Primer to CanTherm

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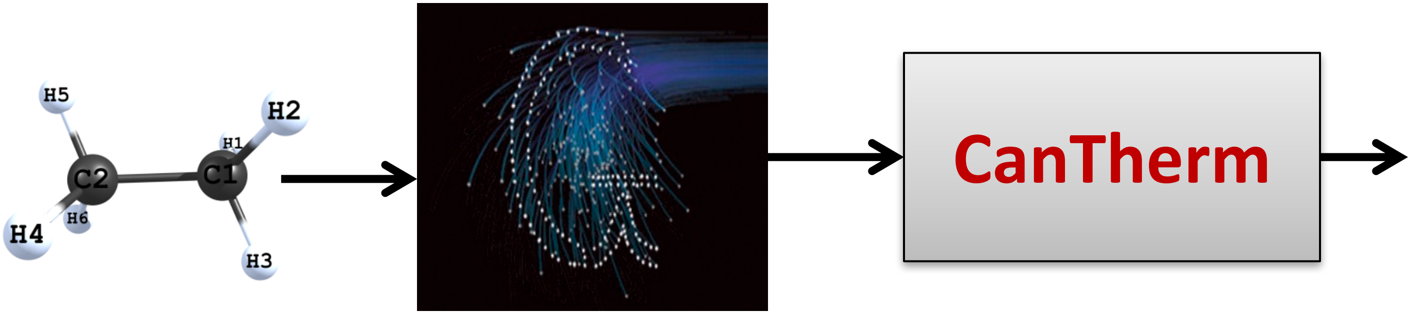
27th Sept 2013

What is CanTherm



Gaussian

CanTherm

1. Thermodynamic Properties
2. Kinetic rate coefficients

What is CanTherm

CanTherm is written in python and can be used for the following calculations

1. Thermodynamic properties of stable molecule (H_{298}, S , Cp(T))
2. High pressure limit rate coefficients
3. Pressure dependent rate coefficients for entire network using either Modified Strong Collision, Reservoir State or Chemically Significant Eigenvalue (CSE) approximations

Theory manual :
https://github.com/GreenGroup/CanTherm/blob/master/manual.pdf

Running CanTherm

For Green group folks it is easiest to use virtual environment setup on pharos on my account
(or alternatively on Connie's)

1. Activate virtualenv

```
source /home/shamel/virtualenv/bin/activate
```

2. Navigate to your input directory

3. Run CanTherm

```
python /home/shamel/RMG-Py/cantherm.py input.py
```

4. Deactivate virtualenv

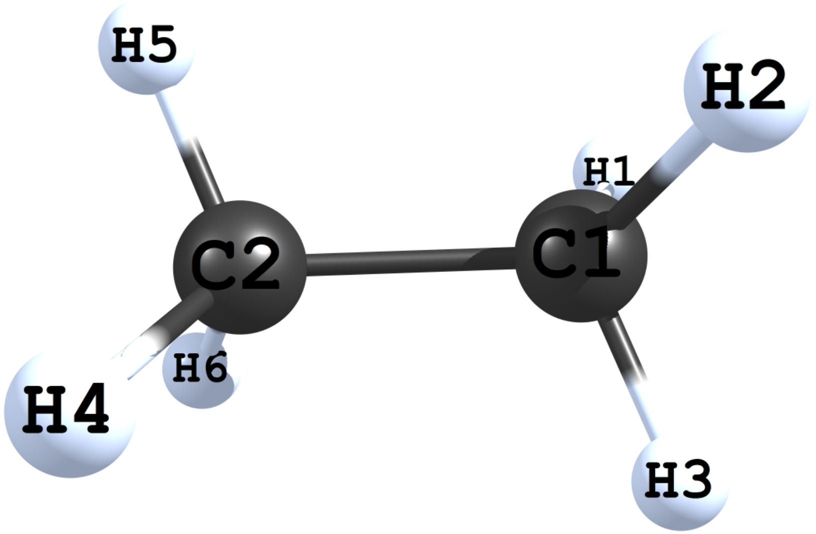
```
deactivate
```

Calculating thermodynamic properties of stable species

What do you need ?

- Gaussian log file containing optimized structure and energy
- Gaussian log file for frequency job with keyword iop(7/33=1) *(only if you want hindered rotors)*
- Gaussian log file for every hindered rotor scan of the system *(only if you want hindered rotors)*
- Species file for CanTherm
- Input file for CanTherm

Species file

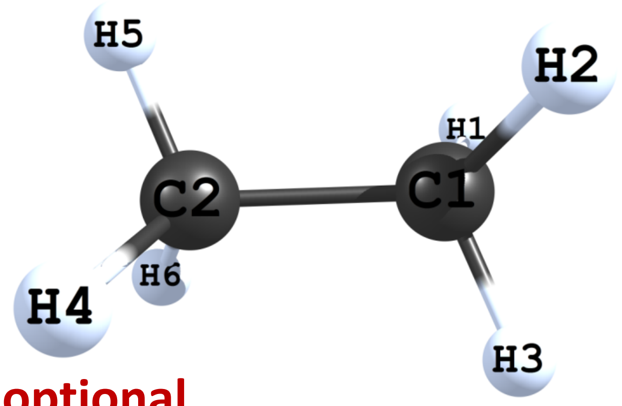


C2H6

Species file

1. Define the number and type of atoms in the molecule

```
atoms =
{
'C': 2,
'H': 6,
}
```



2. Define the different bonds in the molecule, optional.
We have corrections only for CBS-QB3 right now

```
bonds =
{
'C-C': 1,
'C-H': 6,
}
```

