

# *Zacros* Tutorial 1: Demonstration of Ethylene Hydrogenation Example

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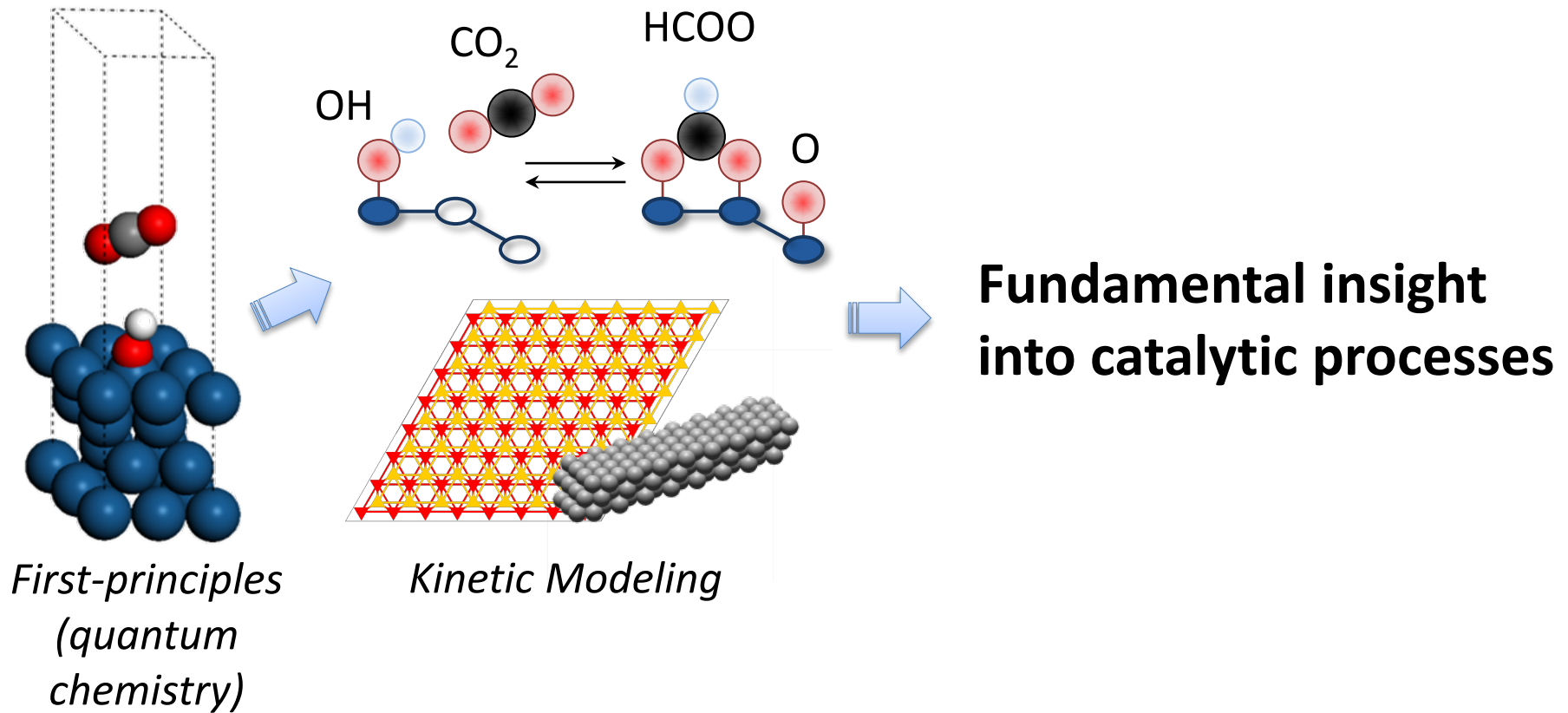
“Workshop on Multiscale Computational Catalysis and Materials Science”

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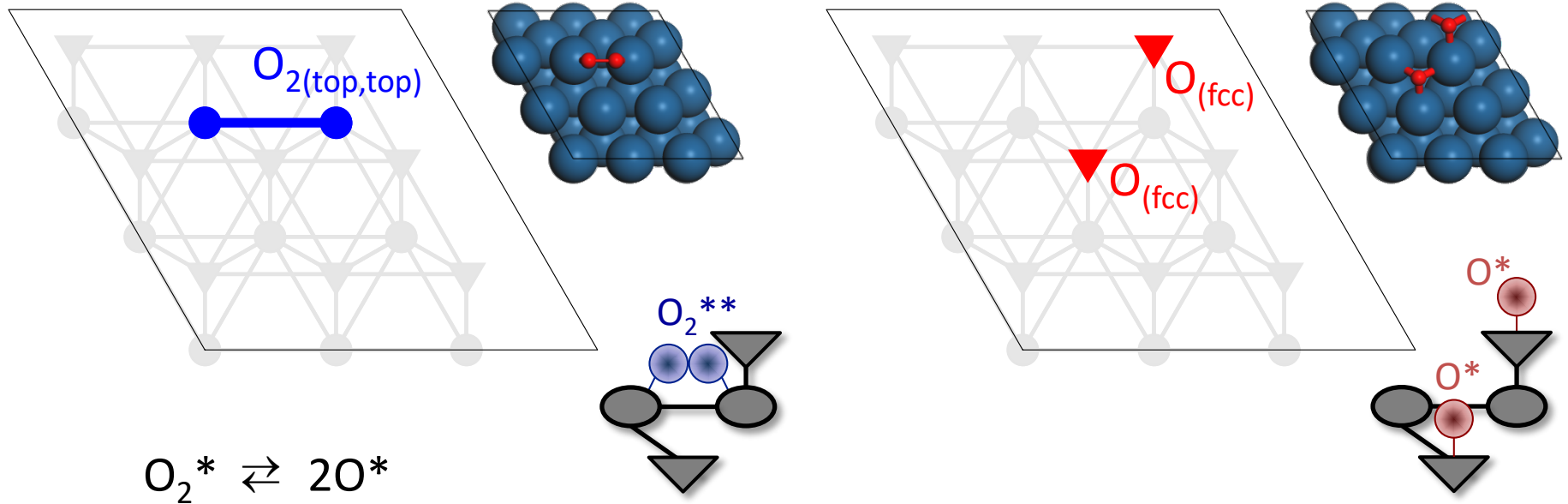
# First-Principles Kinetic Modelling

