Potential Energy Surface
Transition State

Making INPUT 1

- First lines are input of method and basis set
    - #P HF/STO-3G pop=reg
- Empty line
- Title of the calculation: Anything is OK
- Empty line
- Charge and spin multiplicity: usually we consider neutral molecule so charge 0, multiplicity is number of unpaired electrons +1, usually we consider filled electron so 1

Making INPUT 2

- Then define the molecule either using XYZ or Z-matrix input

```
O1          0.000000   0.754227  -0.058812
O2          0.000000  -0.754227  -0.058812
H3         -0.742068  -1.085986   0.470499
H4          0.742068   1.085986   0.470499
```

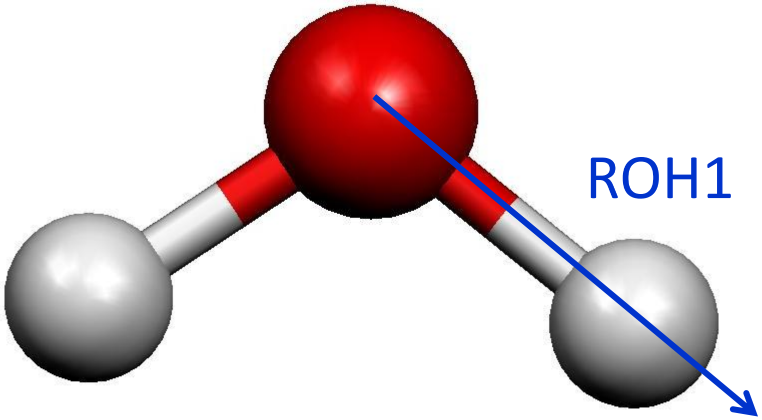
```
O1
O2    1,   RO1O2
H3,   2,   RO2H3,   1,   AO1O2H3
H4,   1,   RO1H4,   2,   AO2O1H4,    3,   DH3O2O1H4

 RO1O2=1.50845307
 RO2H3=0.97
 RO1H4=0.97
 AO1O2H3=110.0
 AO2O1H4=110.0
 DH3O2O1H4=109.
```

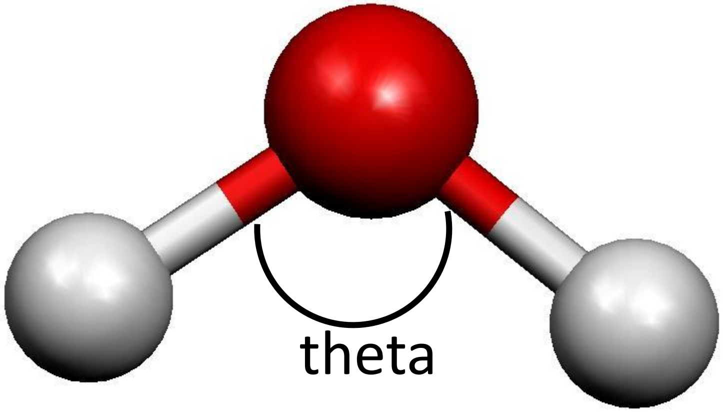
- Then end with one blank line

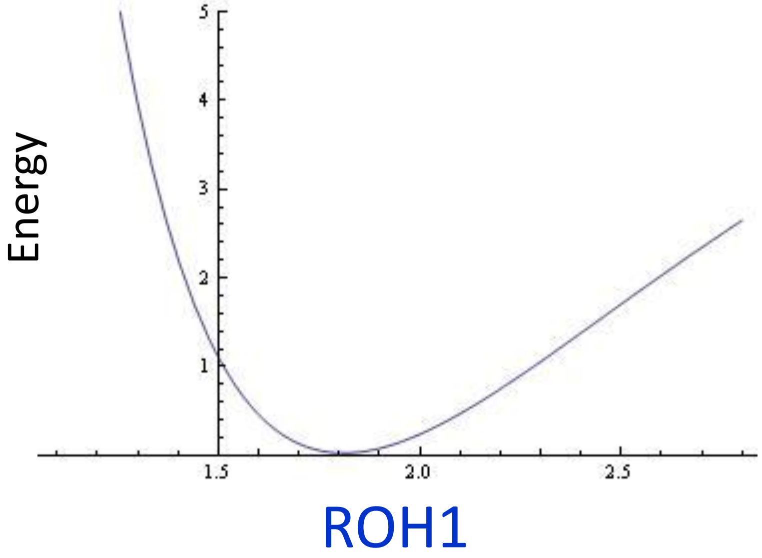
Review

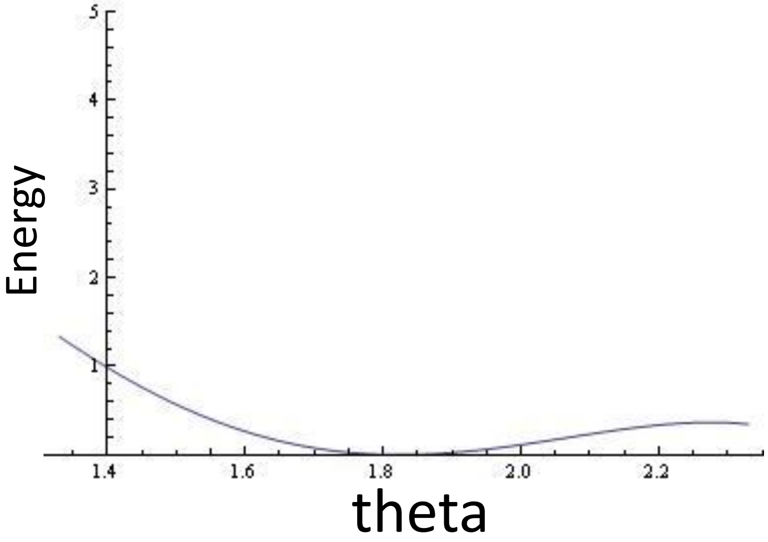
- Last week we did diatomic molecules with only on bond so we only have to think about forming a bond or breaking that bond
- Today we will consider something more complex molecules
- Then we will make and break a bond a the same time REACTION