3. Linearity of molecule

```
linear = False (or True for molecule like acetylene)
```

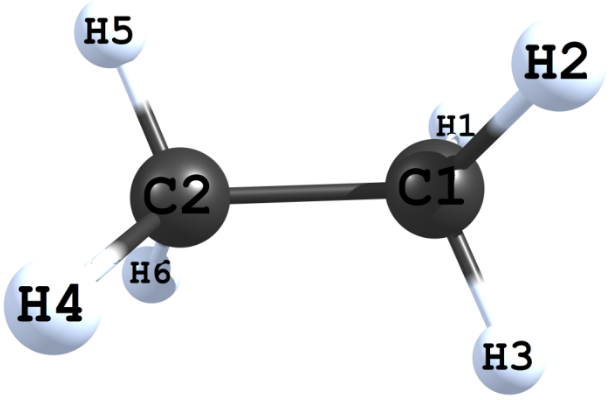
Species file

4. Statistical factors and spin multiplicity

externalSymmetry = 6

spinMultiplicity = 1

opticalIsomers = 1



Statistical factors include symmetry number and chirality correction

Statistical factors are typically introduced via the partition function, *Q*

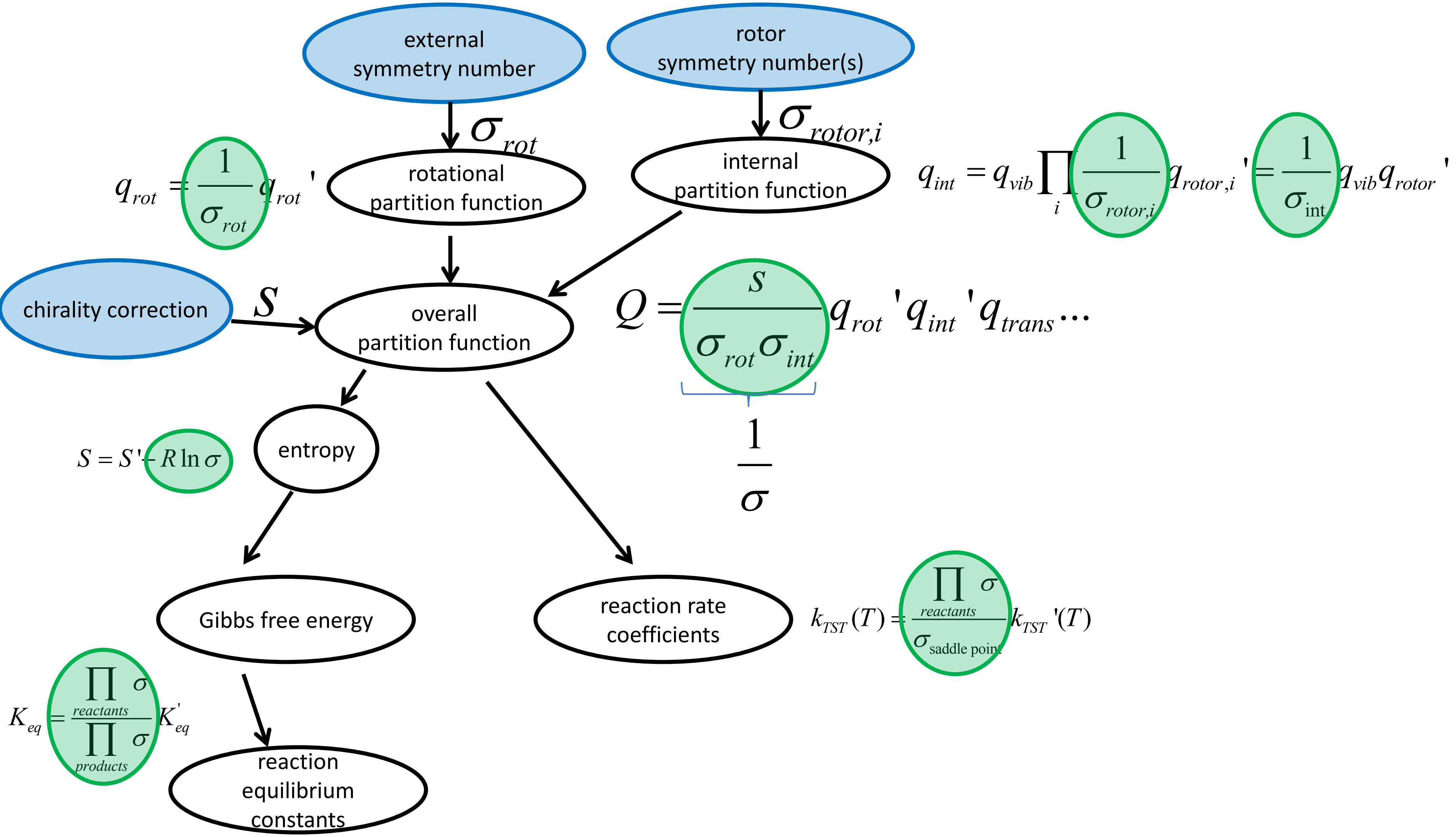
  – Partition functions are multiplied by chirality contribution, divided by the symmetry number

chirality contribution: 2 if chiral; 1 otherwise;
(the number of optical isomers)

$$Q = \frac{s}{\sigma} Q'$$

symmetry number: a positive integer

Statistical effects enter into entropy, equilibrium constants, A-factors, etc.



$$q_{rot} = \frac{1}{\sigma_{rot}} q_{rot}'$$

$$q_{int} = q_{vib} \prod_i \frac{1}{\sigma_{rotor,i}} q_{rotor,i}' = \frac{1}{\sigma_{int}} q_{vib} q_{rotor}'$$

$$Q = \underbrace{\frac{s}{\sigma_{rot}\sigma_{int}}}_{\frac{1}{\sigma}} q_{rot}' q_{int}' q_{trans} \cdots$$

