Tutorial for TUMME – version 3.1

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TUMME: Tsinghua University Minnesota Master Equation solver

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TUMME: Tsinghua University Minnesota Master Equation solver

Introduction – 1

■ What is TUMME ?

- TUMME (Tsinghua University Minnesota Master Equation solver) is a computer program for setting up and solving one-dimensional energy-dependent master equations for gas-phase chemical kinetics.

- TUMME can solve for the phenomenological rate constants and the time evolution of energy-bin populations for a gas-phase reaction network involving single or multiple intermediate energy-wells in a (P, T) ensemble.

■ What can TUMME do ?

☐ Construct the transition matrix of a master equation with discrete energy bins

☐ Calculate rate constants for collisional energy transfer

☐ Calculate microcanonical reaction rates including anharmonicity, recrossing, and tunneling

☐ Calculate phenomenological rate constants for a complicated reaction map

☐ Calculate the time evolution of energy populations

☐ Characterize the pressure and temperature dependences of chemical kinetics

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Basic assumptions of TUMME

- □ **Markov random process**

  The transition process depends on the current state and has no historical memory.

- □ **RRKM assumption**

  The intramolecular vibrational relaxation (IVR) is faster than reaction.

- □ **Bimolecular reagents equilibrated**

  Bimolecular pairs are always in thermal equilibrium.

- □ **Pressure, temperature, and concentrations**

  a) Constant pressure, constant temperature

  b) Bath gas is ideal gas

  c) Bath gas concentration >> reactant and product concentrations

Master equation sketch

TUMME: Tsinghua University Minnesota Master Equation solver
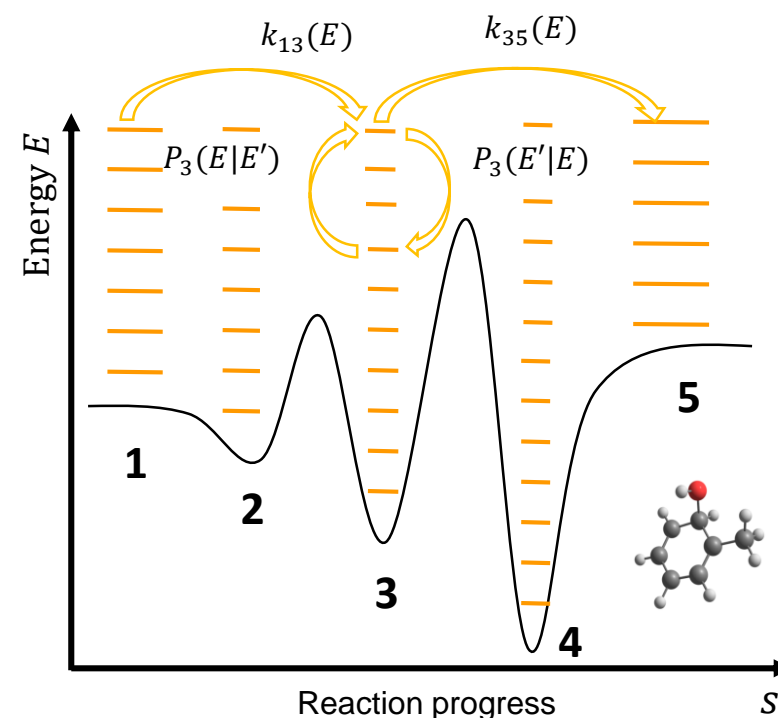
Introduction – 3

■ Features of TUMME

☐ Microcanonical flux coefficients by multistructural variational transition state

theory (MS-VTST) with multidimensional tunneling (SCT, LCT, or μOMT)

☐ Inverse-Laplace transform for microcanonical rate flux coefficients

☐ "Exponential-down" collision relaxation mode with energy-dependent $\langle \Delta E_d \rangle$

☐ Phenomenological rate constants from chemically significant eigenmodes

☐ Pseudo-first order treatment when bimolecular reactions involved

☐ MPI and MP parallelism of computer code

☐ Double/quadruple/octuple precision for floating-point arithmetic

☐ Interfaces available for *Polyrate, MSTor,* and *Gaussian*

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Installation

■ Installation command:

```
[user@~] tar -xvf TUMME3.1.tar.xz
[user@~] cd TUMME3.1/
[user@~/TUMME3.1] ./configure
```

□ TUMME is written using Python3.

□ To run basic TUMME, Anaconda should be installed.

□ To use high-precision libraries, you need the configure file to compile.

□ To use MPI, you need to install *mpi4py* module according to this webpage:

https://mpi4py.readthedocs.io/en/stable/install.html#using-pip

```bash
#!/bin/bash
path=`pwd`
#configure qd must use GNU,      INTEL does NOT work!
cd $path/C++/qd/qd-2.3.7.1
./configure --prefix $path/C++/qd  CXX=g++ CC=gcc FC=gfortran
make clean
make
make install
#compile mini_mpack in dd (quadruple precision)
cd $path/C++/mpack_dd/src
make clean
make
#comile mini_mpack in qd (octuple precision)
cd $path/C++/mpack_qd/src
make clean
make
#compile muti-preicison tumme
cd $path/C++
sed -i "s#^ROOTPATH =.*#ROOTPATH =$path#g" Makefile
make clean
make
#set executble script
cd $path/bin
sed -i "s#^ROOT_PATH=.*#ROOT_PATH=$path#g" tumme
#set enviroment variable
echo "# Enviroment variable of TUMME" >> ~/.bashrc
echo 'export PATH=$PATH:'$path'/bin' >> ~/.bashrc
```

Details in the file configure

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How to run

■ Run command:

[*user@~/TUMME3.1*] *tumme param.in*

□ The script will run different commands according to the keyword **#PARALLEL** defined in the input file.

□ The name of the input file can be any file name.

```sh
#!/bin/sh
ROOT_PATH=/home/work/TUMME/
SRC_PATH=$ROOT_PATH/src
PYTHON_COMMAND=python3
TUMME_MAIN=tumme_main.py
INPUT=$1
# read parallelism
PARALLEL_STR=$(grep "#parallel" $INPUT|tr -d '\n'|sed -e 's/[ \t]*$//g')
PARALLEL_MODE=$(echo ${PARALLEL_STR##* })
NPROC_STR=$(grep "#nproc" $INPUT|tr -d '\n'|sed -e 's/[ \t]*$//g')
NPROC=$( echo ${NPROC_STR##* })
# omit some check code

# run command
if [ "$PARALLEL_MODE" == "MPI" ]
then
    MPI_COMMAND="mpirun -np "$NPROC
else
    MPI_COMMAND=' '
fi
$MPI_COMMAND $PYTHON_COMMAND $SRC_PATH/$TUMME_MAIN $INPUT
```