Water Molecule
Potential Energy Curve

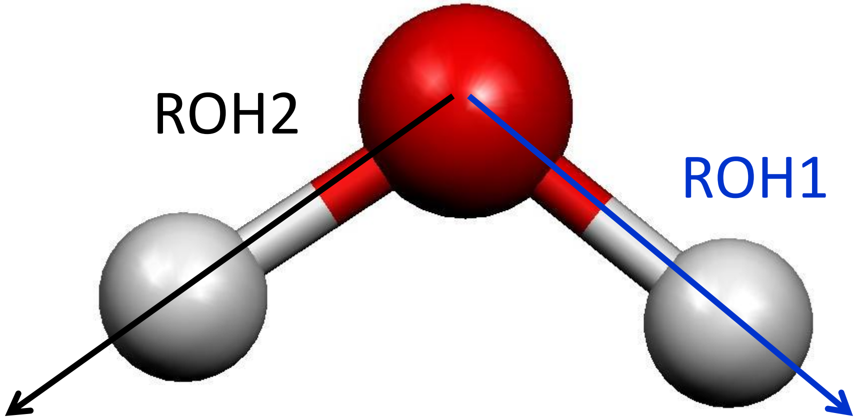


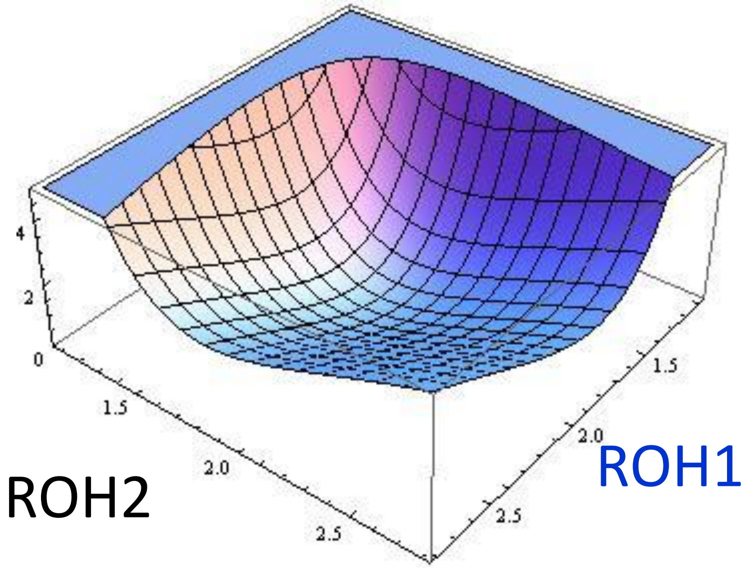


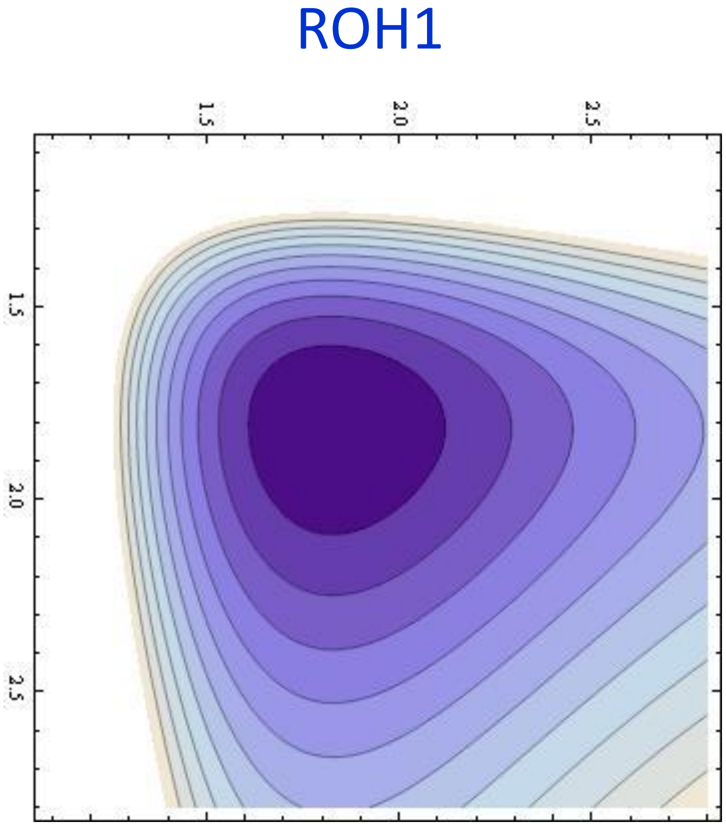




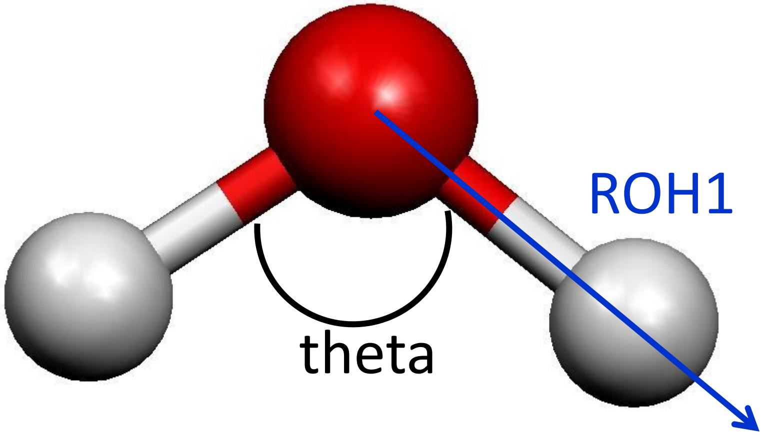
Water Molecule: Stretch Stretch Potential Energy Surface

