# Optimization Techniques – locate a transition state

- Locating minima for functions is fairly easy.

- Finding first-order saddle points, *transition structures* (TS), is much more difficult.

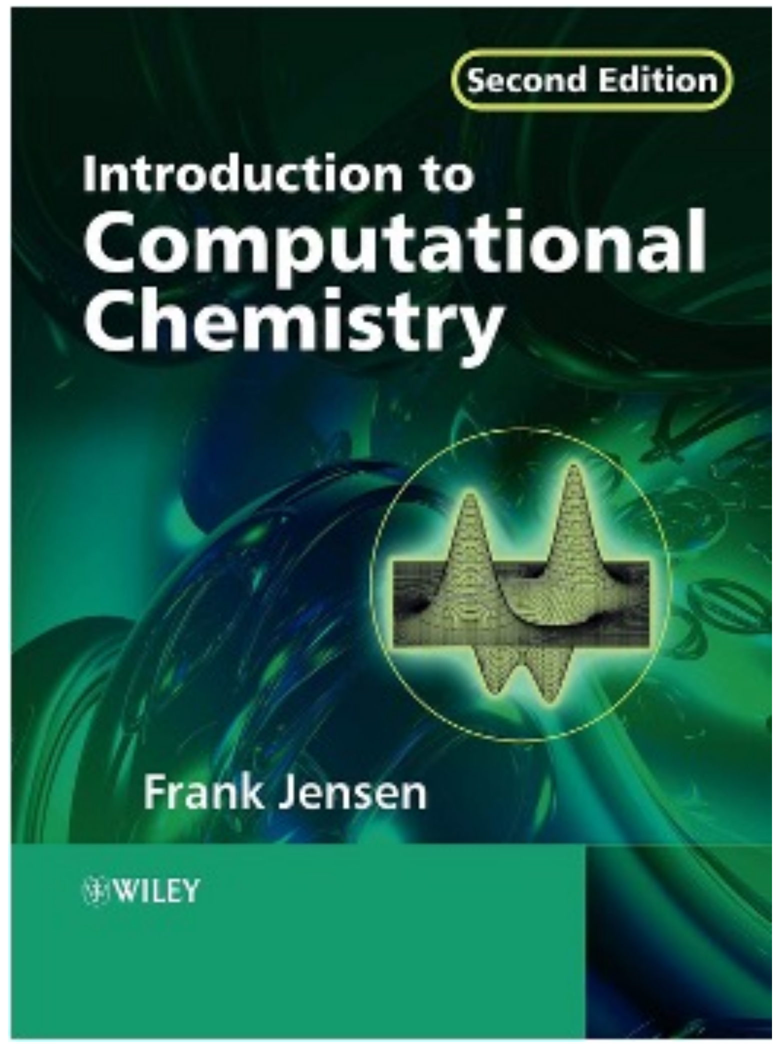
- There are *no* general methods that are guaranteed to work!

- Many different strategies have been proposed.

  - ***One-structure interpolation methods:***
    - ✓ *Linear Synchronous Transit* (LST) method.
    - ✓ *Quadratic Synchronous Transit* (QST).
    - ✓ *Synchronous Transit-guided Quasi-Newton* (STQN).

  - ***Two-structure interpolation methods***
    - ✓ *Saddle* algorithm.
    - ✓ *Step-and-Slide* algorithm.

  - ***Multi-structure interpolation method***
    - ✓ *Self-Penalty Walk* (SPW) method.
    - ✓ *Locally Updated Planes* (LUP) minimization.
    - ✓ *Conjugate Peak Refinement* (CPR) method.
    - ✓ *Nudged Elastic Band* (NEB) method.



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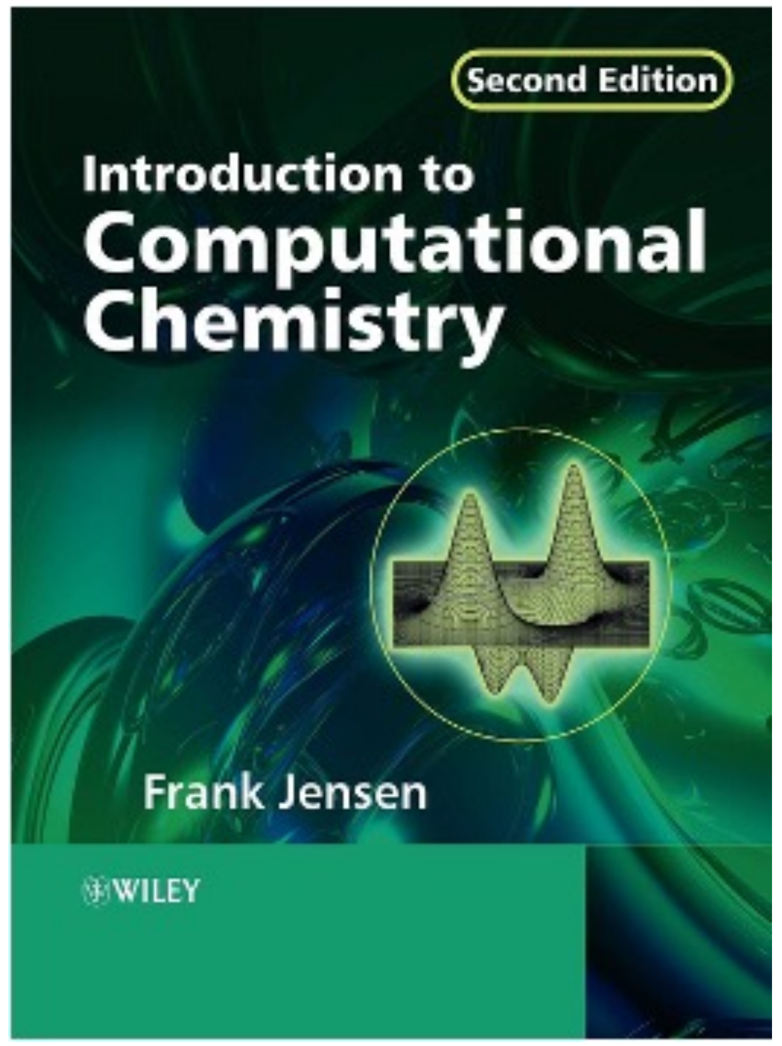
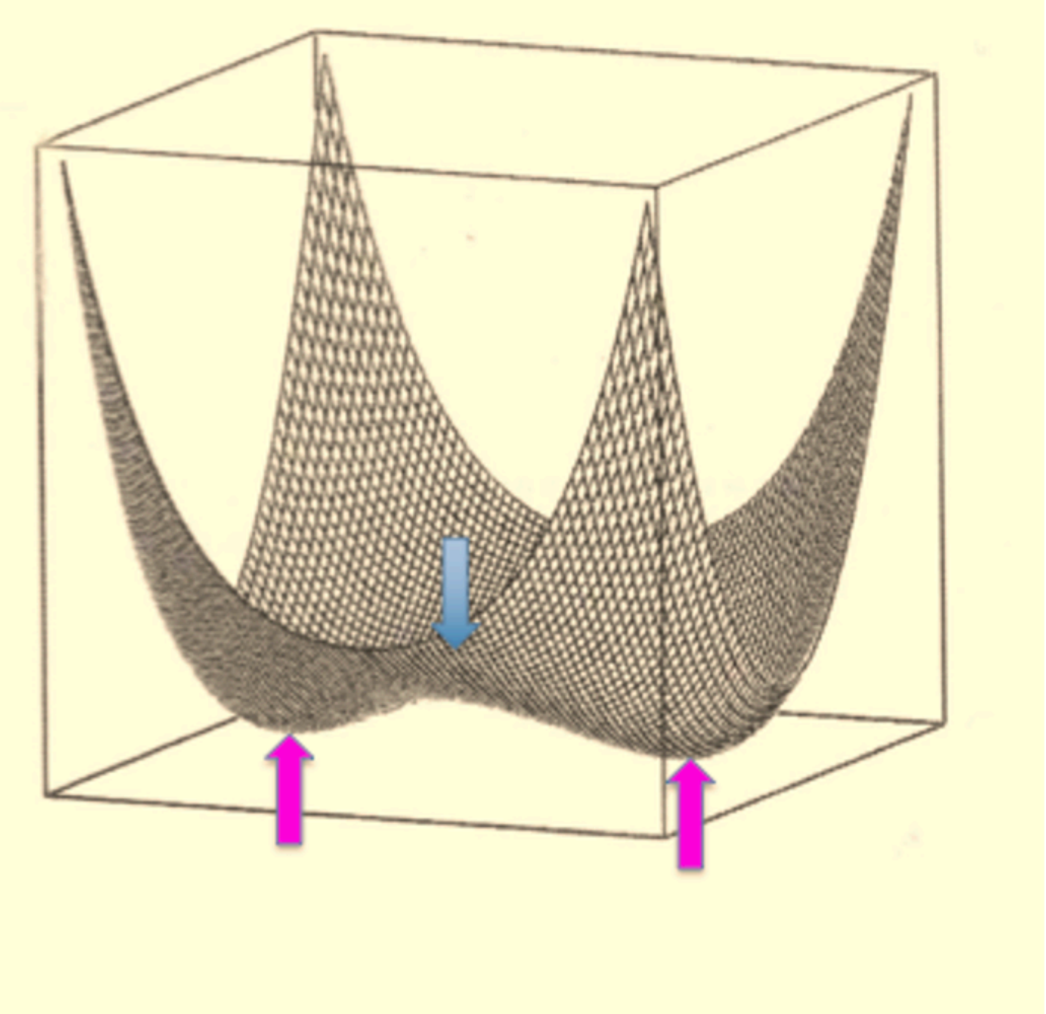
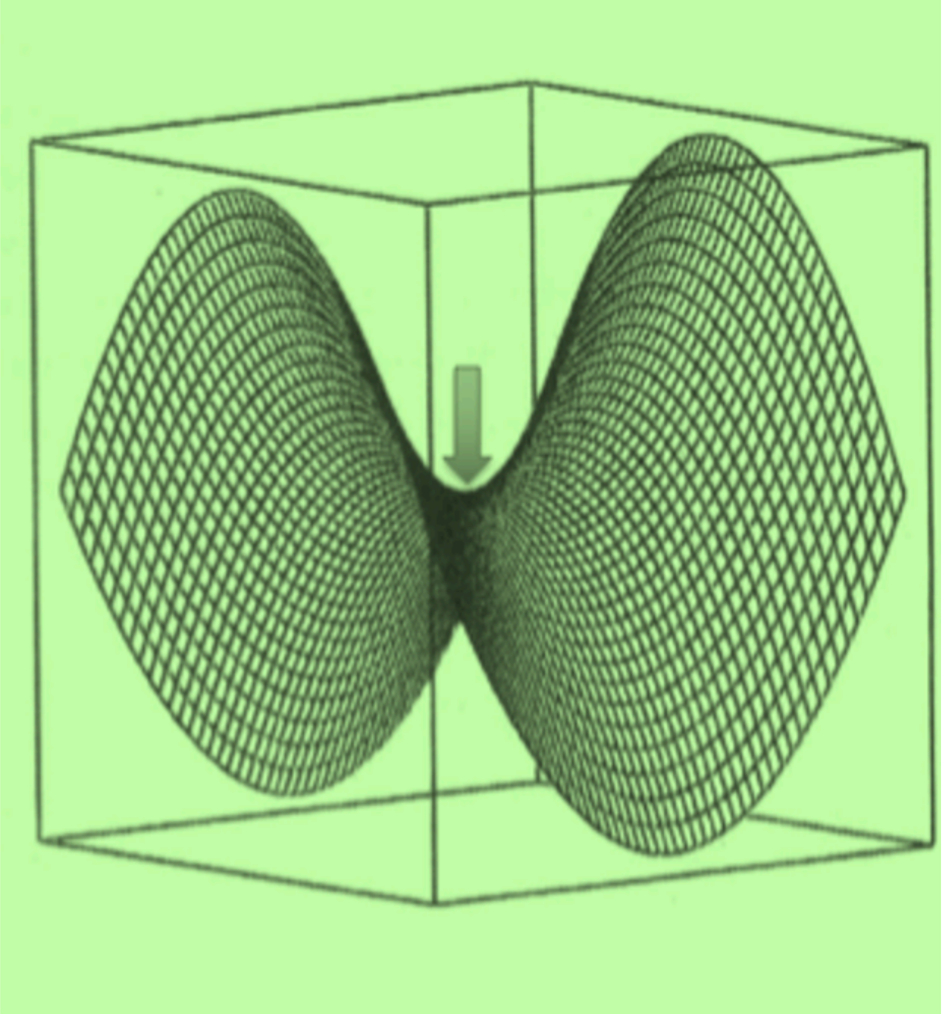



Two minima and a saddlepoint


Saddlepoint
=transition state

ORCA 6.0 TUTORIALS

SEARCH

**FIRST STEPS**

- How to cite
- Installing ORCA
- Hello water! Your first ORCA calculation
- Input and Output
- Running a calculation in parallel
- Graphical User Interfaces (GUI)

# Finding Transition States with NEB-TS

Suppose you wanted to predict the transition state (TS) for the hydrolysis of methyl-acetate into acetic acid and methanol:

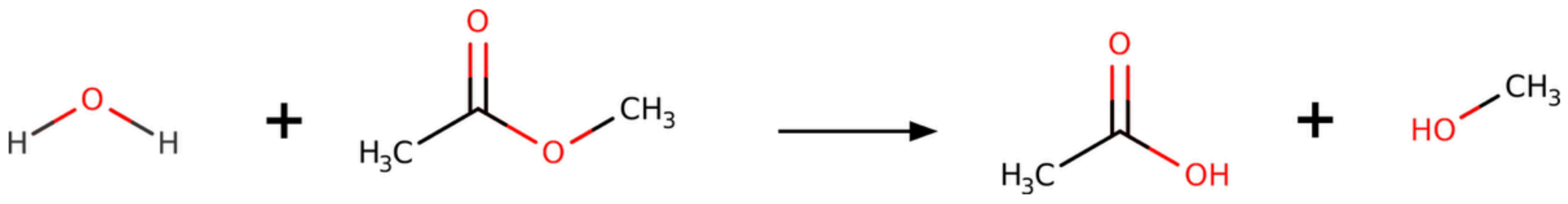


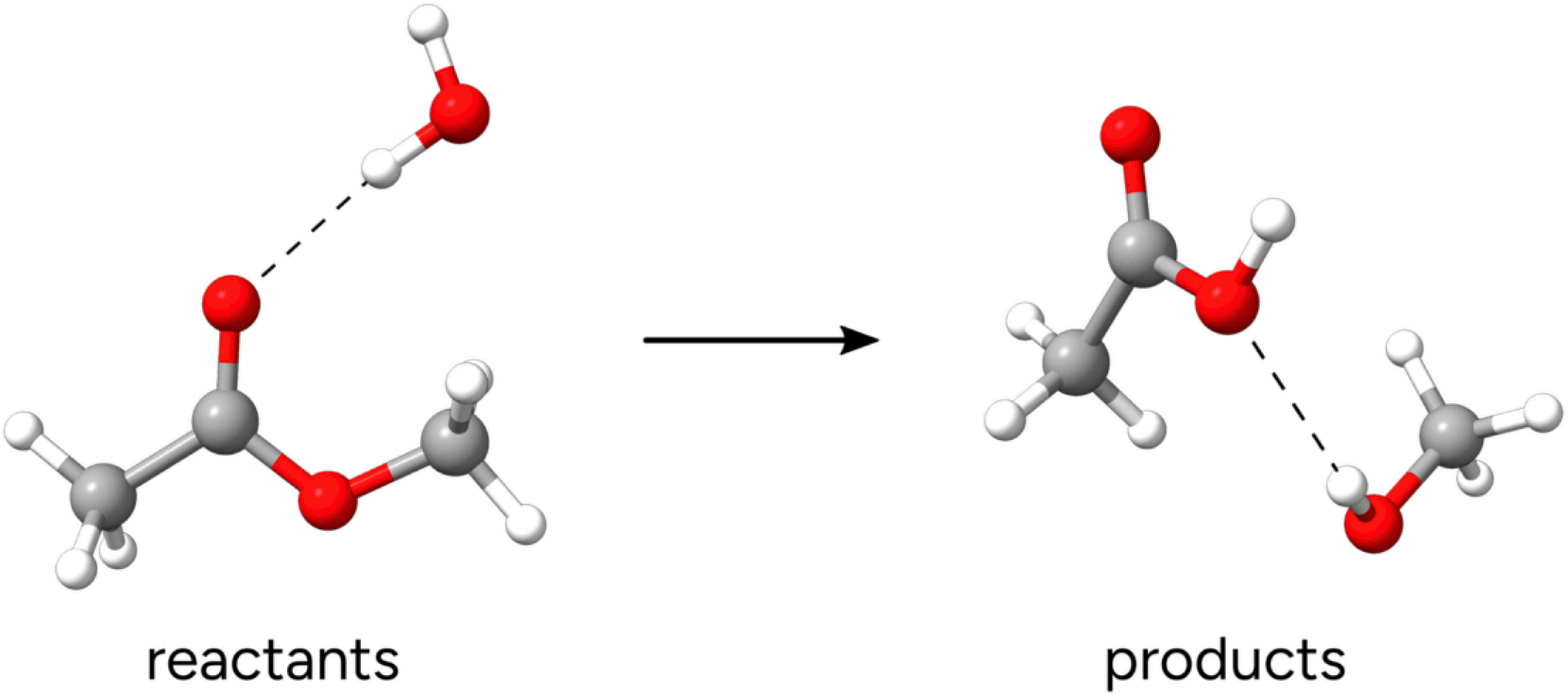
**Figure: Hydrolysis reaction of methyl-acetate.**

