CHEM 260

Assignment 5

Due Monday 10th February 2003

19. a) Assign J values[#] to the following lines from the absorption spectrum of $^{1}H^{35}Cl$, and plot the frequencies (in cm^{-1}) against $J+1$.

    104.13, 124.73, 145.37, 165.89, 186.23, 206.60, 226.86 cm^{-1}.

    b) Use the slope of the best straight line through the points to determine B (in cm^{-1}) and thence the moment of inertia I of the molecule.

    c) Use your value of $I(H^{35}Cl)$ to predict the moment of inertia and rotational constant of $D^{35}Cl$, assuming that the bond length is unchanged. [Use atomic masses 1.0078u, 2.0144u and 34.9688u for H, D and ^{35}Cl, respectively.]

    d) Predict the first line in the rotational spectrum of $D^{35}Cl$ that has a frequency above 100 cm^{-1}.

20. The intensity (A) of individual lines in a microwave (pure rotation) spectrum depends on the product of the degeneracy, $(2J+1)$, and the Boltzmann factor, $\exp\{-E_J/kT\}$. Substituting for rotational energy, E_J,

$$A = A_0(2J+1)\,e^{-BJ(J+1)/kT}$$

    a) By differentiating A with respect to J, show that the maximum intensity occurs at

$$J_{max} \approx \left[\frac{kT}{2B}\right]^{1/2} - \tfrac{1}{2} \qquad \text{(closest integer)}$$

    and calculate J_{max} for DCl at 100, 300, and 700 K.

    b) Use a spreadsheet to calculate A/A_0 for J values from 1 to 10, to see if the maximum is as predicted by the formula (check all three temperatures but you only have to submit one example plot).

21. The Chemistry Department at SFU has NMR facilities described as 100, 400 and 600 MHz spectrometers. By convention the frequency refers to the *proton* precession frequency.

    a) What are the nominal magnetic fields (in kG) of the three spectrometers?

    b) What is the fractional population difference ($\delta N/N$) of nuclear spins in the two energy levels for protons in each spectrometer?

    c) The "400 MHz" spectrometer is often used for ^{13}C NMR. Since the magnetic field is fixed, the radio-frequency probe has to operate at a different frequency – what is it?

[#] Label the lines according to the J value of the *lower* state involved in the transition.