## Assignment A01: Geometry Definition: Cartesian and Internal Coordinates

In Assignment A00 you studied a donor-acceptor substituted (hetero)arene to familiarize yourself with *GaussView* and *G09W* and to learn basics about input (GJF) and output files (LOG, CHK). In Assignment A01, we are considering various ways to define the initial structure in the GJF input file and we learn how to locate minima and simple transition state structures. We will consider the systems $YH_3^{n-}$ ($n$ = 0, X = N, P; $n$ = -1, Y = C, Si). Pick one system (Y, $n$) and perform all computations for that system. It is the goal of this exercise to determine the minimum structure of $YH_3^{n-}$ in $C_{3v}$-symmetry, to determine the transition state structure of $YH_3^{n-}$ in $D_{3h}$-symmetry, and to compute a step-by-step scan of the potential energy surface (PES) along the inversion coordinate.

The specific tasks include (a) the creation of GJF files for $YH_3^{n-}$ with *GaussView* in different symmetries (pyramidal, planar), (b) the setup of entry-level Hartree-Fock computations of this molecule in both symmetries, the optimization of each structure to a minimum, and the computation of vibrational frequencies using *G09W*, (c) the setup of an entry-level Hartree-Fock computations of the inversion transition state structure of $YH_3^{n-}$ starting from a near-planar structure, the optimization of the structure to the inversion transition state structure, and the computation of vibrational frequencies using *G09W*, and (d) the computation of a scan the potential energy surface (PES) along the inversion coordinate while maintaining $C_{3v}$ symmetry.

**(a) Building $YH_3^{n-}$ in $C_{3v}$- and $D_{3h}$-Symmetry.** Consider ammonia as an example. Select "N" and "pyramidal" in the "Element Fragment" window and build ammonia in the **active View window**. Use "Save" in the "File" menu and save the ammonia structure in a GJF file with internal coordinates and then again in a second GJF file with Cartesian coordinates (see examples below). Do these GJF file contain precise $C_{3v}$ symmetry? Why, or why not?

In the "Edit" menu, select "Point Group", mark "Enable Point Group Symmetry", and constrain the subgroup to "C3v". Use "Save" in the "File" menu and save the ammonia structure in a GJF

file with internal coordinates and then again in a second GJF file with Cartesian coordinates (see examples below). Do these GJF file contain precise $C_{3v}$ symmetry? Why, or why not?

How many degrees of freedom are there in $C_{3v}$ symmetric $YH_3^{n-}$? From scratch, setup a GJF file with a Z-matrix for $C_{3v}$-symmetric $YH_3^{n-}$ that has as many variables as there are degrees of freedom. (Hint: You need to place a dummy atom "X" to define the $C_3$ symmetry axis.)

How many degrees of freedom are there in $D_{3h}$ symmetric $YH_3^{n-}$? From scratch, setup a GJF file with a Z-matrix for $D_{3h}$-symmetric $YH_3^{n-}$ that has as many variables as there are degrees of freedom. (Hint: No dummy atoms are required. But you may place a dummy atom X to define the $C_3$ symmetry axis; i.e., setup the $D_{3h}$ symmetric structure as a special case of the $C_{3v}$ symmetric structure.)

**(b) Optimizations and Frequency Computation at RHF/6-31G* Level in Perfect $C_{3v}$ or $D_{3h}$ Symmetry.** You setup GJF files for $YH_3^{n-}$ with Z-matrices with $C_{3v}$-symmetry and $D_{3h}$-symmetry. For each do this: Open the GJF file in *GaussView*; your initial structure will be displayed in the **active View window**. Select menu "Calculate"; the "Gaussian Calculation Setup" window opens. Under "Job Type", select "Opt+Freq". Under "Method", select the 6-31G* basis set. Under "Title", add a job title. Under "Link 0", select memory limit 256 MW and specify "2" shared processors. Click "submit". The *G09W* window opens while each job runs (a few minutes). When *G09W* is done, close the *G09W* window. You now have sets of GJF, LOG and CHK output files for $YH_3^{n-}$ with $C_{3v}$-symmetry and $D_{3h}$-symmetry. Explore the LOG files. Explore the frequencies and note the imaginary mode of the $D_{3h}$-symmetric structure. Compare the energies, compute the relative energy.