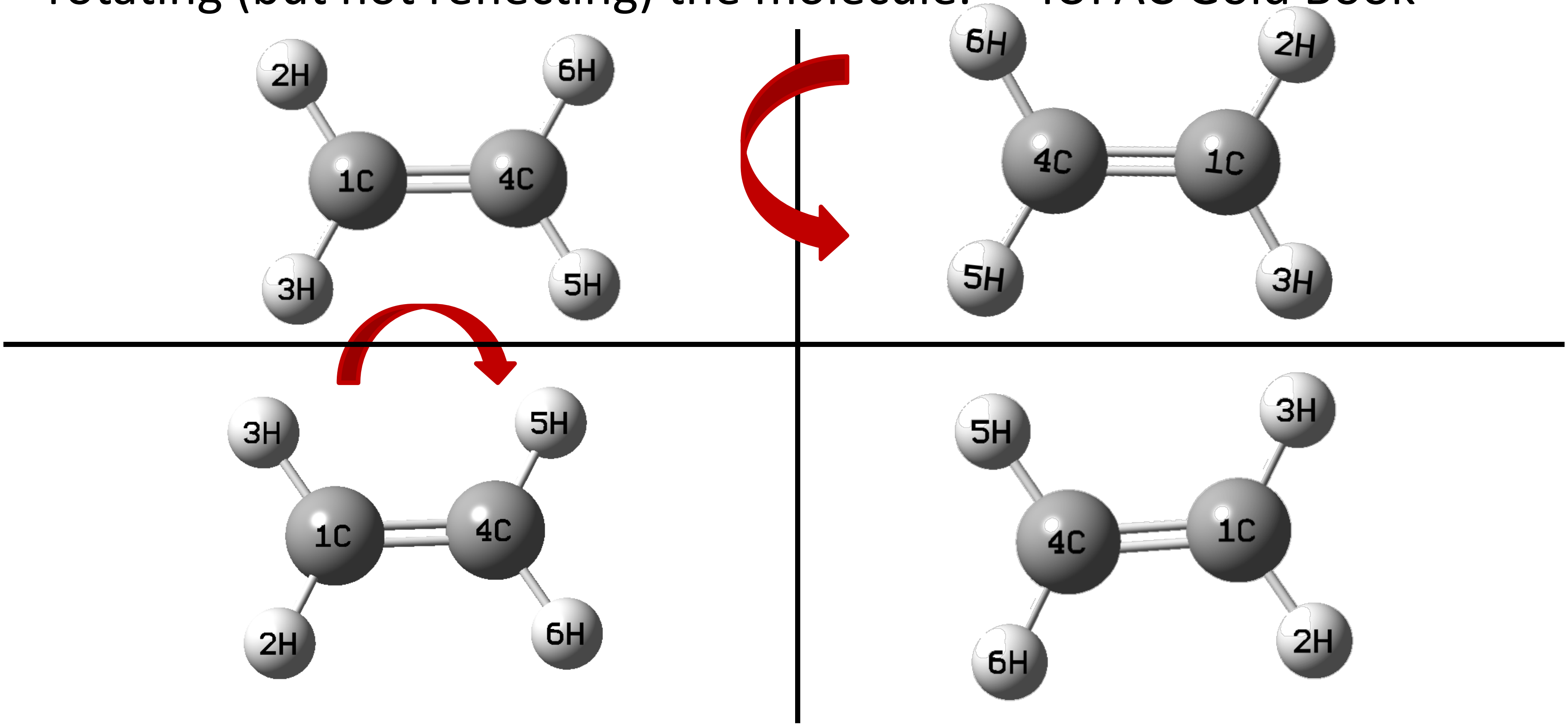
$$S = S' - R\ln\sigma$$

$$k_{TST}(T) = \frac{\prod_{reactants} \sigma}{\sigma_{\text{saddle point}}} k_{TST}'(T)$$

$$K_{eq} = \frac{\prod_{reactants} \sigma}{\prod_{products} \sigma} K_{eq}'$$

External symmetry number

"The symmetry number of a molecule is obtained by imagining all identical atoms to be labeled, and then counting the number of different but equivalent arrangements that can be obtained by rotating (but not reflecting) the molecule."—IUPAC Gold Book



How to figure out external symmetry number

Point group uniquely determines external symmetry number

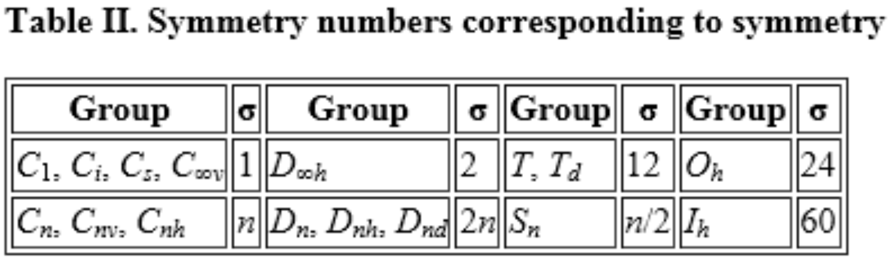
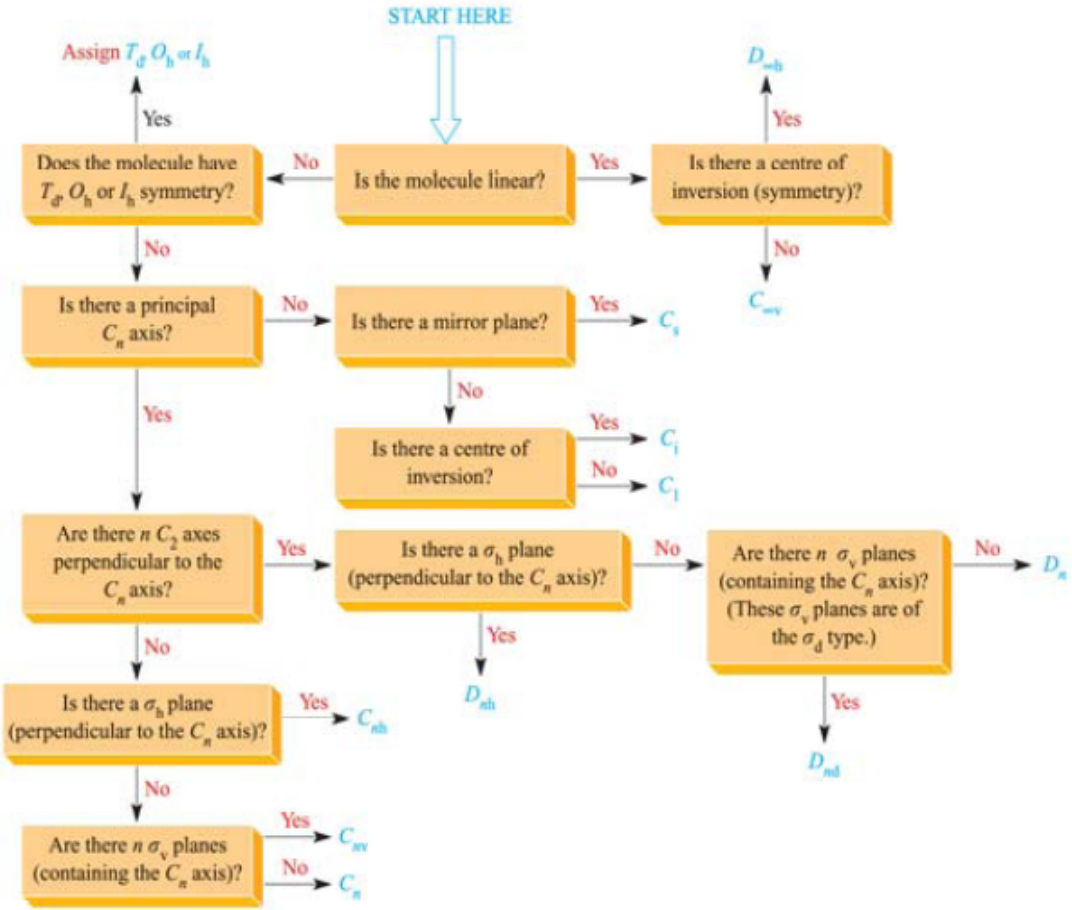