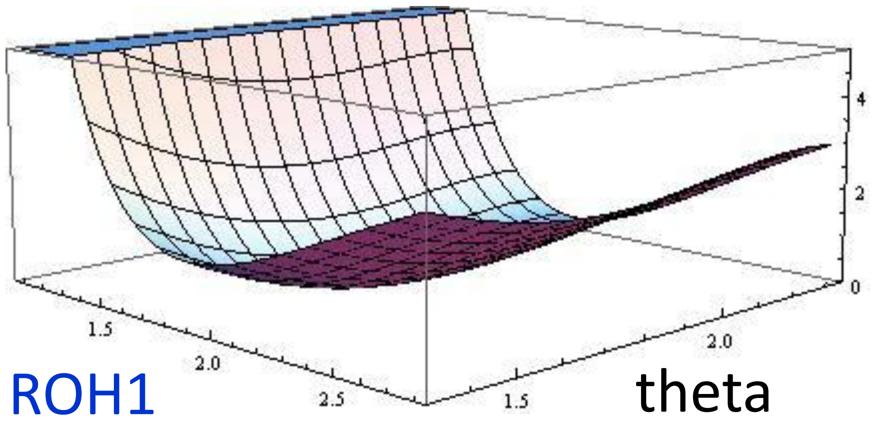


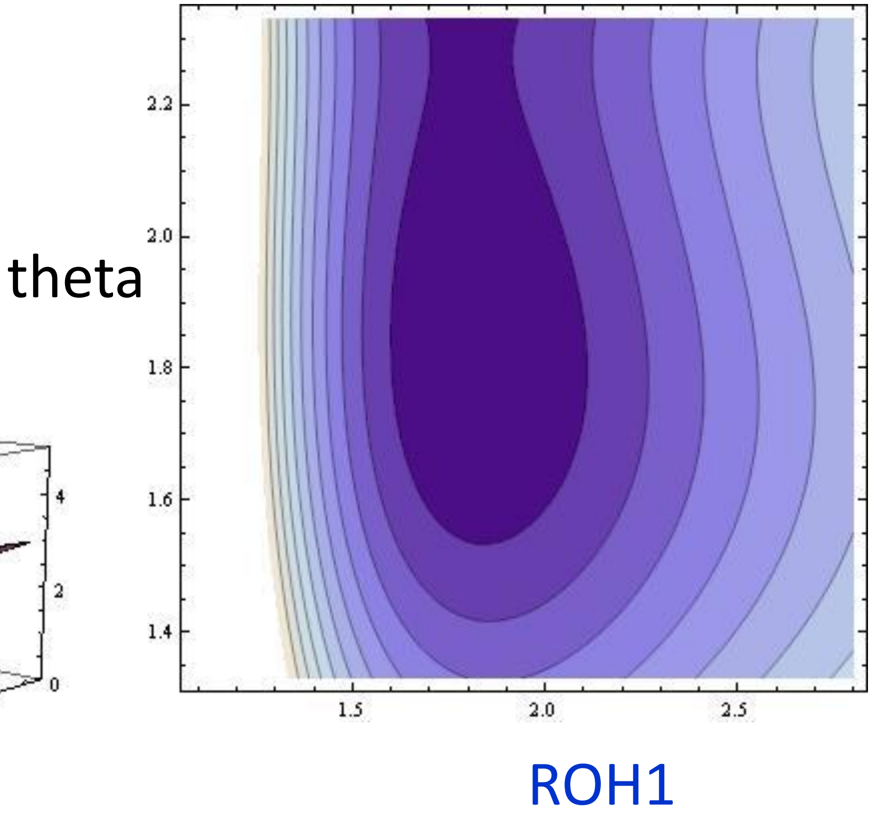




Water Molecule: Stretch Bend Potential Energy Surface







Normal Mode Vibration

First we consider mass –weight Cartesian Coordinates

$$q_1 = m_1^{1/2}\Delta X_1; q_2 = m_1^{1/2}\Delta Y_1; q_3 = m_1^{1/2}\Delta Z_1; q_4 = m_2^{1/2}\Delta x_2;\ldots q_{3N} = m_N^{1/2}\Delta Z_N$$

Next expand the potential energy to second term near equilibrium

$$V = V(0) + \sum_{I}^{3N} K_I q_I + \frac{1}{2}\sum_{I}^{3N}\sum_{J}^{3N} K_{IJ} q_I q_J = \frac{1}{2}\sum_{I}^{3N}\sum_{J}^{3N} K_{IJ} q_I q_J$$

Total energy is given as $E = \frac{1}{2}\sum_{I}^{3N}\dot{q}_I^2 + \frac{1}{2}\sum_{I}^{3N}\sum_{J}^{3N} K_{IJ} q_I q_J$

Cross term

If we diagonalize K_{IJ} $\quad E = \frac{1}{2}\sum_{I}^{3N-5/6}\dot{Q}_I^2 + \frac{1}{2}\sum_{I}^{3N-5/6}\lambda_I Q_I^2$

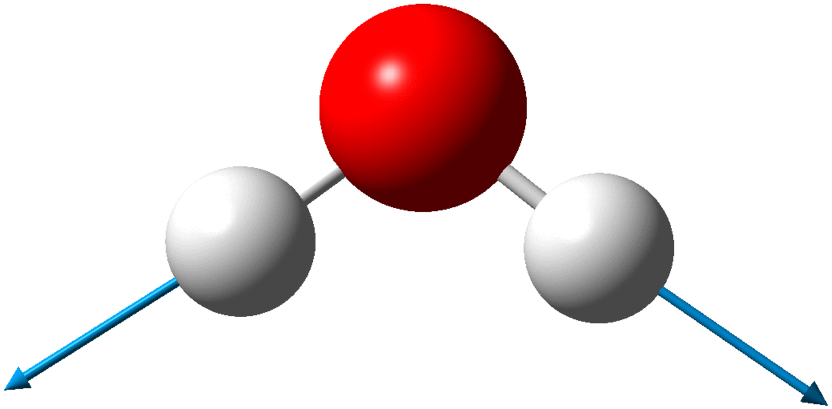
Motion described by 3N-6(5 for linear molecule) NORMAL MODES

$$Q_I = \sum_{J=1}^{3N} L_{IJ} q_J \qquad I = 1,3N - 5/6$$

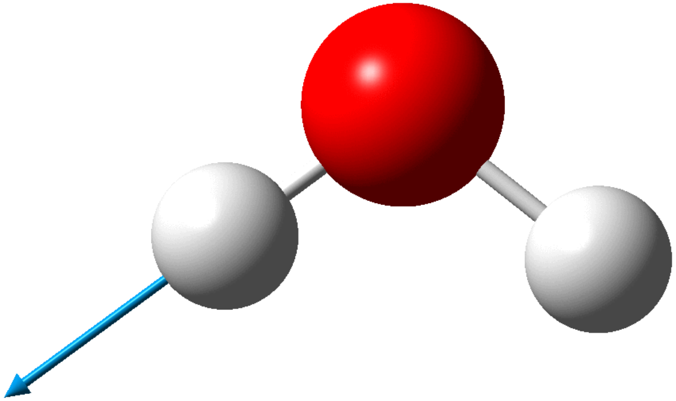
5/6 Modes that are ignored have zero λ_I TRANSLATION/ROTATION

