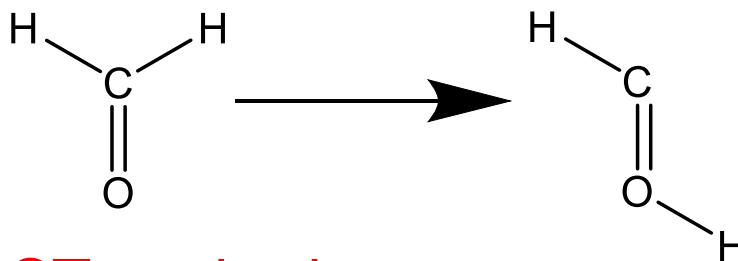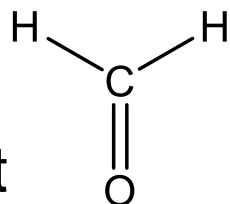# 11月6日上机实习安排

使用MS软件DMoI3模块完成：

Locate the transition state (TS) of Hydrogen Shift Reaction:

by using LST/QST method:

1. Geometry optimizations of **initial state (IS)** and **final state (FS)**

2. Transition state search

3. Transition state confirmation

4. TS further optimization

1. Geometry Optimization of IS

① Put ⟨H₂C=O⟩ as IS into a crystal cell with the volume of 30 Å×30 Å×30 Å

② DMol3 **Geometry Optimization** setting:
- ✓Geometry optimization quality: Fine
- ✓PBE-D (Grimme) functional
- ✓**Charge "0"**
- ✓Integration accuracy: Fine
- ✓SCF tolerance: Medium (1e−5)
- ✓K points: Gamma
- ✓Core treatment: Effective Core Potentials
- ✓Basis set: DNP (4.4)
- ✓Orbital cutoff: 5.0 Å
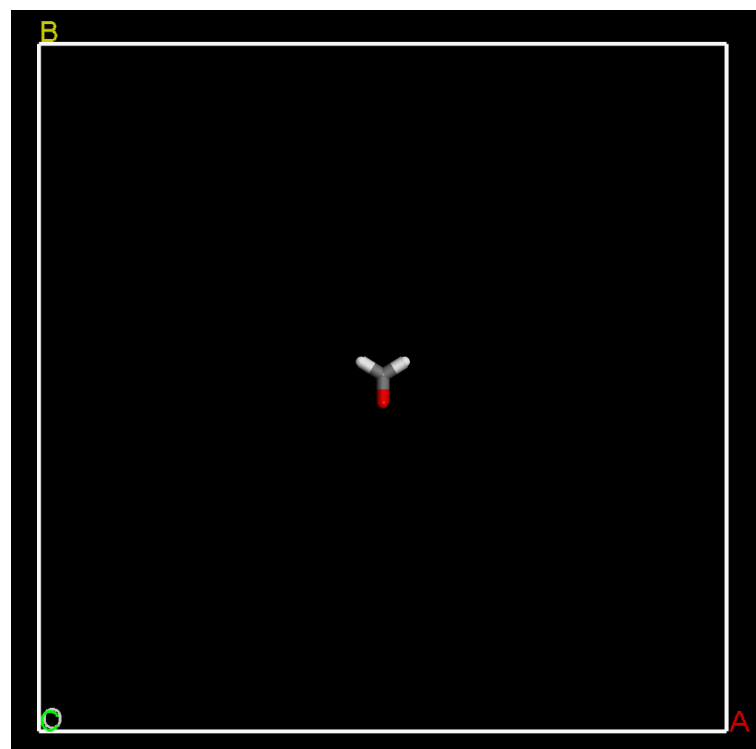
1. Geometry Optimization of FS