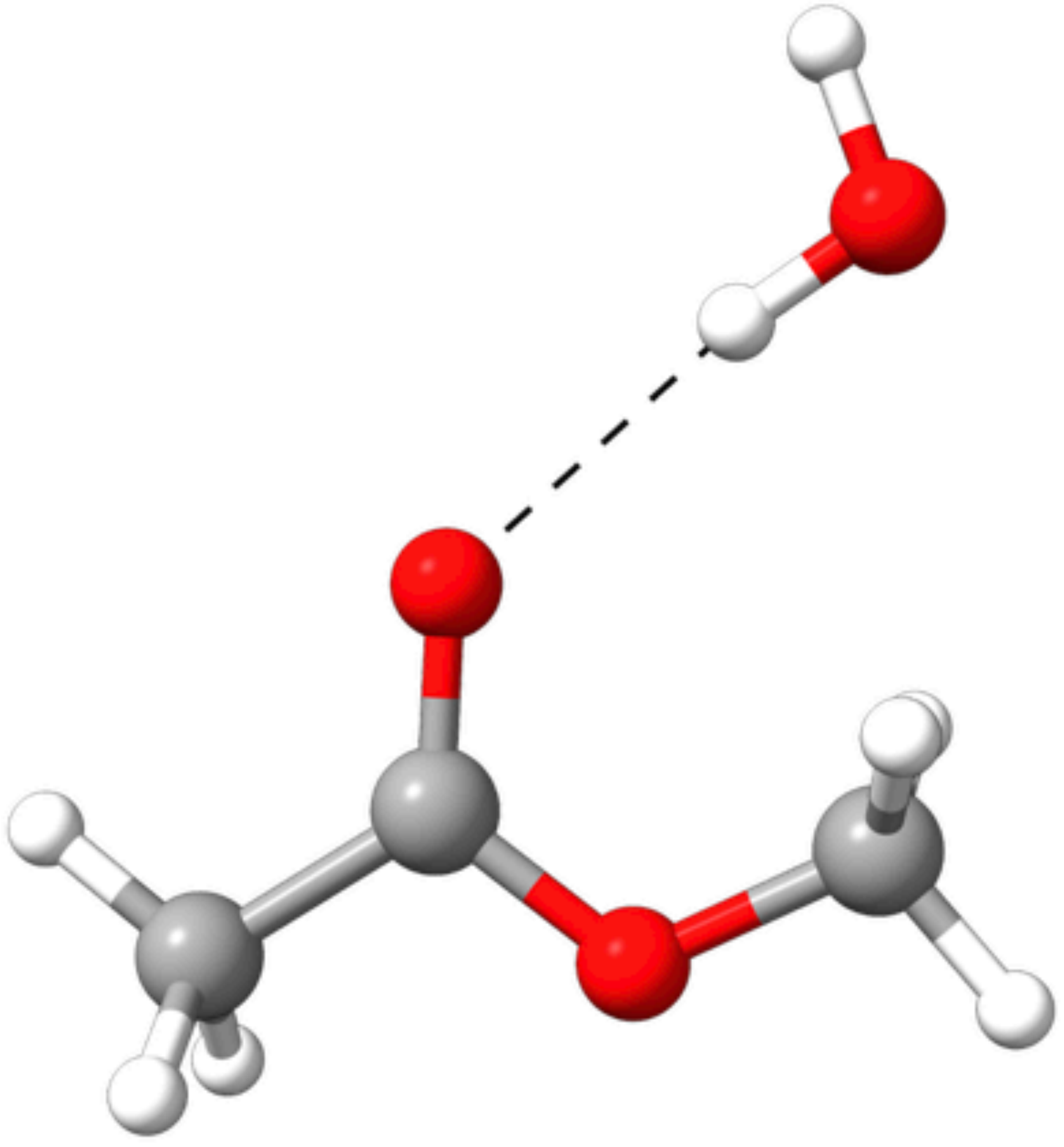
Maybe you need to investigate the mechanism, or even to compute the $\Delta G^{\ddagger}$ and try to predict reaction rates. How could one do that using theory?

In ORCA there is a black box method called NEB-TS (from Nudged Elastic Band with TS optimization), that can find the TS structure only from the geometries of the reactants and products!

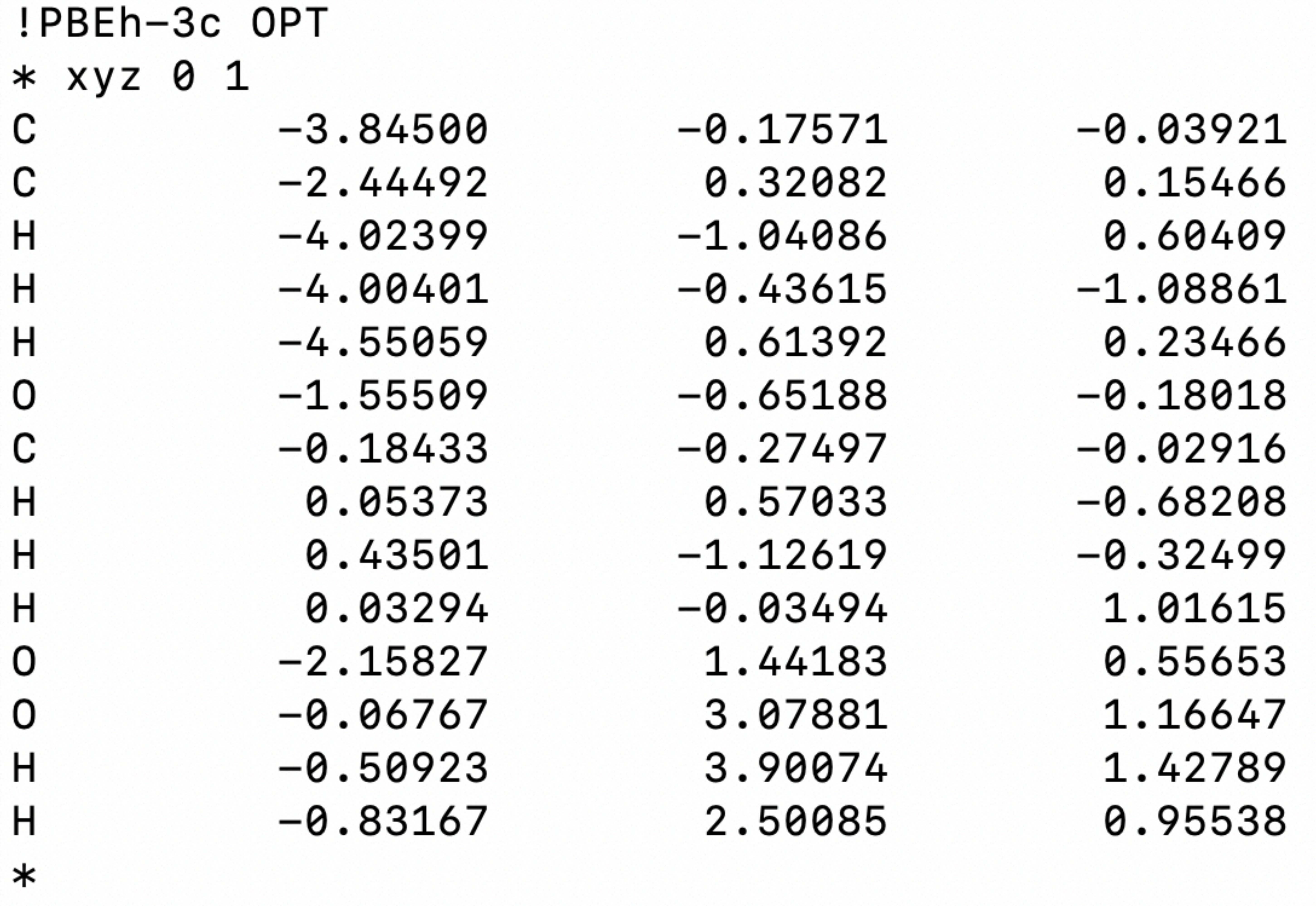
# Defining your reactants and products

So the first step is to optimize the "reactants" and "products".





reactants



```
!PBEh-3c OPT
* xyz 0 1
C            -3.84500         -0.17571         -0.03921
C            -2.44492          0.32082          0.15466
H            -4.02399         -1.04086          0.60409
H            -4.00401         -0.43615         -1.08861
H            -4.55059          0.61392          0.23466
O            -1.55509         -0.65188         -0.18018
C            -0.18433         -0.27497         -0.02916
H             0.05373          0.57033         -0.68208
H             0.43501         -1.12619         -0.32499
H             0.03294         -0.03494          1.01615
O            -2.15827          1.44183          0.55653
O            -0.06767          3.07881          1.16647
H            -0.50923          3.90074          1.42789
H            -0.83167          2.50085          0.95538
*
```

PBEh-3c is a highly efficient electronic structure approach performing particularly well in the optimization of geometries and for interaction energies of non-covalent complexes.[325] Here, a global hybrid variant of the Perdew-Burke-Ernzerhof (PBE) functional with a relatively large amount of non-local Fock-exchange (42%) is employed with a valence-double-zeta Gaussian AO basis set (def2-mSVP). Basis set superposition errors (BSSE) and London dispersion effects are accounted for by the gCP and D3 schemes, respectively (see above). The basis set is constructed such that:

Table 7.8

**Composition of the def2-mSVP basis set.**

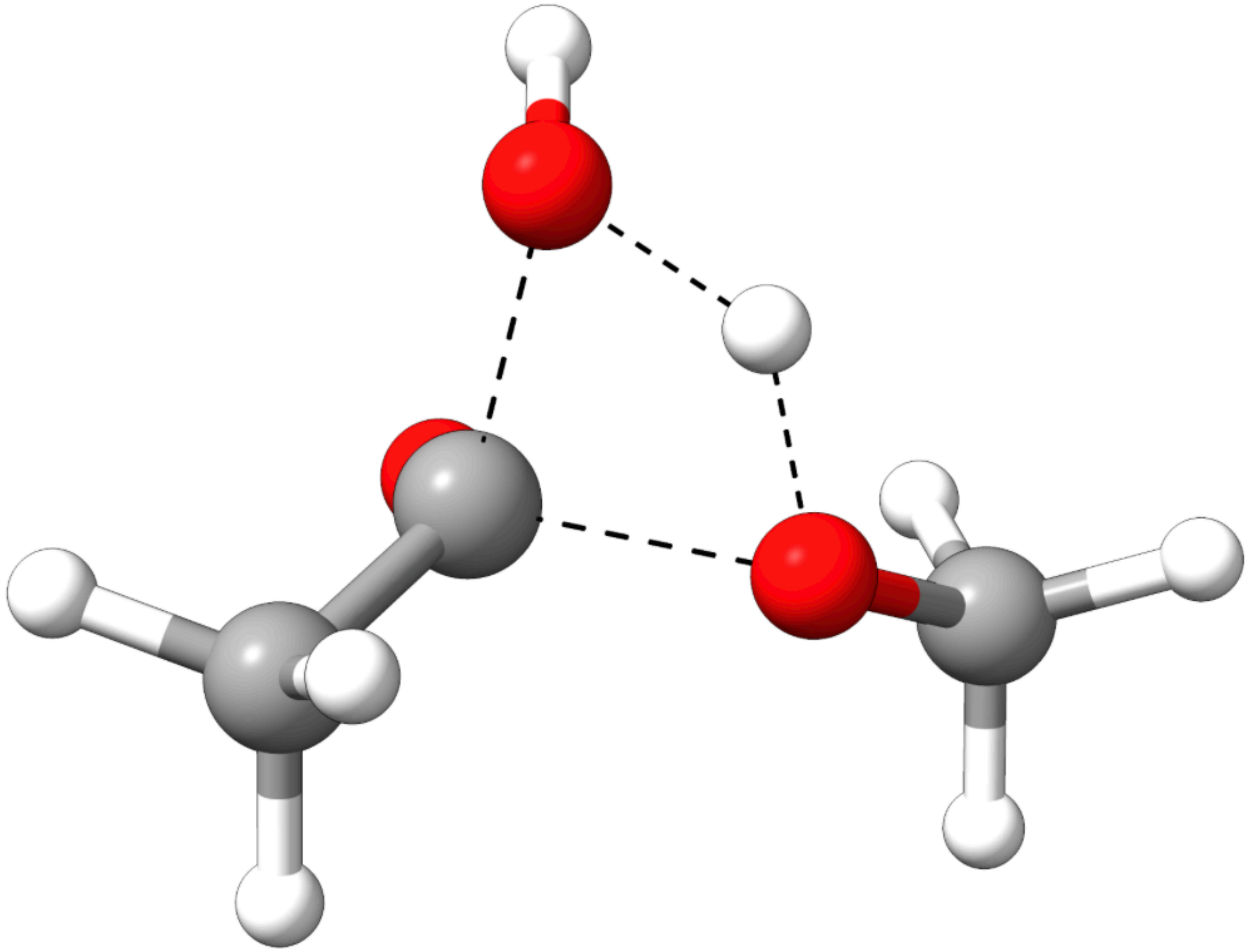
| element | basis |
|---|---|
| H | def2-SV(P) ($\alpha$ scaled by 1.2) |
| He | def2-SVP(-p) |
| Li-Be,Na-Kr | def2-SV(P) |
| B,Ne | Ahlrichs' DZ + Polarization from def2-SVP |
| C-F | Ahlrichs' DZ + Polarization from 6-31G* |
| Rb-Rn | def2-SVP with Stuttgart-Dresden ECPs |

