Zacros Tutorial 1: Demonstration of Ethylene Hydrogenation Example

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"Workshop on Multiscale Computational Catalysis and Materials Science"

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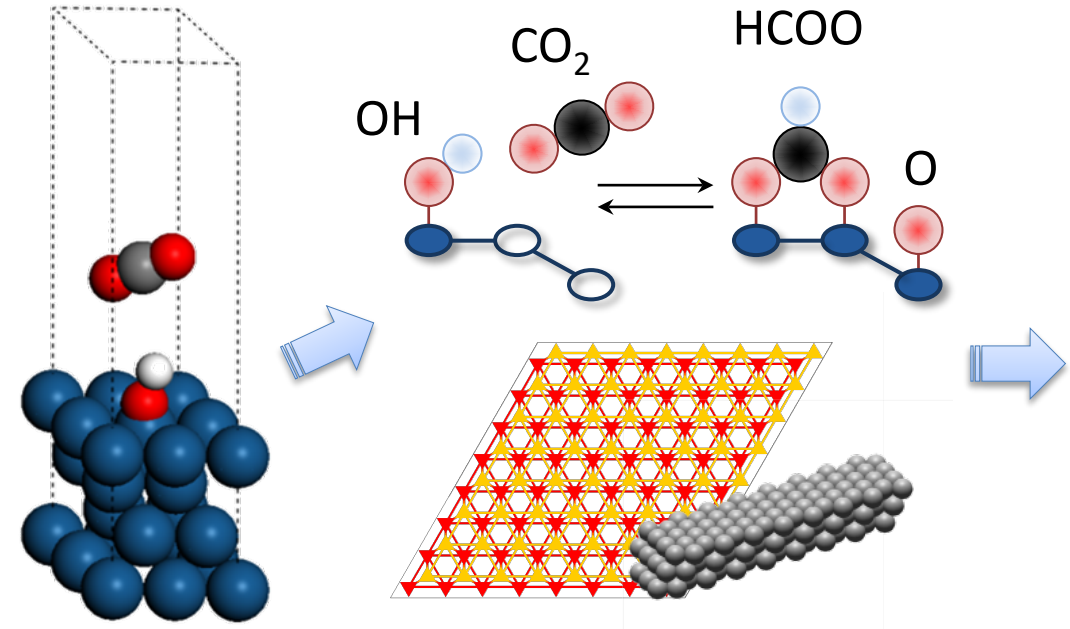
First-Principles Kinetic Modelling



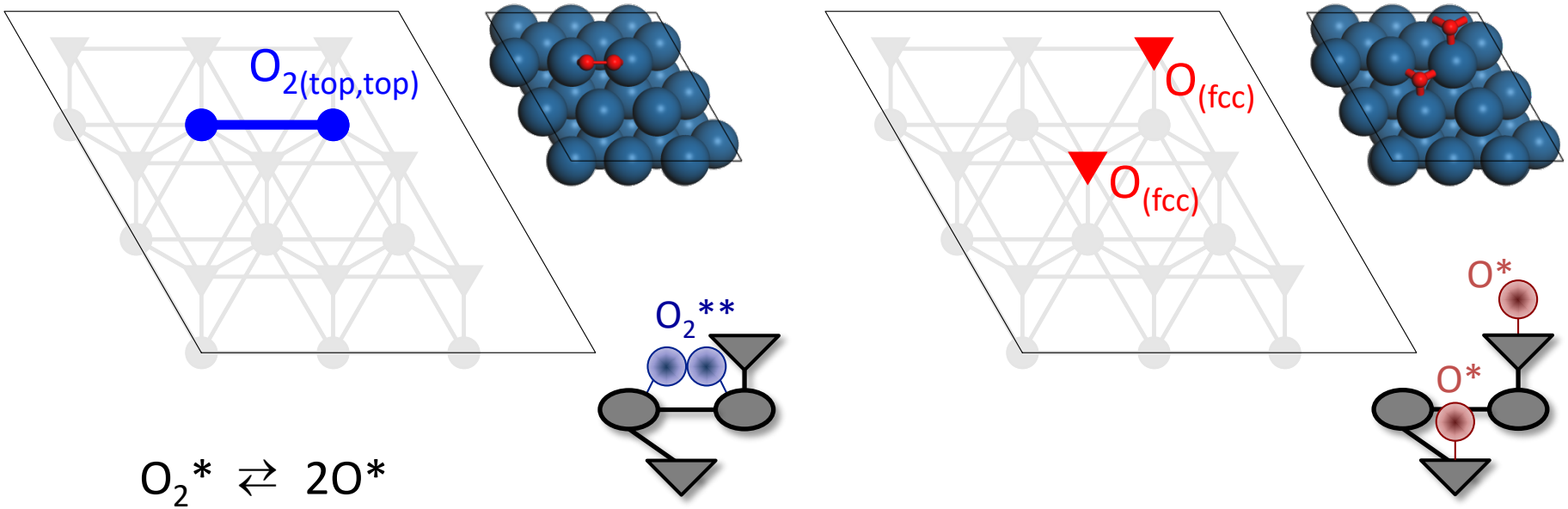
First-principles (quantum chemistry)