➢ Copy IS to new **xsd** file

H—C
‖
O
H
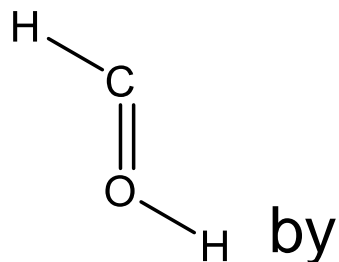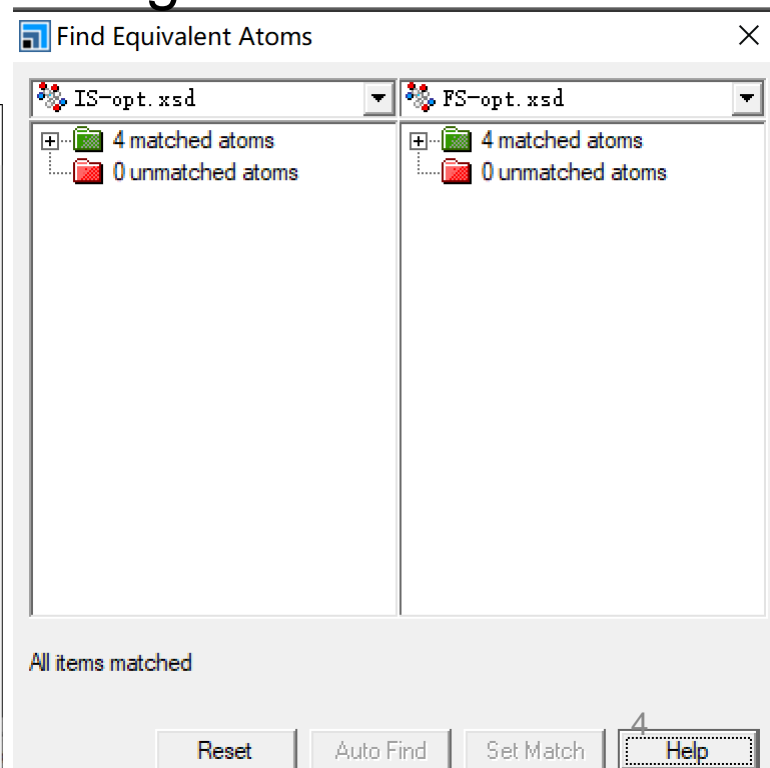
➢ Generate FS by changing coordinates of O and H atoms of IS

➢ **Keep the sequence of atomic coordination as the same as IS**
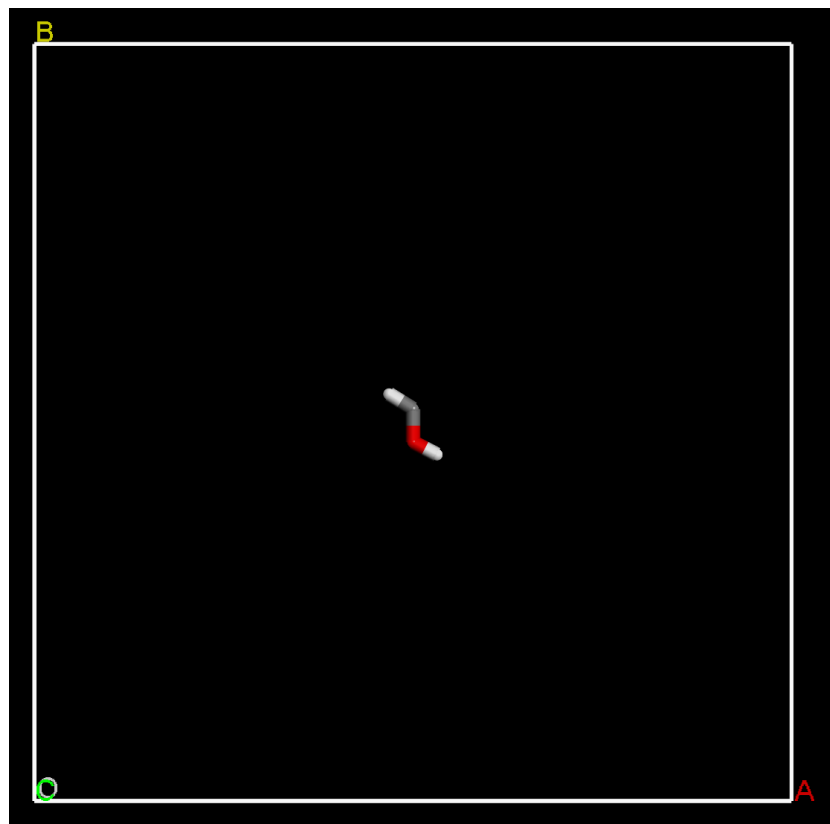
2. Transition State (TS) Search

① Open **IS.xsd and FS.xsd** files

② Tools → Reaction Preview, import two *.xsd files as IS and FS

③ Match atoms

④ Determine how many frames (8) to be generated

⑤ Press "Preview"

