Molecular Energy Levels

Physical Chemistry Tutorials

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[Useful conversion ratio for rotational energy levels: $\frac{h}{8\pi^2 c} = 16.8576$ amu Å^2 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 nx, ny and nz. Calculate the separation between the lowest two translational levels taking m(N) = 14.0 . Given that kT at room temperature is about 208 cm^{-1} (0.414x10^{-20} 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}Cl) = 34.969, m(^{1}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}O) = 15.995, m(^{14}N) = 14.003].

c) 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, m(^{2}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 eV. Its vibrational wavenumber is 323 cm^{-1}. Calculate the value of the dissociation energy De in cm^{-1} (1 eV = 8065 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 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.

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 ← 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?