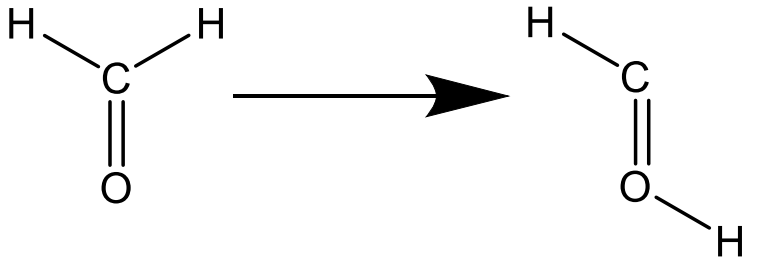
10月12日上机实习安排

使用Gaussian软件完成：

1. $(H_2O)_3$团簇结构的优化，并进一步计算该团簇中氢键的平均键能
2. Hydrogen Shift Reaction机理研究：

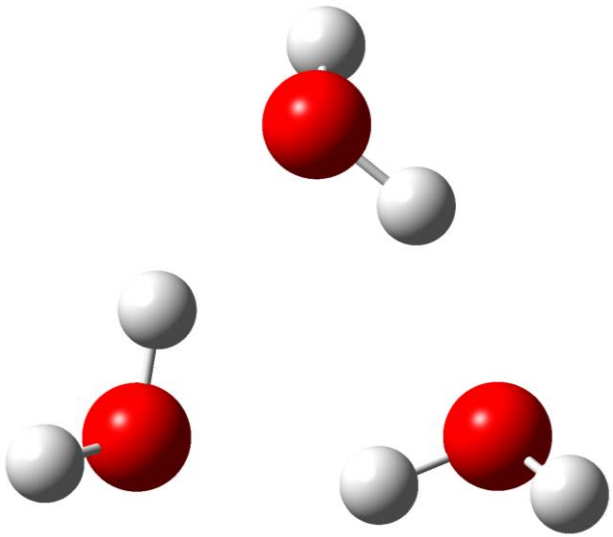


选做：主要反应物、过渡态、产物的IR、UV-vis、NMR光谱比较（时间允许）

上机操作：同学们及时更新QQ群众excel表格，能看到大家的完成情况

1.1 Geometry Optimization of $(H_2O)_3$ Cluster

1. Model building: **approach to a specific local minimum**
2. Optimization:
   - ➢Computational level: B3LYP/6-31G
   - ➢opt