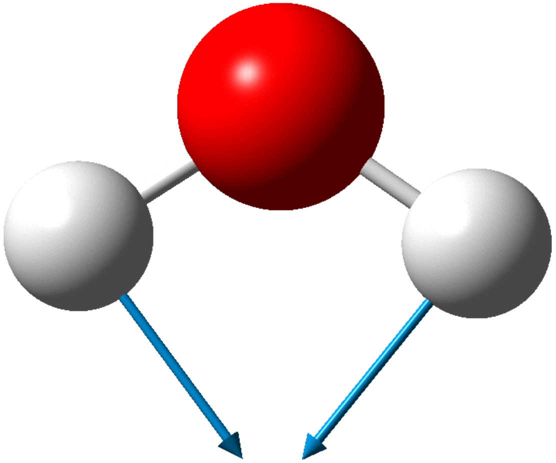
Normal Modes of Water

Symmetric stretch



Antisymmetric stretch

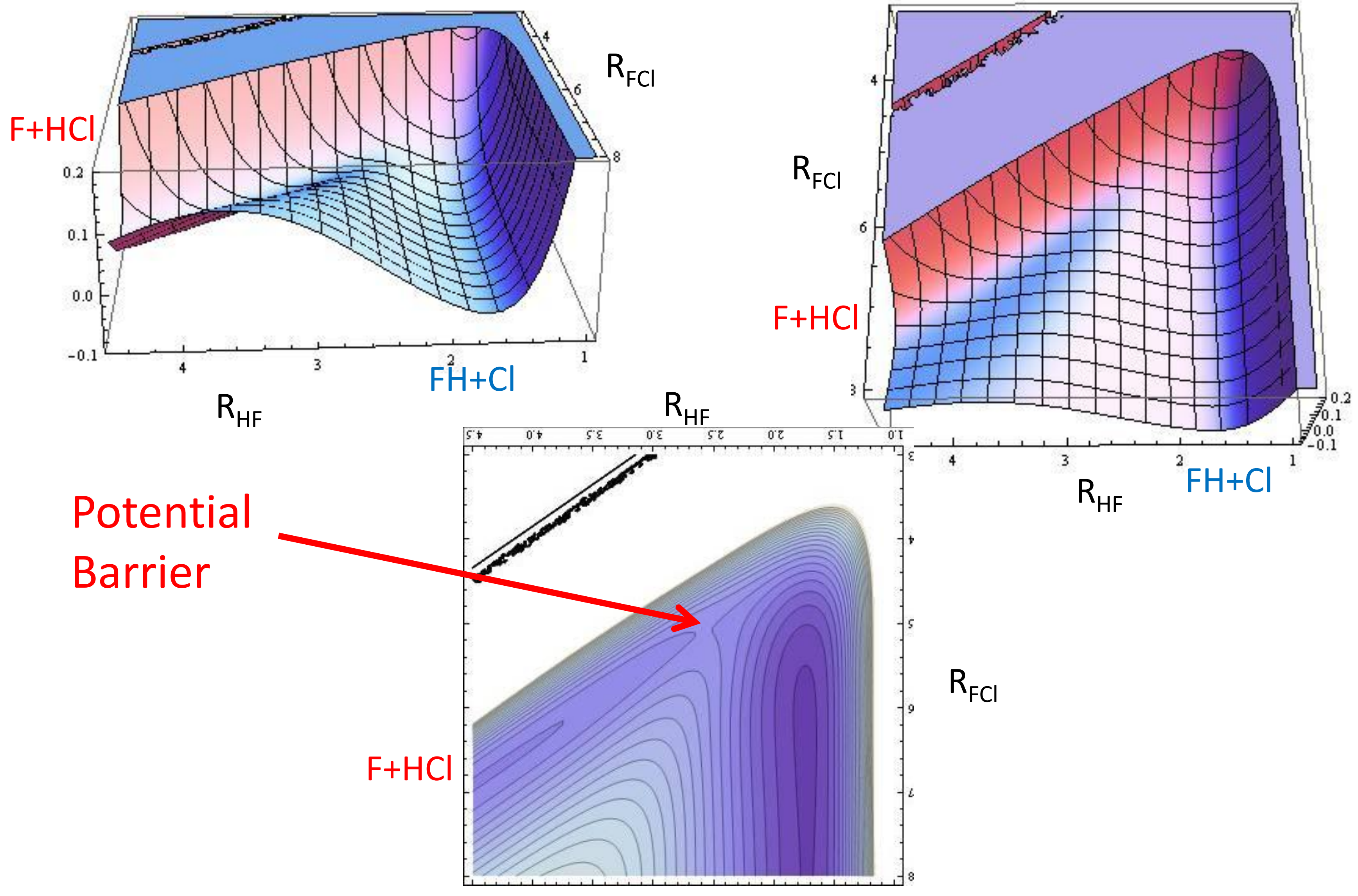




Bend

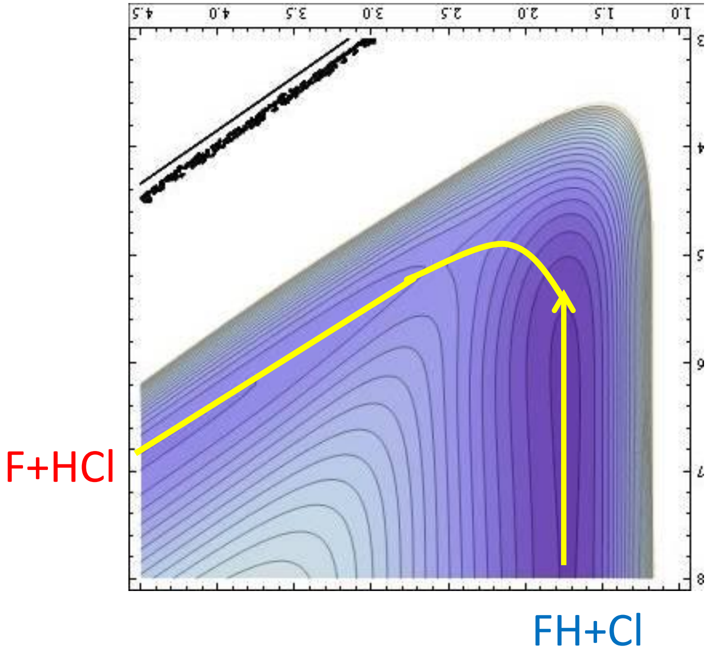
F+HCl→FH+Cl Potential Energy Surface

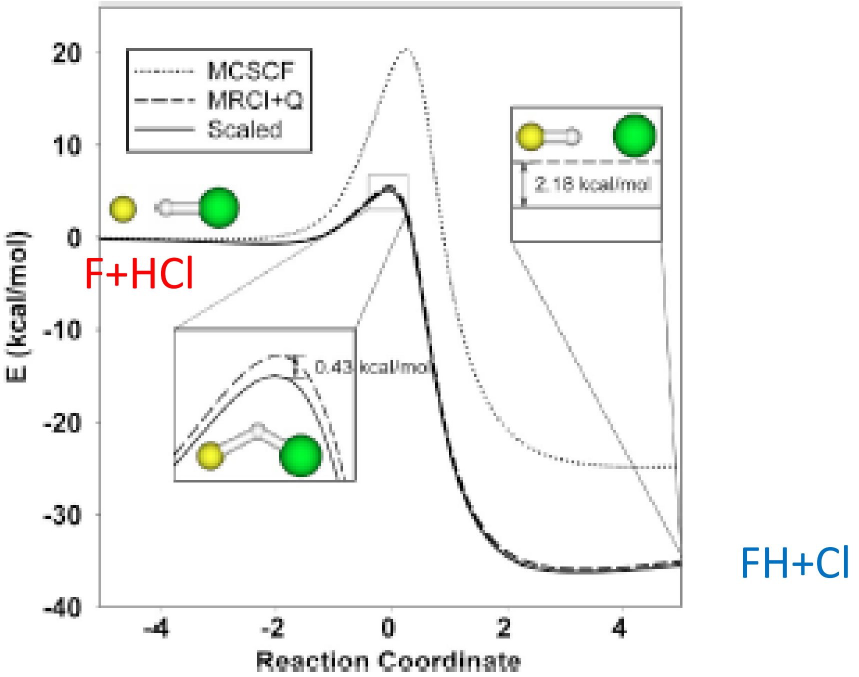
Hydrogen Abstraction Reaction, break a HCl bond form a HF bond



Potential Barrier

Potential Energy Curve along IRC





You need enough energy to go over the potential barrier to react!