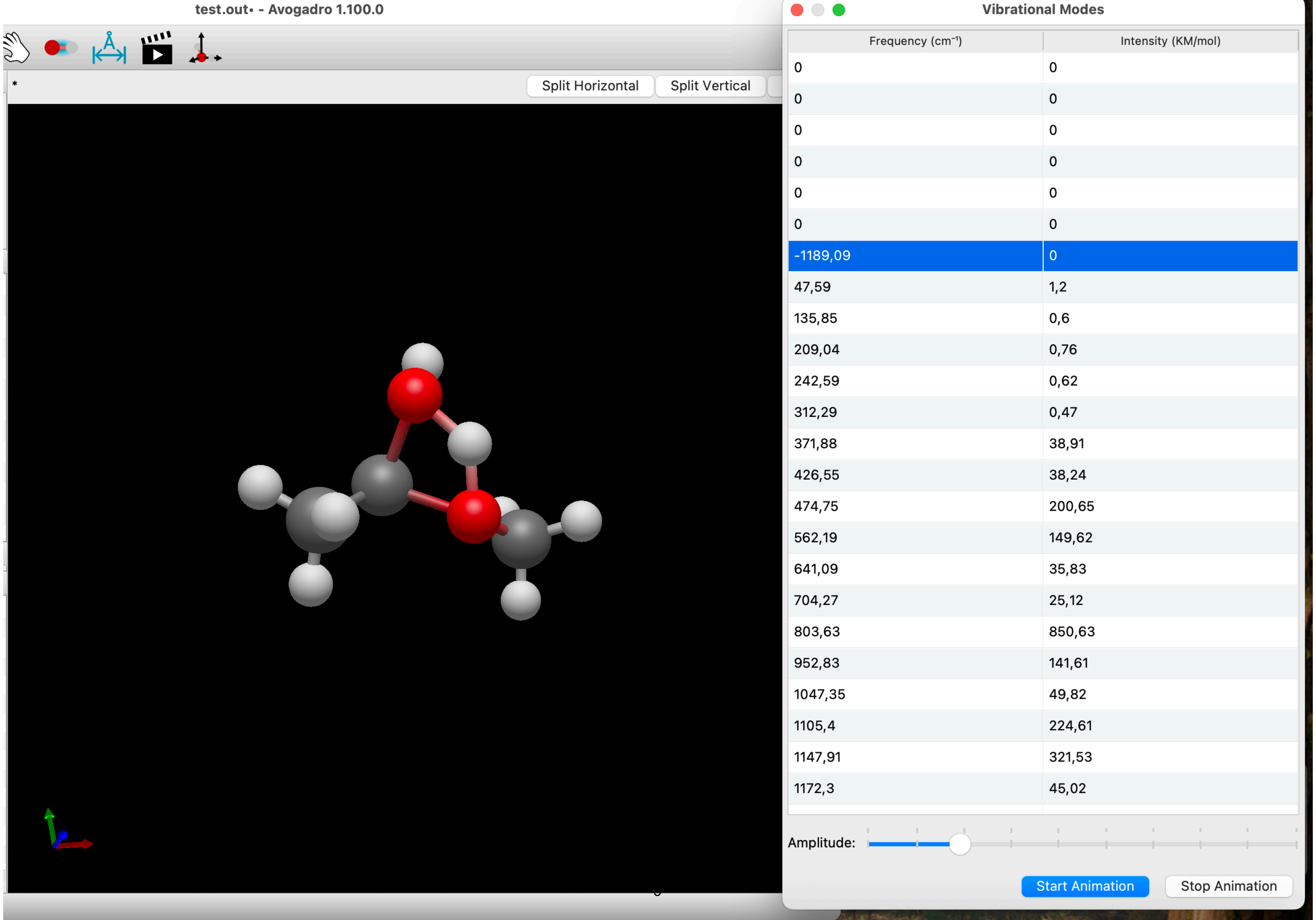
# The NEB-TS input

With the optimized reactants and products at hand, we can create the NEB-TS input which is quite simple. NEB-TS is requested via the `NEB-TS` keyword and all other settings are defined in the `%NEB` block. To verify that our probably found TS is reasonable we also request a final vibrational frequencies calculation.

```
!PBEh-3c NEB-TS FREQ

%NEB
 NEB_END_XYZFILE "product.xyz"
END

*XYZFILE 0 1 reactant.xyz
```

The final trajectory from the reactants to products can be read from `basename_MEP_trj.xyz`, and the final transition state geometry, saved in `basename_NEB-TS_converged.xyz` is:



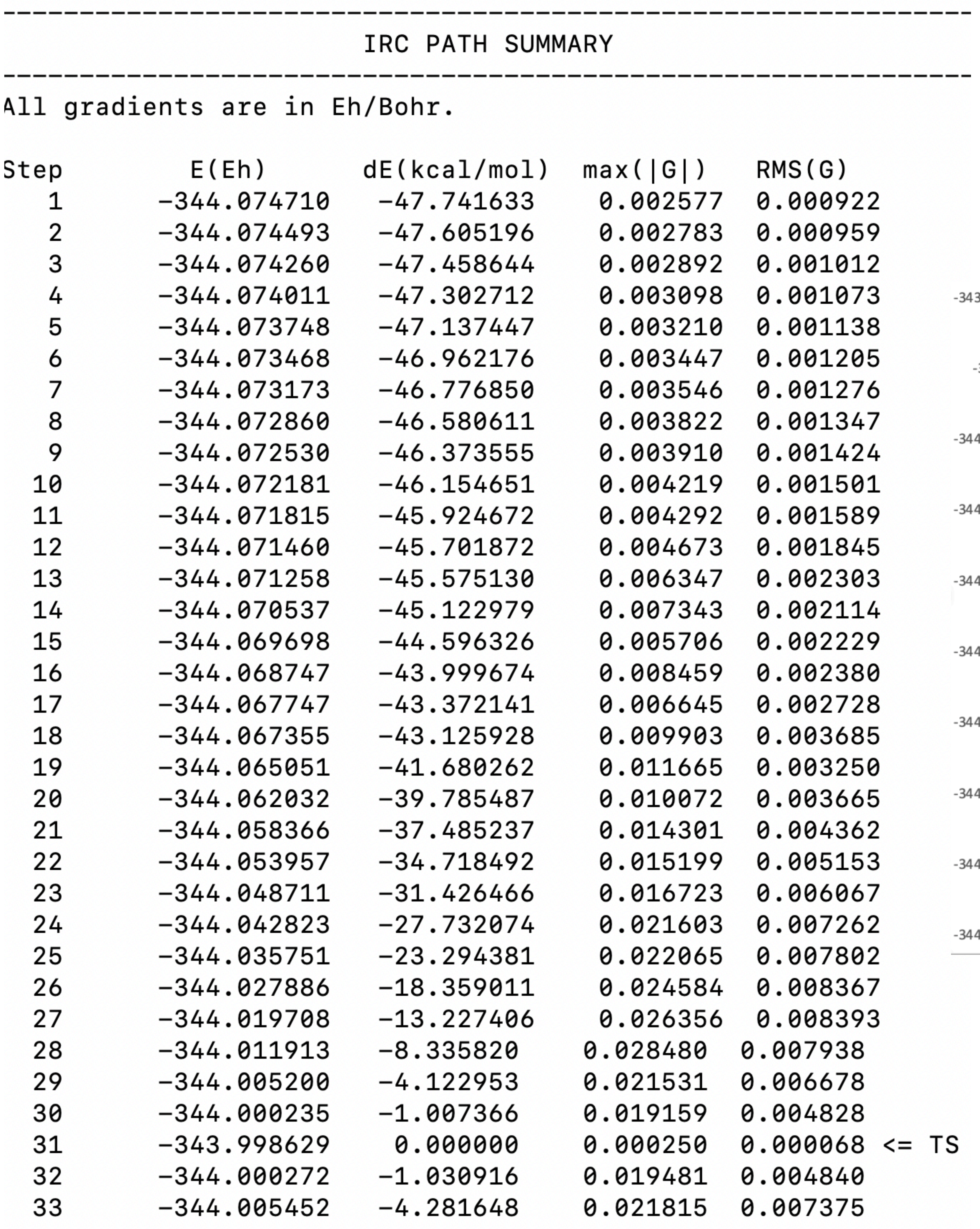


| Frequency (cm⁻¹) | Intensity (KM/mol) |
|---|---|
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| -1189,09 | 0 |
| 47,59 | 1,2 |
| 135,85 | 0,6 |
| 209,04 | 0,76 |
| 242,59 | 0,62 |
| 312,29 | 0,47 |
| 371,88 | 38,91 |
| 426,55 | 38,24 |
| 474,75 | 200,65 |
| 562,19 | 149,62 |
| 641,09 | 35,83 |
| 704,27 | 25,12 |
| 803,63 | 850,63 |
| 952,83 | 141,61 |
| 1047,35 | 49,82 |
| 1105,4 | 224,61 |
| 1147,91 | 321,53 |
| 1172,3 | 45,02 |

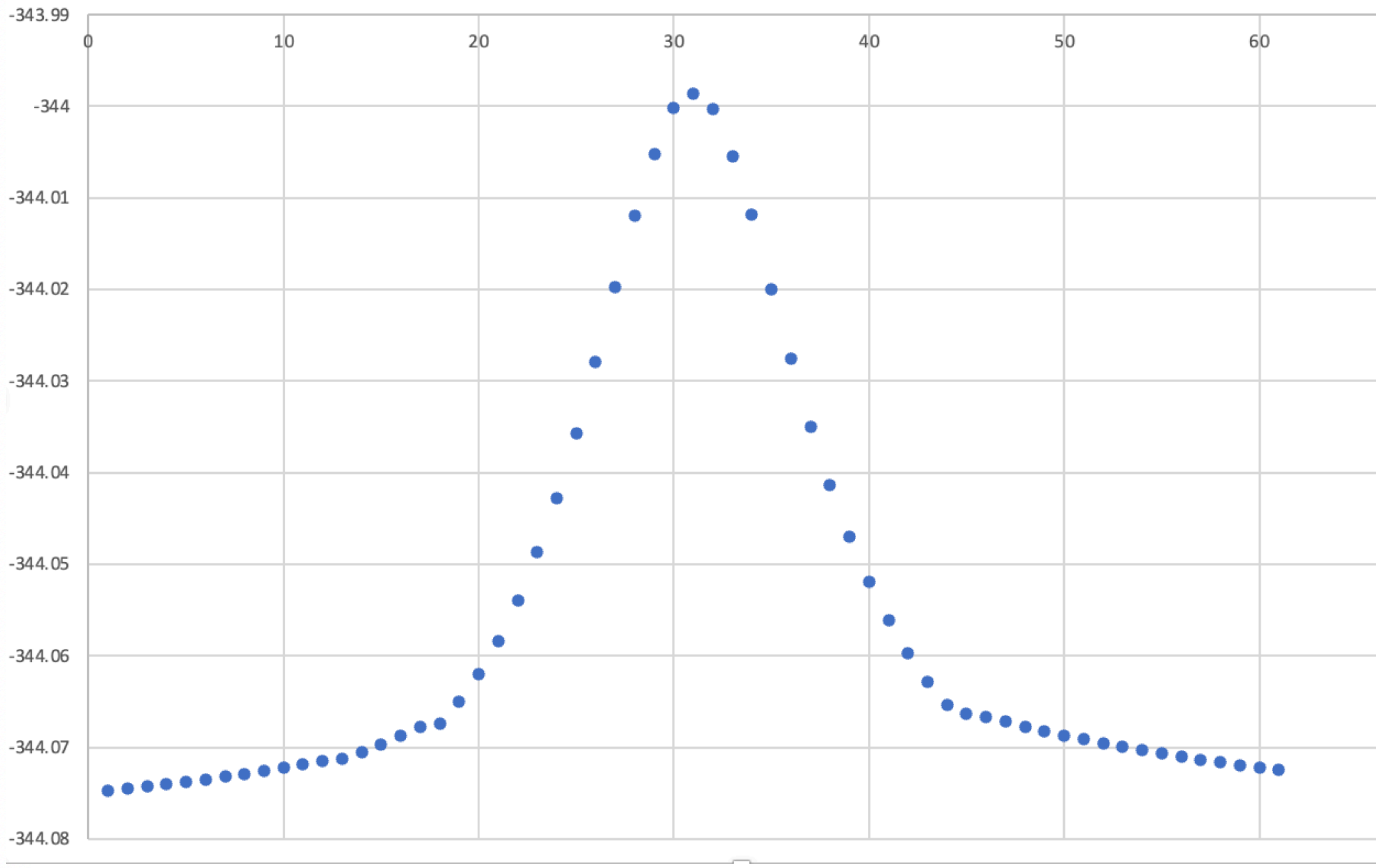
# Intrinsic Reaction Coordinate (IRC)

The Intrinsic Reaction Coordinate (IRC) is a special form of a minimum energy path that connects a transition state (TS) with its downhill-nearest intermediates. A method determining the IRC is thus useful to determine whether a transition state is directly connected to a given reactant and/or product. ORCA features its own implementation of Morokuma and coworkers' popular method.[Morokuma1977] The IRC method can be requested via the `IRC` simple keyword:

```
!PBEh-3c IRC

%IRC
 MAXITER 30
END

*XYZ 0 1
  C        -1.84501632713068    -0.29902338501760     0.13965550783148
  C        -0.60427233047858     0.40801470126327    -0.30748931627626
  H        -1.79969560900340    -0.62542670171715     1.17387028101901
  H        -1.99815116424407    -1.16672099289380    -0.50053987777241
  H        -2.69502981456739     0.37020072397205     0.01415109784312
  O         0.65789072189710    -0.51654995193254     0.40508214427829
  C         1.78743258993764    -0.74092055682896    -0.40589355555236
  H         1.87117376072047    -0.00613885127936    -1.21175769873916
  H         1.73166898217582    -1.73455818935491    -0.85282219990796
  H         2.69041861170014    -0.69167566508163     0.20538781077427
  O        -0.35825727785491     0.87776938984982    -1.37278324761597
  O        -0.19672134435744     1.40575408337574     1.03247158384842
  H         0.17686346937189     2.21194694294315     0.65417696505443
  H         0.58169573183341     0.50732845270191     1.02649050521508
*
```



```
---------------------------------------------------------------
                        IRC PATH SUMMARY
---------------------------------------------------------------
All gradients are in Eh/Bohr.

Step         E(Eh)        dE(kcal/mol)   max(|G|)   RMS(G)
   1     -344.074710    -47.741633     0.002577  0.000922
   2     -344.074493    -47.605196     0.002783  0.000959
   3     -344.074260    -47.458644     0.002892  0.001012
   4     -344.074011    -47.302712     0.003098  0.001073
   5     -344.073748    -47.137447     0.003210  0.001138
   6     -344.073468    -46.962176     0.003447  0.001205
   7     -344.073173    -46.776850     0.003546  0.001276
   8     -344.072860    -46.580611     0.003822  0.001347
   9     -344.072530    -46.373555     0.003910  0.001424
  10     -344.072181    -46.154651     0.004219  0.001501
  11     -344.071815    -45.924672     0.004292  0.001589
  12     -344.071460    -45.701872     0.004673  0.001845
  13     -344.071258    -45.575130     0.006347  0.002303
  14     -344.070537    -45.122979     0.007343  0.002114
  15     -344.069698    -44.596326     0.005706  0.002229
  16     -344.068747    -43.999674     0.008459  0.002380
  17     -344.067747    -43.372141     0.006645  0.002728
  18     -344.067355    -43.125928     0.009903  0.003685
  19     -344.065051    -41.680262     0.011665  0.003250
  20     -344.062032    -39.785487     0.010072  0.003665
  21     -344.058366    -37.485237     0.014301  0.004362
  22     -344.053957    -34.718492     0.015199  0.005153
  23     -344.048711    -31.426466     0.016723  0.006067
  24     -344.042823    -27.732074     0.021603  0.007262
  25     -344.035751    -23.294381     0.022065  0.007802
  26     -344.027886    -18.359011     0.024584  0.008367
  27     -344.019708    -13.227406     0.026356  0.008393
  28     -344.011913    -8.335820     0.028480  0.007938
  29     -344.005200    -4.122953     0.021531  0.006678
  30     -344.000235    -1.007366     0.019159  0.004828
  31     -343.998629     0.000000     0.000250  0.000068 <= TS
  32     -344.000272    -1.030916     0.019481  0.004840
  33     -344.005452    -4.281648     0.021815  0.007375
```



ORCA 6.0 TUTORIALS

SEARCH

FIRST STEPS

How to cite

Installing ORCA

Hello water! Your first ORCA calculation

Input and Output

Running a calculation in parallel

Graphical User Interfaces (GUI)

Solving common issues

WORKFLOWS

Compound Jobs

Extrapolation Techniques

PROPERTIES

Single point energies

Geometry optimization

Vibrational frequencies

# Kinectic Isotope Effects (KIE)

Kinetic isotope effects (KIE) are changes in reaction rates caused by a change in a given isotope in a molecule. That is caused due to the difference in mass, that affects vibrational frequencies and/or tunneling probabilities.

It is an effect often exploited to investigate reaction mechanisms, when there is bond breaking or forming to an atom that can be substituted by an isotope. These KIE are predictable, depending on the mass ratios, and thus can be used to validate proposed mechanisms. The origin of the KIE is related to a change on the **Zero Point Energy** (ZPE) of the system, that is affected when the vibrational frequencies are lowered or increased due to the mass change. For the heavier deuterium the vibrational frequencies are lowered, thus lowering the ZPE and altering the free energy barrier.