Table II. Symmetry numbers corresponding to symmetry point groups

Group	σ	Group	σ	Group	σ	Group	σ
C_1, C_i, C_s, $C_{\infty v}$	1	$D_{\infty h}$	2	T, T_d	12	O_h	24
C_n, C_{nv}, C_{nh}	n	D_n, D_{nh}, D_{nd}	$2n$	S_n	$n/2$	I_h	60

http://cccbdb.nist.gov/thermo.asp

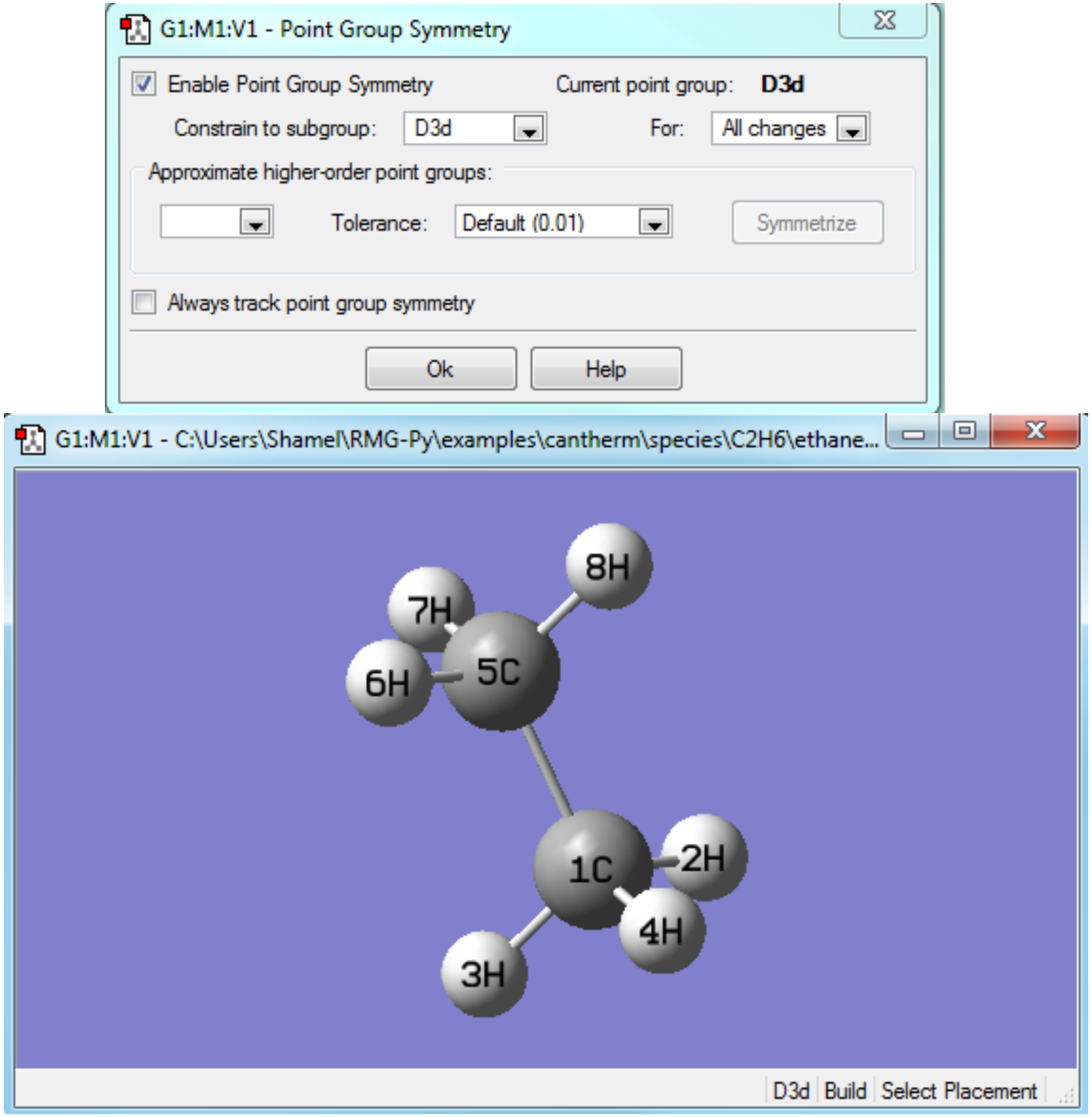
Determining point group



Scheme for assigning point groups of molecules and molecular ions. Apart from the cases of $n = 1$ or ∞, n most commonly has values of 2, 3, 4, 5 or 6.

Catherine E. Housecroft and Alan G.Sharpe: *Inorganic Chemistry* 2e © Pearson Education 2005

Easy way of calculating the point group



G1:M1:V1 - Point Group Symmetry

☑ Enable Point Group Symmetry

Current point group: **D3d**

Constrain to subgroup: D3d

For: All changes

Approximate higher-order point groups:

Tolerance: Default (0.01)

☐ Always track point group symmetry

G1:M1:V1 - C:\Users\Shamel\RMG-Py\examples\cantherm\species\C2H6\ethane...

D3d Build Select Placement

Note: This can be inaccurate, check by making the tolerance loose.

Determining spin multiplicity

Spin multiplicity is determined by the 2S+1 rule

↑ Radical

Multiplicity = 2 (1/2) + 1 = 2 (Doublet)

↑↓ Paired electron

Multiplicity = 2 (0) + 1 = 1 (Singlet)

↑ ↑ Unpaired electron

Multiplicity = 2 (1) + 1 = 3 (Triplet)

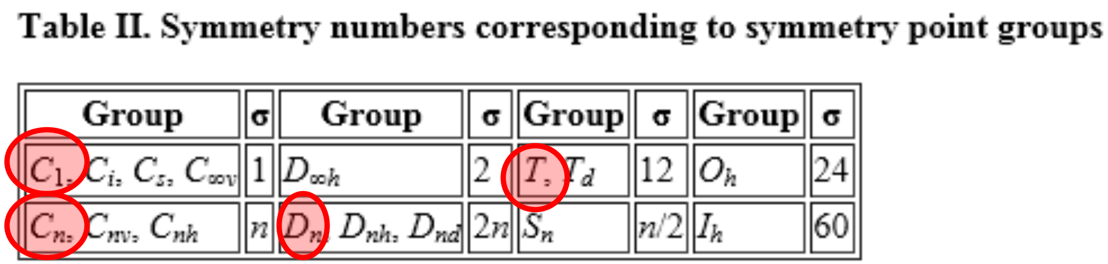
Determining chirality

- **A molecular configuration is chiral if and only if its mirror image is non-superposable**