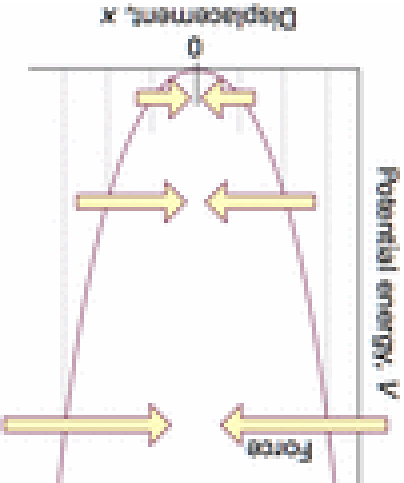
The minimum energy path that connect the barrier with reactant and product is called intrinsic reaction path

For F+HCl case you need about 5 kcal/mol of for reaction to occur

How to quantify Barrier?

- At the barrier the first derivative is zero and the second derivative is negative for one degree of freedom and the rest are always positive. In Gaussian you can use the freq keyword to check if there is imaginary frequency

Harmonic Oscillator approximation at barrier



$$F = m\frac{d^2x}{dt^2} = -kx$$

k: force constant

$$\omega = \sqrt{\frac{k}{m}}$$

In the case of barrier the force constant k is negative so omega is imaginary

Find the potential Barrier

- Input a geometry that is close to the barrier and use the keyword Opt=(ts)
- Check if the optimized structure is a barrier by calculating the frequency by the freq keyword
- Use the IRC keyword to follow the reaction to the reactant and product keyword IRC(forward), IRC(backward)

Transition State Theory

- Once you have the barrier you can estimate the thermal rate constant of the reaction from the calculation results! (Assuming that the reaction proceeds along the IRC)

$$A + B \rightarrow (AB)^{+} \rightarrow \text{product}$$

Activated Complex
(Geomtry at Potential Barrier)

$$-\left(\frac{d[A]}{dt}\right) = \frac{k_B T}{h} K^{+}[A][B]$$

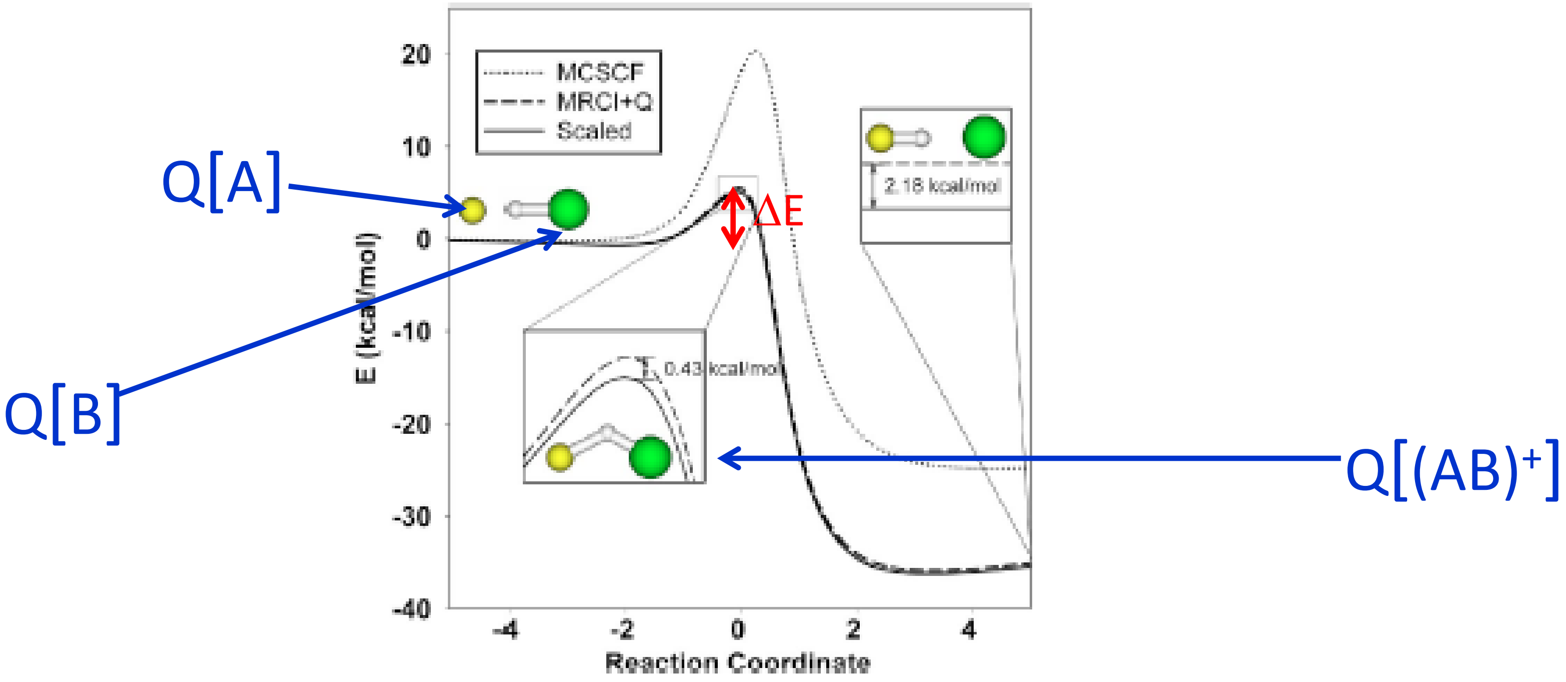
K^{+} is the thermal rate constant that depends on temperature

Things Needed To Calculate Rate Constant

$$K^{+} = \frac{Q\left[(AB)^{+}\right]}{Q[A]Q[B]}\exp\left[-\frac{\Delta E}{k_B T}\right]$$

Q is the partition function of the respective molecules

ΔE is the energy difference from the reactant to the barrier



Q[A]

Q[B]

Q[(AB)$^{+}$]

Partition Function 1

$$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P}$$

Usually you consider 1atm pressure

$$\begin{aligned} Q_{electronic} &= D_0 \exp\left[-\varepsilon_0 / k_B T\right] + D_1 \exp\left[-\varepsilon_1 / k_B T\right] \\ &+ D_2 \exp\left[-\varepsilon_2 / k_B T\right] + \ldots \\ &= D_0 \end{aligned}$$

D is the degeneracy of the electronic state, usually only consider ground electronic state