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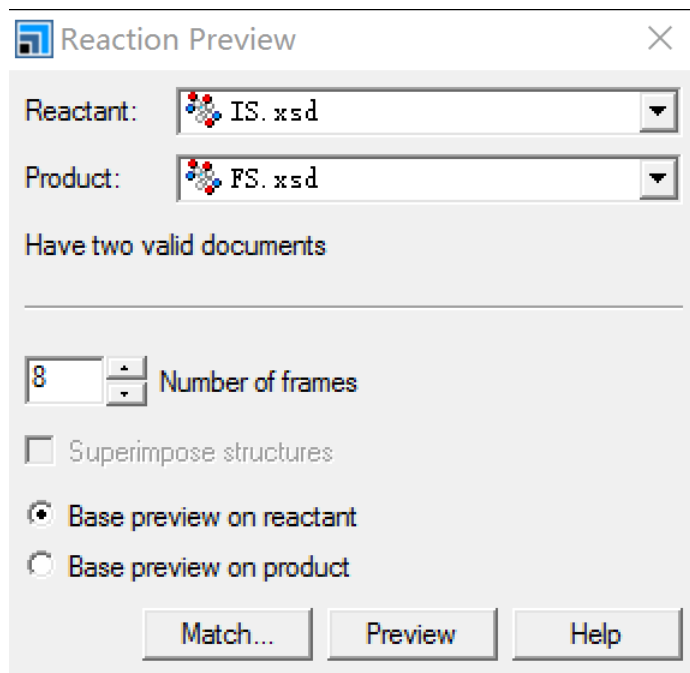
2. Transition State (TS) Search

① Obtain IS-FS.**xtd** file and open it

② DMol3 **TS Search** setting:
- ✓Search protocol: Complete LST/QST
- ✓Quality: Fine
- ✓Properties Tab: mark "Frequency"

③ After TS search, check *.outmol file for reaction barrier and frequency results or open *.xsd file Tools → Vibrational Analysis → Calculate

3. TS Confirmation

① Open TS.**xtd** file

② DMol3 **TS Confirmation** setting:
- ✓ Quality: Fine
- ✓ Path quality: Medium
- ✓ Max. images: The number of intermediate NEB images used during the transition state confirmation.
- ✓ Properties Tab: **Mark "Frequency"!!!**

③ After TS confirmation, check *.xcd and *.xtd files for further information

Hydrogen Shift Reaction (Gaussian)

➢Computational level: B3LYP/6-31G(d)

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

E_a = 91.0 kcal/mol^{-1}

1.118 Å

113.8°

1.171 Å

60.7°

1.122 Å

101.2°

1.321 Å

0.976 Å

122.4°

1.111 Å

1.207 Å

Energy (kcal/mol)