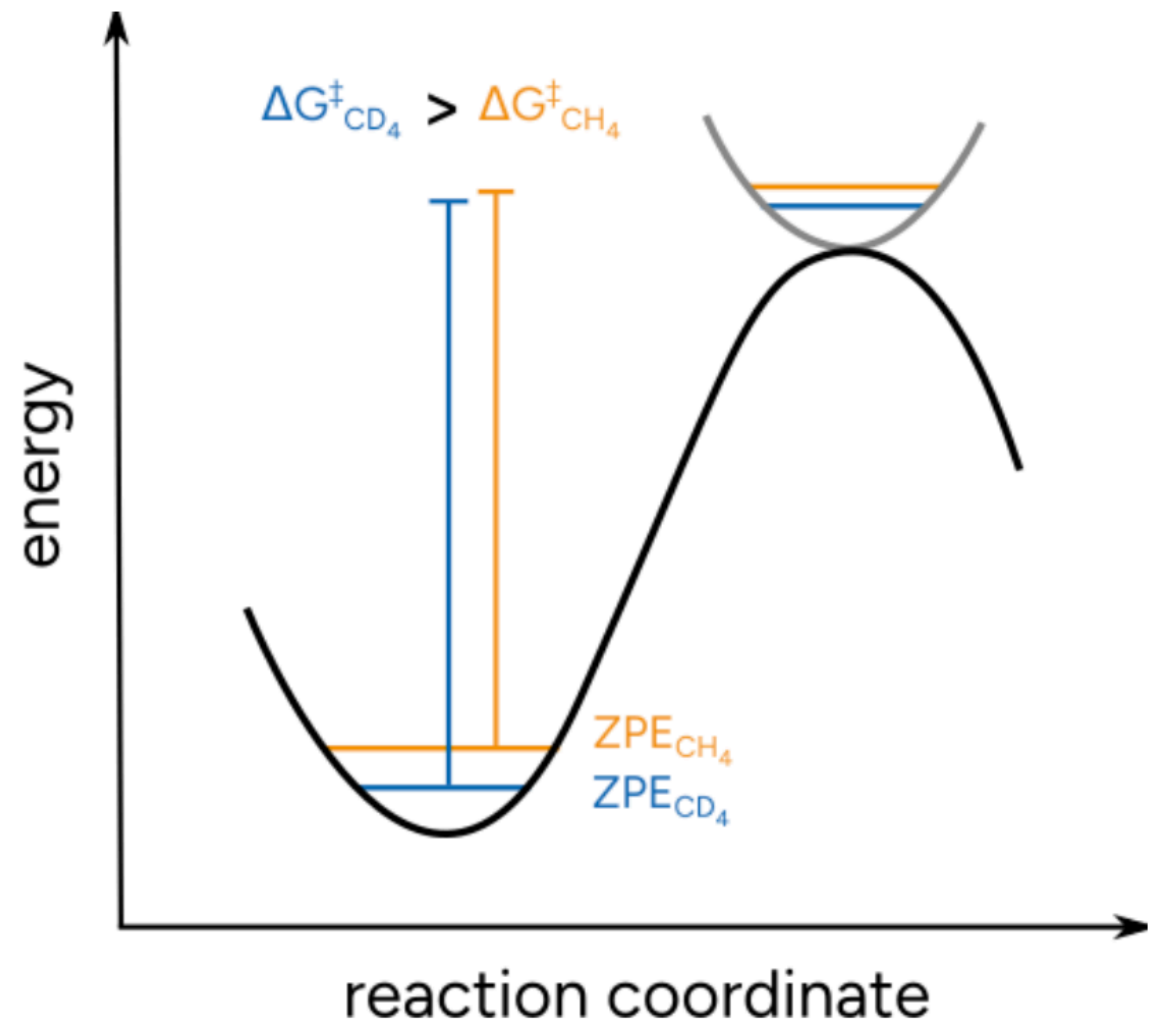
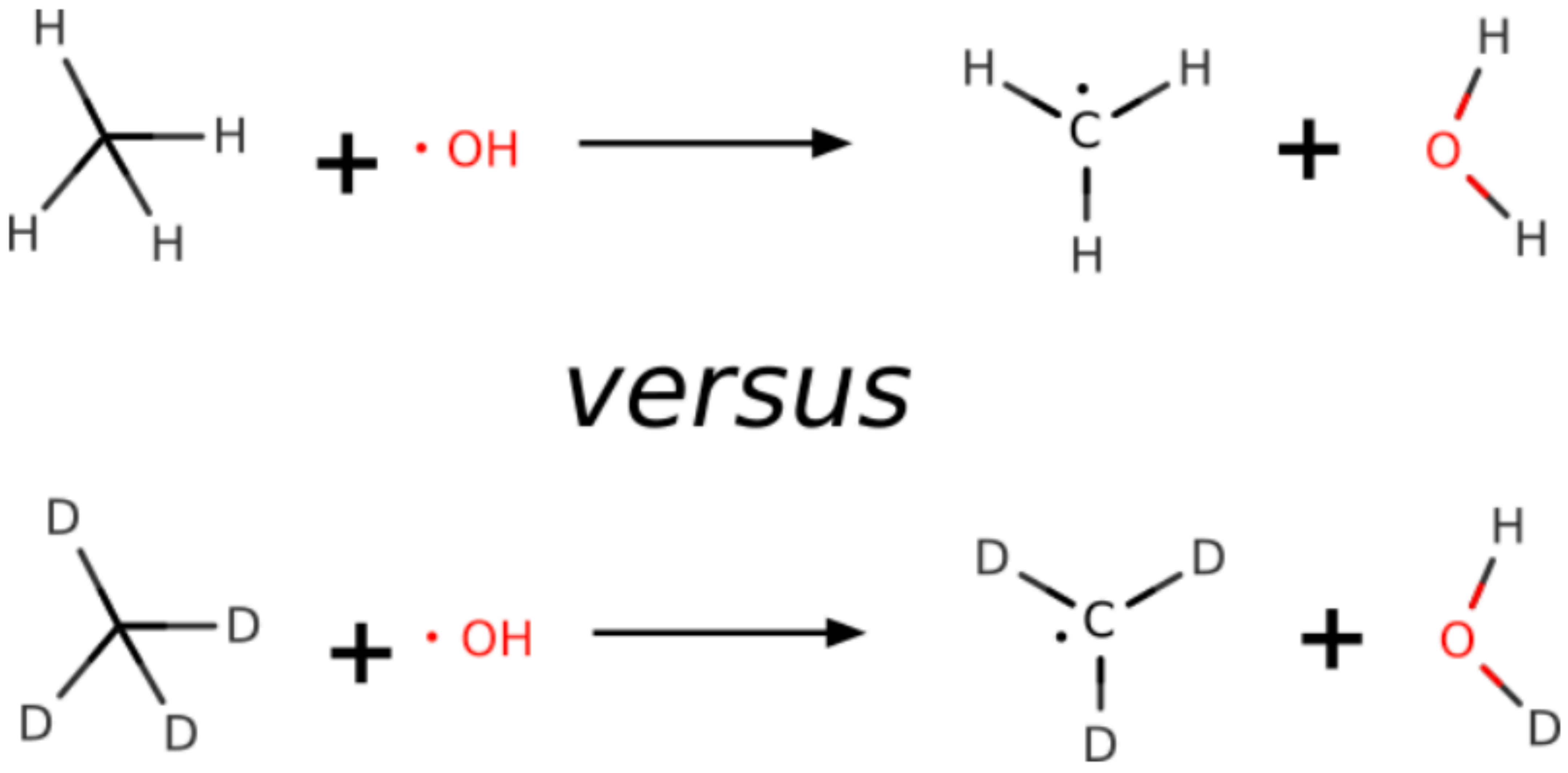


**Figure: Schematic origin of the KIE.**

# Example 1: H-atom Abstraction

In this example, we use ORCA to make a quantum-mechanical prediction of the KIE for the H-atom abstraction from methane by the hydroxyl radical. The respective KIE ratio is known from highly accurate gas-phase experiments ($6.75 \pm 0.83$).[Tully1993]

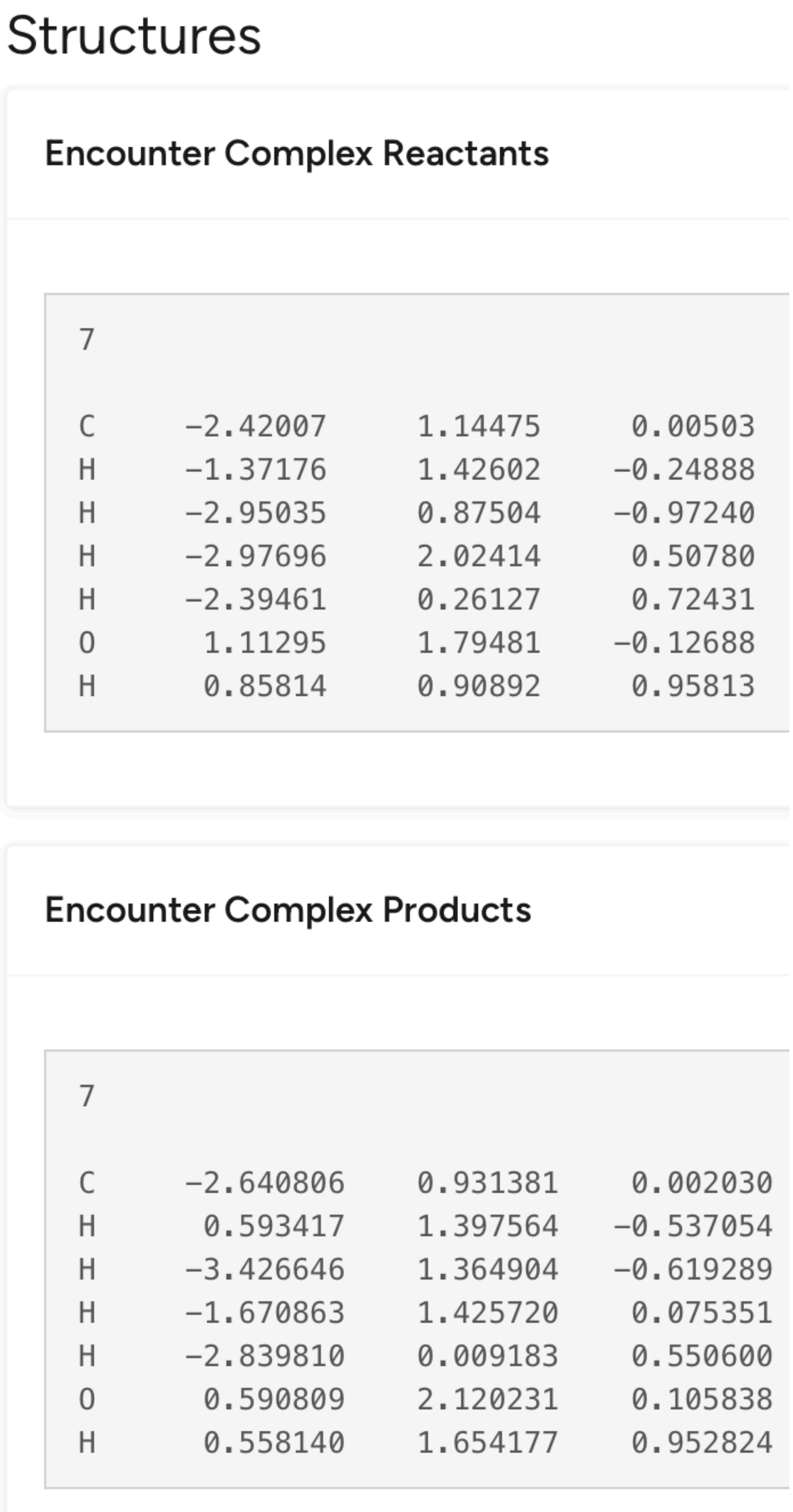


First, we searched for the transition states of the respective reactions with the NEB-TS method. In this case, we employed the ωB97X-3c composite method. It is based on a range-separated hybrid functional that is specifically suited to compute transition states and reaction barriers at a reasonable cost. Note, that we also adjusted the temperature for the thermochemistry calculation to obtain free energies at the same conditions as in the experiment (T = 293 K). We further optimize the isolated reactants for both cases. The respective inputs can be found in the tabs below:

Typically, the KIE is quantified by the ratio of the reaction rates of both reactions $\frac{kH}{kD}$. This can be calculated from the free energy reaction barriers of both reactions according to:

$$\frac{k_H}{k_D} = e^{-(\Delta G^{\ddagger}_H - \Delta G^{\ddagger}_D)/RT}$$

To obtain these barriers, we can use the usual transition state search and optimization algorithms in ORCA, we just have to adjust the mass of the respective atoms to simulate the corresponding isotopes. This can be easily done via the geometry input within the ORCA input file:



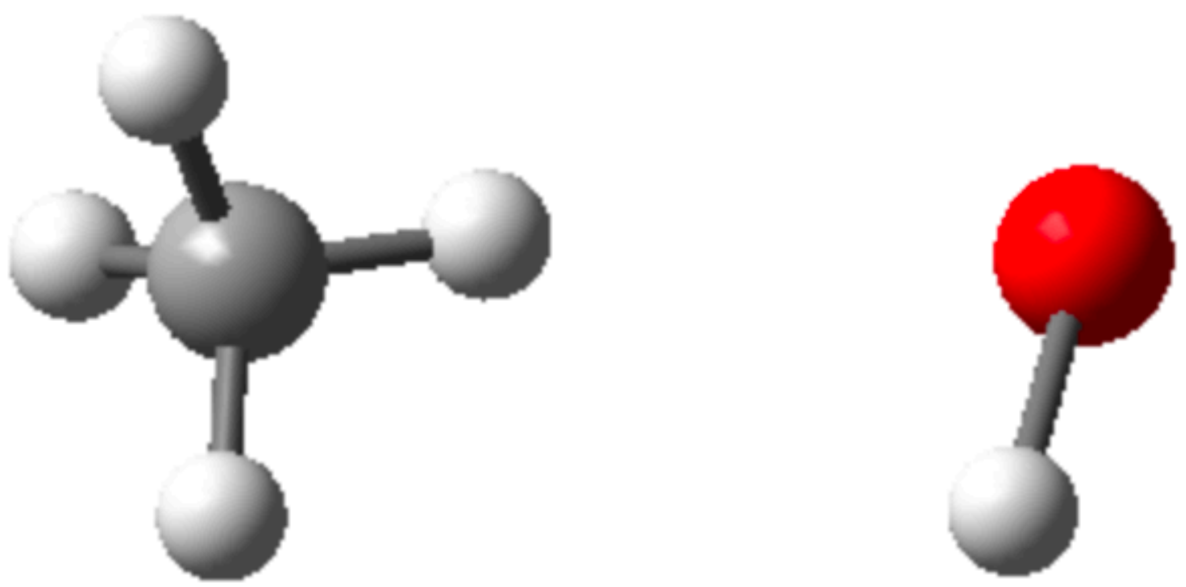
# Structures

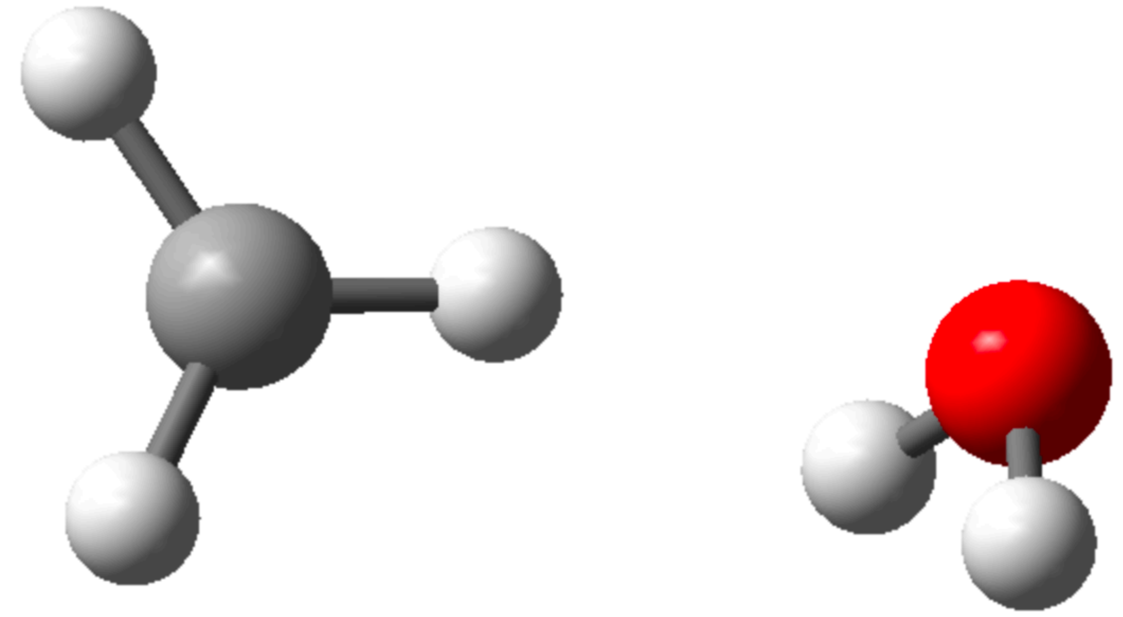
## Encounter Complex Reactants

```
7


C     -2.42007     1.14475     0.00503
H     -1.37176     1.42602    -0.24888
H     -2.95035     0.87504    -0.97240
H     -2.97696     2.02414     0.50780
H     -2.39461     0.26127     0.72431
O      1.11295     1.79481    -0.12688
H      0.85814     0.90892     0.95813
```