**(c) Transition-State Optimizations and Frequency Computation at RHF/6-31G* Level Without Symmetry Constraints.** Open an new molecule window in *GaussView*, build your $YH_3^{n-}$ system, and use the tools in the Builder menu to deform the structure to your best initial guess of the inversion transition state structure. This initial structure will usually not be exactly planar and an optimization with just "opt" in the command line will lead to the pyramidal

minimum structure. Instead, use "opt=TS" as the command to have *G09W* locate the stationary structure with one imaginary eigenvalue. It is usually best to start a TS search with accurate forces and you should use "opt=(TS,calcfc)". Select these options in the "Calculate" menu in the section "Job Type". Continue with the setup as usual and run the job.

You will now have a third set of GJF, LOG and CHK output files for $YH_3^{n-}$. Explore the LOG file. Did you locate the desired inversion TS? Is the structure *de facto* $D_{3h}$-symmetric? Explore the frequencies, note the imaginary mode, and explore the transition vector. Compare the energies, compute the relative energy.

**(d) Step-by-Step Scan of the Inversion Path of $YH_3^{n-}$ in $C_{3v}$-Symmetry.** The inversion coordinate is the angle between the $C_3$ symmetry axis and any one of the H-atoms. Compute a series of structures along the inversion path of $YH_3^{n-}$. A sample input file follows.

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\partd_80.chk
# opt=z-matrix hf/6-31G*

Ammonia with a1 angle 80 degrees

0 1
 N
 X    1         1.0
 H    1          b1    2         a1
 H    1          b1    2         a1     3  120.0     0
 H    1          b1    2         a1     3 -120.0     0