Details in the file tumme

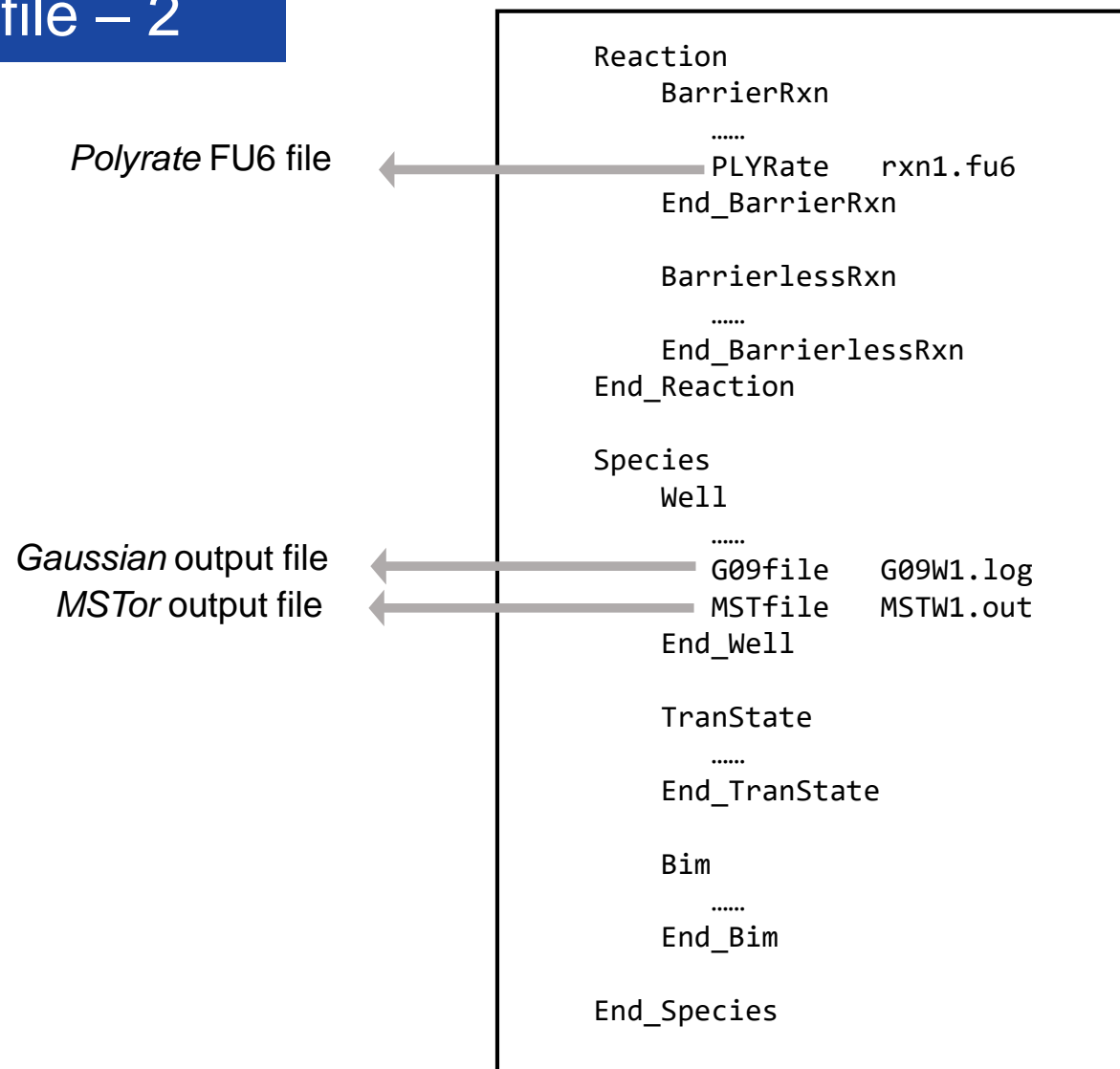*TUMME*: Tsinghua University Minnesota Master Equation solver

Input file – 1

■ **Structure of the standard input**

☐ Parallelism keywords

☐ Parameter section

☐ Reaction section

☐ Species section

```
#nproc 4
#parallel mpi
Parameter
    LJCollision

    …
    End_LJCollision

    Edown

    ……
    End_Edown

    Temperature[K]

        ……
    End_Temperature
    Pressure[torr]

        ……
    End_Pressure

    Energy

    ……
    End_Energy
    GroundSpecies    W1
    MergeThreshold   0.5
    Precision        double

    Prints

        ……
    End_Print
End_Parameter
```

```
Reaction
    BarrierRxn

    ……
    End_BarrierRxn

    BarrierlessRxn

    ……
    End_BarrierlessRxn
End_Reaction

Species
    Well

        ……
    End_Well

    TranState

            ……
    End_TranState

    Bim

        ……
    End_Bim

End_Species
```

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```
Reaction
    BarrierRxn
        ……
        PLYRate    rxn1.fu6
    End_BarrierRxn

    BarrierlessRxn
        ……
    End_BarrierlessRxn
End_Reaction

Species
    Well
        ……
        G09file    G09W1.log
        MSTfile    MSTW1.out
    End_Well

    TranState
        ……
    End_TranState

    Bim
        ……
    End_Bim

End_Species
```

Polyrate FU6 file ←

Gaussian output file ←
MSTor output file ←

■ Interface to external files

Species properties can be read from Polyrate file, Gaussian file, and Species-section, and the priority is

Polyrate file > Gaussian file > Species section

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Output files

- [ ] *.rate

    Temperature-and-pressure-dependent rate constants and high-pressure limits.

- [ ] *.out

    Properties of species and reactions and parameters while solving master equation.

- [ ] File printing microcanonical flux coefficients

- [ ] File printing partition functions

- [ ] File printing collisional energy transfer functions

- [ ] File printing time evolution of energetic-bin populations

- [ ] File printing CSE eigenvalues

- [ ] File printing CSE eigenvectors

    CSE ≡ chemically significant eigenmodes

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Other notes – 1

- ■ About energy

  - ☐ Distinguish concepts of **dE**, **ESOT**, **EMAX**, and **EEOT**.

  - ☐ Ensure **ESOT** > **dE** and **EMAX** > **EEOT.**

  - ☐ The depth of an isomer well may be truncated due to the numerical method of normalization.

  - ☐ If some energies of species are read from **E0** or **EELE** and others from **G09file**, one should ensure they have consistent zeros of energy.

  - ☐ At low temperatures, when molecules mainly populate low energy levels, one should decrease the value of **ESOT**.

  - ☐ At high temperatures, when molecules populate high energy levels, one should increase the value of **ESOT**.

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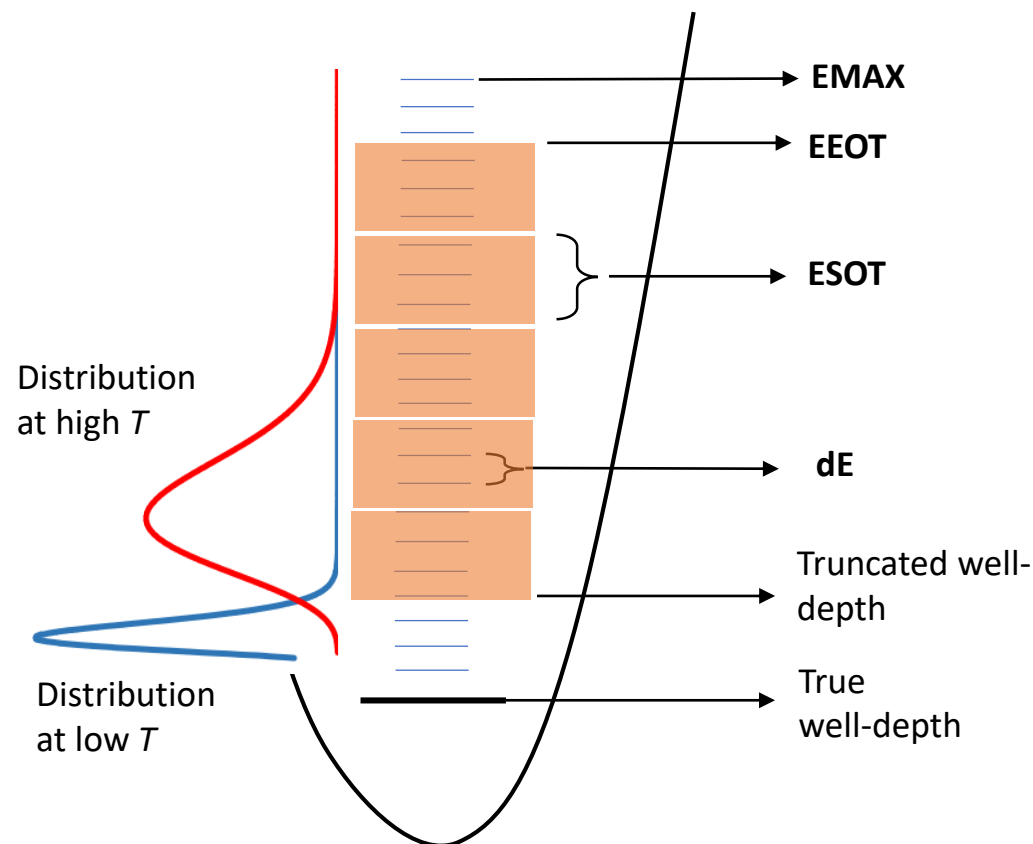
Other notes – 2

■ About symmetry number

Need to define **Rotsigma** when	Not need to define **Rotsigma** when
Read properties from *Polyrate*	Read density of state from *MSTor*
Read properties from **Species** section	Read properties from *Gaussian*

■ About frequency scaling factor

Need to define **Freqscale** when	Not need to define **Freqscale** when
Read properties from *Gaussian*	Read density of state from *MSTor*[a]
Read properties from **Species** section	Read properties from *Polyrate*[a]

[a] If, as usual, the frequency scaling has been done in *MSTor* and *Polyrate*.

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Example 1

1,2-H-shift isomerization of isobutyl

$$(CH_3)_2CHCH_2\bullet \leftrightarrow (CH_3)_3CH\bullet$$
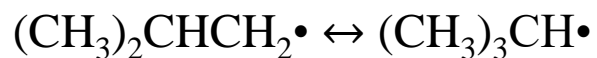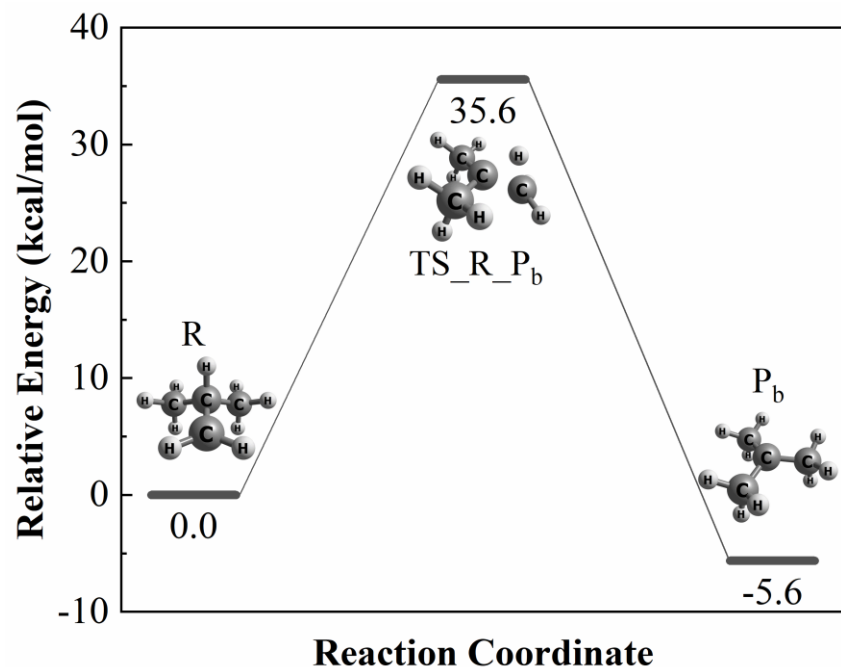
This is an example for the simplest isomerization reaction. In this example, TST(RRKM) is used with the single-structure-rigid-rotor-harmonic-oscillator approximation. The rate constant and time-evolution of species concentrations are extracted from the master equation

$$\frac{d\mathbf{y}}{dt} = -\mathbf{W}\mathbf{y} \tag{1}$$

where $\mathbf{y}$ is a vector containing the population of R and P_b, and $\mathbf{W}$ is the transition matrix.

Input: the standard input file
Output: rate constants and the time evolution of concentrations.

Zhang, R. M.; Xu, X.; Truhlar, D. G., *The Journal of Physical Chemistry A* **2021,** *125* (28), 6303-6313.

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Example 1 (cont.)

■ Standard input file