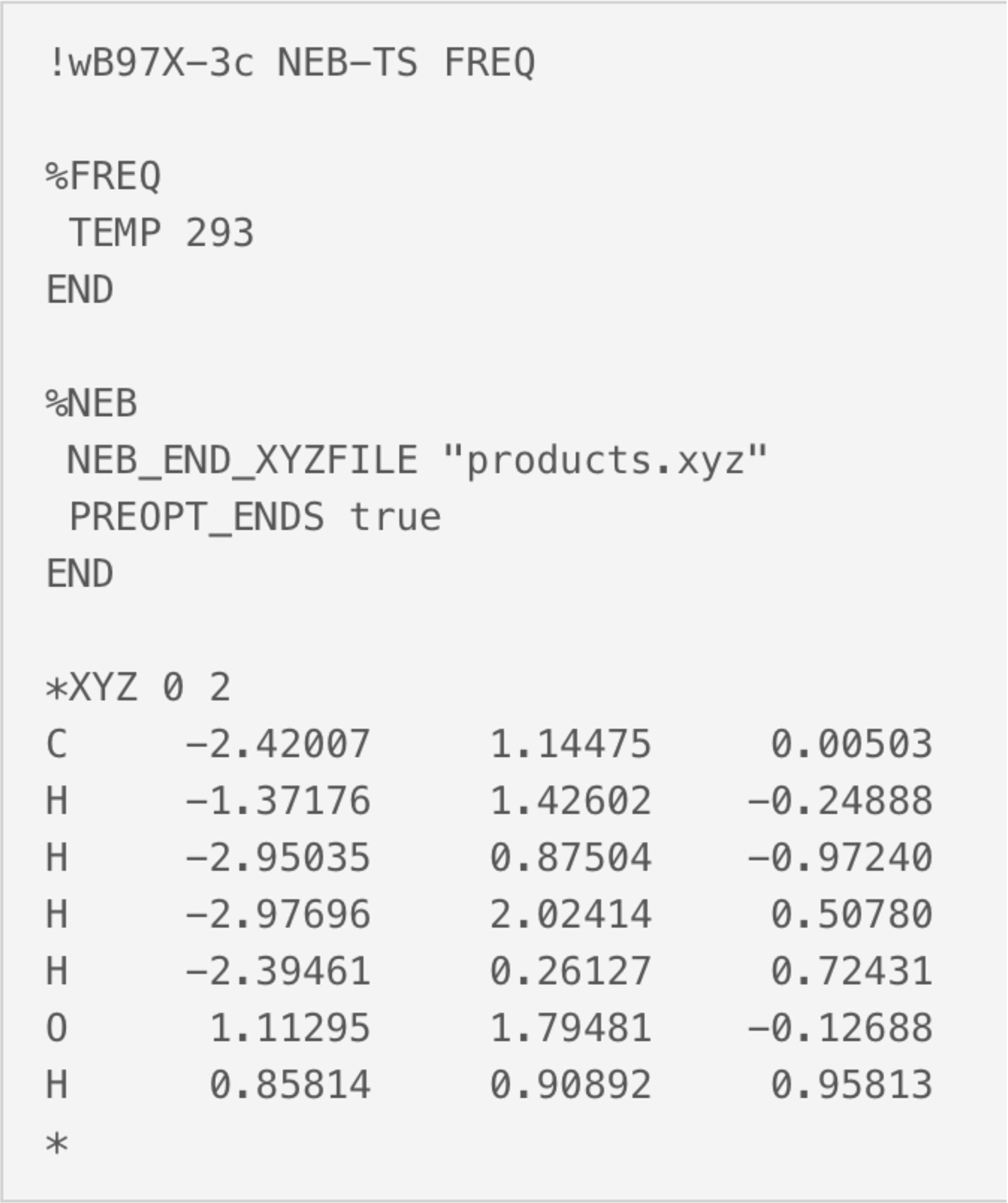
## Encounter Complex Products

```
7


C     -2.640806     0.931381     0.002030
H      0.593417     1.397564    -0.537054
H     -3.426646     1.364904    -0.619289
H     -1.670863     1.425720     0.075351
H     -2.839810     0.009183     0.550600
O      0.590809     2.120231     0.105838
H      0.558140     1.654177     0.952824
```

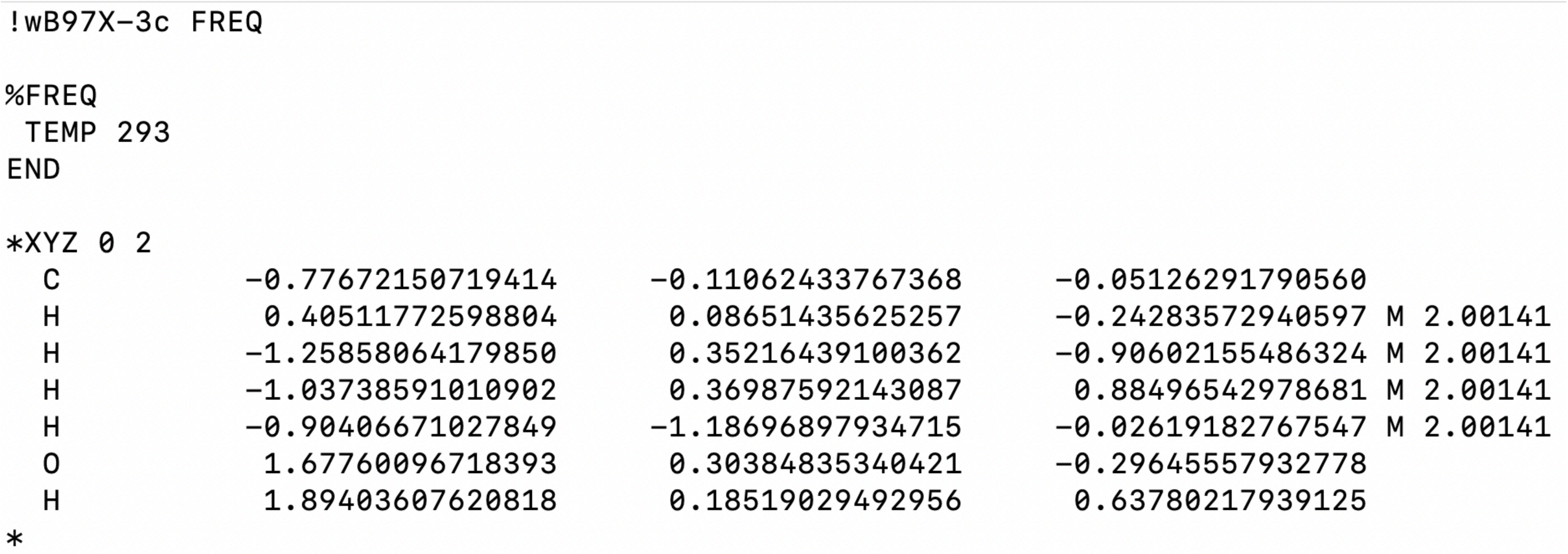




# NEB-TS $CH_4$

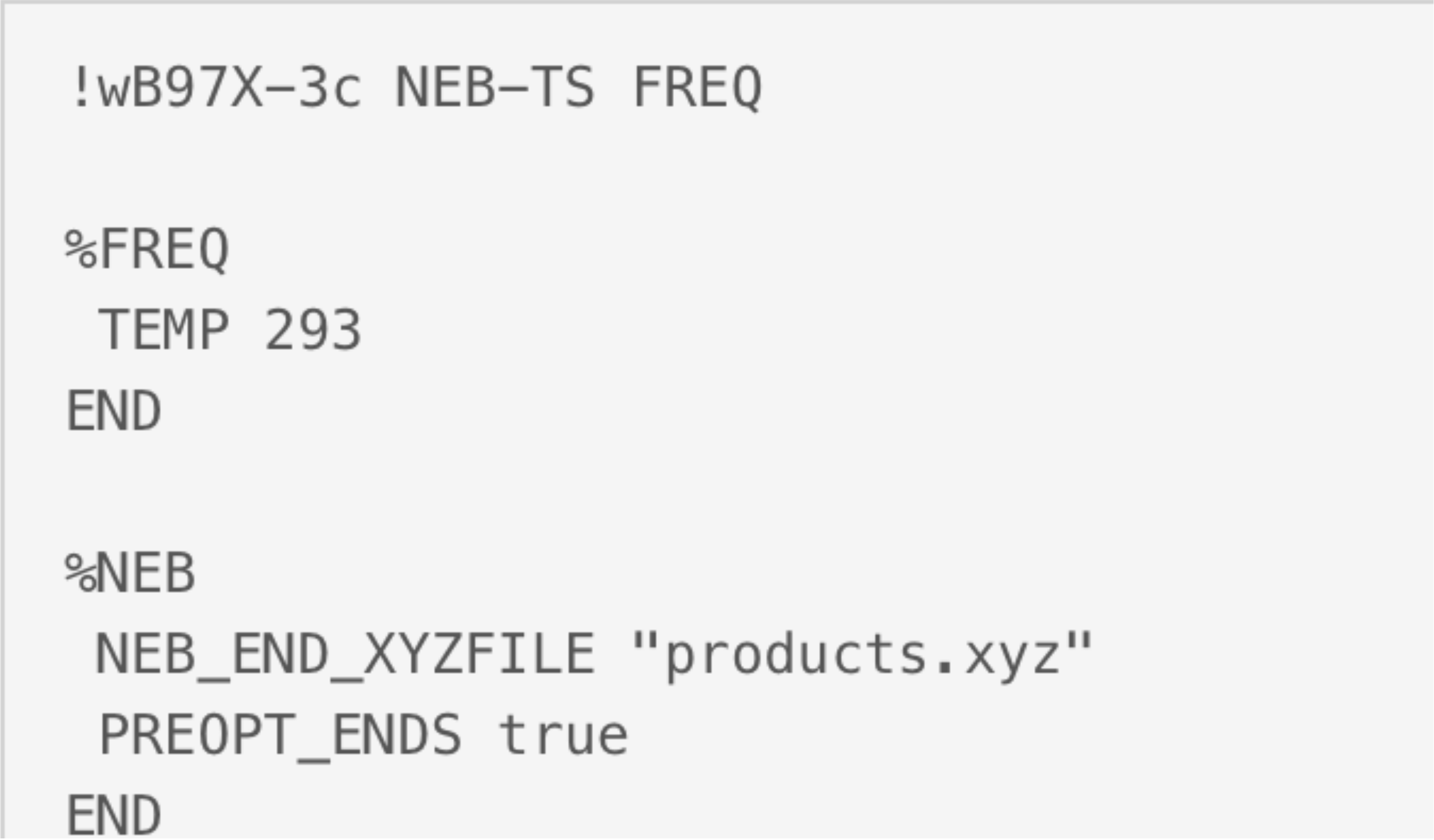


```
!wB97X-3c NEB-TS FREQ

%FREQ
 TEMP 293
END

%NEB
 NEB_END_XYZFILE "products.xyz"
 PREOPT_ENDS true
END

*XYZ 0 2
C      -2.42007      1.14475      0.00503
H      -1.37176      1.42602     -0.24888
H      -2.95035      0.87504     -0.97240
H      -2.97696      2.02414      0.50780
H      -2.39461      0.26127      0.72431
O       1.11295      1.79481     -0.12688
H       0.85814      0.90892      0.95813
*
```

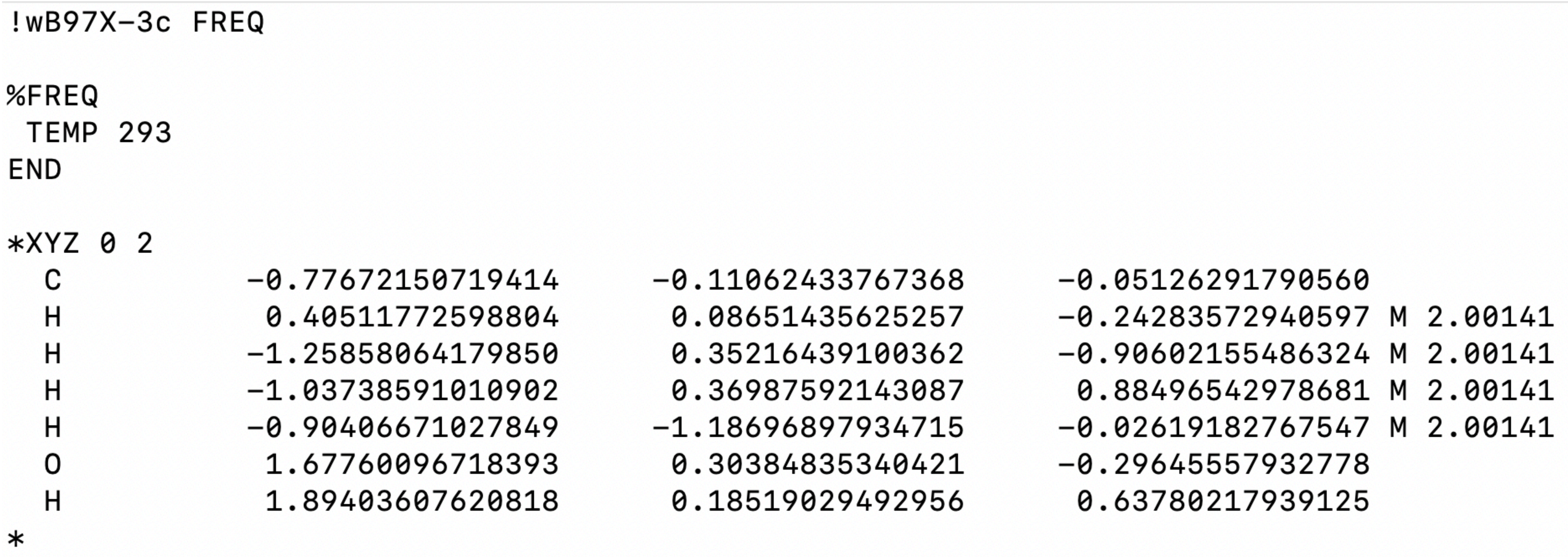


```
!wB97X-3c FREQ

%FREQ
 TEMP 293
END

*XYZ 0 2
  C           -0.77672150719414      -0.11062433767368      -0.05126291790560
  H            0.40511772598804       0.08651435625257      -0.24283572940597 M 2.00141
  H           -1.25858064179850       0.35216439100362      -0.90602155486324 M 2.00141
  H           -1.03738591010902       0.36987592143087       0.88496542978681 M 2.00141
  H           -0.90406671027849      -1.18696897934715      -0.02619182767547 M 2.00141
  O            1.67760096718393       0.30384835340421      -0.29645557932778
  H            1.89403607620818       0.18519029492956       0.63780217939125
*
```