Partition Function 2

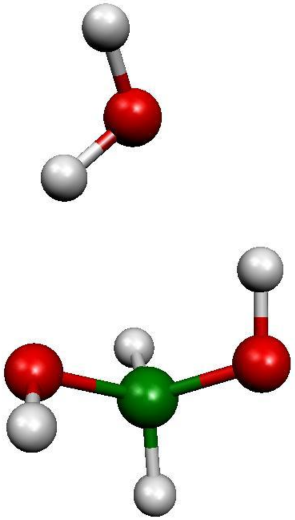
$$Q_{rot} = \frac{\pi^{1/2}}{\sigma_r}\left(\frac{T^{3/2}}{(\theta_A\theta_B\theta_C)^{1/2}}\right) \qquad \theta_{A,B,C} = \frac{h^2}{8\pi^2 I_{A,B,C} k_B}$$

I is the moment of inertia around the respective axis

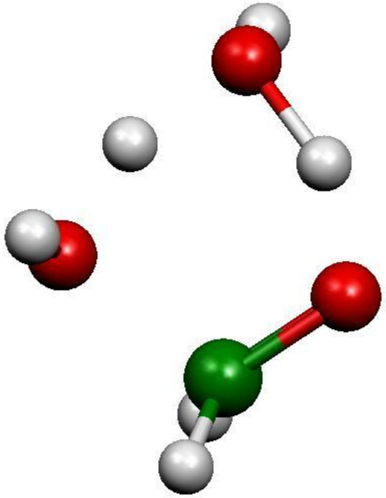
$$Q_{vib} = \prod_{i}^{Nvib} \frac{1}{1 - \exp\left[-\frac{h\nu_i}{k_B T}\right]}$$