```
1  #nproc  15        Parallelism block
2  #parallel mp
3
4  Parameter         Global parameter block
5      HSCollision
6          Bmax[A]              9.0     Collision section
7          MassM[amu]       28.0134
8      End_HSCollision
9
10     Edown
11         EdConst[cm-1]        156.9204    Relaxation section
12     End_Edown
13
14     Temperature[K]
15         1500.          Temperature
16     End_Temperature
17
18     Pressure[torr]
19         3E1 7E1 1E2 3E2 7E2 1E3 3E3 7E3 1E4 3E4 7E4 1E5 3E5 7E5 1E6
20     End_Pressure        Pressure
21
22     GroundSpecies        R    Species where zero
23                               of energy is placed
24     Print
25         Timeevolution
26             Timefile time.txt
27             TimeStep[s] 1E-9
28             TimeNum  100
29             Initspecies      Time-evolution
30                 R
31             END_Initspecies
32         END_Timeevolution
33     End_Print
34
35  End_Parameter
36
37  Reaction          Reaction block
38     BarrierRxn
39         Info  R-TS_R_Pb-Pb   Define the reactant, transition
40     End_BarrierRxn             state, and product
41  End_Reaction
```

```
43  Species           Species block
44     Well           Well/isomer
45         Name R
46         Geometry[A]
47             C              0.00000500    0.05728400    -0.35846700
48             ...            Geometry
49         End_Geometry
50         Frequency[cm-1]
51             137.0475           235.0936           270.3191
52             ...            Frequency
53         End_Frequency
54         E0K[a.u.]   -157.628103   Energy
55     End_Well
56
57     Well
58         Name Pb
59         Geometry[A]
60             C              0.00000000    1.47714300    0.01848500
61             ...
62         End_Geometry
63         Frequency[cm-1]
64             132.2029           137.4214           137.4346
65             ...
66         End_Frequency
67         E0K[a.u.]    -157.637096
68         Rotsigma   3
69     End_Well
70
71     TranState       Transition state
72         Name TS_R_Pb
73         Geometry[A]
74             C              0.00001700    0.02076500    -0.15960900
75             ...
76         End_Geometry
77         Frequency[cm-1]
78             209.6066           217.8881
79             ...
80         End_Frequency
81         E0K[a.u.]    -157.571442
82     End_TranState
83
84  End_Species
```

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Example 1 (cont.)

■ Standard output file

```
43  ********************** Global Parameter **********************
44    Precision:                double
45    MergeThreshold:           2.00000E-01
46    GroundSpecies:            R
47    <DeltaE_d>[a.u.]  =  (T/Tc)^(exponent)[ slope*( E - E_gamma,0) + EdConst ]
48      | Tc[a.u.]:              9.50045E-04
49      | exponent:              0.00000E+00
50      | slope:                 0.00000E+00
51      | EdConst[a.u.]:         7.14982E-04
52    HSCollision
53      | bmax[a.u.]:            1.70075E+01
54      | massM[a.u.]:           5.10653E+04
55      | massA[a.u.]:           None
56
57  ********************** Isomers **********************
58    [MOLECULE PROPERTIES]
59    Name:                     R
60    Read from:                SPECIES block
61    Number of atoms:          13
62 >  Geometry [a.u.]:          ...
76    Freuencies scaling factor: 1.00000E+00
77 >  Frequencies (scaled) [cm-1]: ...
87    E(ele) [ a.u.]:           -0.11720102335749813
88    ZPVE  [ a.u.]:            0.11720102335749813
89    E(0K) [ a.u.]:            0.0
90    Eletronic level [a.u.]:
91      |   1.00000E+00      0.00000E+00
92    Islinear:                 False
93    IABC [a.u.]:              1.11925E+17
94    Symmetry number:          1.00000E+00
95    Optical-isomer number:    1.00000E+00
96    MSTor file:               None
97    [END OF MOLECULE]
```

Global parameters

Isomer properties