2



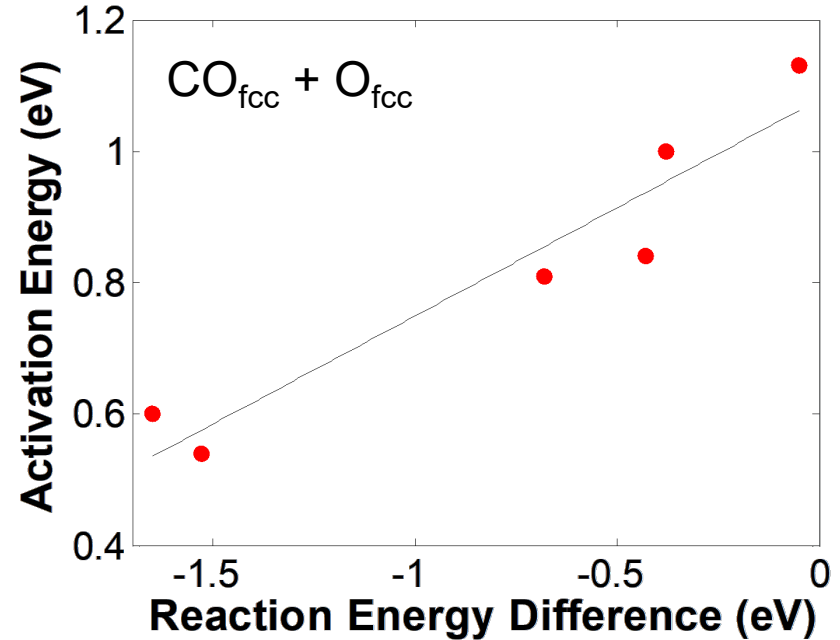
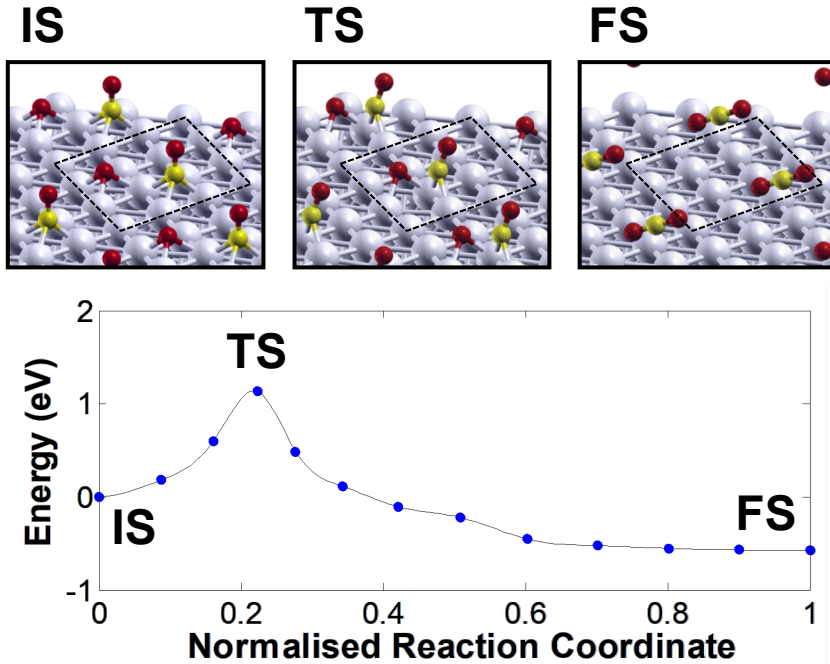
- **Catalytic performance metrics:** activity, selectivity, yield
- **Mechanistic understanding:** dominant pathway, abundant surface species, active sites

# Why Zacros?



- First KMC package to use **graph-theory** for treating:
  - reaction patterns of arbitrary complexity

# Why Zacros?



- First KMC package to use **graph-theory** for treating:
  - reaction patterns of arbitrary complexity
  - coverage effects with consistency and high-accuracy

✓ *High-fidelity KMC simulation in catalysis*

# Software Installation

# Building and creating executable

## Create a build directory and enter the build directory

```
mkdir build; cd build;
```

## Serial build:

```
cmake ../ -DCMAKE_BUILD_TYPE=Release  
          -Ddoopenmp=off -Ddompi=off  
  
-DCMAKE_BUILD_TYPE=Debug: Disables compiler  
optimizations and enables debug flags  
  
-DCMAKE_Fortran_FLAGS='-g -fbounds-check'
```

**Create executable:** `make -j`

# Custom Options for CMake

- Ddoopenmp=on: enables shared-memory parallelization (product-caching); accelerates simulations with long-ranged adsorbate lateral interaction

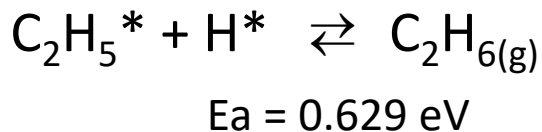
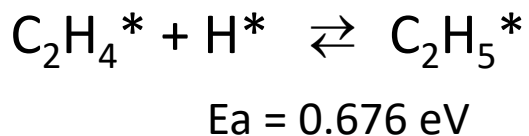
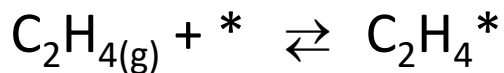
## *Upcoming features*

- Ddmpi=on: Distributed parallelization of kinetic Monte-Carlo by implementing the “Time Warp” algorithm

