Chem 260 Laboratory 8

This lab uses 3-D plots in Excel to investigate a potential energy surface. The surface represents the energy of a triatomic molecule as a function of two bond lengths. (Ideally we would like to vary the bond angle as well, but we don't have enough dimensions to do that at the same time as varying the bond lengths.) Small movements on the P.E. surface correspond to molecular vibrations; larger movements can be used to model chemical reaction dynamics.

P.E. Surface for a Triatomic Molecule

1. Copy the file 260lab8.xls from the network directory to your local hard drive. Open the file with Excel. It has been set up with parameters suitable for the CO_2 molecule.
2. The LEPS surface describes a linear triatomic molecule A–B–C in terms of parameters for pairwise interactions. (It can easily be extended to bent triatomics.) For each pair of atoms there is an equilibrium bond length R_e (in Å), a dissociation energy D_e (kJ mol^{-1}), and a parameter (beta) related to the force constant of the diatomic bond.
3. The diatomic interactions are modelled by Morse curves. Look at the relevant page of the spreadsheet. The two curves correspond to the front edge and a diagonal slice through the 3-D plot. In the former case one parameter (the BC bond length) is held constant; in the latter case the two bond lengths are equal and vary simultaneously.
4. Inspect the 3-D plot and find where the energy is a minimum. You may want to rotate and/or tip the plot. Try looking along the R(A-B) = R(B-C) diagonal while tipping the plot so that the "floor" of the box becomes a horizontal line. By looking at the bottom edge of the potential surface you see what corresponds to the reaction coordinate for the O + CO reaction.
5. Don't be fooled by "bumps" in the surface due to the large steps in bond length. You can change the step sizes and the range plotted in cells B3–B5. By expanding the region around the minimum you can better locate it. Quantitative data can be read from the spreadsheet page labelled Table. Find the bond length and energy at the minimum point of the surface, and report them in your Word document.
6. Try changing the force constant parameter for the C-O bonds from 2.0 to 1.0. Notice how the surface becomes more "gentle" (sharp features are relaxed). The force constant is proportional to the curvature of a potential surface.

Morse parameters for O–C–O

	A-B	B-C	A-C
R_e =	1.13	1.13	1.21
D_e =	1076	1076	497
beta =	2.00	2.00	2.65

REACTION DYNAMICS ON A P.E. SURFACE

1. Now change the model to represent the P.E. surface for the H + H_2 reaction. This is simply the H-H-H surface. The relevant Morse parameters are R_e =0.74 Å, D_e =458 kJ mol^{-1}, β = 1.94. You will have to adjust the axis ranges to see the important part of the surface.
2. Rotate the 3-D view so that it looks like a contour plot. Paste it into your report.
3. Where is the minimum energy on the surface? What molecular structure does this point represent?
4. The low energy "channel" corresponds to the minimum energy path for the reaction. Where is the transition state? Expand the region around the transition state (use steps of 0.05 Å or smaller. Adjust the z-axis units to give plenty of contours. Paste the expanded contour plot in your report.
5. Rotate the 3-D plot to give the reaction coordinate view, as described in step 4 above. It should be obvious why the transition state is sometimes called the "saddle point".
6. Use the Table page to identify the energy and bond lengths of the transition state. Once you find a rough value change the step sizes to find the transition state to an accuracy of 0.01 Å. Report the values in your Word document..

OPTIONAL EXERCISE

(non-credit; for those want a challenge and have time to play)

Modify the LEPS surface to describe a non-collinear reaction trajectory, i.e. a bent transition state. You need to change the formula for Rac (use the cosine rule in the ABC triangle). Keep the angle as an adjustable constant. How does the activation energy for the reaction change with angle?