```
187  ********************** Reaction Stack **********************
188  [ REACTION INFO ]
189    Reactant:                 R
190    TS:                       TS_R_Pb
191    Product:                  Pb
192    Polyrate file:            None
193    Variation:                tst
194    Tunneling:                None
195    Lower limit of MEP:       None
196    Upper limit of MEP:       None
197    The k(E) will be calculated from the analytical expression.
198  [ END OF INFO ]
199
200  [ REACTION INFO ]
201    Reactant:                 Pb
202    TS:                       TS_R_Pb
203    Product:                  R
204    Polyrate file:            None
205    Variation:                tst
206    Tunneling:                None
207    Lower limit of MEP:       None
208    Upper limit of MEP:       None
209    The k(E) will be calculated from the analytical expression.
210  [ END OF INFO ]
211
212  ********************** Reaction Map **********************
213  ( Barrier with ZPVE in a.u.; X denotes none reaction )
214    | From/to          R              Pb
215  R                    X         5.66610E-02
216  Pb          6.56540E-02          X
217
218  (  Reaction energy with ZPVE in a.u.; X denotes none reaction )
219    | From/to          R              Pb
220  R                    X         -8.99300E-03
221  Pb          8.99300E-03          X
222
```

Elementary reactions

Energies

```
224  ********************** Solve master equation **********************
225
226  =================  Cycle  =================
227
228    Temperature[K]:           1.500E+03
229    Pressure[Torr]:           3.000E+01
230    Energy step[cm-1]:        1.04255E+02
231    Energy reference[cm-1]:   4.37123E+04
232
233  [ RELAXATION INFO ]
234    Name:                     R
235    Size:                     418
236    bmax[a.u.]:               17.007535
237    Z[1/s]:                   6.389267E+08
238    Truncated well E0[cm-1]:  237.776
239    True well E0:[cm-1]       0.000
240  [ END OF INFO ]
241
242  [ RELAXATION INFO ]
243    Name:                     Pb
244    Size:                     436
245    bmax[a.u.]:               17.007535
246    Z[1/s]:                   6.389267E+08
247    Truncated well E0[cm-1]:  -1638.820
248    True well E0:[cm-1]       -1973.735
249  [ END OF INFO ]
250
251  [ ME INFO ]
252    Size                      854
253    Min CSE eigenvalue[1/s]:  0.00000E+00
254    Max CSE eigenvalue[1/s]:  4.06206E+05
255    Min IERE eigenvalue[1/s]: 4.84188E+05
256    Max IERE eigenvalue[1/s]: 1.35205E+10
257
258    EPCS:
259      CSE No.         1              2
260      R            -3.80037E-01  5.14525E-01
261      Pb           -9.24971E-01  -2.11400E-01
262
263    Binding:
264      Pb well corresponds to eigen mode 1
265      R well corresponds to eigen mode 2
266
267    Merge Pairs:
268      |   | R -    Pb
269
270  [ END OF INFO ]
```

Parameters for each (T, p) condition.

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Example 1 (cont.)

■ Rate constants output file

```
48  ******************* Rate constants map *******************
49 >*   The diagonal denotes sum of the off-diagonal in a row. ···
80
81  T = 1500.00 K, p = 3.000E+03
82  From/To                        R              Pb
83  R                    9.48752E+06    9.48752E+06
84  Pb                   1.60158E+06    1.60158E+06
```

```
204  ******************* Rate constants in temperature *******************
205
206  R -> other species
207  │T[K]/p[torr]              3.000E+01      7.000E+01      1.000E+02      3.000E+02
208  1.500E+03                    #              #              #              #
209
224  ******************* High-pressure limit flux coefficient *******************
225
226  T[K]                      R->Pb          Pb->R
227  1.500E+03             6.92012E+07    1.16818E+07
228
```
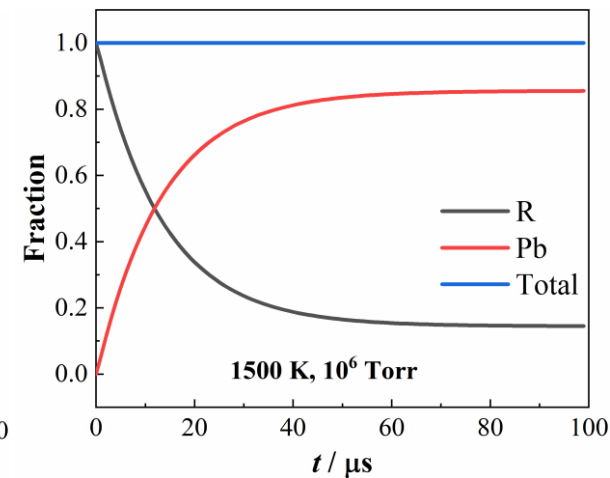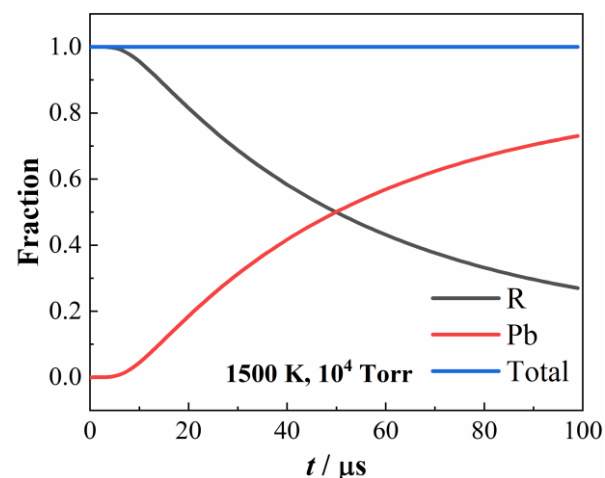
Phenomenological
rate constants

```
128  ******************* Rate constants in pressure *******************
129
130 ˅ R -> other species
131  │p[torr]/T[K]              1500.00
132  3.000E+01                    #
133  7.000E+01                    #
134  1.000E+02                    #
135  3.000E+02                    #
136  7.000E+02                    #
137  1.000E+03                    #
138  3.000E+03              9.48752E+06
139  7.000E+03              1.51666E+07
140  1.000E+04              1.81750E+07
141  3.000E+04              2.95969E+07
```
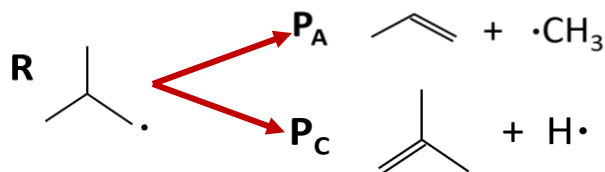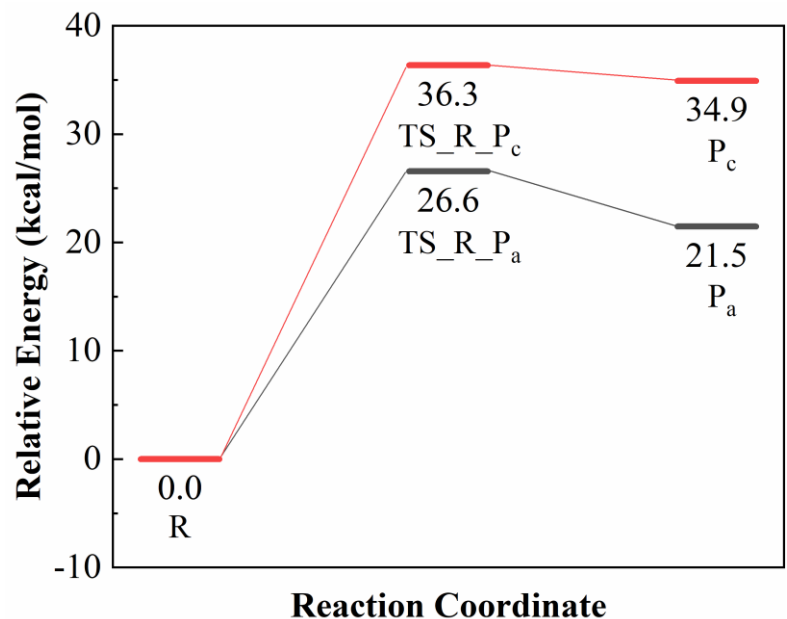
"Merge" happened

The time-evolution of isomers

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Example 2

C-C and C-H *β*-scission of isobutyl

This is an example of competing unimolecular reactions. In this example, TST(RRKM) is used with the single-structure-rigid-rotor-harmonic-oscillator approximation. Rate constants are extracted from the master equation

$$\frac{d\mathbf{y}}{dt} = -\mathbf{W}\mathbf{y} + \mathbf{Bs} \qquad (2)$$

based on CSE theory, where **y** is a vector containing the population of R. For the time evolution, TUMME neglect the **Bs** term of eq (2) and uses the following homogeneous master equation:

$$\frac{d\mathbf{y}}{dt} = -\mathbf{W}\mathbf{y} \qquad (3)$$

Input: the standard input file
Output: rate constants and the time-evolution of concentrations.

Zhang, R. M.; Xu, X.; Truhlar, D. G., *The Journal of Physical Chemistry A* **2021,** *125* (28), 6303-6313.

Example 2 (cont.)

■ Standard input file