# Input Files: Structure and Content



# Demonstration: Ethylene Hydrogenation



Gas species		Surface species	
$\text{H}_{2(\text{g})}$	0 eV	$\text{H}^*$	-0.468 eV
$\text{C}_2\text{H}_{4(\text{g})}$	0 eV	$\text{C}_2\text{H}_4^*$	-0.607 eV
		$\text{C}_2\text{H}_5^*$	-0.733 eV
$\text{C}_2\text{H}_6(\text{g})$	-1.379 eV		

- On Pd(100) the reaction proceeds via two subsequent hydrogenation steps after adsorption of reactants<sup>1</sup>

<sup>1</sup> Hansen & Neurock, Journal of Catalysis 196, 241–252 (2000)

# General Simulation Input

```

random_seed      71543
temperature      380.0
pressure         2.00

n_gas_species    3
gas_specs_names  H2      C2H4      C2H6
gas_energies     0.000    0.000    -1.379 # eV
gas_molec_weights 2.016    28.053    30.069 # g/mol
gas_molar_fracs  0.100    0.100    0.000

n_surf_species   3
surf_specs_names H*  C2H4*  C2H5*
surf_specs_dent  1  2     1

snapshots        on time 1e-5
process_statistics on time 1e-5
species_numbers  on time 1e-5

event_report      on

max_steps         infinity
max_time          1.0e+50
wall_time         5000

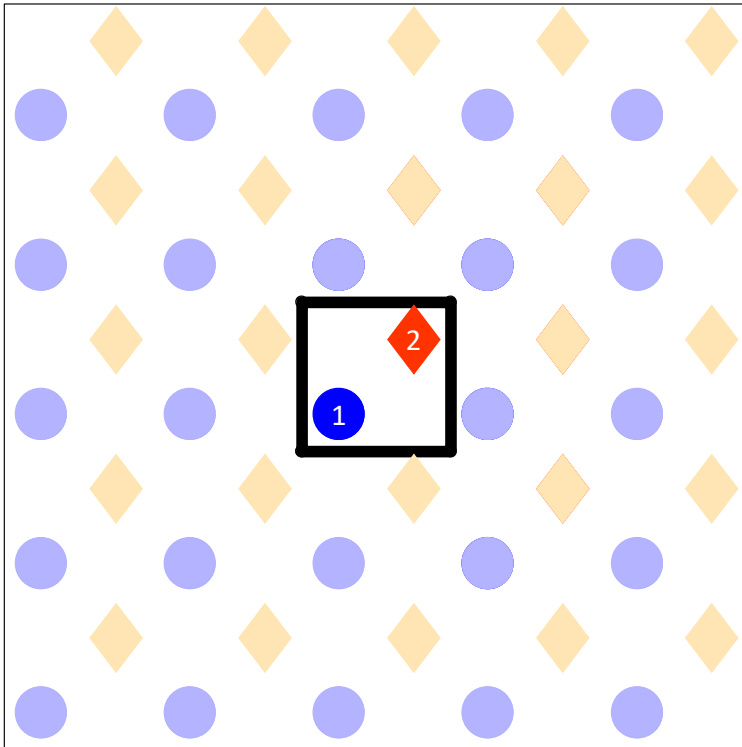
finish

```

- Zacros's input files:
  - General parameters
  - Lattice structure
  - Energetics
  - Reaction mechanism
  - Initial state (optional)
- General parameters appear in file: `simulation_input.dat`
  - Conditions
  - Species information
  - Gas energetics
  - Simulation flags and parameters

# Lattice Input

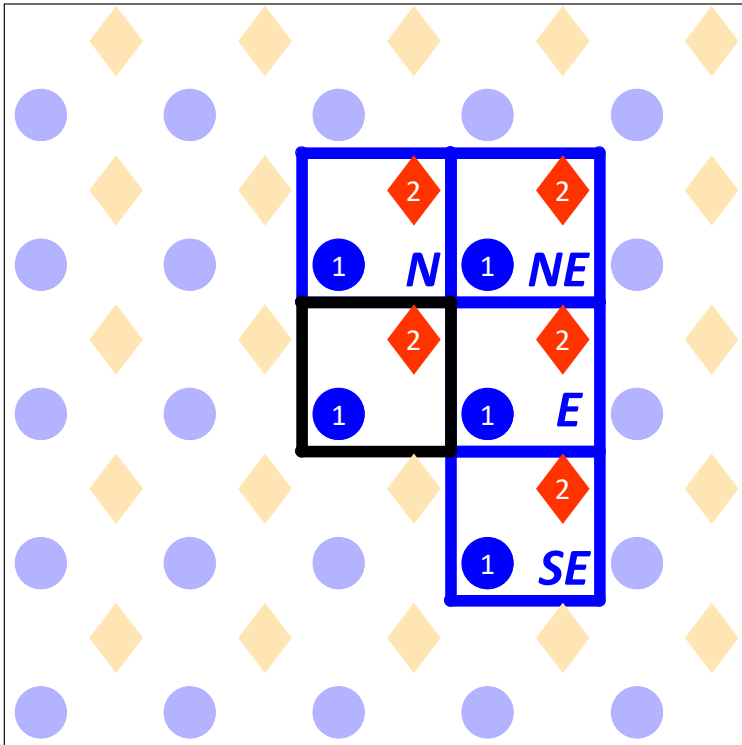
- *Zacros* incorporates a lattice generator for easily defining any periodic 2D lattice structure



