spectrum of H^{37}Cl occur at

$$2837.6, 2858.8, 2899.2 \text{ and } 2918.6 \text{ cm}^{-1}.$$

Deduce as much as possible about the molecule.

Would the corresponding lines in H^{35}Cl lie at the same spectral positions?

$$[{}^1\text{H} = 1.0078 \text{ amu}, {}^{37}\text{Cl} = 36.9659 \text{ amu}]$$

32. a) Sketch the normal modes of dichloroacetylene (dichloroethyne), $\text{Cl}-\text{C}\equiv\text{C}-\text{Cl}$, indicating their symmetries and which are degenerate.
- c) For each normal mode, determine the symmetry of the $\nu = 0, 1$, and 2 vibrational levels, and hence determine whether or not the $\nu = 0 \rightarrow 1$ transition for each mode is allowed. For the allowed transitions, state the direction of the transition dipole moment.
- More difficult:* do the same for the $\nu = 1 \rightarrow 2$ transitions.
- d) If the vibrations are anharmonic, transitions with $\Delta\nu = \pm 2$ may be weakly allowed. Determine which (if any) of the $\nu = 0 \rightarrow 2$ transitions are allowed by symmetry considerations.
- e) Identify a combination line which is symmetry allowed.

33. The vibration-rotation spectrum of CS_2 shows strong bands at 397 cm^{-1} (IR active, perpendicular band) 685 cm^{-1} (Raman active) and 1510 cm^{-1} (IR active, parallel band). The corresponding transitions in OCS lie at $520, 859$ and 2062 cm^{-1} but appear in both the IR and Raman spectra.

- Explain what is meant by *parallel* and *perpendicular* bands.
- Assign the fundamental modes of vibration and discuss the geometry of these molecules.
- The line spacing in the rotational Raman spectrum of CO_2 and CS_2 are 3.122 and 0.873 cm^{-1} respectively. Calculate the C–O bond length in CO_2 and the C–S bond length in CS_2 .
- Explain fully why the line spacing in the rotational Raman spectrum of OCS is very close to that of CS_2

n.b., Assume integral relative molecular masses. The nuclear spins of ${}^{16}\text{O}$ and ${}^{32}\text{S} = 0$.

34. a) In the idealized IR spectrum of acetylene (ethyne) a strong absorption is seen at 3290 cm^{-1} ; this is attributed to the fundamental ($\nu = 0 \rightarrow 1$) of mode 3 (for the normal modes, see the lecture notes). A second strong absorption at 730 cm^{-1} is attributed to the fundamental of mode 5. Combination lines in which *only two* modes are involved are observed at the following wavenumbers (in cm^{-1}):

$$1340 \quad 2700 \quad 3900 \quad 4100 \quad 5260 \quad 6660$$

Determine the wavenumbers of the other three normal modes (it is not necessary to identify which is which; anharmonicity is ignored throughout).

- b) Account for the following combination lines, which involve *more than two modes*

$$1950 \quad \text{and} \quad 3310 \text{ cm}^{-1}$$

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

226 cm^{-1}	Infrared active exhibiting PQR branches
506 cm^{-1}	Raman active
848 cm^{-1}	Raman active
2149 cm^{-1}	Infrared active exhibiting PR branches only
2322 cm^{-1}	Raman active

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 nm, determine the C–C bond length.

Section 4: Molecular electronic spectroscopy

36. The $v = 0 \leftarrow 0$ vibrational band in the $A^1\Pi \leftarrow X^1\Sigma^+$ electronic transition in BeO shows a band head in the R -branch.

- a) Derive a general expression for the wavenumber of a line in the R -branch ($J''+1 \leftarrow J''$) and show that the wavenumber is a maximum when

$$J'' = -\frac{B_0'' - 3B_0'}{2(B_0'' - B_0')}$$

- b) The highest wavenumber lines in the R -branch are those corresponding to transitions out of $J'' = 4$ and $J'' = 5$ which lie at essentially the same wavenumber. The microwave spectrum of the ground state gives $B_0'' = 1.642 \text{ cm}^{-1}$. Obtain an approximate value for B_0' , the rotational constant in the A -state giving an estimate of uncertainty in your answer.
- c) Calculate the bond lengths of BeO in both electronic states and account qualitatively for any difference between them. (*n.b.* BeO is isoelectronic with C_2)
- d) Which electronic state would you expect to find lying lower in energy than the $A^1\Pi$ state?