- Carbon atom bonded to 4 distinct ligands?
  Sufficient for chiral *center* ("local" chirality)
  Neither necessary nor sufficient for overall chirality
    Chirality can also arise from:
      Axial chirality (helicity)
      Planar chirality
      Inherent chirality

- A molecular configuration is not chiral if it contains a plane of symmetry
- Certain conformations can have chiral molecular configurations even when the molecule is not optically active

Easy way of calculating chirality



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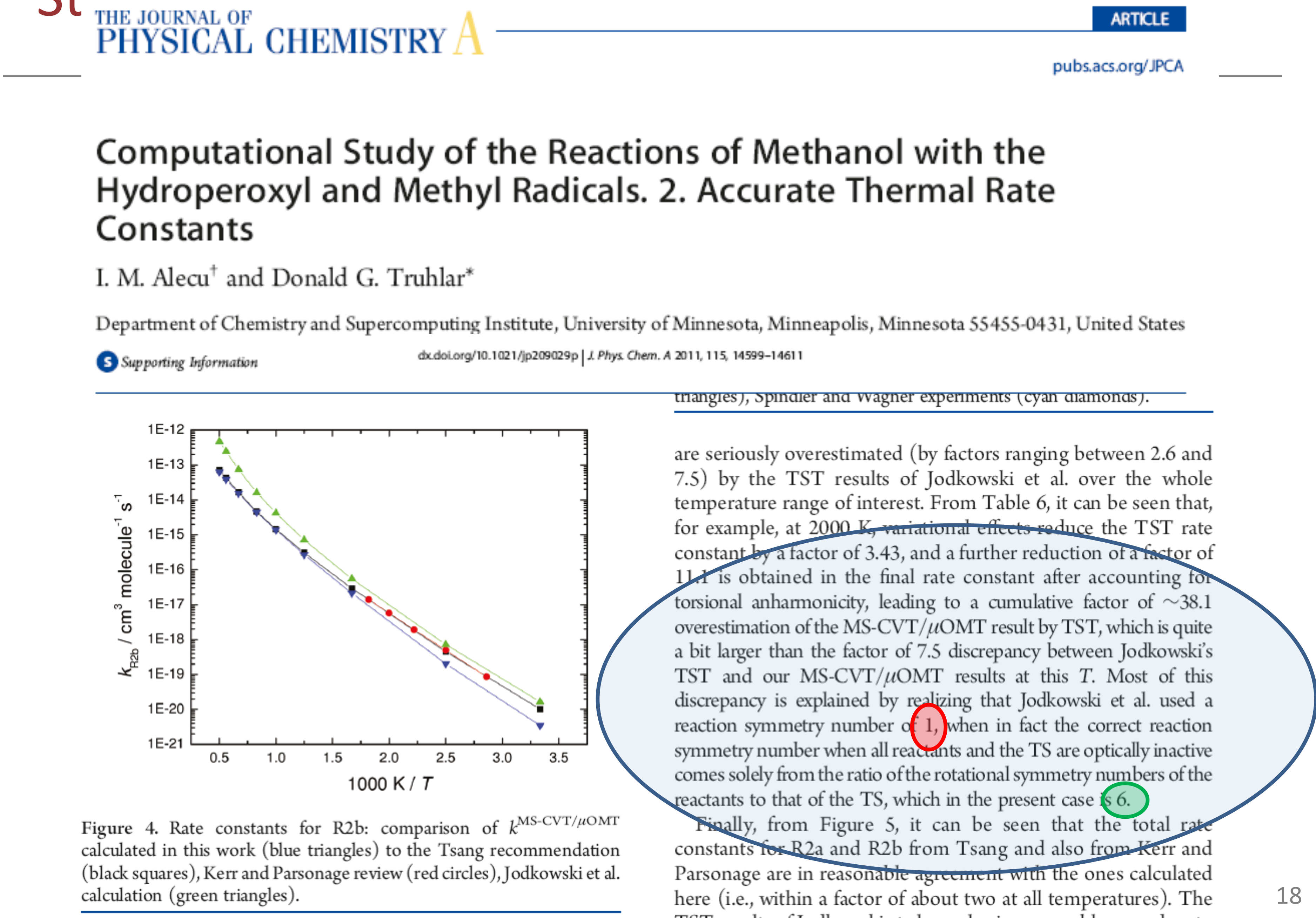
C_n, C_{nv}, C_{nh}	n	D_n, D_{nh}, D_{nd}	$2n$	S_n	$n/2$	I_h	60

Point groups (circled above) lacking σ_v, σ_d, σ_h (planes of symmetry) and S_n (improper rotation axis) symmetry elements correspond to chiral molecular configurations

St



THE JOURNAL OF PHYSICAL CHEMISTRY A

ARTICLE

pubs.acs.org/JPCA

Computational Study of the Reactions of Methanol with the Hydroperoxyl and Methyl Radicals. 2. Accurate Thermal Rate Constants

I. M. Alecu[†] and Donald G. Truhlar[*]

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States

Supporting Information

dx.doi.org/10.1021/jp209029p | J. Phys. Chem. A 2011, 115, 14599–14611

Figure 4. Rate constants for R2b: comparison of $k^{\text{MS-CVT}/\mu\text{OMT}}$ calculated in this work (blue triangles) to the Tsang recommendation (black squares), Kerr and Parsonage review (red circles), Jodkowski et al. calculation (green triangles).

triangles), Spindler and Wagner experiments (cyan diamonds).

are seriously overestimated (by factors ranging between 2.6 and 7.5) by the TST results of Jodkowski et al. over the whole temperature range of interest. From Table 6, it can be seen that, for example, at 2000 K, variational effects reduce the TST rate constant by a factor of 3.43, and a further reduction of a factor of 11.1 is obtained in the final rate constant after accounting for torsional anharmonicity, leading to a cumulative factor of ~38.1 overestimation of the MS-CVT/μOMT result by TST, which is quite a bit larger than the factor of 7.5 discrepancy between Jodkowski's TST and our MS-CVT/μOMT results at this T. Most of this discrepancy is explained by realizing that Jodkowski et al. used a reaction symmetry number of 1, when in fact the correct reaction symmetry number when all reactants and the TS are optically inactive comes solely from the ratio of the rotational symmetry numbers of the reactants to that of the TS, which in the present case is 6.