- *Draw the unit cell with all sites therein*

# Lattice Input

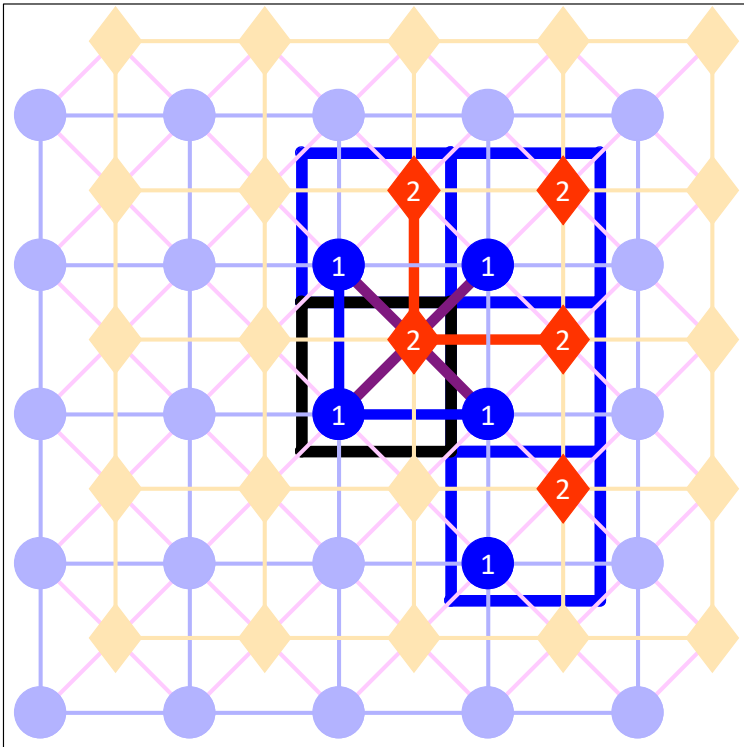
- *Zacros* incorporates a lattice generator for easily defining any periodic 2D lattice structure



- *Draw the unit cell with all sites therein*
- *Draw the periodic images clockwise from N to SE*

# Lattice Input

- *Zacros* incorporates a lattice generator for easily defining any periodic 2D lattice structure



- *Draw the unit cell with all sites therein*
- *Draw the periodic images clockwise from N to SE*
- *Mark all links with neighbouring sites on these cells*

# Lattice Input

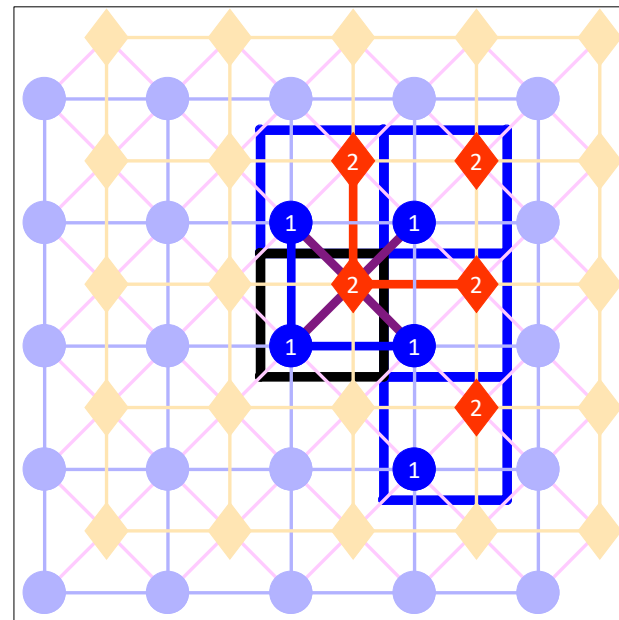
```

lattice periodic_cell
cell_vectors # in row format (Angstroms)
  2.751140353562500 0.000000000000000
  0.000000000000000 2.751140353562500
repeat_cell      7 7
n_site_types     2
site_type_names  top hol
n_cell_sites     2
site_types       top hol
site_coordinates # fractional coord. (x,y) in rows
  0.250000000000000 0.250000000000000
  0.750000000000000 0.750000000000000

neighboring_structure # site-neighsite cell
1-2 self
1-1 north
1-1 east
2-1 north
2-1 northeast
2-1 east
2-2 north
2-2 east
end_neighboring_structure

end_lattice

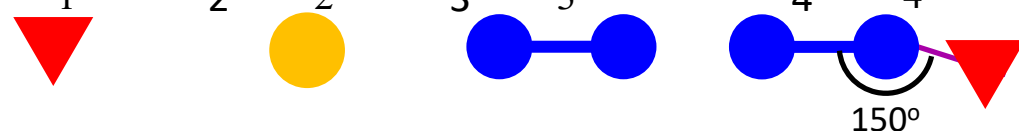
```



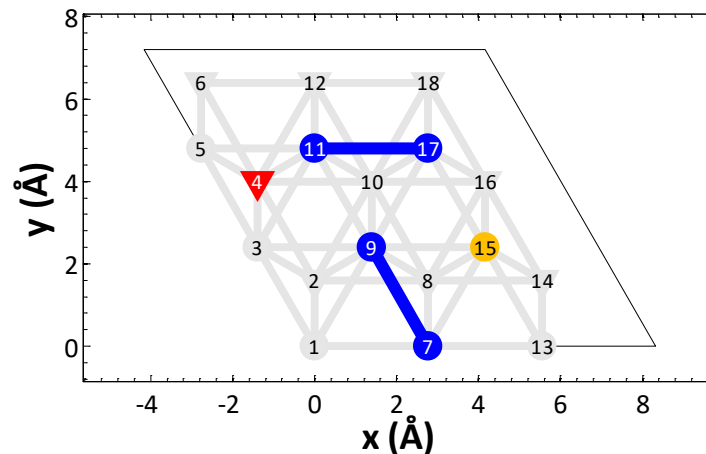
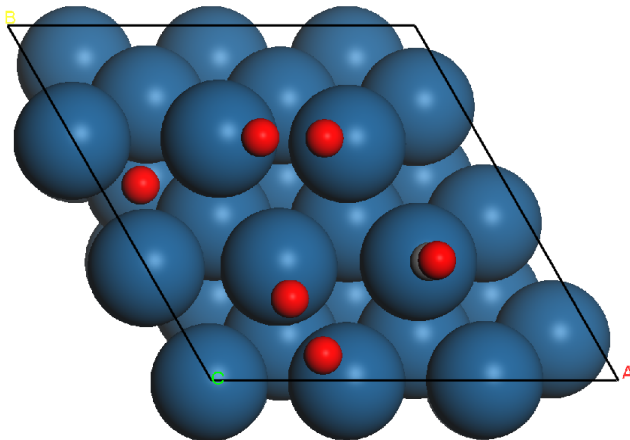
- Straightforward translation of the figure into file:  
lattice\_input.dat