37. For Br_2 , the equilibrium internuclear distances of the ground state and of an excited electronic state are $R_e = 228 \text{ pm}$ and $R_e' = 266 \text{ pm}$, respectively.

The vibrational wavenumber, $\left(\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \right)$, for the excited state is 168 cm^{-1} .

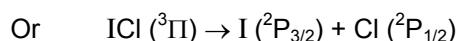
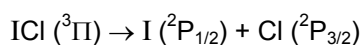
Assuming that the upper state potential energy curve may be approximated as a simple harmonic oscillator, use the classical version of the Franck-Condon principle to predict which is the most probable (vertical) change in vibrational quantum number for a transition in absorption from $v = 0$ of the ground state.

38. The figure below shows the $v'' = 0$ progression for a weakly allowed, ${}^3\Pi \leftarrow X^1\Sigma^+$, electronic transition in ICl. The wavenumbers marked correspond to the band origin, ν_{00} and the onset of a dissociative continuum.



- What conclusions can one draw from the fact that so few vibrational levels are supported in the excited state?
- What is the dissociation energy, D'_0 , of the excited state?

The ground state of ICl dissociates to two ground-state (*i.e.*, ${}^2P_{3/2}$) atoms. There are two possibilities for the dissociation of the excited state:



- Given that the ground-state spin-orbit splitting for I is 7603 cm^{-1} and for Cl is 881 cm^{-1} , deduce possible values for the dissociation energy of the ground state of ICl.
- The dissociation energies of I_2 and Cl_2 are 12452 and 19972 cm^{-1} , respectively. Use these to deduce the likely dissociation products of $\text{ICl} ({}^3\Pi)$.
- Sketch the potential energy curves for the two states and mark on the quantities you have calculated.

39. The table below gives data for the ground and a low-lying excited state of CN

	T_e	$\omega_e / \text{cm}^{-1}$	$\omega_e x_e / \text{cm}^{-1}$	R_e / nm
$X \ {}^2\Sigma^+$	0	2068.6	13.1	0.11718
$A \ {}^2\Pi$	9245.3	1812.5	12.6	0.12333

- Sketch an MO diagram for CN and show the occupancies for the X and A states and use it to account for the observed changes in vibrational constant and equilibrium bond-length.
- Use a Morse potential model to estimate the number of accessible vibrational levels and the dissociation energies for each state.
- At what wavenumber is the band origin (the 0-0 transition) observed?
- Combine your results for parts b) and c) to show that the potential energy curves must cross at large separation.
- Sketch the two potential energy curves and show mark all the quantities you have calculated.
- There is a higher energy state, $B \ {}^2\Sigma^+$ for which $T_e = 25,752.0 \text{ cm}^{-1}$. The dominant features of the B – X electronic band system are the 0–0 and 1–0 vibrational bands which have relative intensities of 11 : 1. Deduce what you can about the potential energy curve for the B state and propose an electronic configuration consistent with your conclusion.

Section 5: Raman Scattering

40. The wavenumber of the incident radiation in a Raman spectrometer is 20487 cm^{-1} . What is the wavenumber of the scattered Stokes radiation for the $J = 2 \leftarrow 0$ in $^{15}\text{N}_2$ ($B = 1.9896\text{ cm}^{-1}$)?
41. The rotational Raman spectrum of H_2 was recorded at 350K. The displacements of the first 5 lines of the Stokes branch from the exciting line are listed below, together with their relative intensities.

Displacement / cm^{-1}	Relative 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 .
42. Explain the following observations:
The ratio of the frequencies (measured from the Rayleigh line) of the first and second pure rotational Stokes Raman lines of $^{16}\text{O}_2$ is 5/9. This ratio is 3/7 for C^{16}O_2 and 3/5 for $^{17}\text{O}_2$.
[The nuclear spin of ^{16}O is 0 and that of ^{17}O is 5/2]
43. a) The rotational Raman spectrum of $^{35}\text{Cl}_2$ 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) 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 .