ν_{i} is the vibrational frequency of the i-th vibrational mode

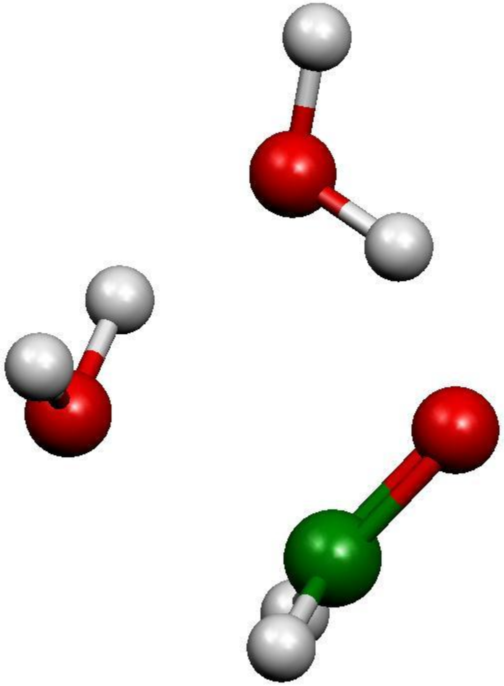
Methanediol Dehydration



$CH_2(OH)_2...H_2O$

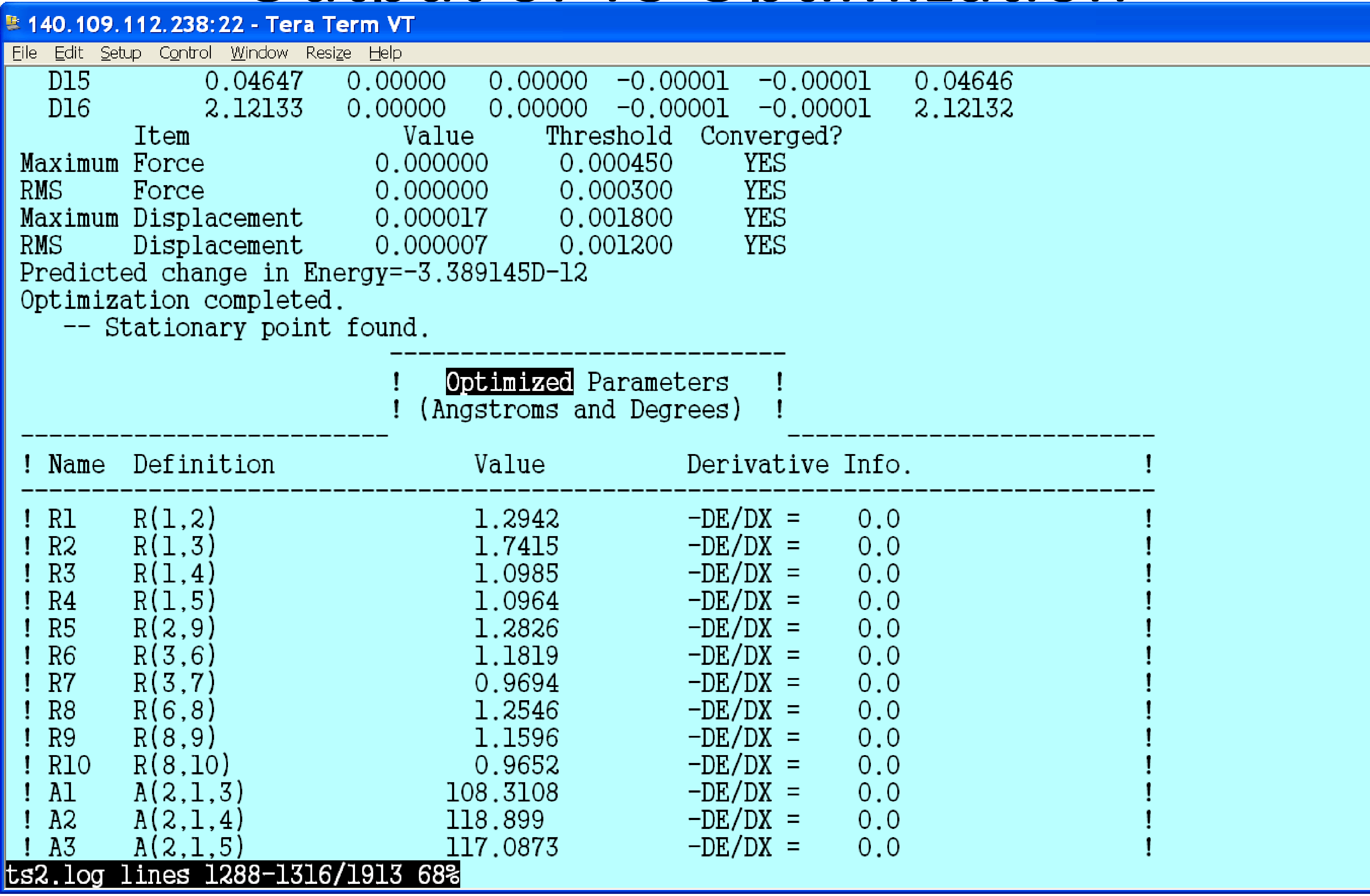


TS Complex



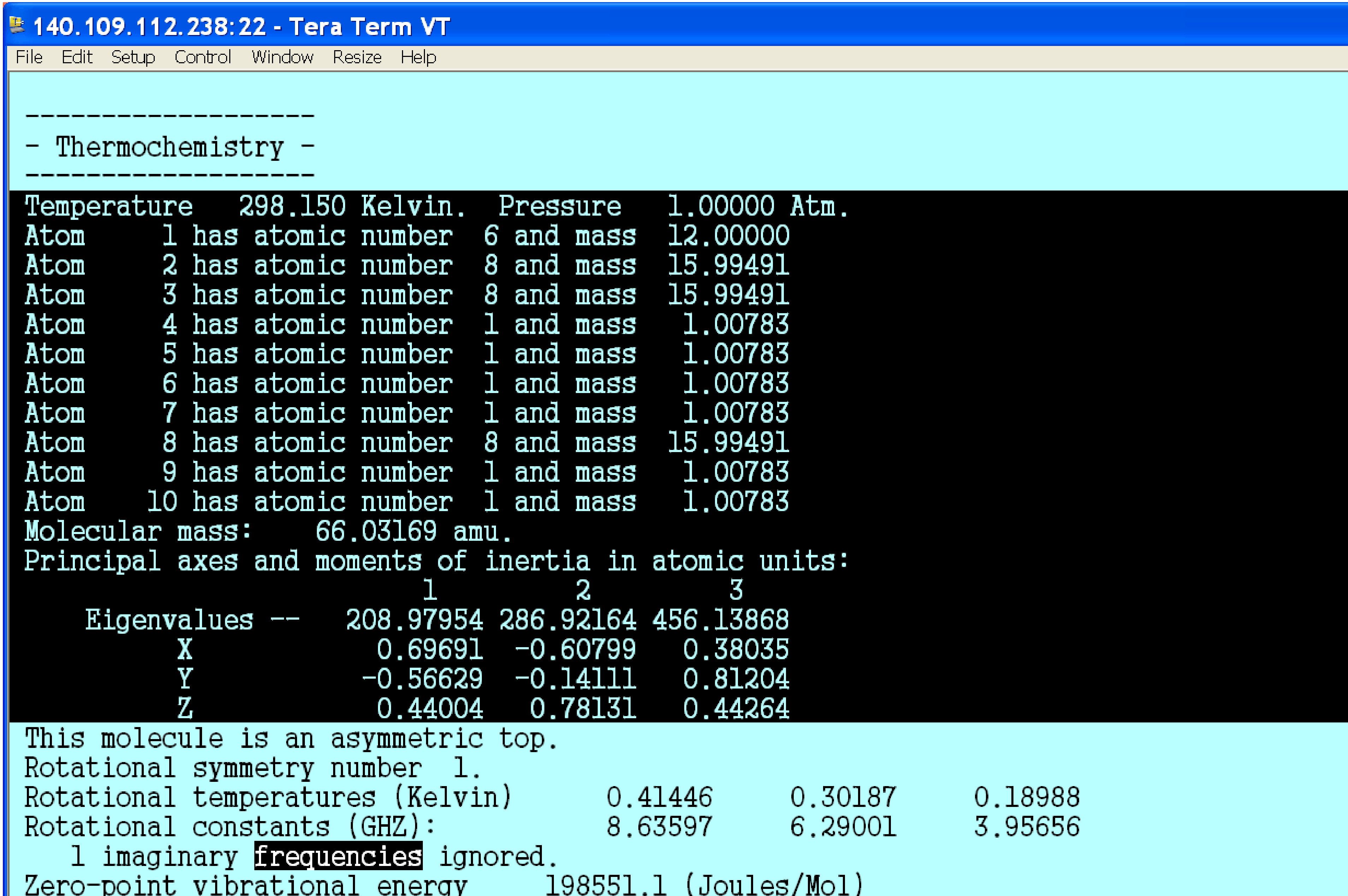
$CH_2O...H_2O...H_2O$

Output of TS Optimization



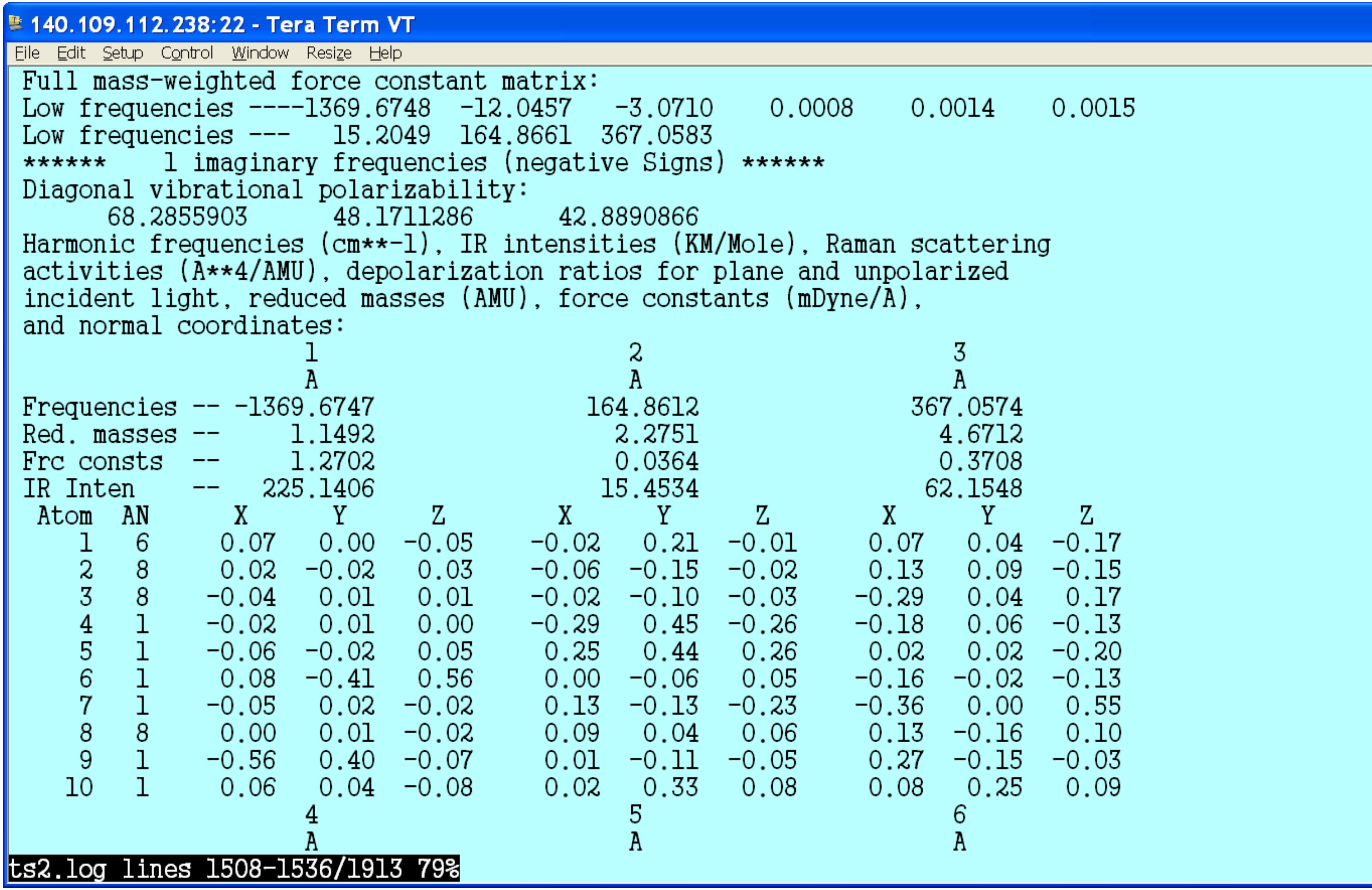
```
  D15         0.04647   0.00000   0.00000  -0.00001  -0.00001   0.04646
  D16         2.12133   0.00000   0.00000  -0.00001  -0.00001   2.12132
        Item               Value     Threshold  Converged?
 Maximum Force            0.000000     0.000450     YES
 RMS     Force            0.000000     0.000300     YES
 Maximum Displacement     0.000017     0.001800     YES
 RMS     Displacement     0.000007     0.001200     YES
 Predicted change in Energy=-3.389145D-12
 Optimization completed.
    -- Stationary point found.
                           ----------------------------
                           !   Optimized Parameters   !
                           ! (Angstroms and Degrees)  !
 --------------------------                            --------------------------
 ! Name  Definition              Value          Derivative Info.                !
 --------------------------------------------------------------------------------
 ! R1    R(1,2)                  1.2942         -DE/DX =    0.0                 !
 ! R2    R(1,3)                  1.7415         -DE/DX =    0.0                 !
 ! R3    R(1,4)                  1.0985         -DE/DX =    0.0                 !
 ! R4    R(1,5)                  1.0964         -DE/DX =    0.0                 !
 ! R5    R(2,9)                  1.2826         -DE/DX =    0.0                 !
 ! R6    R(3,6)                  1.1819         -DE/DX =    0.0                 !
 ! R7    R(3,7)                  0.9694         -DE/DX =    0.0                 !
 ! R8    R(6,8)                  1.2546         -DE/DX =    0.0                 !
 ! R9    R(8,9)                  1.1596         -DE/DX =    0.0                 !
 ! R10   R(8,10)                 0.9652         -DE/DX =    0.0                 !
 ! A1    A(2,1,3)              108.3108         -DE/DX =    0.0                 !
 ! A2    A(2,1,4)              118.899          -DE/DX =    0.0                 !
 ! A3    A(2,1,5)              117.0873         -DE/DX =    0.0                 !
ts2.log lines 1288-1316/1913 68%
```

Output of TS Optimization



```
 -------------------
 - Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
 Atom     1 has atomic number  6 and mass  12.00000
 Atom     2 has atomic number  8 and mass  15.99491
 Atom     3 has atomic number  8 and mass  15.99491
 Atom     4 has atomic number  1 and mass   1.00783
 Atom     5 has atomic number  1 and mass   1.00783
 Atom     6 has atomic number  1 and mass   1.00783
 Atom     7 has atomic number  1 and mass   1.00783
 Atom     8 has atomic number  8 and mass  15.99491
 Atom     9 has atomic number  1 and mass   1.00783
 Atom    10 has atomic number  1 and mass   1.00783
