Molecular Energy Levels

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

Q 1.1 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(N) = 14.0. Given that k_BT at room temperature is about 208 cm^{-1} (or 0.414 x 10^{-20} J molecule^{-1}), deduce what you can about the quantised motion of the nitrogen molecules.

Q 1.2 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}Cl) = 34.969 a.u., m(^{1}H) = 1.0078 a.u.].

Q 2.1 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 and $x_e\omega_e$ and the zero point energy.

Q 2.2 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}O) = 15.995 a.u., m(^{14}N) = 14.003 a.u.].

Q 2.3 The vibrational parameters for H^{35}Cl are ω_e = 2990.95 cm^{-1} and $\omega_e x_e$ = 52.819 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}Cl) = 36.966 a.u., m(^{2}H) = 2.0141 a.u. See also Q 1.2].

Q 3.1 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 ΔJ = +1 and those in the P branch ΔJ = -1. How can you confirm the assignment of the rotational numbering? What are the B values for the two vibrational levels?

Q 3.2 a) The molecule Br_2 has a dissociation energy D_0 = 1.971 eV. Its vibrational wavenumber is 323 cm^{-1}. Calculate the value of the dissociation energy D_e in cm^{-1} (1 eV = 8065 cm^{-1}).

b) 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 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 7194cm^{-1}. Comment.

Q 4.1 The first excited electronic state of a molecule lies 200 kJ mol^{-1} above the ground state. Using the Boltzmann distribution law and the fact that at room temperature RT is roughly 2.5 kJ mol^{-1}, find the proportion of molecules in this excited state.

Q 4.2 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?

Q 4.3 The molecule BF has a rotational constant of 1.52 cm^{-1}. Which will be the most highly populated rotational level at 500 K?