```
1   #nproc  15              Parallelism block
2   #parallel mp
3
4   Parameter               Parameter block
5       HSCollision
6           Bmax[A]                    9.0      Collision section
7           MassM[amu]                 28.0134
8       End_HSCollision
9
10      Edown
11          EdConst[cm-1]          111.0324     Relaxation section
12      End_Edown
13
14      Temperature[K]
15          700.                        Temperature
16      End_Temperature
17
18      Pressure[torr]         Pressure
19       1E-10 1E-9 1E-8 1E-7 1E-6 1E-5 1E-4 1E-3 1E-2 1E-1 1.0 1E1 1E2 1E4 1E6
20      End_Pressure
21
22      GroundSpecies          R      Species where zero
23                                     of energy is placed
24      Precision quadruple    Precision of the transition matrix
25  End_Parameter
26
27
28  Reaction                   Reaction block
29      BarrierRxn
30          Info  R-TS_R_Pa-Pa   Define the reactant, transition state and product
31      End_BarrierRxn
32
33      BarrierRxn
34          Info  R-TS_R_Pc-Pc
35      End_BarrierRxn
36  End_Reaction
```

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Example 2 (cont.)

■ Standard input file

```
37  Species
38     Well                    Species block
39        Name R
40        Geometry[A]
41           C                    0.00000100    0.06835100   -0.36837900
42           ...
43        End_Geometry
44        Frequency[cm-1]
45           76.5658                 150.8529              176.9492
46           ...
47        End_Frequency
48        E0K[eV]    2.937894765
49     End_Well      Wells / isomers
50
51
52     TranState
53        Name TS_R_Pc
54        Geometry[A]
55           C                   -0.00000900    0.10844500    0.01394900
56           ...
57        End_Geometry
58        Frequency[cm-1]
59           83.0861                 115.2996
60           ...
61        End_Frequency
62        E0K[eV]        4.514114916
63     End_TranState
64                        Transition states
65     TranState
66        Name TS_R_Pa
67        Geometry[A]
68           C                   -0.31875100   -0.23524300   -0.46905000
69           ...
70        End_Geometry
71        Frequency[cm-1]
72           73.3727                 118.3417
73           ...
74        End_Frequency
75        E0K[eV]        4.089317803
76     End_TranState
```

```
78     Bim            Bimolecular pairs
79        Name Pa
80        Sp1Mol      The first molecular fragment species
81           Name   Pa_1 #sp1
82           Geometry[A]
83              C                   0.00000000    0.00000000    0.00000000
84              ...
85           End_Geometry
86           Frequency[cm-1]
87              920.0904                1304.9899             1304.9899
88              ...
89           End_Frequency
90           E0K[eV]    0.0
91           EleLevel[a.u.]
92              1 0
93           End_EleLevel
94           Rotsigma          6
95        End_Sp1Mol
96
97        Sp2Mol  The second molecular fragment species
98           Name   Pa_2 #sp2
99           Geometry[A]
100             C                  -1.26496100   -0.21881800    0.03958700
101             ...
102          End_Geometry
103          Frequency[cm-1]
104             80.0033                 438.0612              576.8934
105             ...
106          End_Frequency
107          E0K[kcal/mol]   0.0
108          Rotsigma          1.0
109       End_Sp2Mol
110       E0K[eV]   3.868742222
111    End_Bim
```

```
113    Bim
114       Name Pc
115       Sp1Mol
116          Name   Pc_1 #sp1
117          Geometry[A]
118             C                  0.000000    0.000000    1.456933
119             ...
120          End_Geometry
121          Frequency[cm-1]
122             29.8139                87.0421           393.0655
123             ...
124          End_Frequency
125          E0K[kcal/mol]   0.0
126          Rotsigma          2.0
127       End_Sp1Mol
128
129       Sp2Atom        The atomic fragment species
130          Name       13_r #sp2
131          Symbol      H
132          E0K[kcal/mol]  0.0
133       End_Sp2Atom
134       E0K[eV]    4.452257969
135    End_Bim
136
137 End_Species
```

12/30/2022

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Example 2 (cont.)

■ Standard output file

```
43  ****************** Global Parameter *********************
44    Precision:              quadruple
45    MergeThreshold:         2.00000E-01
46    GroundSpecies:          R
47    <DeltaE_d>[a.u.] = (T/Tc)^(exponent)[ slope*( E - E_gamma,0) + EdConst ]
48       Tc[a.u.]:            9.50045E-04
49       exponent:            0.00000E+00
50       slope:              0.00000E+00
51       EdConst[a.u.]:       5.05901E-04
52  HSCollision
53       bmax[a.u.]:          1.70075E+01
54       massM[a.u.]:         5.10653E+04
55       massA[a.u.]:         None
56
57  ******************** Isomers ********************
58  [MOLECULE PROPERTIES]
59    Name:                   R
60    Read from:              SPECIES block
61    Number of atoms:        13
62 >  Geometry [a.u.]:        ...
76    Freuencies scaling factor: 1.00000E+00
77 >  Frequencies (scaled) [cm-1]: ...
87    E(ele) [ a.u.]:         -0.10796549924632348
88    ZPVE [ a.u.]:           0.10796549924632348
89    E(0K) [ a.u.]:          0.0
90    Eletronic level [a.u.]:
91          1.00000E+00      0.00000E+00
92    Islinear:               False
93    IABC [a.u.]:            1.11655E+17
94    Symmetry number:        1.00000E+00
95    Optical-isomer number:  1.00000E+00
96    MSTor file:             None
97  [END OF MOLECULE]
```

Global parameters

Isomer properties

Elementary reactions

```
306 ********************** Reaction Stack **********************
307 [ REACTION INFO ]
308   Reactant:                R
309   TS:                      TS_R_Pa
310   Product:                 Pa
311   Polyrate file:           None
312   Variation:               tst
313   Tunneling:               None
314   Lower limit of MEP:      None
315   Upper limit of MEP:      None
316   The k(E) will be calculated from the analytical expression.
317 [ END OF INFO ]
318
319 [ REACTION INFO ]
320   Reactant:                Pa
321   TS:                      TS_R_Pa
322   Product:                 R
323   Polyrate file:           None
324   Variation:               tst
325   Tunneling:               None
326   Lower limit of MEP:      None
327   Upper limit of MEP:      None
328   The k(E) will be calculated from the analytical expression.
329 [ END OF INFO ]
```

```
371 ================= Cycle =================
372
373    Temperature[K]:          7.000E+02
374    Pressure[Torr]:          1.000E-10
375    Energy step[cm-1]:       4.86525E+01
376    Energy reference[cm-1]:  2.73088E+04
377
378 [ RELAXATION INFO ]
379    Name:                    R
380    Size:                    560
381    bmax[a.u.]:              17.007535
382    Z[1/s]:                  3.117643E-03
383    Truncated well E0[cm-1]: 112.075
384    True well E0:[cm-1]      0.000
385 [ END OF INFO ]
386
387 [ ME INFO ]
388    Size                     560
389    Min CSE eigenvalue[1/s]: 7.19400E-07
390    Max CSE eigenvalue[1/s]: 7.19400E-07
391    Min IERE eigenvalue[1/s]: 1.45896E-05
392    Max IERE eigenvalue[1/s]: 3.15746E+10
393
394    EPCS:
395       CSE No.               1
396       R                     9.61931E-01
397
398    Kappa:
399       Bim Name             Pa           Pc
400       R                    7.40531E-02  1.21092E-07
401
402    Binding:
403       R well corresponds to eigen mode 1
404
405 [ END OF INFO ]
```

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Example 2 (cont.)

■ Rate constants output file