 Molecular mass:    66.03169 amu.
 Principal axes and moments of inertia in atomic units:
                           1         2         3
     Eigenvalues --   208.97954 286.92164 456.13868
           X            0.69691  -0.60799   0.38035
           Y           -0.56629  -0.14111   0.81204
           Z            0.44004   0.78131   0.44264
 This molecule is an asymmetric top.
 Rotational symmetry number  1.
 Rotational temperatures (Kelvin)      0.41446     0.30187     0.18988
 Rotational constants (GHZ):           8.63597     6.29001     3.95656
    1 imaginary frequencies ignored.
 Zero-point vibrational energy     198551.1 (Joules/Mol)
```

Output of TS Optimization



```
Full mass-weighted force constant matrix:
Low frequencies ----1369.6748  -12.0457   -3.0710    0.0008    0.0014    0.0015
Low frequencies ---   15.2049  164.8661  367.0583
******    1 imaginary frequencies (negative Signs) ******
Diagonal vibrational polarizability:
      68.2855903      48.1711286      42.8890866
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
activities (A**4/AMU), depolarization ratios for plane and unpolarized
incident light, reduced masses (AMU), force constants (mDyne/A),
and normal coordinates:
                    1                      2                      3
                    A                      A                      A
Frequencies -- -1369.6747               164.8612               367.0574
Red. masses --     1.1492                 2.2751                 4.6712
Frc consts  --     1.2702                 0.0364                 0.3708
IR Inten    --   225.1406                15.4534                62.1548
 Atom  AN      X      Y      Z        X      Y      Z        X      Y      Z
    1   6   0.07   0.00  -0.05    -0.02   0.21  -0.01     0.07   0.04  -0.17
    2   8   0.02  -0.02   0.03    -0.06  -0.15  -0.02     0.13   0.09  -0.15
    3   8  -0.04   0.01   0.01    -0.02  -0.10  -0.03    -0.29   0.04   0.17
    4   1  -0.02   0.01   0.00    -0.29   0.45  -0.26    -0.18   0.06  -0.13
    5   1  -0.06  -0.02   0.05     0.25   0.44   0.26     0.02   0.02  -0.20
    6   1   0.08  -0.41   0.56     0.00  -0.06   0.05    -0.16  -0.02  -0.13
    7   1  -0.05   0.02  -0.02     0.13  -0.13  -0.23    -0.36   0.00   0.55
    8   8   0.00   0.01  -0.02     0.09   0.04   0.06     0.13  -0.16   0.10
    9   1  -0.56   0.40  -0.07     0.01  -0.11  -0.05     0.27  -0.15  -0.03
   10   1   0.06   0.04  -0.08     0.02   0.33   0.08     0.08   0.25   0.09
                    4                      5                      6
                    A                      A                      A
ts2.log lines 1508-1536/1913 79%
```

Hartree Fock Projects 2

- Vinyl alcohol H2C=CHOH, CH3CHO isomer energy and barrier energy (IRC check)
- $R_1R_2C=O$ optimization effect of substituent on the C=O vibrational frequency and intensity
- CO2+H2O carbonic acid formation barrier
- $R_1R_2R_3C\text{-}CR_4R_5R_6$ and $R_1R_2C=CR_3R_4$ torsion barrier and potential curve