Kinetic Modeling

Fundamental insight into catalytic processes

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

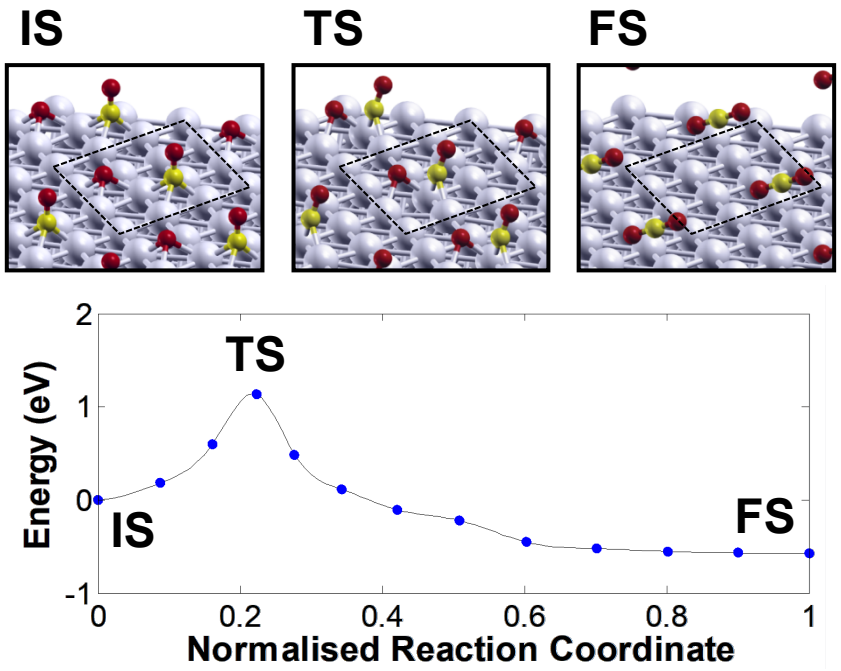
Why *Zacros*?

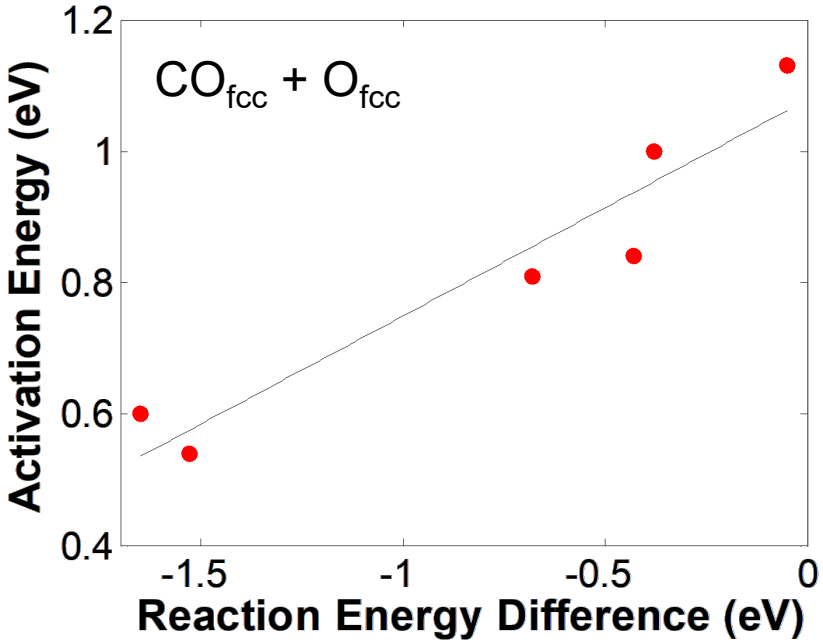


$O_2^* \rightleftarrows 2O^*$

- 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

- `-Ddompi=on`: Distributed parallelization of kinetic Monte-Carlo by implementing the "Time Warp" algorithm

