

## Chem 260 Laboratory 4

This week there are two unrelated labs; both use HyperChem. The first one allows you to inspect the rotational symmetry of various molecules, and to view their inertial axes.

The second lab introduces you to free radicals. By working through this lab you should get a feel for the probability distribution of the unpaired electron in two free radicals. This determines their ESR spectra, which you will simulate in a later lab (in two weeks time).

### MOLECULAR SYMMETRY AND MOMENTS OF INERTIA

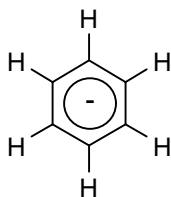
Inspect each of the following molecules, using HyperChem's 3-D rotation tool. (Structure files for many of the molecules can be found on your local hard drive or on the HyperChem CD, in ChemLite\Samples\VSEPR or Aromatic.) Use Display/Show Inertial Axes to see the axes about which the principal moments of inertia are defined.

CO<sub>2</sub>, SF<sub>6</sub>, XeF<sub>4</sub>, HCN, NH<sub>3</sub>, PF<sub>5</sub>, C<sub>6</sub>H<sub>6</sub>, CH<sub>4</sub>, C<sub>60</sub>, HCCH, H<sub>2</sub>O, SF<sub>4</sub>.

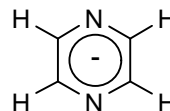
In each case classify the molecule as a spherical top, a symmetric top, an asymmetric top, or linear. Report your findings in table form in your lab report.

### FREE RADICALS

Free radicals are molecules with one or more unpaired electrons (some definitions include single atoms with unpaired electrons). This lab explores the molecular orbitals of two  $\pi$  radicals:



the benzene anion



the pyrazine anion.

1. Open the benzene.hin file in HyperChem. Make sure the structure is optimized. Open a log file (EHT print level 1).
2. Select Setup/EHT and Setup/Options and enter -1 for the charge and 2 for the spin multiplicity (a single unpaired electron spin has two orientations).
3. Perform a single point calculation and look at the orbital window to find the molecular orbital in which the unpaired spin resides. HyperChem puts it in one of the two degenerate HOMO orbitals. Display these two orbitals. If the electron were confined to one of them, this would suggest preferential location on some carbons. Is this likely? What if the unpaired electron is shared between the degenerate orbitals; would that result in an even distribution across all six carbons?

4. Look at the  $p_z$  coefficients of the relevant molecular orbitals in the log file. Transfer them to a spreadsheet. [A convenient way to do this is to open the log file in Word, delete unwanted lines, and save the result as a text file, which can then be opened by Excel.]
5. For each molecular orbital the sum of the six carbon  $p_z$  coefficients is zero. Try summing the squares of the coefficients. Since the answer is not 1.00 it is clear that the  $\pi$  orbitals are not normalized. Divide each squared coefficient by the sum over all carbons so that you have the probabilities of finding the unpaired electron in the individual carbon  $2p_z$  atomic orbitals.
6. By combining (averaging) the probabilities for the two degenerate HOMOs you get the probability of finding the unpaired electron on each carbon. Record the answer in your lab report. Does it make sense?
7. Edit the benzene anion in HyperChem to change it to the pyrazine anion. Optimize the geometry and perform an EHT calculation.
8. Use the HyperChem log, as before, to find the probability of finding the unpaired electron on the carbon and nitrogen atoms. Record the results in your lab report and compare with your findings for the benzene anion.