```
48  ********************* Rate constants map *********************
49  *   The diagonal denotes sum of the off-diagonal in a row.
50
51  | T = 700.00 K, p = 1.000E-10
52  | From/To                  R            Pa           Pc
53  R                   7.19400E-07   7.19400E-07   4.65869E-28
54  Pa                  2.58261E-26   2.53198E-18   2.53198E-18
55  Pc                  1.93973E-41   2.93664E-12   2.93664E-12


143 ********************* Rate constants in pressure *********************
144
145 ▾ R -> other species
146  | p[torr]/T[K]              700.00
147  1.000E-10                 7.19400E-07
148  1.000E-09                 7.19367E-06
149  1.000E-08                 7.19043E-05
150  1.000E-07                 7.16146E-04
151  1.000E-06                 7.01463E-03
152  1.000E-05                 6.69286E-02
153  1.000E-04                 6.14926E-01
154  1.000E-03                 5.35435E+00
155  1.000E-02                 4.32060E+01
156  1.000E-01                 3.12770E+02
157  1.000E+00                 1.94093E+03
158  1.000E+01                 9.71923E+03
159  1.000E+02                 3.61678E+04
160  1.000E+04                 1.47466E+05
161  1.000E+06                 1.76960E+05
```
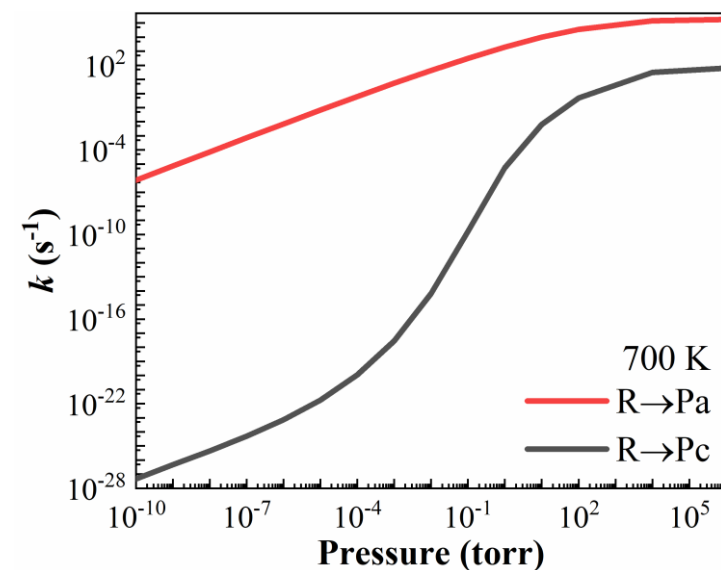
```
309 ********************* Rate constants in temperature *********************
310
311 R -> other species
312  | T[K]/p[torr]        1.000E-10      1.000E-09      1.000E-08      1.000E-07
313  7.000E+02            7.19400E-07    7.19367E-06    7.19043E-05    7.16146E-04

349 ********************* High-pressure limit flux coefficient *********************
350
351  T[K]                   R->Pa          R->Pc          Pa->R          Pc->R
352  7.000E+02            1.77507E+05    6.53738E+01    6.88689E-15    2.94171E-12
```
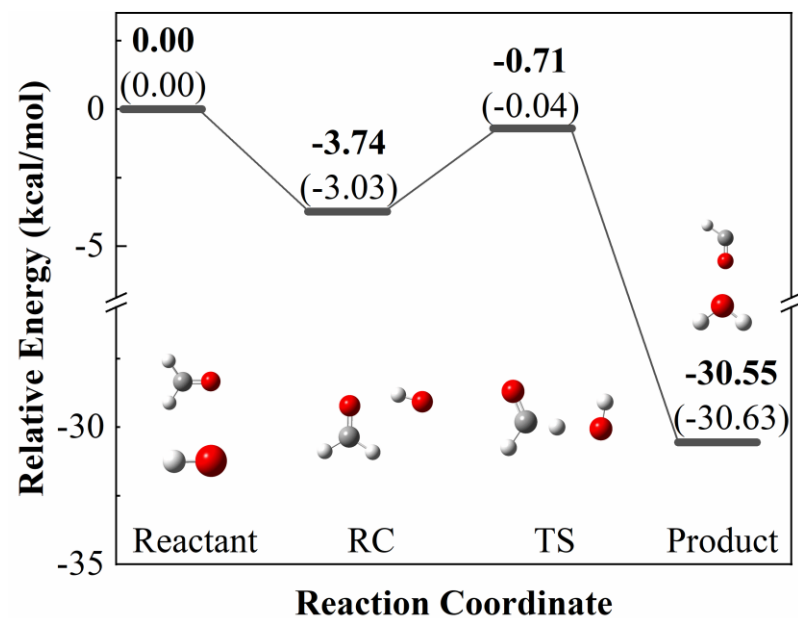
Phenomenological rate constants

Falloff curves

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Example 3

Hydrogen Abstraction from HCHO by OH (TST)

This is an example of a bimolecular reaction. This example uses TST(RRKM) theory with the single-structure-rigid-rotor-harmonic-oscillator is used for reaction 2, and the reaction 1 is estimated by the inverse-Laplacian transform to the hard-sphere model. Based on the CSE theory, the rate constant is extracted from

$$\frac{d\mathbf{y}}{dt} = -\mathbf{W}\mathbf{y} + \mathbf{B}n_{\text{HCHO}}n_{\text{OH}} \tag{4}$$

where the $n_{\text{HCHO}}n_{\text{OH}}$ is left unknown. For time-evolution calculations, the reaction is assumed to be pseudo-first order, and eq. (4) is converted to homogeneous form by appending the n_{HCHO} concentration to the population vector $\mathbf{y}$ to get vector $\mathbf{y}^*$,

$$\frac{d\mathbf{y}^*}{dt} = -\mathbf{W}^*\mathbf{y}^* \tag{5}$$

$$\text{HCHO} + \text{OH} \overset{1}{\rightarrow} \text{HCHO}\cdots\text{HO} \overset{2}{\rightarrow} \text{HCO} + \text{H}_2\text{O}$$

Input: the standard input file, *Polyrate* file for the reaction 2.
Output: rate constants and the time-evolution of concentrations.

Zhang, R. M.; Chen, W.; Truhlar, D. G.; Xu, X., *Faraday Discussions* **2022**, **238**, 431-460. doi.org/10.1039/D2FD00024E.

TUMME: Tsinghua University Minnesota Master Equation solver

Example 3 (cont.)

■ Standard input file

```
 1  Parameter
 2      LJCollision
 3          EpsilonM[cm-1]        56.993
 4          EpsilonA[cm-1]       191.134
 5          DiameterM[A]           3.74
 6          DiameterA[A]           4.94
 7          MassM[amu]            28
 8          MassA[amu]            47
 9      End_LJCollision
10
11      Edown
12          EDCONST[cm-1]    200
13          Tc[K]            300
14          Exponent         0.85
15      END_Edown
16
17      Temperature[K]
18          600. 1000. 1500.
19      End_Temperature
20
21      Pressure[torr]
22          1E-2
23      End_Pressure
24  |
25      PBimol
26          BimolName
27              R
28          End_BimolName
29
30          ExcessConc[mol/L]
31              1E-5
32          End_ExcessConc
33      End_PBimol
34
35      GroundSpecies          R
36  End_Parameter
37
38  Reaction
39      BarrierRxn
40          Info        RC-TS-P
41          Pyrfile    Rxn1.fu6
42      End_BarrierRxn
43
44      BarrierlessRxn
45          Info              R-RC
46          Avgdiameter[A]     4.11
47          Rxnenergy[kcal/mol]  -3.734532
48      End_BarrierlessRxn
49  End_Reaction
```

Global parameters block

Collision

Relaxation

Bimolecular pair(s)
with pseudo-first
order assumption

Reactions block

Barriered elementary
reaction, read from
Polyrate file

Barrierless elementary
reaction , ILT + hard-sphere