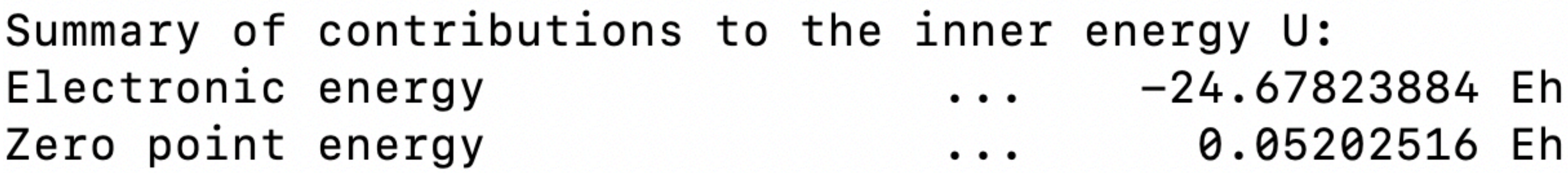
## NEB-TS $CH_4$



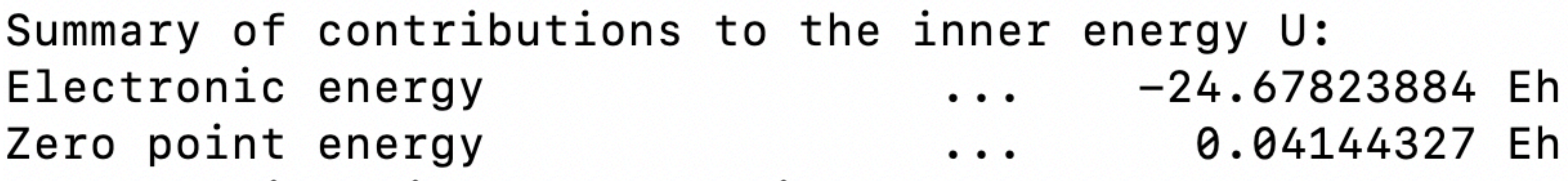
```
!wB97X-3c NEB-TS FREQ

%FREQ
 TEMP 293
END

%NEB
 NEB_END_XYZFILE "products.xyz"
 PREOPT_ENDS true
END
```



```
!wB97X-3c FREQ

%FREQ
 TEMP 293
END

*XYZ 0 2
  C          -0.77672150719414     -0.11062433767368     -0.05126291790560
  H           0.40511772598804      0.08651435625257     -0.24283572940597 M 2.00141
  H          -1.25858064179850      0.35216439100362     -0.90602155486324 M 2.00141
  H          -1.03738591010902      0.36987592143087      0.88496542978681 M 2.00141
  H          -0.90406671027849     -1.18696897934715     -0.02619182767547 M 2.00141
  O           1.67760096718393      0.30384835340421     -0.29645557932778
  H           1.89403607620818      0.18519029492956      0.63780217939125
*
```



```
Summary of contributions to the inner energy U:
Electronic energy                ...    -24.67823884 Eh
Zero point energy                ...      0.05202516 Eh
```



```
Summary of contributions to the inner energy U:
Electronic energy                ...    -24.67823884 Eh
Zero point energy                ...      0.04144327 Eh
```

```
Final Gibbs free energy         ...    -24.65155581 Eh
```

```
Final Gibbs free energy         ...    -24.66300026 Eh
```

# Infrared and Raman

The prediction of infrared (IR) and (non-resnonant) Raman spectra are nowadays a straightforward task in computational chemistry. Let us use ORCA to predict the fundamental frequencies and intensities for benzene.

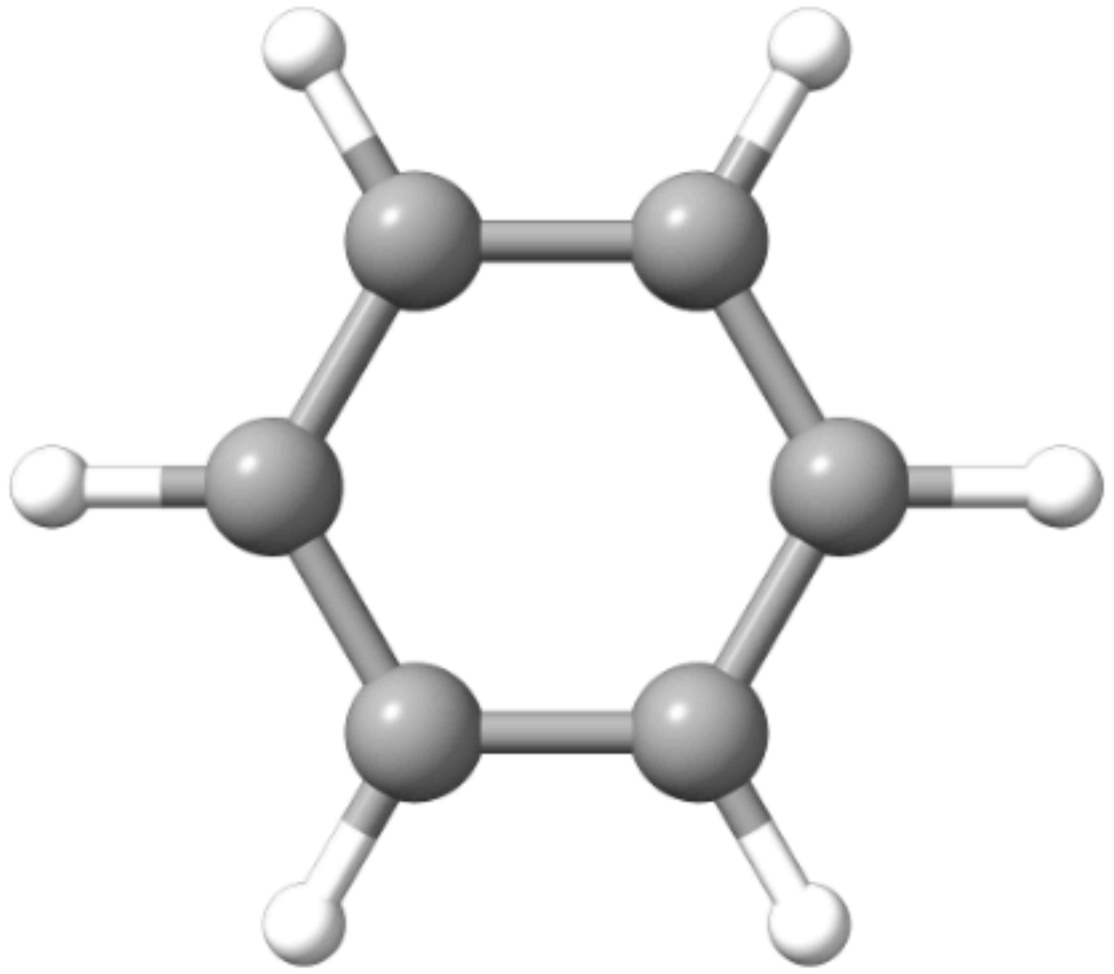


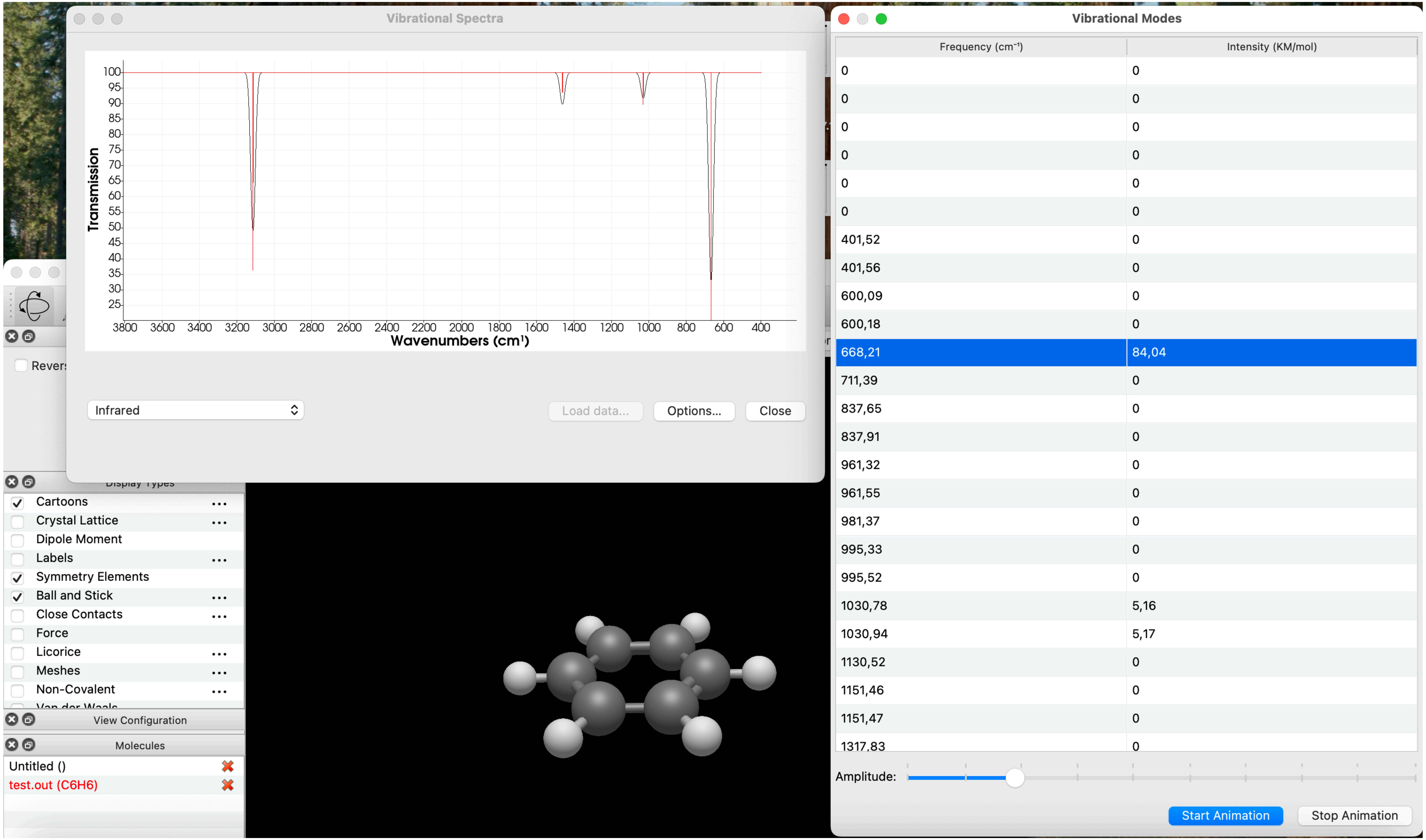
**Figure: $D_{6h}$ symmetric structure of benzene.**

# Predicting infrared spectra

The optimization of the molecular structure and subsequent calculation of the vibrational frequencies, e.g. with DFT can be envoked via simple keywords `OPT` and `FREQ`:

```
!BP86 DEF2-SVP OPT FREQ

*XYZ 0 1
H        -1.242909   -2.152782    0.000000
C        -0.695566   -1.204756    0.000000
C         0.695566   -1.204756    0.000000
H         1.242909   -2.152782    0.000000
C         1.391133    0.000000    0.000000
H         2.485819    0.000000    0.000000
C         0.695566    1.204756    0.000000
H         1.242909    2.152782    0.000000
C        -0.695566    1.204756    0.000000
H        -1.242909    2.152782    0.000000
C        -1.391133    0.000000    0.000000
H        -2.485819    0.000000    0.000000
*
```

```
VIBRATIONAL FREQUENCIES
-----------------------

Scaling factor for frequencies =  1.000000000

    0:         0.00 cm**-1
    1:         0.00 cm**-1
    2:         0.00 cm**-1
    3:         0.00 cm**-1
    4:         0.00 cm**-1
    5:         0.00 cm**-1
    6:       401.52 cm**-1
    7:       401.56 cm**-1
    8:       600.09 cm**-1
    9:       600.18 cm**-1
   10:       668.21 cm**-1
   11:       711.39 cm**-1
   12:       837.65 cm**-1
   13:       837.91 cm**-1
   14:       961.32 cm**-1
   15:       961.55 cm**-1
```



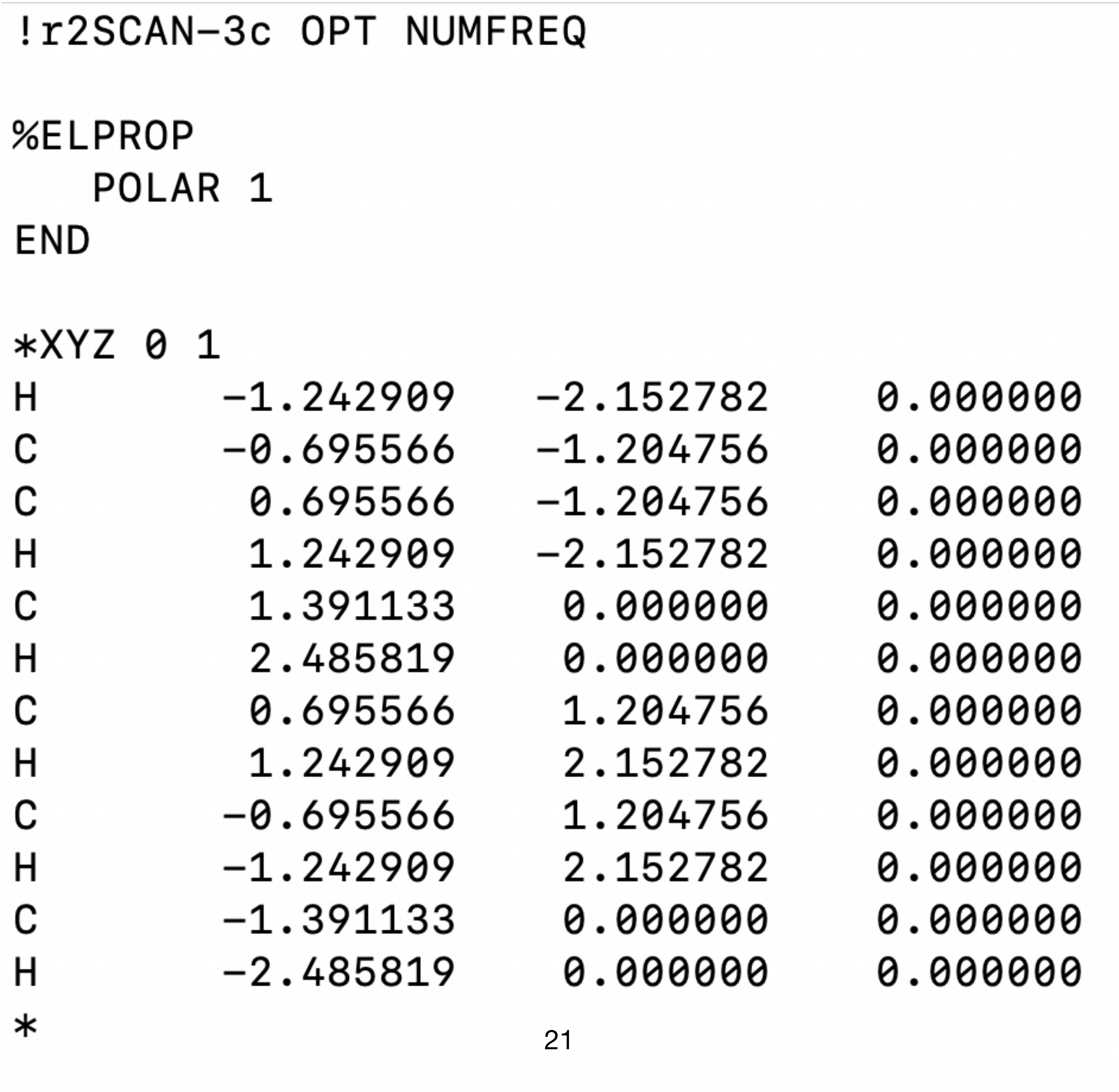
☑ Cartoons
☐ Crystal Lattice
☐ Dipole Moment
☐ Labels
☑ Symmetry Elements
☑ Ball and Stick
☐ Close Contacts
☐ Force
☐ Licorice
☐ Meshes
☐ Non-Covalent
☐ Van der Waals

Untitled ()
test.out (C6H6)