# Energetics Model

- Zacros* incorporates cluster expansion Hamiltonians for the accurate representation of adsorbate lateral interactions

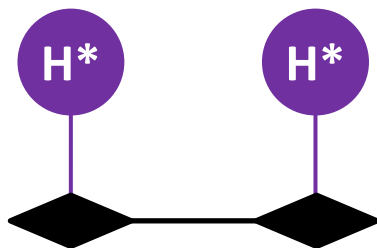
$$\text{Energy} = N_1 \times \varepsilon_1 + N_2 \times \varepsilon_2 + N_3 \times \varepsilon_3 + N_4 \times \varepsilon_4 + \dots$$


Energy = -5.191008 eV

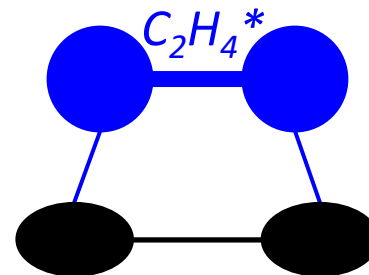


# Energetics Input

- To define each pattern (cluster) in the Hamiltonian:



Adsorbed  
hydrogen pair  
repulsion



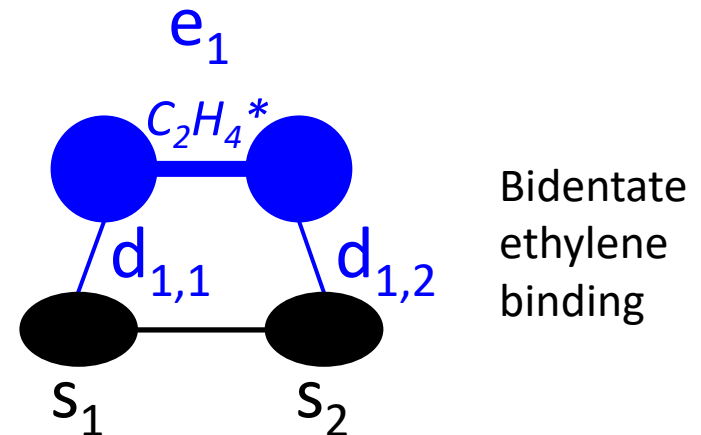
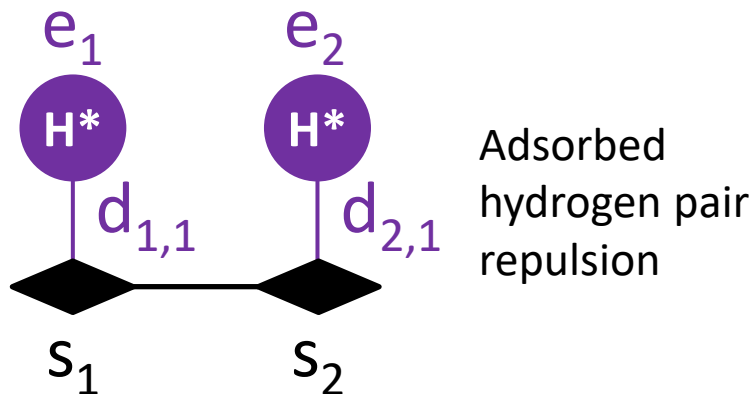
Bidentate  
ethylene  
binding

- Draw all the sites and species involved in the pattern*



# Energetics Input

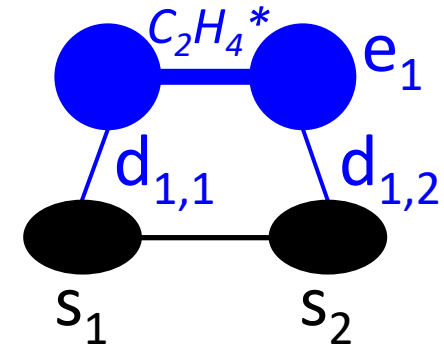
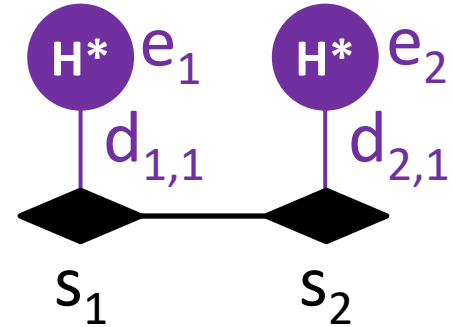
- To define each pattern (cluster) in the Hamiltonian:



- Draw all the sites and species involved in the pattern*
- Number all the sites, adsorbates (surface entities), and dentates thereof*

# Energetics Input

```
energetics
#####
cluster H_Pair_hollow
  sites 2
  neighboring 1-2
  lattice_state
    1 H* 1
    2 H* 1
  site_types          hol hol
  graph_multiplicity  2
  cluster_eng         -0.100 # eV
end_cluster
#####
cluster C2H4_top-top
  sites 2
  neighboring 1-2
  lattice_state
    1 C2H4* 1
    1 C2H4* 2
  site_types          top top
  graph_multiplicity  1
  cluster_eng         -0.607 # eV
end_cluster
##### ...
end_energetics
```



- Straightforward translation of the figure into file:  
energetics\_input.dat

# Reaction Mechanism

- Reactions are similarly represented as graphs with an initial and a final state (reactants, products)

## *Ethylene hydrogenation step*



*Initial state: ethylene next to a hydrogen adatom*

*Final state: ethyl and empty sites pseudo-species*

# Mechanism Input

```
mechanism
```

```
##### ...
```

```
reversible_step C2H4_hydrogenation
```

```
  sites 3
```

```
  neighboring 1-2 2-3
```

```
  initial # (entity, species, dentate)
```

```
    1 C2H4* 1
```

```
    1 C2H4* 2
```

```
    2 H* 1
```

```
  final
```

```
    1 C2H5* 1
```

```
    2 * 1
```

```
    3 * 1
```

```
  site_types      top top hol
```

```
  pre_expon      1.000e+13
```