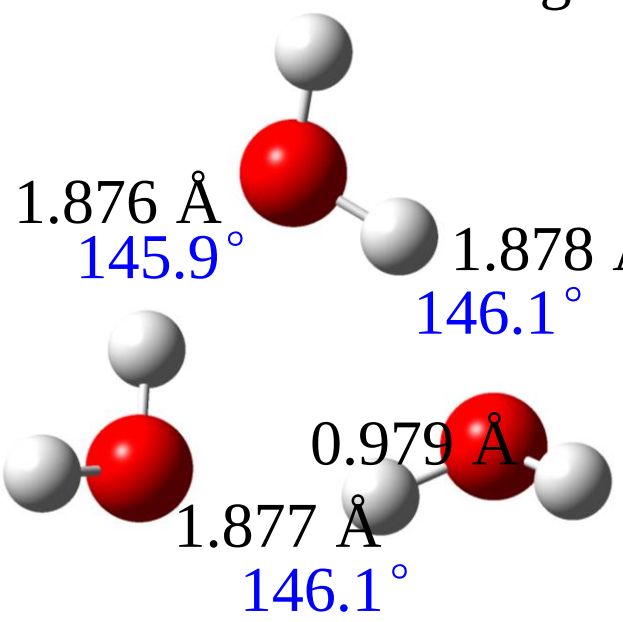


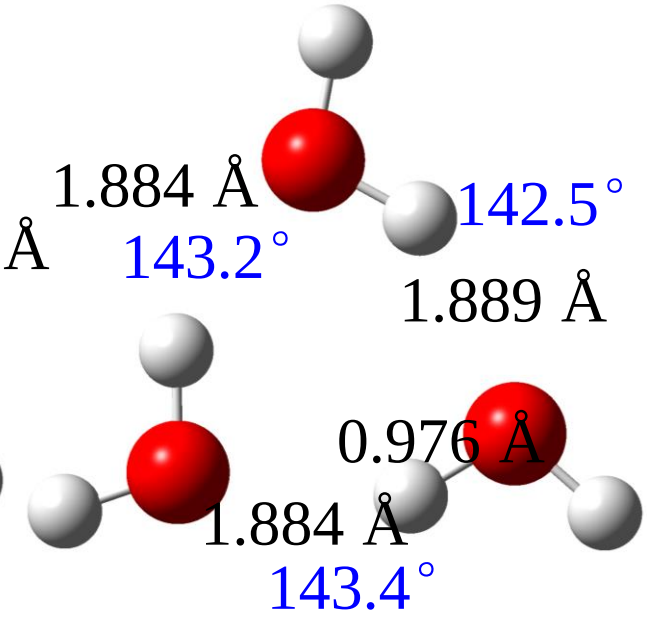
Isomer

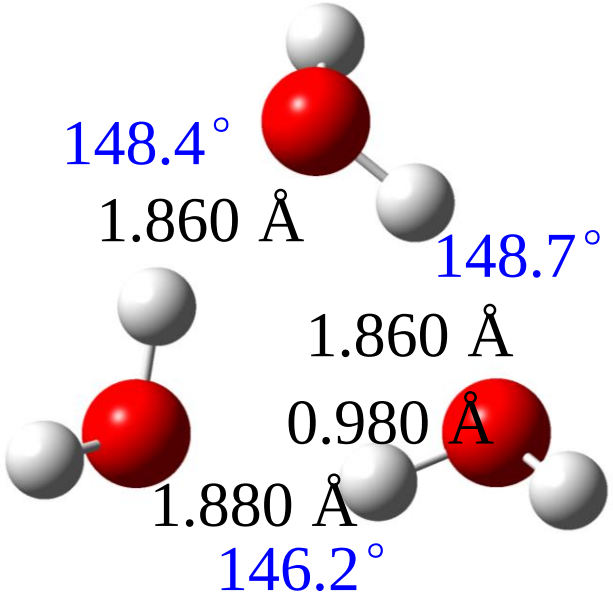
```
%chk=C:\G09W\Scratch\CMS\3-H2OS-3-OPT.chk
#p opt b3lyp/6-31g geom=connectivity

optimization

0 1
 O                  1.62463338   -0.14124280   -0.20864362
 H                  0.78243543   -0.51793364    0.05669884
 O                 -0.92793600   -1.28279800   -0.05682200
 H                 -0.71269337   -0.34811429   -0.01636250
 O                 -0.64788300    1.44519500   -0.05753400
 H                 -1.29180827   -1.56414656    0.78581669
 H                  2.13380442    0.08629922    0.57274584
 H                 -0.19687316    2.25308712   -0.31346454
 H                  0.13811517    0.89649171   -0.10979848

 1 2 1.0 7 1.0
 2
 3 4 1.0 6 1.0
 4
 5 8 1.0 9 1.0
 6
 7
 8
```

1.1 Geometry Optimization of $(H_2O)_3$ Cluster

- Take my successful optimized $(H_2O)_3$ isomers (my computational level: M06-2X/6-31+G(d)) as examples for model building





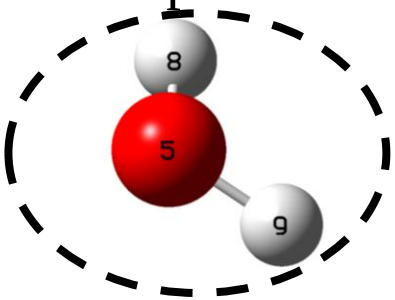


Isomer I **Isomer II** **Isomer III**

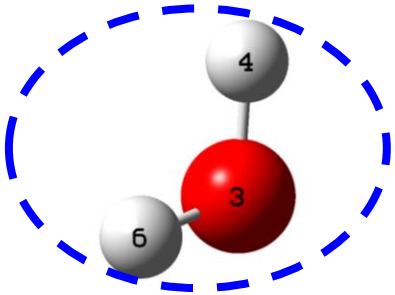
-229.18487148 a.u. -229.18436347 a.u. **-229.18657639 a.u.**