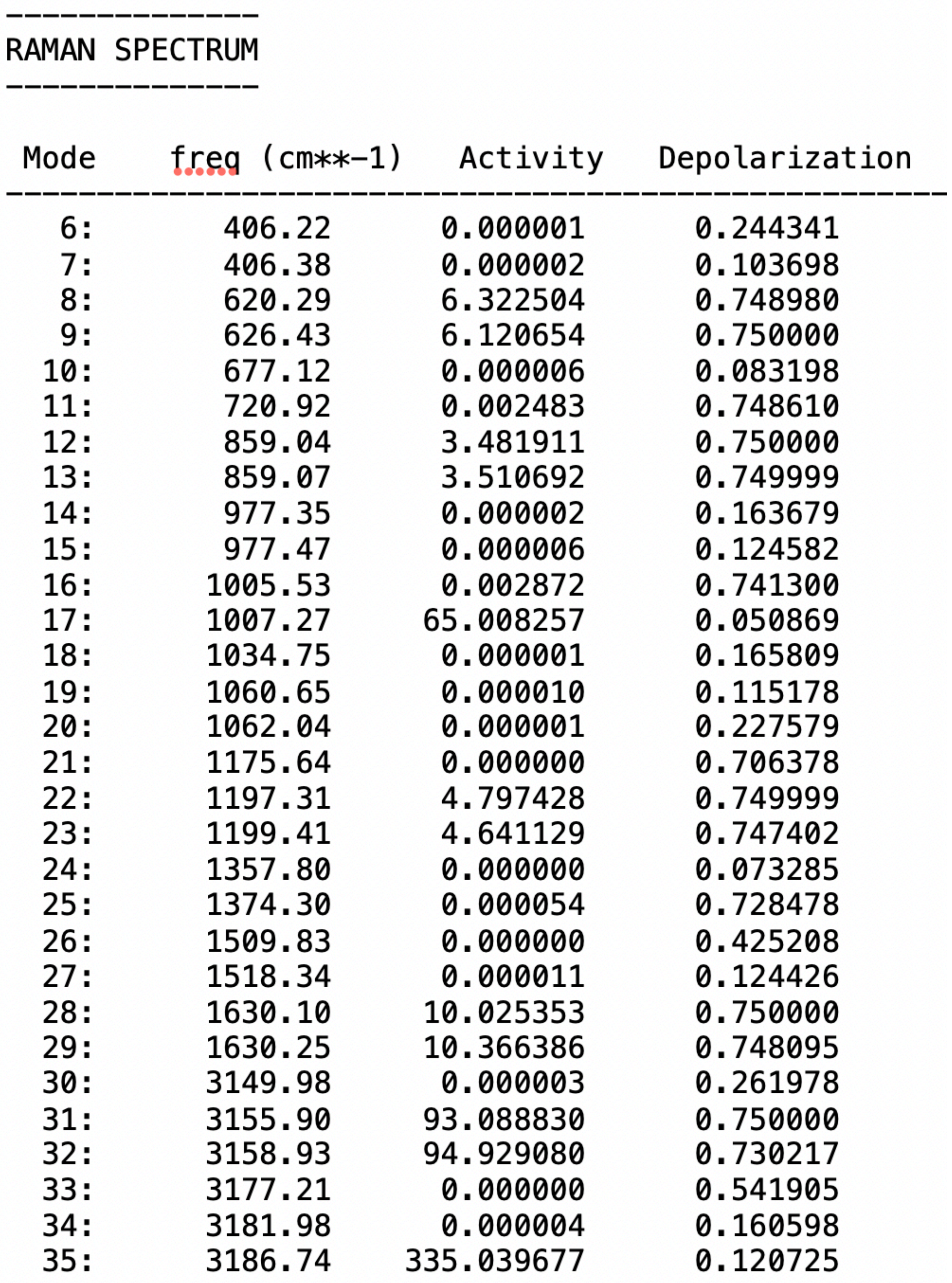
| Frequency (cm$^{-1}$) | Intensity (KM/mol) |
|---|---|
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| 0 | 0 |
| 401,52 | 0 |
| 401,56 | 0 |
| 600,09 | 0 |
| 600,18 | 0 |
| 668,21 | 84,04 |
| 711,39 | 0 |
| 837,65 | 0 |
| 837,91 | 0 |
| 961,32 | 0 |
| 961,55 | 0 |
| 981,37 | 0 |
| 995,33 | 0 |
| 995,52 | 0 |
| 1030,78 | 5,16 |
| 1030,94 | 5,17 |
| 1130,52 | 0 |
| 1151,46 | 0 |
| 1151,47 | 0 |
| 1317,83 | 0 |

# Predicting Raman spectra

In a similar way, the non-resonant Raman spectra composed of fundamental transitions can be predicted. The main difference here is that the derivatives of the polarizability have to be computed numerically, so that the !NUMFREQ flag has to be used, together with a keyword under %ELPROP to request the calculation of polarizabilties:



```
!r2SCAN-3c OPT NUMFREQ

%ELPROP
   POLAR 1
END

*XYZ 0 1
H       -1.242909   -2.152782    0.000000
C       -0.695566   -1.204756    0.000000
C        0.695566   -1.204756    0.000000
H        1.242909   -2.152782    0.000000
C        1.391133    0.000000    0.000000
H        2.485819    0.000000    0.000000
C        0.695566    1.204756    0.000000
H        1.242909    2.152782    0.000000
C       -0.695566    1.204756    0.000000
H       -1.242909    2.152782    0.000000
C       -1.391133    0.000000    0.000000
H       -2.485819    0.000000    0.000000
*
```



```
--------------
RAMAN SPECTRUM
--------------

 Mode    freq (cm**-1)   Activity   Depolarization
-------------------------------------------------------------------
   6:       406.22      0.000001      0.244341
   7:       406.38      0.000002      0.103698
   8:       620.29      6.322504      0.748980
   9:       626.43      6.120654      0.750000
  10:       677.12      0.000006      0.083198
  11:       720.92      0.002483      0.748610
  12:       859.04      3.481911      0.750000
  13:       859.07      3.510692      0.749999
  14:       977.35      0.000002      0.163679
  15:       977.47      0.000006      0.124582
  16:      1005.53      0.002872      0.741300
  17:      1007.27     65.008257      0.050869
  18:      1034.75      0.000001      0.165809
  19:      1060.65      0.000010      0.115178
  20:      1062.04      0.000001      0.227579
  21:      1175.64      0.000000      0.706378
  22:      1197.31      4.797428      0.749999
  23:      1199.41      4.641129      0.747402
  24:      1357.80      0.000000      0.073285
  25:      1374.30      0.000054      0.728478
  26:      1509.83      0.000000      0.425208
  27:      1518.34      0.000011      0.124426
  28:      1630.10     10.025353      0.750000
  29:      1630.25     10.366386      0.748095
  30:      3149.98      0.000003      0.261978
  31:      3155.90     93.088830      0.750000
  32:      3158.93     94.929080      0.730217
  33:      3177.21      0.000000      0.541905
  34:      3181.98      0.000004      0.160598
  35:      3186.74    335.039677      0.120725
```

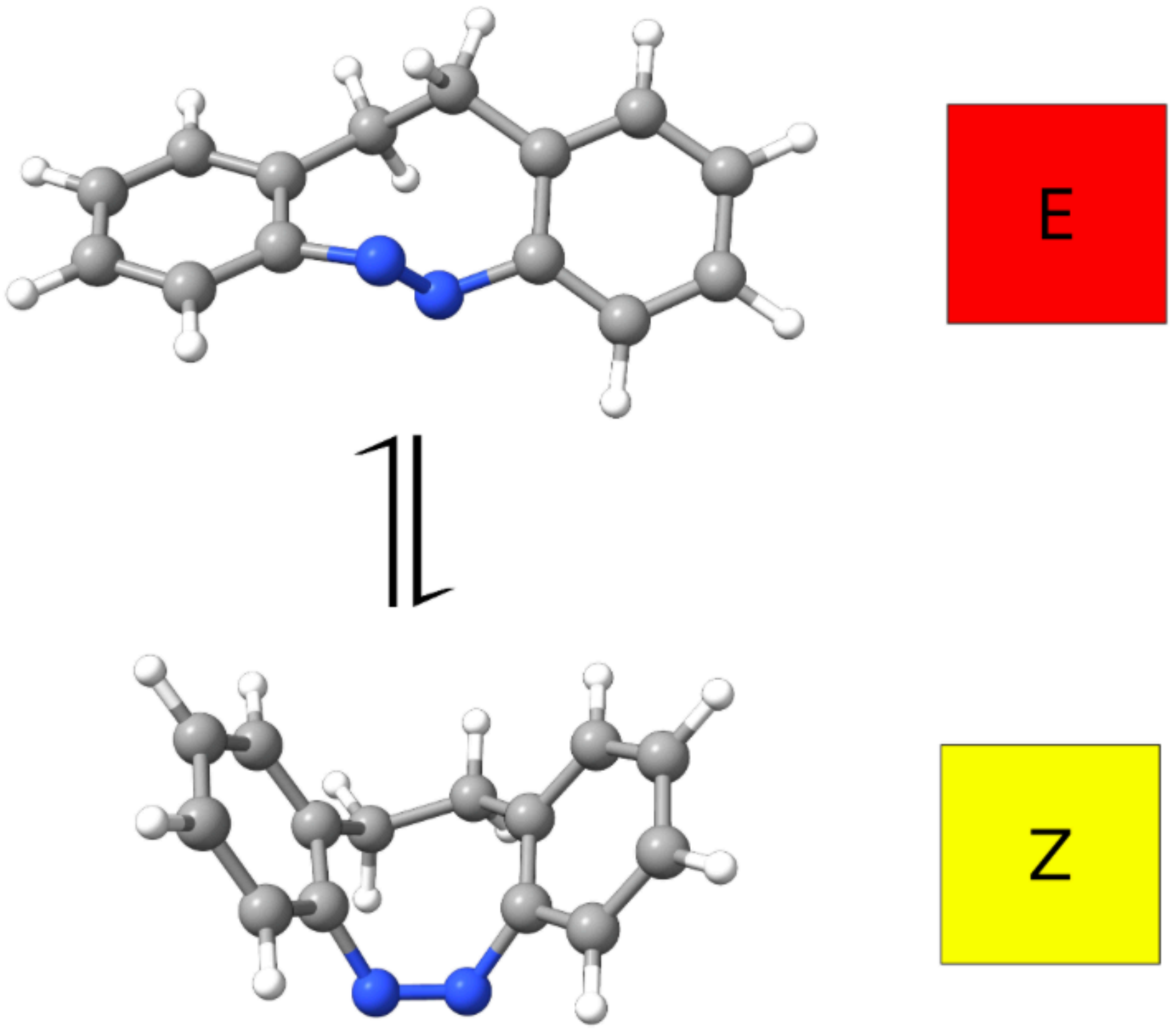
# UVVis spectroscopy (UV/Vis)

Predicting the UV/Vis spectrum is, essentially, predicting the electronic excited states of a system, their energies and the probabilities of transition between them.

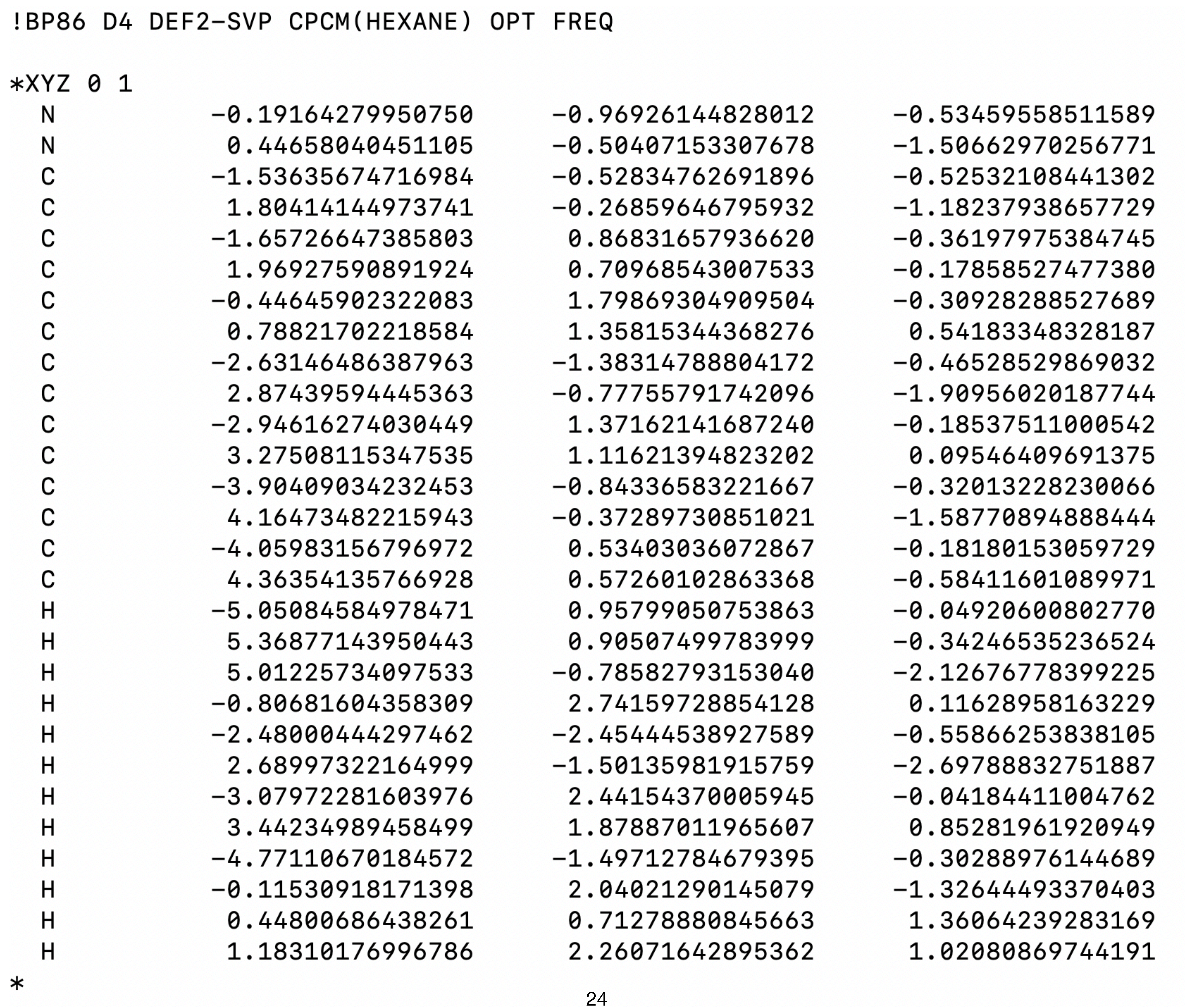
In ORCA, there are several methods that can compute excited state properties with higher or lower accuracy, but here we will discuss only two of them: the simpler and widely used TD-DFT, that presents a good speed to accuracy trade-off, and the newer STEOM-DLPNO-CCSD, that is closer to the high-end of excited state methods.