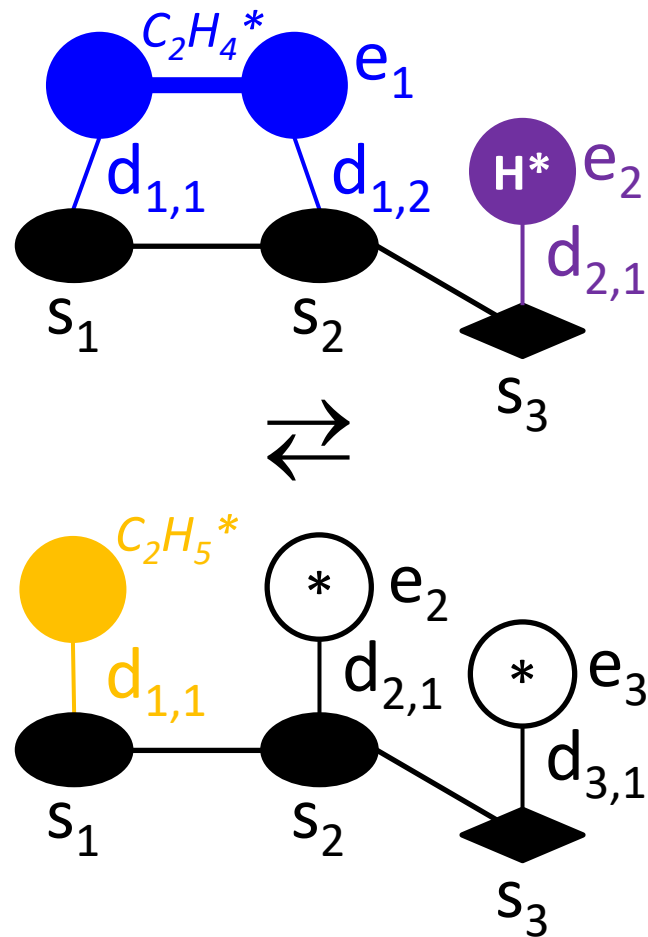
```
  pe_ratio       1.000
```

```
  activ_eng      0.676
```

```
end_reversible_step
```

```
##### ...
```

```
end_mechanism
```

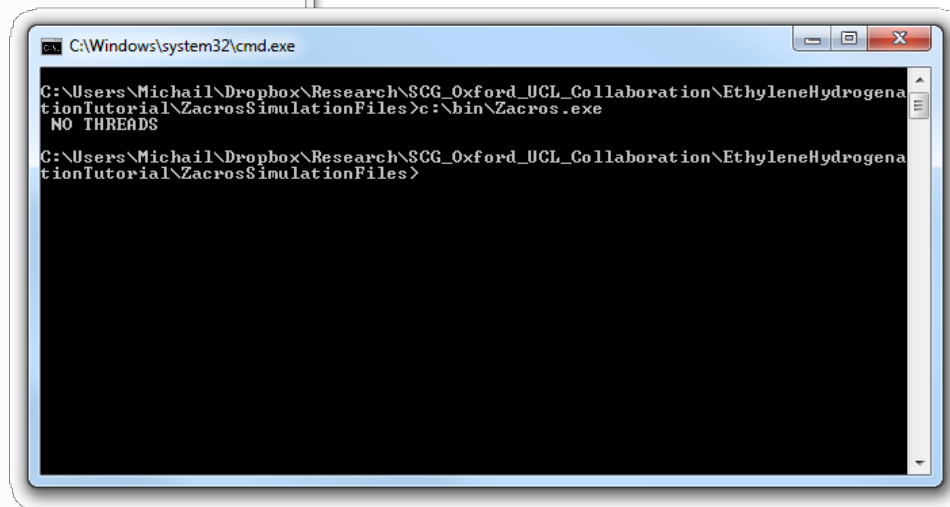
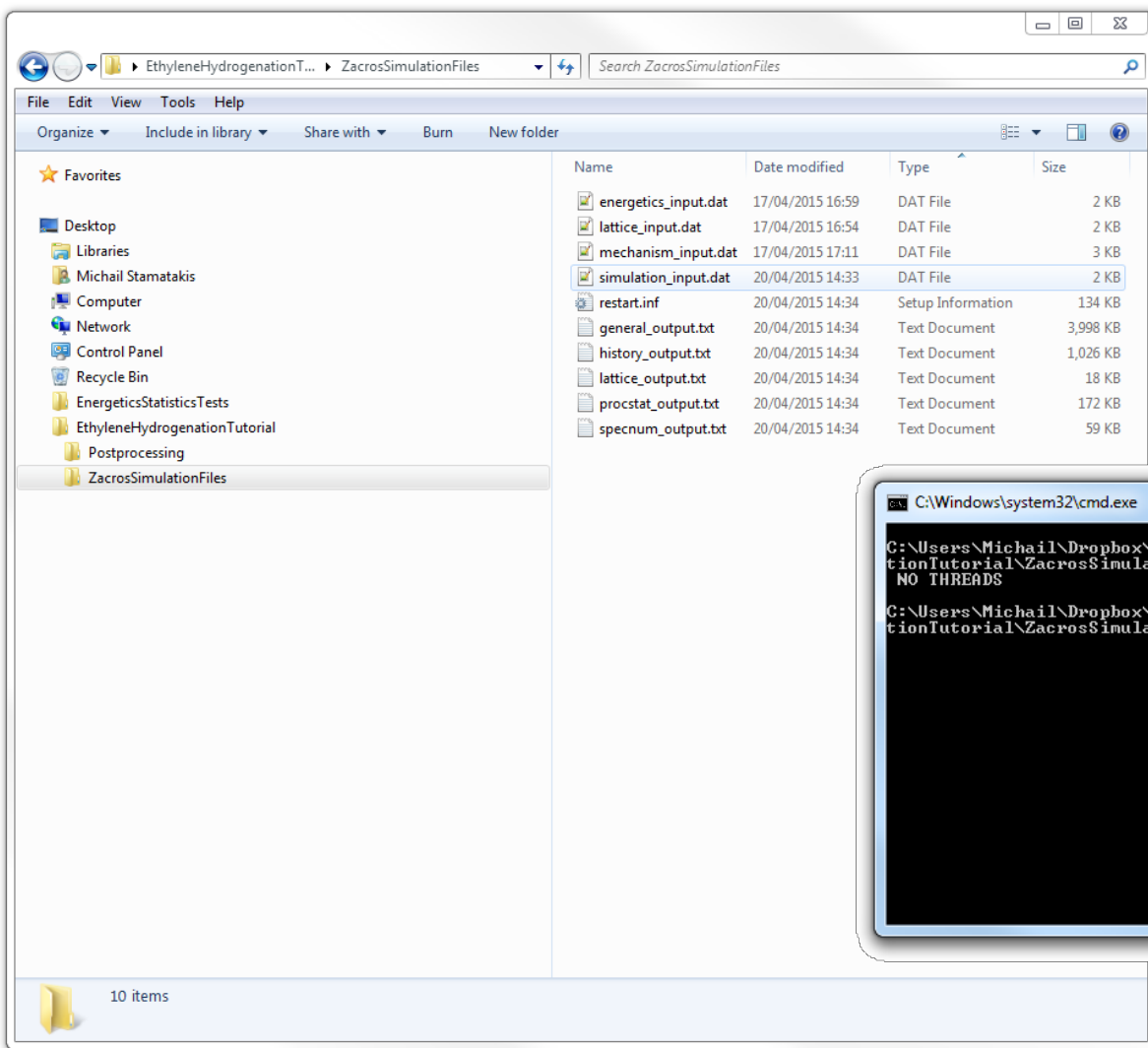


