Chem 260 Laboratory 7

BOND VIBRATIONS

This lab explores the potential energy curve for a bond vibration. To simulate a "real" chemical bond you will use HyperChem to calculate the energy of the F_2 molecule as a function of bond length. The results will then be compared with two common approximations:

Simple Harmonic Oscillator $E = k(r - r_e)^2 - D_e$

The Morse Potential $E = D_e\left[1 - e^{-a(r-r_e)}\right]^2 - D_e$

Note that both equations have been written with a final term that shifts the energy scale so that $E \rightarrow 0$ as $r \rightarrow \infty$.

1. Copy the Excel file 260lab7.xls from the network drive to your local hard drive (C:).
2. Open the Excel file. To save time the worksheet and plot have been pre-programmed, so take care what you alter. You need to provide the missing data in column A by means of Extended Hückel calculations.
3. Open HyperChem and create a F_2 molecule. Open a log file (EHT print level 0 is sufficient).
4. Set the bond length by selecting the bond and using Edit/Set Bond Length. Suitable values are given in the spreadsheet. Perform a single-point EHT calculation.
5. Repeat the EHT calculation for other bond lengths. Don't forget the 10 Å (or larger) point, which is needed to shift the energy scale to satisfy the convention that separated atoms have zero energy.
6. Transfer the energies from your log file to the spreadsheet (column A) and check that the plot looks as you expect.
7. At what bond length is the energy a minimum? Due to the limitations of the EHT method your value of r_e will differ from experiment (1.42 Å) and the optimum geometry found by molecular modelling. This is why we don't use EHT for structure optimization! The bond dissociation energy (D_e) is a much better approximation.
8. Compare the curve for a simple harmonic oscillator with your vibrational potential curve. The SHO curve has parabolic shape, so it is defined by only two parameters (k and r_e). However, a third parameter (D_e) is needed to shift the energy scale, as explained above. The relevant parameters should be entered in cells E18-E20 of the spreadsheet. Rough values of D_e and r_e are easy to guess, but k is harder.
9. k represents the force constant. What happens when you increase its value? Decrease it? Choose a value that makes the SHO curve roughly similar to the EHT results.
10. Now try to find the best fit. This is done by minimizing the square deviations between the curves (the relevant sum is given in cell G16). Use Tools/Solver. Set the window to minimize the Target Cell (G16) by Changing Cells E18-E20. Click Solve and Accept.

11. Notice that the fit is good near the potential minimum but less so for larger deviations from r_e. This is because not all points were used in the fit (some cells in column G were left empty). By changing the formula in G16 (e.g. sum G6:G12) you can get a better fit at the minimum.
12. Now try the Morse function. The parameters D_e and r_e have the same meaning as before, so you already have good starting parameters. The Morse exponent a is related to the force constant (k) but it will be necessary to experiment to find its magnitude. Once you have a crude fit you can use the Solver tool. Again, it may be desirable to adjust the range of points included in the fit to achieve a satisfactory fit at the potential minimum.
13. Save the Excel file and copy it to the subdirectory where you leave your lab report. There is no need to copy it into a Word document.