Finally, from Figure 5, it can be seen that the total rate constants for R2a and R2b from Tsang and also from Kerr and Parsonage are in reasonable agreement with the ones calculated here (i.e., within a factor of about two at all temperatures). The

Species file

5. Energy, geometry and frequencies

```
energy = {
'CBS-QB3': GaussianLog('ethane_cbsqb3.log'),
‘CCSD(T)-F12/cc-pVDZ-F12': -79.64199436,
}

geometry = GaussianLog('ethane_cbsqb3.log')
frequencies = GaussianLog('ethane_cbsqb3.log')
```

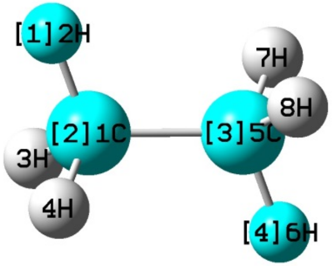
Energy in Hartrees
does not include ZPE

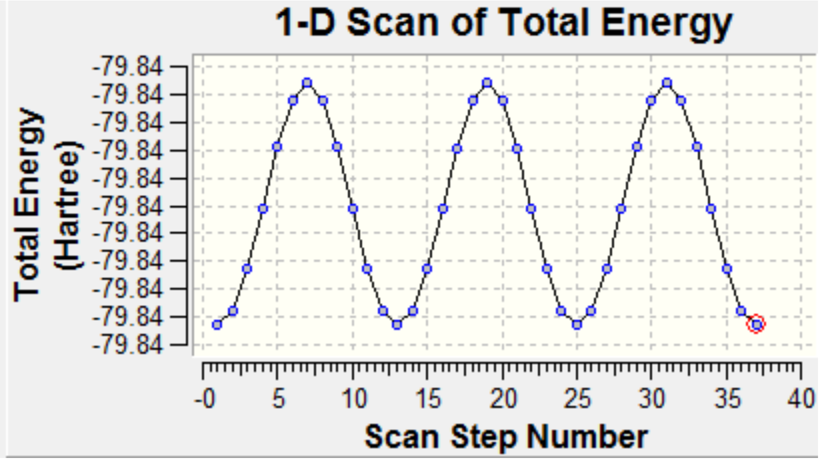
Species file

6. Hindered rotors

```
rotors = [
HinderedRotor(
scanLog=GaussianLog('ethane_scan_1.log'), pivots=[1,5], top=[1,2,3,4],
symmetry=3, fit='best‘
),
]
```

Fit potential to Fourier series or cosine





Internal symmetry number of 3

Input file for thermo

```
modelChemistry = “CBS-QB3“

frequencyScaleFactor = 0.99
useHinderedRotors = True
useBondCorrections = False

species('C2H6', 'C2H6.py')
statmech('C2H6')
thermo('C2H6', 'NASA')
```

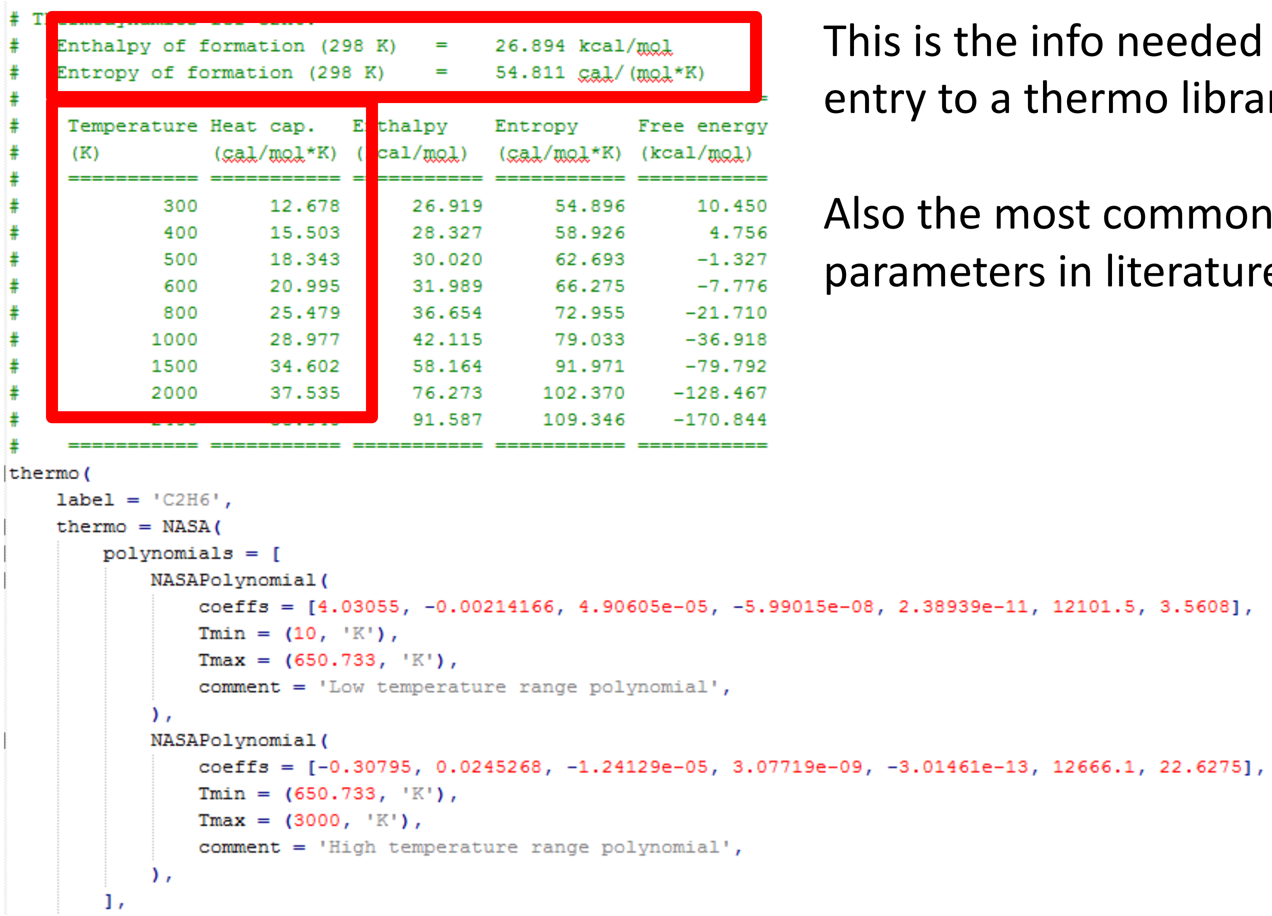
Which model chemistry energy you want to use? (Remember your species file can have multiple methods)