- File: mechanism\_input.dat

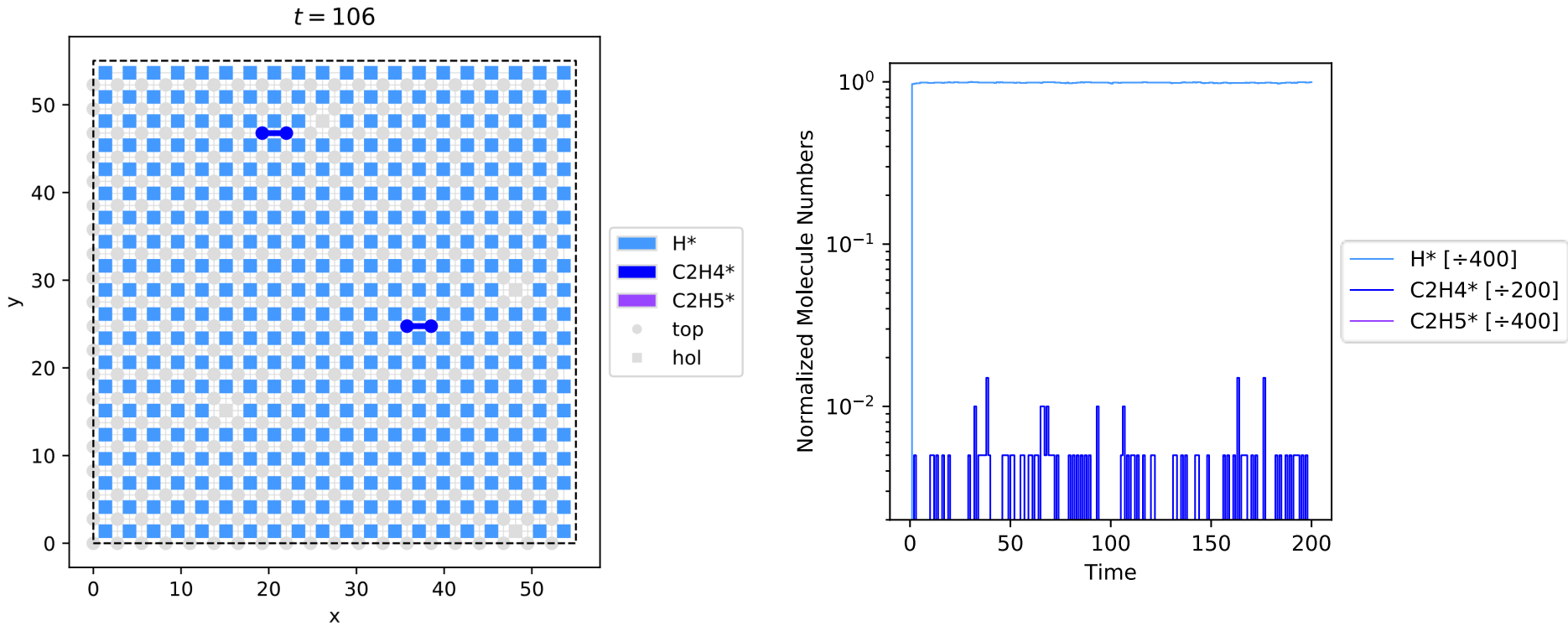
# Running a Simulation

# Running *Zacros*

- Put all input files in one directory and invoke *Zacros*

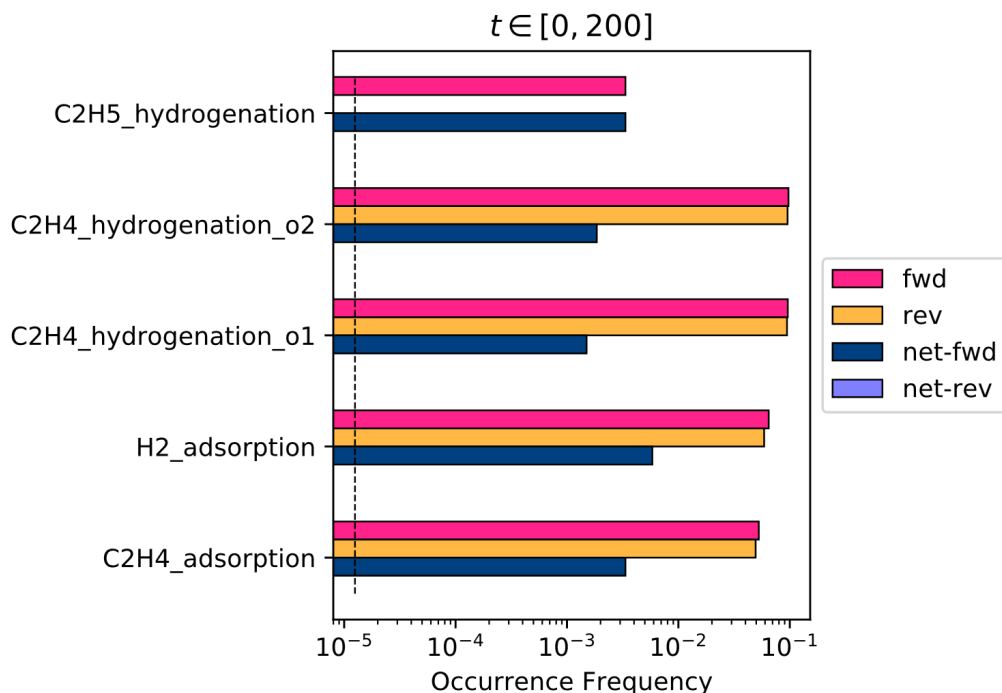


# Post-processing the Results

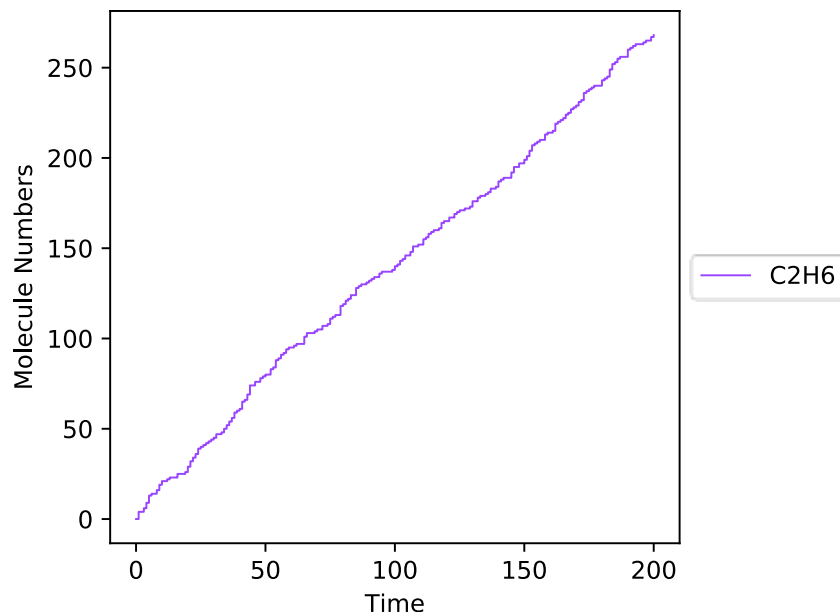


- “Zacros-post” tool available for post-processing output (standalone GUI and Python importable libraries)
- Surface coverages can be investigated and most abundant species identified

# Post-processing the Results



**Turnover Frequency:**  
 268 molecules / 200 s / 400 sites =  $0.003 \text{ s}^{-1}$



- Statistical analysis of reaction events can identify major pathways and rate-determining steps
- Catalytic activity and selectivity can be estimated



# For more information...



The screenshot shows the Zacros website homepage. The browser address bar displays <http://zacros.org/>. The website features a navigation menu with links for Home, Development, Software, Tutorials, and Publications. A search bar is located in the top right corner. The main content area includes a large image of a molecular structure and a smaller image of a scientific publication cover titled "Catalysis Science & Technology". Below the images, there is a section titled "About Zacros" which provides a detailed description of the software package and its capabilities.

**Zacros**  
Advanced lattice-KMC made easy

keyword(s) ...  
Search

Home Development Software Tutorials Publications

Catalysis Science & Technology

Used in studies published in top peer-reviewed journals