```
43  Species
44      Bim
45          Name R
46          Sp1Mol
47              Name R_f
48              Geometry[A]
49                  C        0.00000E+00        0.00000E+00        -5.23675E-01
50                  ......
51              End_Geometry
52
53              Frequency[cm-1]
54                  1.17074E+03 1.22857E+03 1.48038E+03 1.82298E+03 2.83467E+03 2.90356E+03
55              End_Frequency
56              EleLevel
57                  1 0
58              End_EleLevel
59              RotSigma      2
60              E0K[kcal/mol]  0
61          End_Sp1Mol
62
63          Sp2Mol
64              Name R_h
65              Geometry[A]
66                  O        0.00000E+00        0.00000E+00        1.07801E-01
67                  H        0.00000E+00        0.00000E+00        -8.62409E-01
68              End_Geometry
69
70              Frequency[cm-1]
71                  3.69902E+03
72              End_Frequency
73
74              EleLevel
75                  2 0
76                  2 0.000637887
77              End_EleLevel
78
79              E0K[kcal/mol] 0
80          End_Sp2Mol
81          E0K 0
82      End_Bim
83
84      Bim
85          Name P
86          Sp1Mol
87              Name P_f
88          End_Sp1Mol
89
90          Sp2Mol
91              Name P_w
92              RotSigma  2
93          End_Sp2Mol
94      End_Bim
95  End_Species
```

Species block

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TUMME: Tsinghua University Minnesota Master Equation solver

Example 3 (cont.)

■ Time-evolution file

```
1    #
2    # Time evolution ouput for TUMME
3    # the unit for energy is kcal/mol; the unit for time is second
4    #
5
6    T =          100.00   K, p =  1.000E+01 torr                        time
7    y(E)/time               0.00000E+00   2.00000E-07   4.00000E-07   6.00000E-07
8    RC
9    7.94883E+00             6.85012E-32   8.33291E-22   7.96635E-22   7.61593E-22
10   7.90908E+00            -1.07883E-27   9.98076E-22   9.54173E-22   9.12200E-22
11   7.86934E+00            -3.32792E-28   1.19544E-21   1.14285E-21   1.09258E-21
12   7.82959E+00            -2.60212E-28   1.43168E-21   1.36871E-21   1.30850E-21
13   7.78985E+00             3.93483E-26   1.71456E-21   1.63914E-21   1.56703E-21
14   7.75011E+00            -4.70048E-27   2.05319E-21   1.96287E-21   1.87653E-21
15   7.71036E+00            -4.78735E-27   2.45852E-21   2.35037E-21   2.24698E-21
16   7.67062E+00            -3.84387E-27   2.94387E-21   2.81437E-21   2.69057E-21
17   7.63087E+00            -5.38489E-29   3.52505E-21   3.36998E-21   3.22174E-21
18   7.59113E+00             2.27151E-27   4.22076E-21   4.03509E-21   3.85760E-21
19   7.55139E+00            -1.03427E-26   5.05372E-21   4.83142E-21   4.61889E-21
20   7.51164E+00            -4.83806E-27   6.05073E-21   5.78457E-21   5.53012E-21
21   7.47190E+00            -1.73190E-26   7.24373E-21   6.92509E-21   6.62047E-21
22   7.43215E+00            -2.21353E-26   8.67143E-21   8.28999E-21   7.92533E-21
23   7.39241E+00            -5.47684E-27   1.03799E-20   9.92332E-21   9.48681E-21
24   7.35267E+00            -2.23638E-26   1.24241E-20   1.18776E-20   1.13551E-20
25   7.31292E+00            -2.15904E-26   1.48711E-20   1.42169E-20   1.35915E-20
26   7.27318E+00            -1.11184E-26   1.77991E-20   1.70162E-20   1.62676E-20
27   7.23343E+00            -2.36191E-26   2.13020E-20   2.03649E-20   1.94691E-20
28   7.19369E+00            -1.19291E-26   2.54929E-20   2.43715E-20   2.32994E-20
```

energy   microscopic population of RC

```
302    R
303    [n]                    1.00000E+00   9.56011E-01   9.13957E-01   8.73754E-01   8.35318E-01
304
```
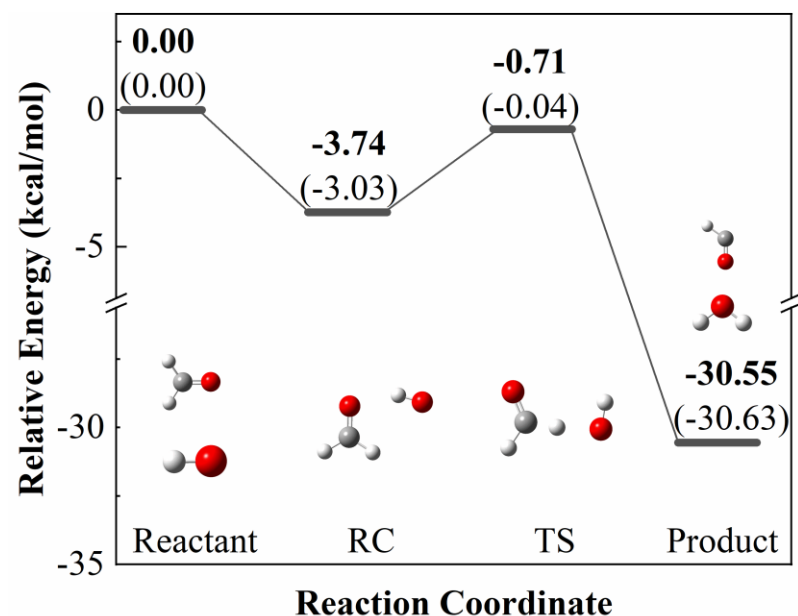
macroscopic concentration of R

The time-evolution of n_{OH} (solid lines) and n_{RC} (dash-dot lines). The initial condition is set as $n_{OH}(t)=0=10^{-7}$ mol/L, $n_{RC}(t)=0$ and n_{HCHO} is assumed to be constant at 10^{-5} mol/L.

TUMME: Tsinghua University Minnesota Master Equation solver

Example 4

■ Hydrogen Abstraction from HCHO by OH (MS-VTST/SCT)

This is an example of a bimolecular reaction. In this example, MS-CVT/SCT is used for reaction 2, and rate constants for reaction 1 are estimated by an inverse Laplace transform applied to the hard-sphere model. The rate constant is extracted from eq. (4) based on CSE theory, and the time evolution is estimated from eq. (5).

Input: the standard input file,
Polyrate file for reaction 2,
MStor files for RC and TS
Output: rate constants and the time-evolution of concentrations.

$$HCHO + OH \xrightarrow{1} HCHO \cdots HO \xrightarrow{2} HCO + H_2O$$

Zhang, R. M.; Chen, W.; Truhlar, D. G.; Xu, X., *Faraday Discussions* **2022**, **238**, 431-460. doi.org/10.1039/D2FD00024E.

TUMME: Tsinghua University Minnesota Master Equation solver

Example 4 (cont.)

■ Standard input file

Global parameters block

```
1   Parameter
2       LJCollision
3           EpsilonM[cm-1]              56.993
4           EpsilonA[cm-1]             191.134
5           DiameterM[A]                  3.74
6           DiameterA[A]                  4.94
7           MassM[amu]                28
8           MassA[amu]                47
9       End_LJCollision
10
11      Edown
12          EDCONST[cm-1]     200
13          Tc[K]             300
14          Exponent          0.85
15      END_Edown
16
17      Temperature[K]
18          100.
19        End_Temperature
20
21      Pressure[torr]
22          10 1E4 1E7
23      End_Pressure
24
25      PseuBimolecular
26          PseuBimName
27              R
28          End_PseuBimName
29
30          ExcessConc[mol/L]
31              1E-5
32          End_ExcessConc
33      End_PseuBimolecular
34
35      GroundSpecies          R
36  End_Parameter
```

Collision

Relaxation

Bimolecular pair(s) with pseudo-first order assumption