Frequency scale factor

Output the thermo in NASA or Wilhoit form

Cantherm Thermo Output

Scroll down to the bottom of output.py:



```
# T
#   Enthalpy of formation (298 K)   =     26.894 kcal/mol
#   Entropy of formation (298 K)    =     54.811 cal/(mol*K)
#                                                           =
#    Temperature Heat cap.   E thalpy    Entropy     Free energy
#    (K)         (cal/mol*K) ( cal/mol)  (cal/mol*K) (kcal/mol)
#    =========== =========== =========== =========== ===========
#            300      12.678      26.919      54.896      10.450
#            400      15.503      28.327      58.926       4.756
#            500      18.343      30.020      62.693      -1.327
#            600      20.995      31.989      66.275      -7.776
#            800      25.479      36.654      72.955     -21.710
#           1000      28.977      42.115      79.033     -36.918
#           1500      34.602      58.164      91.971     -79.792
#           2000      37.535      76.273     102.370    -128.467
#                                 91.587     109.346    -170.844
#    =========== =========== =========== =========== ===========
thermo(
    label = 'C2H6',
    thermo = NASA(
        polynomials = [
            NASAPolynomial(
                coeffs = [4.03055, -0.00214166, 4.90605e-05, -5.99015e-08, 2.38939e-11, 12101.5, 3.5608],
                Tmin = (10, 'K'),
                Tmax = (650.733, 'K'),
                comment = 'Low temperature range polynomial',
            ),
            NASAPolynomial(
                coeffs = [-0.30795, 0.0245268, -1.24129e-05, 3.07719e-09, -3.01461e-13, 12666.1, 22.6275],
                Tmin = (650.733, 'K'),
                Tmax = (3000, 'K'),
                comment = 'High temperature range polynomial',
            ),
        ],
```

This is the info needed to make an entry to a thermo library

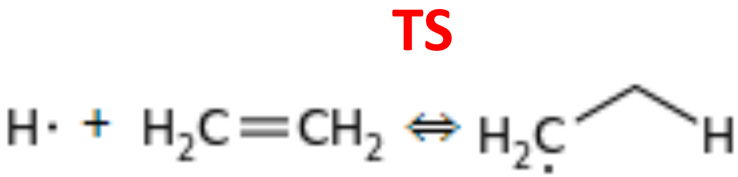
Also the most commonly listed parameters in literature.

To calculate the high pressure limit rate coefficient

You need to setup the species file for all the species in your system

Setup the input file for transition state

Setup input file for the reaction



In all will need to setup 5 files to calculate the rate coefficient

Input file for rate coefficient

```
modelChemistry = "CBS-QB3“
frequencyScaleFactor = 0.99
useHinderedRotors = True
useBondCorrections = False
```

Model chemistry

```
species('H', '../../species/H/H.py')
species('C2H4', '../../species/C2H4/ethene.py')
species('C2H5', '../../species/C2H5/ethyl.py')
transitionState('TS', 'TS.py')
```

Location of the species file

```
reaction(
label = 'H + C2H4 <=> C2H5',    reactants = ['H', 'C2H4'],
products = ['C2H5'],
transitionState = 'TS',
tunneling='Eckart',
)
```

Definition of the reaction

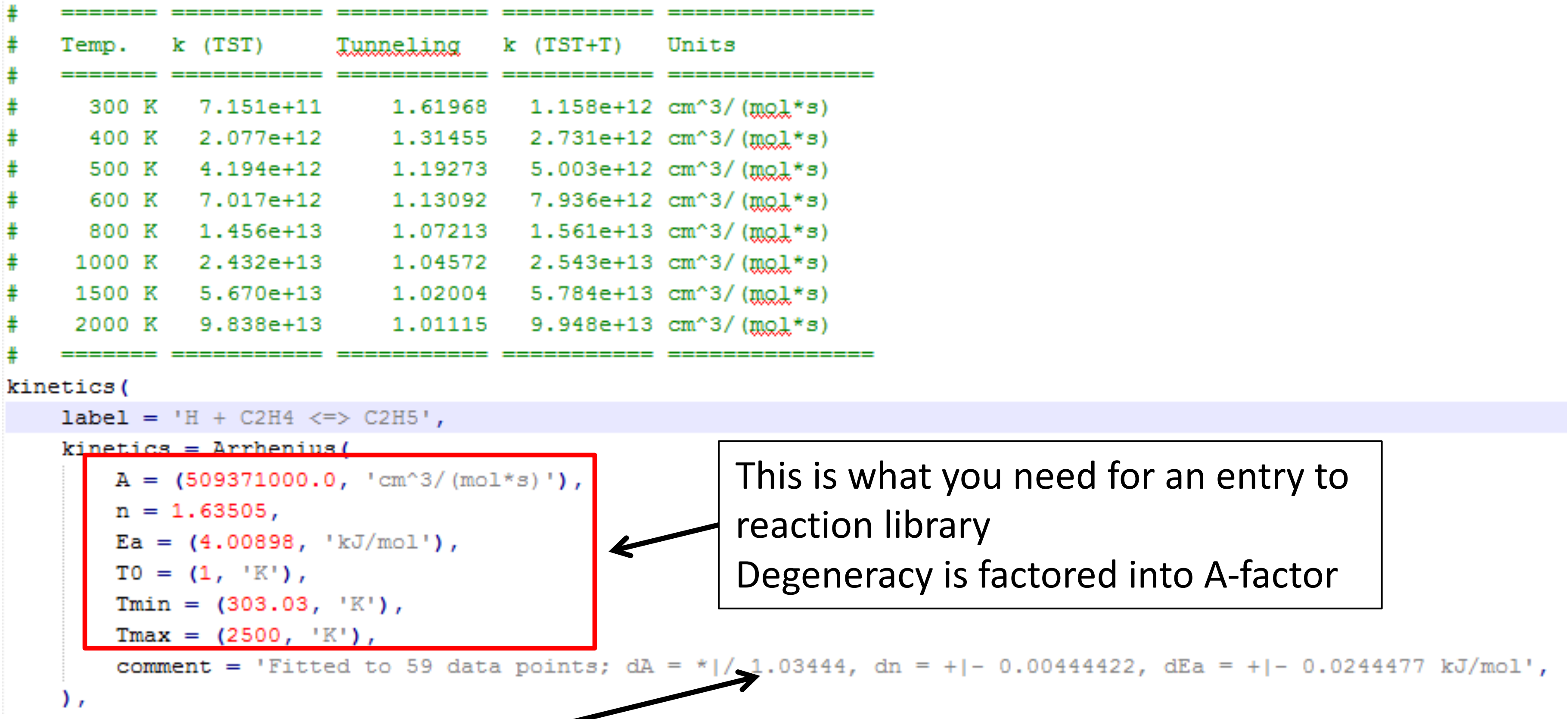
Type of tunneling
Eckart or Wigner

```
kinetics('H + C2H4 <=> C2H5')
```