### About Zacros

Zacros is a **Kinetic Monte Carlo software package** written in Fortran, for simulating molecular phenomena on catalytic surfaces. The tool enables researchers in the areas of Computational Catalysis and Surface Science to perform dynamic modelling of adsorption, desorption, surface diffusion, and reaction processes on heterogeneous catalysts. The rates of these elementary processes are typically computed from *ab initio* simulations, thereby enabling the prediction of catalytic performance metrics (such as activity and selectivity) from first principles. Zacros can also perform simulations of temperature programmed desorption/reaction spectra, enabling Surface Scientists to validate in detail hypothesised kinetic mechanisms against experimental data.

The package employs the **Graph-Theoretical KMC** methodology coupled with **cluster expansion Hamiltonians** for the adlayer energetics and Brønsted-Evans-Polanyi relations for the activation energies of elementary events. This framework can naturally capture:

- steric exclusion effects for species that bind in more than one catalytic sites,
- complex reaction patterns involving adsorbates in specific binding configurations and neighbouring patterns,

- Tutorials
- Exemplar input files
- Scientific publications
- Software development news and updates

<http://zacros.org>

# Activity

- Install *Zacros* on your computer or on the cluster under your account.
  - You may have to run the command: **export FC=ifort** before the cmake commands, in order to instruct cmake to use the Intel Fortran Compiler.
- Download **Zacros\_Tutorial\_01\_SimulationFiles.zip** (containing the input files for the ethylene hydrogenation example).
- Make a new directory, move the file there and unzip.
- Run the simulation, and when it completes, visualise the contents of **specnum\_output.dat** using Excel (or *Zacros-post* if you have it installed in your computer).