

[Useful conversion ratio for rotational energy levels: $\frac{h}{8\pi^2c} = 16.8576 \text{ amu } \text{\AA}^2 \text{ cm}^{-1}$]

Question 1

- a) A sample of nitrogen gas is confined to a cubic volume 10 cm x 10 cm x 10 cm at 300 K. Write down the expression for the translational energy levels of a nitrogen molecule, using the three quantum numbers n_x , n_y and n_z . Calculate the separation between the lowest two translational levels taking $m(\text{N}) = 14.0$. Given that kT at room temperature is about 208 cm^{-1} ($0.414 \times 10^{-20} \text{ J molecule}^{-1}$), deduce what you can about the quantised motion of the nitrogen molecules.
- b) Some consecutive rotational energy levels of H^{35}Cl in the $v=0$ level occur at 125.201, 208.584, 312.716 and 437.534 cm^{-1} . Identify the J value for each level; hence deduce the moment of inertia and bond length of the molecule. What is the degeneracy of each level and to what does this degeneracy correspond physically? [$m(^{35}\text{Cl}) = 34.969$, $m(^1\text{H}) = 1.0078$].

Question 2

- a) The vibrational levels of the diatomic molecule sodium iodide (NaI) lie at the following wavenumbers: 142.8, 427.3, 710.3, 991.8 cm^{-1} . Deduce the values for the constants ω_e , $\omega_e x_e$ and the zero point energy.
- b) The molecules O_2 and N_2 have harmonic vibrational wavenumbers of 1580 and 2359 cm^{-1} respectively. Calculate the bond force constants for these two molecules and comment on their respective values. [$m(^{16}\text{O}) = 15.995$, $m(^{14}\text{N}) = 14.003$].
- c) The vibrational parameters for H^{35}Cl are $\omega_e = 2990.95 \text{ cm}^{-1}$ and $\omega_e x_e = 52.819 \text{ cm}^{-1}$. Calculate the ^{35}Cl to ^{37}Cl isotope shift for the $v=1-0$ vibrational interval for both HCl and DCl. Can you explain why one is larger than the other? Estimate the dissociation energies D_0 for H^{35}Cl and H^{37}Cl , explaining clearly why the two values are not the same. [$m(^{37}\text{Cl}) = 36.966$, $m(^2\text{H}) = 2.0141$. See also Question 1.b].

Question 3

- a) The following are observed wavenumbers of lines in the 0-0 band of an electronic spectrum of BeO.

J	R(J)	P(J)
0	21199.8	
1	21202.9	21193.3
2	21205.7	21189.9
3	21208.5	21186.4
4	21211.1	21182.7
5	21213.6	21178.9
6	21215.6	21174.8
7		21170.7

The transitions in the R branch obey the selection rule $\Delta J = +1$ and those in the P branch $\Delta J = -1$. How can you confirm the assignment of the rotational numbering? What are the B values for the two vibrational levels?

- b) The molecule Br_2 has a dissociation energy $D_0 = 1.971 \text{ eV}$. Its vibrational wavenumber is 323 cm^{-1} . Calculate the value of the dissociation energy D_e in cm^{-1} ($1 \text{ eV} = 8065 \text{ cm}^{-1}$).
- c) A series of absorption bands is observed in the electronic spectrum of O_2 in the ultraviolet region. The origins of the first three bands are at 49363 , $50\,046$ and $50\,710 \text{ cm}^{-1}$. Sketch an energy level diagram for the transitions (all of which originate from the $v = 0$ level of the ground state) and estimate the dissociation energy D_0 of the excited state. The dissociation energy is actually 7194 cm^{-1} . Comment.

Question 4

- a) The first excited electronic state of a molecule lies 200 kJmol^{-1} above the ground state. Using the Boltzmann distribution law and the fact that at room temperature RT is roughly 2.5 kJmol^{-1} , find the proportion of molecules in this excited state.
- b) For CO , the spacing between vibrational levels 0 and 1 is around 2100 cm^{-1} . What proportion of molecules are in the state with $v = 1$ at room temperature? Would you expect to see the transition $v = 2 \leftarrow 1$ in the absorption spectrum?
- c) The molecule BF has a rotational constant of 1.52 cm^{-1} . Which will be the most highly populated rotational level at 500 K ?