1.2 Interaction Energy Calculation of $(H_2O)_3$ Cluster

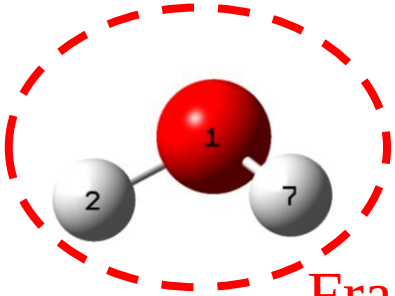
1. After geometry optimization, save *.chk file to obtain the final optimized $(H_2O)_3$ structure
2. Perform single-point energy calculations to estimate the hydrogen bonding energy
   - ➢Computational level: M06-2X/6-31G(d)
   - ➢counterpoise = 3



Fragment 1



Fragment 2



Fragment 3

```
%chk=C:\G09W\Scratch\CMS\3-H2OS-final-HB.chk
#p m062x/6-31g(d) counterpoise=3 geom=connectivity

hydrogen bonding energy estimation

0 1 0 1 0 1 0 1
O(fragment=3)      1.62463338   -0.14124280   -0.20864362
H(fragment=3)      0.78243543   -0.51793364    0.05669884
O(fragment=2)     -0.92793600   -1.28279800   -0.05682200
H(fragment=2)     -0.71269337   -0.34811429   -0.01636250
O(fragment=1)     -0.64788300    1.44519500   -0.05753400
H(fragment=2)     -1.29180827   -1.56414656    0.78581669
H(fragment=2)      2.13380442    0.08629922    0.57274584
H(fragment=1)     -0.19687316    2.25308712   -0.31346454
H(fragment=1)      0.13811517    0.89649171   -0.10979848

1 2 1.0 7 1.0
2
3 4 1.0 6 1.0
4
5 8 1.0 9 1.0
6
7
8
```