Calculate the kinetics

Cantherm Kinetics Output

Scroll down to the bottom of output.py:

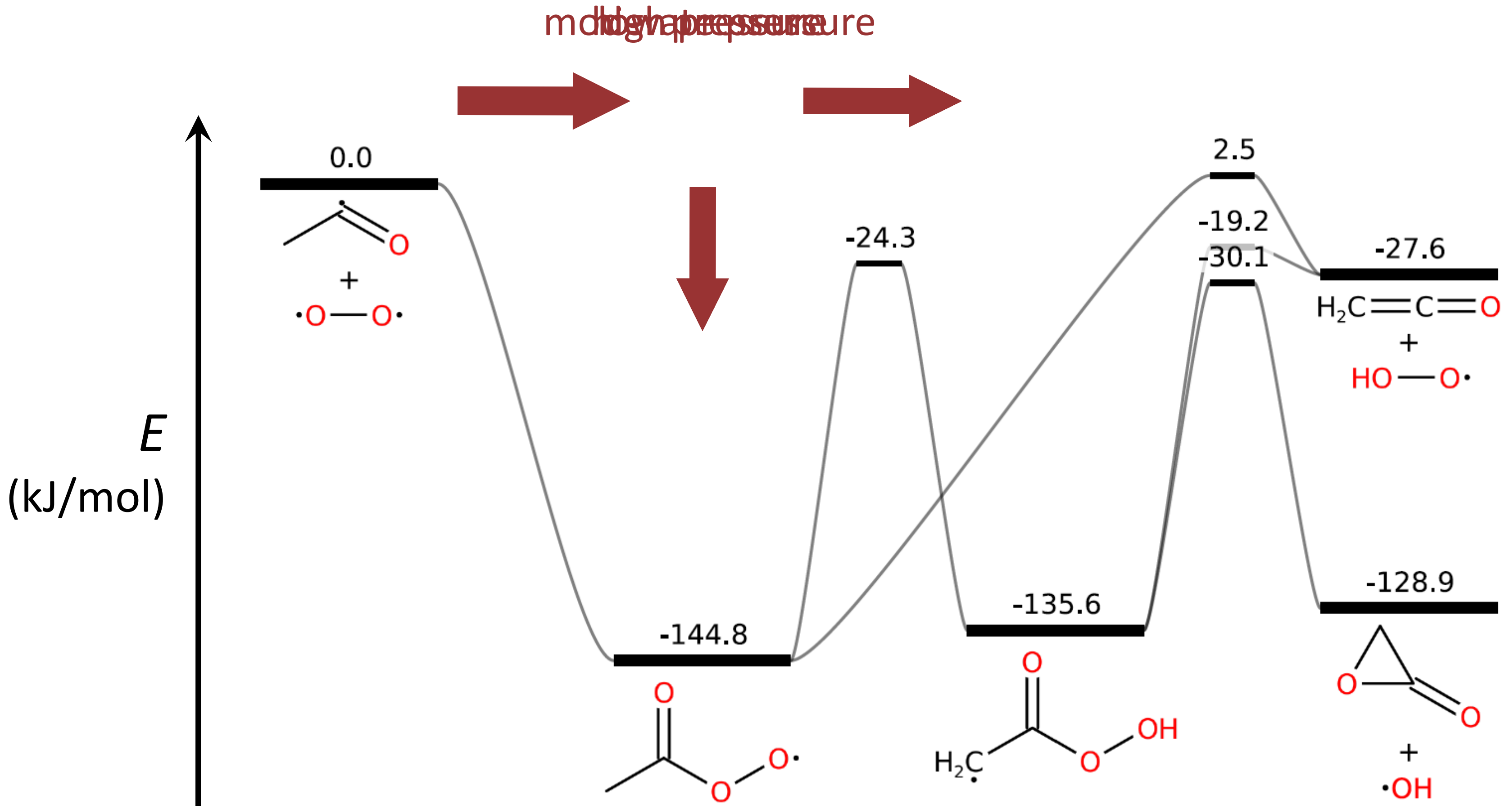


```
#   ======= =========== =========== =========== ===============
#   Temp.   k (TST)     Tunneling   k (TST+T)   Units
#   ======= =========== =========== =========== ===============
#     300 K   7.151e+11     1.61968   1.158e+12 cm^3/(mol*s)
#     400 K   2.077e+12     1.31455   2.731e+12 cm^3/(mol*s)
#     500 K   4.194e+12     1.19273   5.003e+12 cm^3/(mol*s)
#     600 K   7.017e+12     1.13092   7.936e+12 cm^3/(mol*s)
#     800 K   1.456e+13     1.07213   1.561e+13 cm^3/(mol*s)
#    1000 K   2.432e+13     1.04572   2.543e+13 cm^3/(mol*s)
#    1500 K   5.670e+13     1.02004   5.784e+13 cm^3/(mol*s)
#    2000 K   9.838e+13     1.01115   9.948e+13 cm^3/(mol*s)
#   ======= =========== =========== =========== ===============
kinetics(
    label = 'H + C2H4 <=> C2H5',
    kinetics = Arrhenius(
        A = (509371000.0, 'cm^3/(mol*s)'),
        n = 1.63505,
        Ea = (4.00898, 'kJ/mol'),
        T0 = (1, 'K'),
        Tmin = (303.03, 'K'),
        Tmax = (2500, 'K'),
        comment = 'Fitted to 59 data points; dA = *|/ 1.03444, dn = +|- 0.00444422, dEa = +|- 0.0244477 kJ/mol',
    ),
```

This is what you need for an entry to reaction library
Degeneracy is factored into A-factor

Error from fitting is **NOT** total error on kinetics

Changing pressure can dramatically change product branching ratios in multi-well networks.



moderate pressure

low pressure

high pressure

Questions

$$k = \kappa \frac{k_b T}{h} \frac{Q_{ts}}{\Pi Q_R} \exp(\frac{-E_0}{k_b T})$$

$Q = Q_{trans} Q_{rot} Q_{vib} Q_{el}$

$S = k_b \ln Q + k_b T \frac{d \ln Q}{dT}$