

MOLECULAR ENERGY LEVELS

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

Q 1.1 A sample of nitrogen gas is confined to a cubic volume $10\text{cm} \times 10\text{cm} \times 10\text{cm}$ 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} (or $0.414 \times 10^{-20} \text{ J molecule}^{-1}$), 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?
[$m(^{35}\text{Cl}) = 34.969 \text{ a.u.}$, $m(^1\text{H}) = 1.0078 \text{ a.u.}$].

Q 2.1 The vibrational levels of the diatomic molecule sodium iodide (NaI) lie at the following wavenumbers:

$$142.8, 427.3, 710.3, 991.8 \text{ cm}^{-1}.$$

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.
[$m(^{16}\text{O}) = 15.995 \text{ a.u.}$, $m(^{14}\text{N}) = 14.003 \text{ a.u.}$].

Q 2.3 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.

[$m(^{37}\text{Cl}) = 36.966 \text{ a.u.}$, $m(^2\text{H}) = 2.0141 \text{ a.u.}$ 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 $\Delta J = +1$ 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?

- Q 3.2 a) 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} ($1 \text{ eV} = 8065 \text{ cm}^{-1}$).
- 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 $50\,710 \text{ cm}^{-1}$. 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.
- 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 ?