100

80

60

40

20

0

-3   -2   -1   0   1   2

Reaction Coordinate
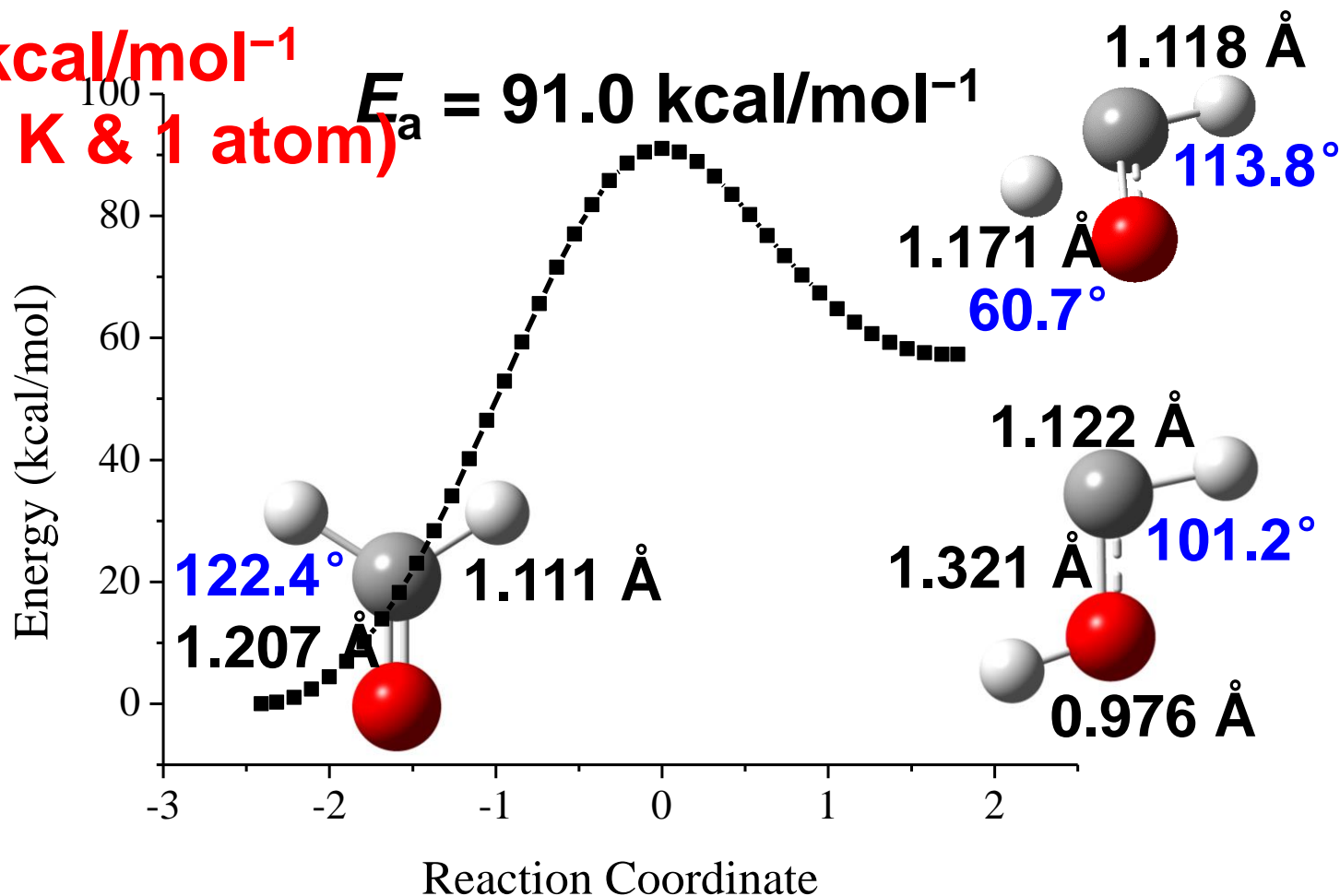
4. TS Further Optimization (if TS search fail)

① Open TS.**xsd** file

② DMol3 **TS Optimization** setting:
 ✓Quality: Fine
 ✓Properties Tab: mark "Frequency"

Done by VASP

VASP Calculations

➢**INCAR (input parameter setting)**

➢KPOINTS (*k*-point setting)

➢POSCAR (coordination for structure, cif (from MS)→*.vasp generated by **VESTA** software)

➢POTCAR (PW-PP information)

INCAR for Geometry Optimization

ALGO = Fast
PREC = Normal
ENCUT = 500
EDIFF = 1E-5
EDIFFG = -0.05

Output: CONTCAR (final structure)
OUTCAR (summary file)

ISMEAR = 0   #smearing method for the Gaussian smearing
SIGMA = 0.02   #determines the width of the smearing in eV
LREAL = Auto   #determines the projection operators evaluated in real or reciprocal space
NELM = 100   #the maximum number of electronic SC (self-consistency) steps
#optimization setting
IBRION = 2   #optimization method for the conjugate gradient algorithm
ISIF = 3   #update lattice parameters, atomic position, force
NSW = 600   #optimization cycle
#print control
LORBIT = 11
LWAVE = .FALSE.
LCHARG = .FALSE.
#add vdW corrections
IVDW = 11   #D3

KPOINTS File

Automatic-mesh
0
Monkhorst-Pack
12 12   1
  0.   0. 0.