## Example: Azobenzene E/Z Isomers

To make this rather abstract topic into something more concrete, we will try to simulate the experimental results obtained for an azobenzene derivative [Temps2009]:



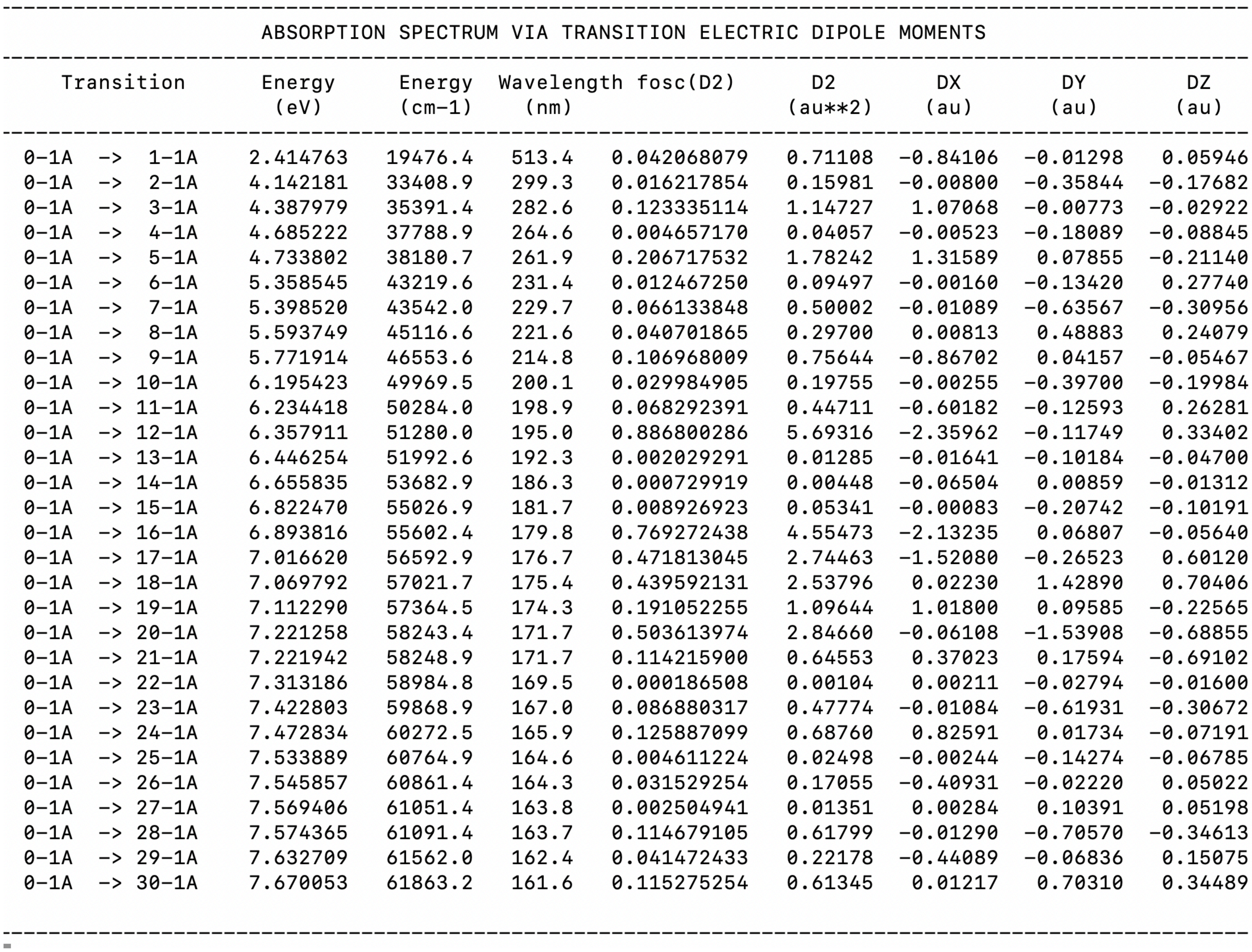
# Optimize the structure



```
!BP86 D4 DEF2-SVP CPCM(HEXANE) OPT FREQ

*XYZ 0 1
  N         -0.19164279950750    -0.96926144828012    -0.53459558511589
  N          0.44658040451105    -0.50407153307678    -1.50662970256771
  C         -1.53635674716984    -0.52834762691896    -0.52532108441302
  C          1.80414144973741    -0.26859646795932    -1.18237938657729
  C         -1.65726647385803     0.86831657936620    -0.36197975384745
  C          1.96927590891924     0.70968543007533    -0.17858527477380
  C         -0.44645902322083     1.79869304909504    -0.30928288527689
  C          0.78821702218584     1.35815344368276     0.54183348328187
  C         -2.63146486387963    -1.38314788804172    -0.46528529869032
  C          2.87439594445363    -0.77755791742096    -1.90956020187744
  C         -2.94616274030449     1.37162141687240    -0.18537511000542
  C          3.27508115347535     1.11621394823202     0.09546409691375
  C         -3.90409034232453    -0.84336583221667    -0.32013228230066
  C          4.16473482215943    -0.37289730851021    -1.58770894888444
  C         -4.05983156796972     0.53403036072867    -0.18180153059729
  C          4.36354135766928     0.57260102863368    -0.58411601089971
  H         -5.05084584978471     0.95799050753863    -0.04920600802770
  H          5.36877143950443     0.90507499783999    -0.34246535236524
  H          5.01225734097533    -0.78582793153040    -2.12676778399225
  H         -0.80681604358309     2.74159728854128     0.11628958163229
  H         -2.48000444297462    -2.45444538927589    -0.55866253838105
  H          2.68997322164999    -1.50135981915759    -2.69788832751887
  H         -3.07972281603976     2.44154370005945    -0.04184411004762
  H          3.44234989458499     1.87887011965607     0.85281961920949
  H         -4.77110670184572    -1.49712784679395    -0.30288976144689
  H         -0.11530918171398     2.04021290145079    -1.32644493370403
  H          0.44800686438261     0.71278880845663     1.36064239283169
  H          1.18310176996786     2.26071642895362     1.02080869744191
*
```

# UVVis spectroscopy (UV/Vis)

```
!CAM-B3LYP DEF2-TZVP CPCM(HEXANE)

%TDDFT
   NROOTS   30
END

*XYZ 0 1
  N          -0.20233261350251     -0.98352101890508     -0.53864256798465
  N           0.45685574902912     -0.51593952720020     -1.51407147792640
  C          -1.54295554443568     -0.53876036443078     -0.52338042376975
  C           1.81047923822707     -0.27363430990024     -1.19077727859341
  C          -1.66606508184945      0.87410430721721     -0.35993830396083
  C           1.97855314383950      0.71486214506290     -0.17459021080388
  C          -0.44773448184299      1.80225286700293     -0.30896092469013
  C           0.78948412680428      1.36020875322509      0.54510911346728
  C          -2.65381442370950     -1.39733328617257     -0.46389898574428
  C           2.89596537305414     -0.78576040510117     -1.92161237307395
  C          -2.96659540316517      1.38180597015202     -0.18218068923252
  C           3.29639462441249      1.12503336545013      0.10079423690754
  C          -3.93670500857494     -0.85115653182447     -0.31568401546832
  C           4.19686278079702     -0.37488772643820     -1.59757363771191
  C          -4.09256770697750      0.53953556166117     -0.17641062039320
  C           4.39655119246363      0.57983393435534     -0.58449547923311
  H          -5.09610744215582      0.97122299710821     -0.04214572972590
  H           5.41464813117020      0.91837638262705     -0.33879587329159
  H           5.05650224604636     -0.79336459000480     -2.14300862182110
  H          -0.80850536474706      2.76323802254608      0.11108295421499
  H          -2.50021523125569     -2.48230731271427     -0.56052627767440
  H           2.70846633153024     -1.52059816927113     -2.71842687644395
  H          -3.09839031437952      2.46660305246919     -0.03788187466031
  H           3.46294010586585      1.89769331824380      0.86906392310715
  H          -4.81629333350793     -1.51271331070769     -0.29910927668970
  H          -0.11161962454321      2.04413840612430     -1.33961211731954
  H           0.44430346858122      0.70407700657517      1.37223745987253
  H           1.18524406282586      2.26909346285000      1.04237194864337
*
```



```
-----------------------------------------------------------------------------------------------
                       ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
-----------------------------------------------------------------------------------------------
    Transition      Energy     Energy  Wavelength fosc(D2)      D2        DX        DY        DZ
                     (eV)      (cm-1)    (nm)                 (au**2)    (au)      (au)      (au)
-----------------------------------------------------------------------------------------------
  0-1A  ->  1-1A    2.414763   19476.4   513.4   0.042068079   0.71108  -0.84106  -0.01298   0.05946
  0-1A  ->  2-1A    4.142181   33408.9   299.3   0.016217854   0.15981  -0.00800  -0.35844  -0.17682
  0-1A  ->  3-1A    4.387979   35391.4   282.6   0.123335114   1.14727   1.07068  -0.00773  -0.02922
  0-1A  ->  4-1A    4.685222   37788.9   264.6   0.004657170   0.04057  -0.00523  -0.18089  -0.08845
  0-1A  ->  5-1A    4.733802   38180.7   261.9   0.206717532   1.78242   1.31589   0.07855  -0.21140
  0-1A  ->  6-1A    5.358545   43219.6   231.4   0.012467250   0.09497  -0.00160  -0.13420   0.27740
  0-1A  ->  7-1A    5.398520   43542.0   229.7   0.066133848   0.50002  -0.01089  -0.63567  -0.30956
  0-1A  ->  8-1A    5.593749   45116.6   221.6   0.040701865   0.29700   0.00813   0.48883   0.24079
  0-1A  ->  9-1A    5.771914   46553.6   214.8   0.106968009   0.75644  -0.86702   0.04157  -0.05467
  0-1A  -> 10-1A    6.195423   49969.5   200.1   0.029984905   0.19755  -0.00255  -0.39700  -0.19984
  0-1A  -> 11-1A    6.234418   50284.0   198.9   0.068292391   0.44711  -0.60182  -0.12593   0.26281
  0-1A  -> 12-1A    6.357911   51280.0   195.0   0.886800286   5.69316  -2.35962  -0.11749   0.33402
  0-1A  -> 13-1A    6.446254   51992.6   192.3   0.002029291   0.01285  -0.01641  -0.10184  -0.04700
  0-1A  -> 14-1A    6.655835   53682.9   186.3   0.000729919   0.00448  -0.06504   0.00859  -0.01312
  0-1A  -> 15-1A    6.822470   55026.9   181.7   0.008926923   0.05341  -0.00083  -0.20742  -0.10191
  0-1A  -> 16-1A    6.893816   55602.4   179.8   0.769272438   4.55473  -2.13235   0.06807  -0.05640
  0-1A  -> 17-1A    7.016620   56592.9   176.7   0.471813045   2.74463  -1.52080  -0.26523   0.60120
  0-1A  -> 18-1A    7.069792   57021.7   175.4   0.439592131   2.53796   0.02230   1.42890   0.70406
  0-1A  -> 19-1A    7.112290   57364.5   174.3   0.191052255   1.09644   1.01800   0.09585  -0.22565
  0-1A  -> 20-1A    7.221258   58243.4   171.7   0.503613974   2.84660  -0.06108  -1.53908  -0.68855
  0-1A  -> 21-1A    7.221942   58248.9   171.7   0.114215900   0.64553   0.37023   0.17594  -0.69102
  0-1A  -> 22-1A    7.313186   58984.8   169.5   0.000186508   0.00104   0.00211  -0.02794  -0.01600
  0-1A  -> 23-1A    7.422803   59868.9   167.0   0.086880317   0.47774  -0.01084  -0.61931  -0.30672
  0-1A  -> 24-1A    7.472834   60272.5   165.9   0.125887099   0.68760   0.82591   0.01734  -0.07191
  0-1A  -> 25-1A    7.533889   60764.9   164.6   0.004611224   0.02498  -0.00244  -0.14274  -0.06785
  0-1A  -> 26-1A    7.545857   60861.4   164.3   0.031529254   0.17055  -0.40931  -0.02220   0.05022
  0-1A  -> 27-1A    7.569406   61051.4   163.8   0.002504941   0.01351   0.00284   0.10391   0.05198
  0-1A  -> 28-1A    7.574365   61091.4   163.7   0.114679105   0.61799  -0.01290  -0.70570  -0.34613
  0-1A  -> 29-1A    7.632709   61562.0   162.4   0.041472433   0.22178  -0.44089  -0.06836   0.15075
  0-1A  -> 30-1A    7.670053   61863.2   161.6   0.115275254   0.61345   0.01217   0.70310   0.34489

-----------------------------------------------------------------------------------------------
```

ORCA 6.0 TUTORIALS

SEARCH

Plotting Fukui functions

Automated docking (DOCKER)

SPECTROSCOPY

Infrared and Raman

UVVis spectroscopy (UV/Vis)

Electronic Circular Dichroism (ECD)

Vibrational Circular Dichroism (VCD)

Nuclear Magnetic Resonance (NMR)

Electron Paramagnetic Resonance (EPR)

Spin-orbit coupling

MULTISCALE METHODS

# Starting with Multiscale models - QM/XTB ONIOM

Let's start our incursion on the world of multiscale calculations. Multiscale here means that we will use different levels of theory/methods for different parts of our system.

These multiscale models can be useful for a variety of problems: treating the active site of a protein on a higher level and the rest of the protein on a simpler level, modeling a chromophore on a higher level and the surrounding explicit solvent on a lower level, or even splitting a medium-sized system into smaller parts for improved efficiency.

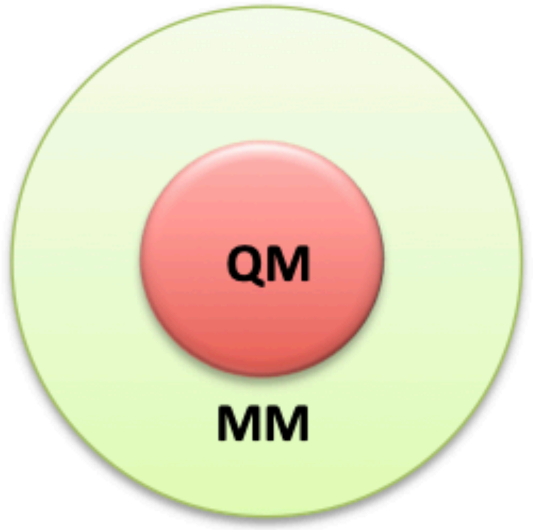
In ORCA, there are different approaches to run multiscale simulations, based on three main categories:

1. ONIOM methods mixing different "Quantum Mechanical" (QM) methods,
2. QM/MM methods mixing QM with "Molecular Mechanics" (MM) methods that rely on predefined force-fields, and
3. Crystal-QM/MM methods which treat a small part of a periodic crystal (e.g. the unit cell) at a high QM level and embed this in a lower level model of the large super-cell model.

It is important to emphasize that our implementation is focused in all cases on a "QM-centric" perspective, meaning it is aimed at users familiar with QM approaches, and so will be these tutorials.

```
!QM/XTB revPBE D4 DEF2-TZVP
%QMMM QMATOMS {0:11} END END
* XYZ 0 1
C   -0.701502936  -0.290627698   2.406884396
H   -1.183295956   0.395647770   3.098874220
H    0.349561571  -0.030321572   2.307833035
H   -0.794056854  -1.291605451   2.824039291
C   -1.448546246  -0.244876636   1.091815299
O   -2.660450004  -0.428479088   1.034345768
N   -0.670056563   0.005916557   0.009776912
H    0.326675319   0.122563958   0.141592839
C   -1.227054574   0.089793737  -1.319967541
H   -2.292024256  -0.106501186  -1.240877562
H   -1.077801692   1.079940300  -1.748543540
H   -0.776628489  -0.647999190  -1.983372734
C    2.041774914  -2.351697968   0.686397615
H    2.599999718  -3.261701204   0.480489612
H    1.113083056  -2.358227418   0.122072198
H    1.782555985  -2.328251269   1.743338615
C    2.809410856  -1.097285929   0.350160876
O    2.264224213   0.004150876   0.293188485
N    4.136169069  -1.266099696   0.136412906
H    4.512490369  -2.193345392   0.213170232
C    5.023407253  -0.159633723  -0.152535629
H    4.409214873   0.731176053  -0.232359342
H    5.750821803  -0.020167991   0.644867678
H    5.548397546  -0.319615451  -1.091677965
*
```

# Quantum mechanics/molecular mechanics (QM/MM) methods



$$\hat{H} = \hat{H}_{QM} + \hat{H}_{MM} + \hat{H}_{Interactions}$$

$$E_{Total}(\mathrm{QM{:}\,MM}) = E_{QM}(\mathrm{QM}) + E_{MM}(\mathrm{MM}) + E_{Interactions}(\mathrm{QM{:}\,MM})$$

---

$$E_{Interactions}(\mathrm{QM{:}\,MM}) = E_{MM}(\mathrm{QM{:}\,MM}) - [E_{MM}(\mathrm{QM}) + E_{MM}(MM)]$$

$$\boxed{E_{Total}(\mathrm{QM{:}\,MM}) = E_{QM}(\mathrm{QM}) + E_{MM}(\mathrm{QM{:}\,MM}) - E_{MM}(\mathrm{QM})}$$

*Our own n-layered integrated molecular orbital and molecular mechanics (ONIOM) method*

F. Maseras, K. Morokuma, *J. Comput. Chem.* 1995, *16*, 1170.
S. Humbel, S. Sieber, K. Morokuma, *J. Chem. Phys.* 1996, 105, 1959.
M. Svensson, S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber, and K. Morokuma, *J. Phys. Chem.* 1996, 100, 19357.
L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H-B. Li, L. Ding and K. Morokuma, *Chem. Rev.* 2015, 115, 5678-5796.