QMS Problem set 4 (due 11.2.2021)

Warm-up: (Each warm-up is connected to one of the problems (first warm-up to first problem etc.))

W1: The spectrum of interstellar radiation contains peaks from CH and CN rotations. Answer problem P11B12 (2 points)

P11B.12 A. Dalgarno, in *Chemistry in the interstellar medium*, *Frontiers of Astrophysics*, ed. E.H. Avrett, Harvard University Press, Cambridge, MA (1976), notes that although both CH and CN spectra show up strongly in the interstellar medium in the constellation Ophiuchus, the CN spectrum has become the standard for the determination of the temperature of the cosmic microwave background radiation. Demonstrate through a calculation why CH would not be as useful for this purpose as CN. The rotational constants $\tilde{B}$ for CH and CN are 14.190 cm^{-1} and 1.891 cm^{-1}, respectively.

Hint: The cosmic background radiation distribution can be approximated as black-body radiation (Topic 7A, Figure 7A.2). From equation 7A.1 the wavenumber of the radiation density maximum (for black-body radiation) can be obtained by substituting T=2.7K (the temperature of cosmic background radiation).

W2: Answer problem E11C.5(b) (2 points)

E11C.5(b) Calculate the relative numbers of Br_2 molecules ($\tilde{\nu}$ = 321 cm^{-1}) in the second and first excited vibrational states at (i) 298 K, (ii) 800 K.

W3: Answer problem E8A.2(a) (3 points)

E8A.2(a) The wavefunction for the ground state of a hydrogen atom is Ne^{-r/a_0}. Evaluate the normalization constant N.

Problems:

P1: Answer P11C.12 Sketch the spectrum. Discuss the relative intensities of the different peaks in relation to the Boltzmann distribution (4 points)

P11C.12 Absorptions in the $v = 1 \leftarrow 0$ vibration–rotation spectrum of $^{1}H^{35}Cl$ were observed at the following wavenumbers (in cm^{-1}):

2998.05	2981.05	2963.35	2944.99	2925.92
2906.25	2865.14	2843.63	2821.59	2799.00

Assign the rotational quantum numbers and use the method of combination differences to calculate the rotational constants of the two vibrational levels.

P2: Answer P11B.11 Plot the relative populations of the 10 lowest rotational energy levels for methane at 25 ºC and 100 ºC. Interpret your results. (6 points)

P11B.11 Develop an expression for the value of J corresponding to the most highly populated rotational energy level of a diatomic rotor at a temperature T remembering that the degeneracy of each level is $2J + 1$. Evaluate the expression for ICl (for which $\tilde{B} = 0.1142\ cm^{-1}$) at 25 °C. Repeat the problem for the most highly populated level of a spherical rotor, taking note of the fact that each level is $(2J + 1)^2$-fold degenerate. Evaluate the expression for CH_4 (for which $\tilde{B} = 5.24\ cm^{-1}$) at 25 °C. *Hint:* To develop the expression, recall that the first derivative of a function is zero when the function reaches either a maximum or minimum value.

P3: Answer P8A.7 (4 points)

P8A.7 The 'size' of an atom is sometimes considered to be measured by the radius of a sphere within which there is a 90 per cent probability of finding the electron in the outermost occupied orbital. Calculate the 'size' of a hydrogen atom in its ground state according to this definition. Go on to explore how the 'size' varies as the definition is changed to other percentages, and plot your conclusion.

P4: In this task we delve into the vibrational spectra of many atomic molecules. a) Use the NIST database to find the experimental liquid and gas phase methanol spectra. Analyse the peaks and the differences in them to your best ability. b) Open the file benz-freq.pdf, which contains the computational IR –spectrum of benzene (among other computational results). Find an experimental spectrum and match the calculated frequencies to the experimental peaks. Remember to make use of the calculated peak intensities (T**2 –values). (3 points)