```
38  Reaction
39
40      BarrierRxn
41          Info          RC-TS-P
42          Pyrfile     Rxn1.fu6
43          Variation    cvt
44          Tunneling    sct
45          slower[A]    -0.12
46          supper[A]     0.23
47      End_BarrierRxn
48
49      BarrierlessRxn
50          Info                  R-RC
51          Avgdiameter[A]         4.11
52          Rxnenergy[kcal/mol]  -3.734532
53      End_BarrierlessRxn
54
55  End_Reaction
56
57  Species
58      Bim
59          Name R
60          Sp1Mol
61              Name R_f
62              Geometry[A]
63                  .
64                  .
65                  .
```

Reactions block

Barriered elementary reaction, read from Polyrate file

Variation

Tunneling

Range of reaction coordinates

Barrierless elementary reaction , ILT + hard-sphere

Species block

TUMME: Tsinghua University Minnesota Master Equation solver

Example 4 (cont.)

■ Time-evolution file

```
1    #
2    # Time evolution ouput for TUMME
3    # the unit for energy is kcal/mol; the unit for time is second
4    #
5
6    T =          100.00   K, p =  1.000E-03 torr
7    y(E)/time             0.00000E+00   2.00000E-07   4.00000E-07   6.00000E-07   8.00000E-07
8    RC
9    9.93603E+00          -7.69770E-42   4.93115E-26   4.77741E-26   4.62847E-26   4.48416E-26
10   9.91602E+00           0.00000E+00   5.40583E-26   5.23729E-26   5.07401E-26   4.91581E-26
11   9.89601E+00           2.30931E-41   5.92603E-26   5.74127E-26   5.56227E-26   5.38885E-26
12   9.87599E+00          -6.15816E-41   6.49632E-26   6.29379E-26   6.09756E-26   5.90746E-26
13   9.85598E+00           1.53954E-41   7.12143E-26   6.89940E-26   6.68430E-26   6.47590E-26
14   9.83596E+00           0.00000E+00   7.80675E-26   7.56336E-26   7.32755E-26   7.09910E-26
15   9.81595E+00           7.69770E-41   8.55779E-26   8.29098E-26   8.03249E-26   7.78206E-26
16   9.79594E+00          -1.53954E-41   9.38099E-26   9.08852E-26   8.80516E-26   8.53064E-26
17   9.77592E+00           1.53954E-41   1.02833E-25   9.96269E-26   9.65208E-26   9.35115E-26
18   9.75591E+00          -3.07908E-41   1.12723E-25   1.09209E-25   1.05804E-25   1.02505E-25
19   9.73589E+00           9.23724E-41   1.23566E-25   1.19713E-25   1.15981E-25   1.12365E-25
20   9.71588E+00          -1.53954E-40   1.35448E-25   1.31225E-25   1.27134E-25   1.23170E-25
21   9.69587E+00           9.23724E-41   1.48469E-25   1.43840E-25   1.39355E-25   1.35010E-25
22   9.67585E+00           3.07908E-41   1.62743E-25   1.57669E-25   1.52754E-25   1.47991E-25
23   9.65584E+00          -6.15816E-41   1.78390E-25   1.72828E-25   1.67440E-25   1.62219E-25
24   9.63582E+00           1.84745E-40   1.95535E-25   1.89439E-25   1.83533E-25   1.77811E-25
25   9.61581E+00          -1.53954E-40   2.14328E-25   2.07646E-25   2.01172E-25   1.94900E-25
```
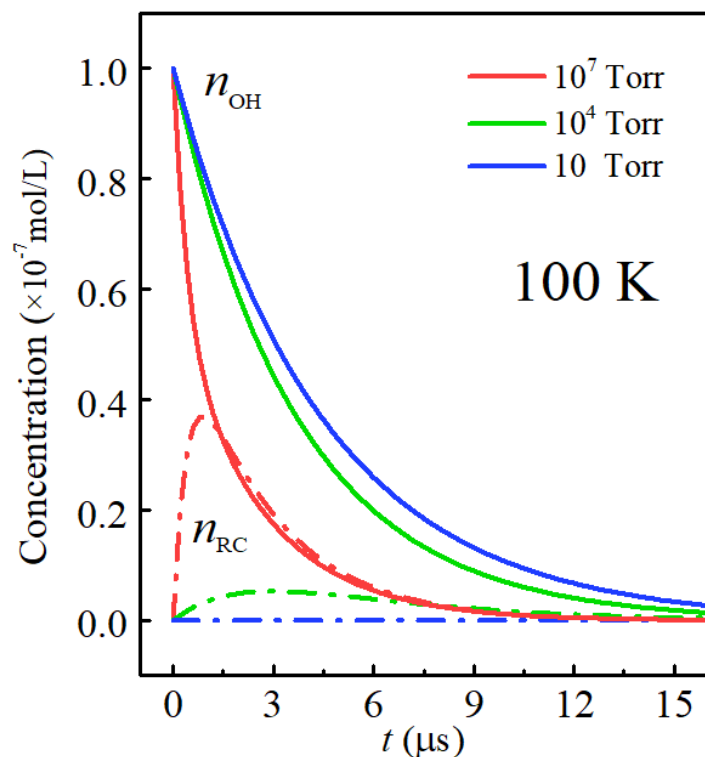
time

energy

microscopic population of RC

```
691  R
692  [n]                    1.00000E+00   9.68821E-01   9.38616E-01   9.09352E-01   8.81001E-01
693
```
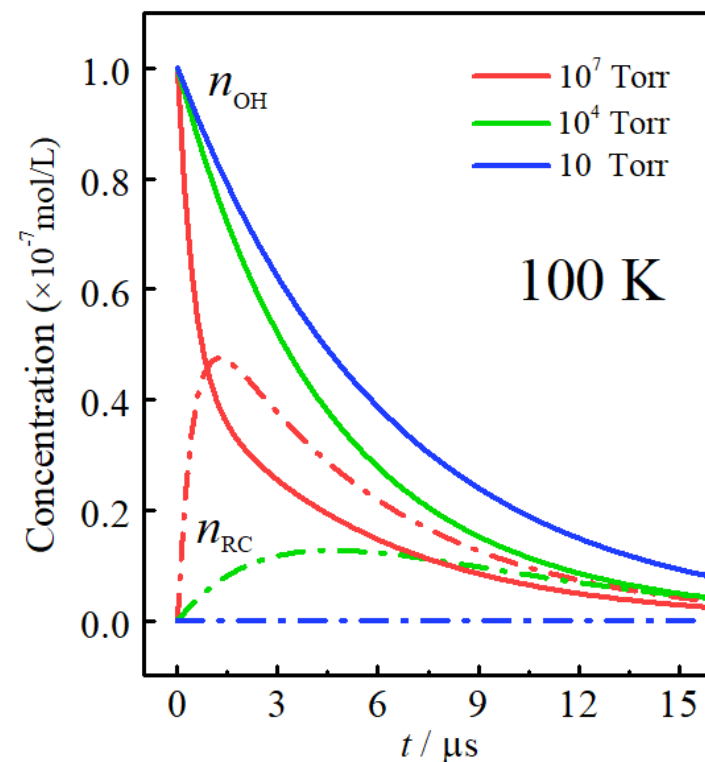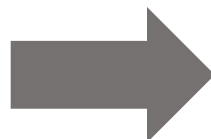
macroscopic concentration of R

The time evolution of n_{OH} (solid lines) and n_{RC} (dash-dot lines). The initial condition is set as $n_{OH}(t=0)=10^{-7}$ mol/L; $n_{RC}(t=0)$ and n_{HCHO} are assumed to be constant at 10^{-5} mol/L.

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Example 4 (cont.)

Comparison with example 3

Time-evolution of the example 3 (TST)

Time-evolution of the example 4 (VTST)

TUMME: Tsinghua University Minnesota Master Equation solver

Thank you for your interest in TUMME.

You are invited to provide feedback to: xuxuefei@tsinghua.edu.cn   and   truhlar@umn.edu

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TUMME: Tsinghua University Minnesota Master Equation solver