b1=1.          Variable will be optimized

a1=80.         Variable after the extra line with NOT be optimized
```

Setup a number of files with different a1 values using a text editor. The points along the path shall not differ by more than 5 degrees. Run these jobs directly with *G09W*. Launch *G09W*. Drop the GJF file into the *G09W* window. Under "Process", click "Begin Processing".

**(e) Write-Up.** Submit one Excel file "A01_'your_last_name(s)'.xlsx" containing computed data for all of the structures along the inversion scan (including all stationary structures) on sheet #1

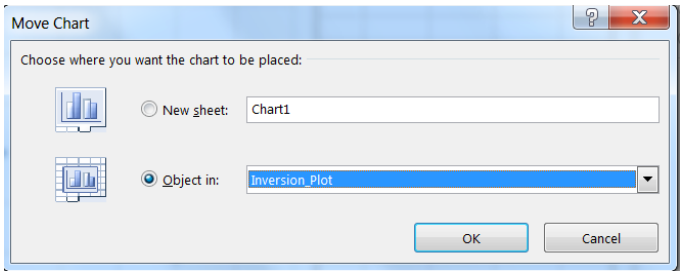
(sheet label "Inversion Scan Data") and with a plot of the inversion scan on a separate sheet (sheet label "Inversion Plot"). Write author name(s) clearly visible on sheet #1 (because we will need the author name(s) on the hardcopies).

The data sheet should contain five columns: the (X-Y-H) angle in degrees (to 2 digits), the *d*(Y-H) bond length in Angstroms (to 3 digits), the total energy in atomic units (to 6 digits), the relative energy in kcal/mol (relative to energy of minimum, to 2 digits), and the dipole moment in Debye (to 3 digits). Include headers on top of each column that clearly state the content of the column and the units.

The plot should show relative energy in kcal/mol versus the (X-Y-H) angle in degrees. The plot should be of the type "scatter with smooth lines and markers". The relative energy is computed with reference to the minimum, all relative energy values are positive, and the x-axis should cross the y-axis at y = 0. Adjust the marker type and color as you like; adjust the line type, width, and color as you like.

Use different marks for points that correspond to stationary structures. To do this, you plot the data for the stationary structures into the same plot ("select data", "add") using the type "scatter" (i.e., there will be marks, but no line). Adjust the marker type and color as you like.

**Move the graph** to its own sheet. Right-click on the graph area but *outside of the plot area*. A menu will pop up which includes the "Move Chart" option and will produce the menu shown:




Select "New sheet" and click "OK". Or select "New sheet", enter the name of the label you want for the new sheet instead of "Chart1", and then click "OK".

Graphs usually have a line around the plot area ("format plot area") but not around the chart area ("format chart area"). Graphs usually do not have gridlines, but you may have gridlines if you like.

Use appropriate **major and minor tick marks**. Major tick marks are labeled. For the x-axis, for example, the major tick marks must include a mark at "90" because "90" is of special significance in the current plot. The major tick mark spacing could be "5" or "10"; a major tick mark spacing of "15" also works well for angles. The total number of labels per axis should be somewhere between 5 and 10. Always show minor tick marks: For a major tick mark spacing of "5", use minor tick marks with a spacing of "1". For a major tick mark spacing of "10", use minor tick marks with a spacing of "1" or "2". For a major tick mark spacing of "15", use minor tick marks with a spacing of "5". For the y-axis, the major tick mark setting will depend on the system you work on. If the barrier is a single-digit value, then use a major tick mark spacing of "1" or "0.5". If the barrier is a mid-range double-digit value, then use a major tick mark spacing of "5" or even "10". Use minor ticks following the above considerations.

The **format of the labels** defaults to the format of the numbers set in the columns with the (x,y) data. In most cases, you want a different format for the labels. Your relative energy data will be to two digits in the column with relative energies in kcal/mol. But you do not want the labels to be "0.00", "1.00", 2.00", …, "10.00"; you want the labels to be "0", "1", "2", …, "10". Or you want them to be "0.0", "0.5", "1.0", "1.5", …, "5.0". So, make sure you have "appropriate label formatting" on both axes. Make sure the labels are clearly readable. The font size should be the same as the text of the body of the paper *once the image is inserted into the paper*.

Include **axis titles**. Show units in axis titles. The font size of the axis title should be 2 or 4 points larger than for the axis labels.

Include **graph title**. The graph title must be outside of the plot area. The font size of the graph title should be 2 or 4 points larger than for the axis title. (If we use the graph in a paper, then the graph title will be part of the Figure legend and we generate the graph without a graph title.)

Enthusiastic students may search the literature for the experimentally measured inversion barrier of their $YH_3^{n-}$ systems.

Submission & Deadlines: Submit "A01_'your_last_name(s)'.xlsx" as attachment to email on Tuesday, 09/06/16 by midnight. Bring one (stapled) hardcopy to class on Wednesday, 09/07/16, for evaluation by peer review.

| |
|---|
| Global: The subject line of any submission by email should contain the assignment number, i.e., "A01 submission". |
| Global: If you work together with another student, there should be one submission for the pair and the collaborator must be copied. |

## Draw $NH_3$ in Active Window without using Point Group

**Save as internal coordinates from "File" menu**

```
%chk=C:\Users\glaserr\Desktop\ammonia.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N
 H                  1            B1
 H                  1            B2    2            A1
 H                  1            B3    3            A2    2            D1    0

   B1             1.00000000
   B2             1.00000000
   B3             1.00000000
   A1           109.47120255
   A2           109.47125080
   D1          -119.99998525

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

**Save as Cartesian coordinates from "File" menu (mark "Write Cartesians")**

```
%chk=C:\Users\glaserr\Desktop\ammonia_coord.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N                  0.00000000    0.00000000    0.00000000
 H                  0.00000000    0.00000000    1.00000000
 H                  0.94280915    0.00000000   -0.33333304
 H                 -0.47140478   -0.81649655   -0.33333304

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

## Draw $NH_3$ in Active Window with using Point Group and C3v

**Save as internal coordinates from "File" menu**

```
%chk=C:\Users\glaserr\Desktop\ammonia_C3v.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N
 H                  1    0.99999994
 H                  1    0.99999994    2  109.47122406
 H                  1    0.99999994    2  109.47122406    3 -120.00000838    0

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

**Save as Cartesian coordinates from "File" menu (mark "Write Cartesians")**

```
%chk=C:\Users\glaserr\Desktop\ammonia_C3v_coord.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N                  0.00000000    0.00000000    0.00000000
 H                  0.00000000    0.00000000    0.99999994
 H                  0.94280897    0.00000000   -0.33333337
 H                 -0.47140460    0.81649645   -0.33333337

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```