POSCAR File

CIF file
1.0
        2.4600000381   0.0000000000   0.0000000000
       -1.2300000191   2.1304225263   0.0000000000
        0.0000000000   0.0000000000   20.0000000000
   C
   2
Direct
   0.000000000   0.000000000   0.000000000
   0.666670024   0.333330005   0.000000000

POTCAR File

PAW_PBE C_GW 28Sep2005
  4.00000000000000
 parameters from PSCTR are:
  VRHFIN =C: s2p2
  LEXCH = PE
  EATOM =   147.1560 eV,   10.8157 Ry

  TITEL = PAW_PBE C_GW 28Sep2005
  LULTRA =   F   use ultrasoft PP ?
  IUNSCR =   0   unscreen: 0-lin 1-nonlin 2-no
  RPACOR =   0.000   partial core radius
  POMASS =   12.011; ZVAL   =   4.000   mass and valenz
  RCORE =   1.500   outmost cutoff radius
  RWIGS =   1.630; RWIGS =   0.863   wigner-seitz radius (au A)
  ENMAX = 413.992; ENMIN = 310.494 eV
  ICORE =   2   local potential
  LCOR   =   T   correct aug charges
  LPAW   =   T   paw PP
......

INCAR for **High-Accuracy** Single-Point Calculation (Charge Density)

ALGO = Normal **Enlarge *K* points**

ENCUT = 500 **Output: CHGCAR**

PREC = Accurate

LREAL = Auto

ISTART = 0 #determines whether to read the file WAVECAR or not

ICHARG = 2 #determines how to construct the 'initial' charge density

ISMEAR = 0

SIGMA = 0.02

LORBIT = 11

LWAVE = .TRUE.

LCHARG = .TRUE.

IVDW = 11

NELM = 300

EDIFF = 10E-6

INCAR for Band Structure

ALGO = Normal
ENCUT = 500   **Output: EIGENVAL**
PREC = Accurate
LREAL = Auto
LORBIT = 11
LWAVE = .FALSE.
LCHARG = .FALSE.
IVDW = 11
ISTART = 1
ICHARG = 11   #for a given charge density read from CHGCAR
ISMEAR = 0
SIGMA = 0.02
NELM = 300
EDIFF = 10E-6

KPOINTS for Band Structure

```
k-points along high symmetry lines
30   ! 30 intersections
Line-mode
rec
0.000  0.000  0.000   ! GM
0.500  0.000  0.000   ! M

0.500  0.000  0.000   ! M
0.500  0.000  0.500   ! L

0.500  0.000  0.500   ! L
0.667  0.333  0.500   ! H

0.667  0.333  0.500   ! H
0.667  0.333  0.000   ! K

0.667  0.333  0.000   ! K
0.000  0.000  0.000   !GM
```

INCAR for DOS

ALGO = Normal
ENCUT = 500
PREC = Accurate
LREAL = Auto
LORBIT = 11
LWAVE = .FALSE.
LCHARG = .FALSE.
IVDW = 11
ISTART = 1
ICHARG = 11
ISMEAR = 0
SIGMA = 0.02
NELM = 300
EDIFF = 10E-6
#control DOS
EMIN = -5.24   #minimum energy for evaluation of DOS
EMAX = 4.76   #maximum energy for evaluation of DOS
NEDOS = 301   #number of grid points in DOS

Output: DOSCAR

Determined by Fermi Level

INCAR for PDOS

ALGO = Normal
ENCUT = 500
PREC = Accurate
LREAL = Auto
IVDW = 11
ISTART = 1
ICHARG = 11
ISMEAR = 0
SIGMA = 0.02
NELM = 300
EDIFF = 10E-6
LORBIT = 11
LWAVE = .FALSE.
LCHARG = .FALSE.

Output: PARCHG.261.ALLK
PARCHG.262.ALLK

\# VB and CB partial charge
LPARD = .TRUE. #Evaluate partial (band and/or k-point) decomposed charge density
IBAND = 261 262
NBMOD = 2 #Number of values in the array IBAND
LSEPB = .TRUE. #Specifies the charge density calculated for every band separately

INCAR for Magnetism

#open the spin-orbital
LSORBIT = .TRUE.

Output: OUTCAR

LNONCOLLINEAR = .TRUE.   #perform fully non-collinear magnetic structure calculations
SAXISR = 0 1 0   #direction of the magnetic field
RWIGS = 1.630 1.100 1.400 2.200   #Wigner Seitz radius read from POTCAR
MAGMOM = 216*0.0 0.866 -0.5 0.0 0.866 0.5 0.0 0.0 1.0 0.0
LMAXMIX = 4   #for d elements
GGA_COMPAT = .FALSE.   #apply spherical cutoff on gradient field