1.2 Interaction Energy Calculation of $(H_2O)_3$ Cluster

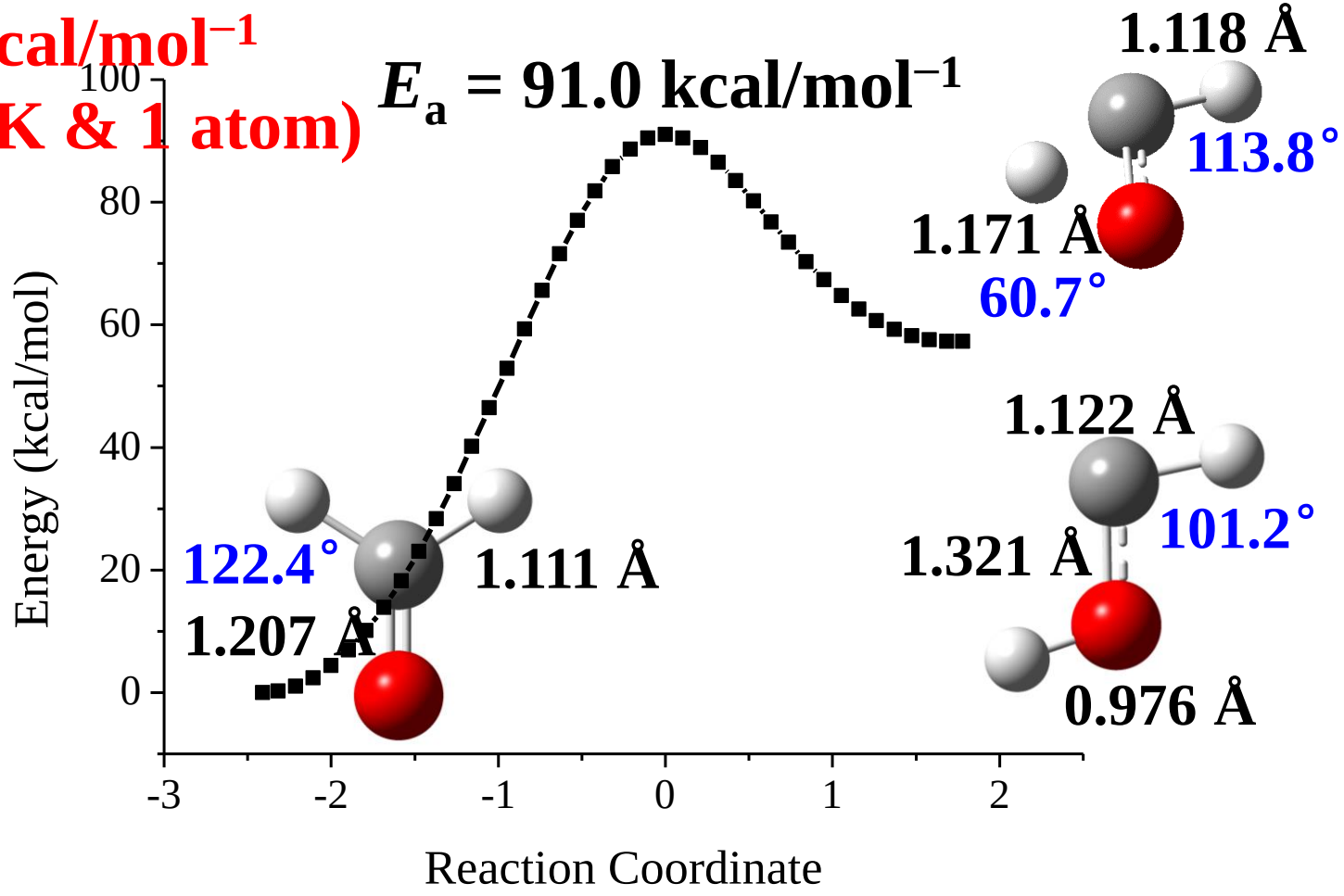
3. Estimate the hydrogen bonding energy

- open *.log file to find $E_{corrected}$ (search by **"Counterpoise: corrected energy ="**)
- Read E_{4th}, E_{5th}, and E_{6th} (search by **"SCF Done:"**)
- Calculate $E_{HB} = (E_{corrected} - E_{4th} - E_{5th} - E_{6th})/3$

2.1 Hydrogen Shift Reaction Mechanism

➢Computational level: B3LYP/6-31G(d)

E_a = ? kcal/mol^{-1}
(298.15 K & 1 atom)



2.1 Hydrogen Shift Reaction Mechanism

1. Reactant and product optimization: opt freq

```
%chk=C:\G09W\Scratch\CMS_2019\H2CO-1-2-hydrogen-shift-reaction\H2CO-reactant-opt.chk
#p opt freq b3lyp/6-31g(d) geom=connectivity

reactant

0 1
 C                    -0.19434629    -1.59010598     0.00000000
 H                     0.33881746    -2.51781090     0.00000000
 H                    -1.26434629    -1.59010598     0.00000000
 O                     0.43269414    -0.49905564     0.00000000
```

2. Transition state optimization:
   - ➢opt=(maxcycle=300,ts,calcfc,noeigentest) freq

```
%chk=C:\G09W\Scratch\CMS_2019\H2CO-1-2-hydrogen-shift-reaction\HCHO-TS-opt-2.chk
#p opt=(calcfc,ts,maxcycle=100,noeigentest) freq rb3lyp/6-31g(d)
geom=connectivity

TS
0 1
 C                     0.00041226     0.66983382     0.00000000
 H                     1.01817584     1.13037976     0.00000000
 O                     0.00041226    -0.63669135     0.00000000
 H                    -1.02394749    -0.05585178     0.00000000
```

3. IRC test: (obtain the optimized transition state first)
   - ➢irc=(maxpoints=30,forward,reverse,calcfc)

```
%chk=C:\G09W\Scratch\CMS_2019\H2CO-1-2-hydrogen-shift-reaction\HCHO-TS-IRC-forward.chk
#p rb3lyp/6-31g(d) irc=(forward,calcfc,maxpoints=30)

IRC test
0 1
 C                    -0.00007448     0.67155691     0.00000000
 H                     1.02292846     1.12362989     0.00000000
 O                    -0.00007448    -0.63614241     0.00000000
 H                    -1.02188569    -0.06383210     0.00000000
```

4. Energy barrier estimation: $E_{TS} - E_R$

2.2 Properties of Reactant, Transition States & Product

- Computational level: B3LYP/6-31G(d)
- IR: freq
- NMR: nmr test
- UV-vis: TD=(50-50,nstates=50)