Input Files:
Structure and Content

Demonstration: Ethylene Hydrogenation

$H_{2(g)} + 2* \rightleftarrows 2H*$

$C_2H_{4(g)} + * \rightleftarrows C_2H_4*$

$C_2H_4* + H* \rightleftarrows C_2H_5*$

Ea = 0.676 eV

$C_2H_5* + H* \rightleftarrows C_2H_{6(g)}$

Ea = 0.629 eV

Gas species		Surface species	
$H_{2(g)}$	0 eV	H*	-0.468 eV
$C_2H_{4(g)}$	0 eV	C_2H_4*	-0.607 eV
		C_2H_5*	-0.733 eV
$C_2H_{6(g)}$	-1.379 eV		

- On Pd(100) the reaction proceeds via two subsequent hydrogenation steps after adsorption of reactants[1]

[1] Hansen & Neurock, Journal of Catalysis 196, 241–252 (2000)

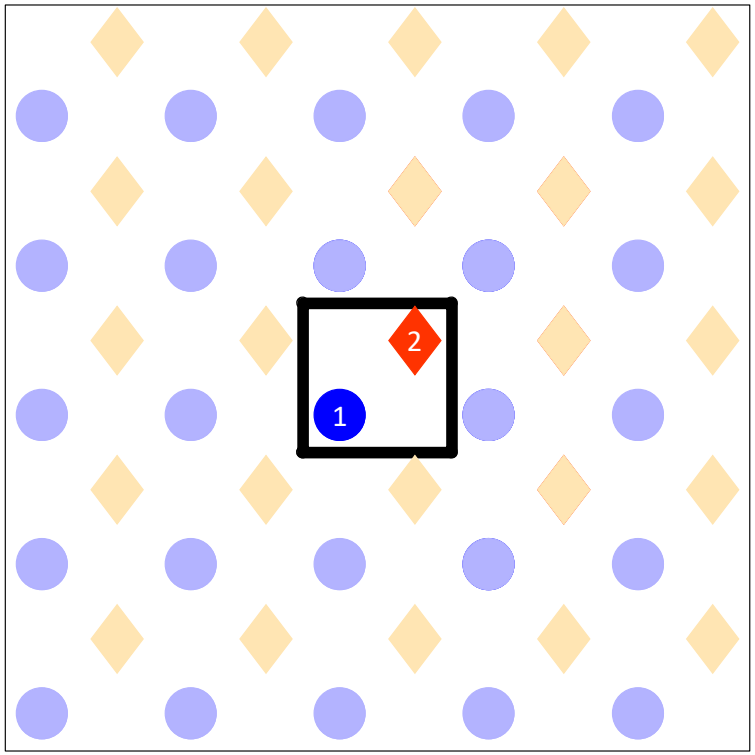
General Simulation Input

```
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*

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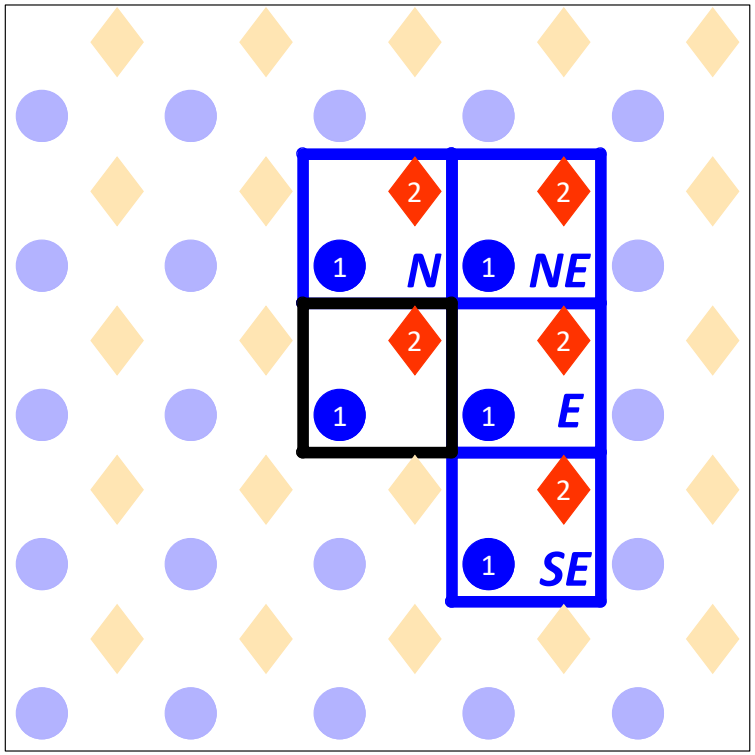

- *Draw the unit cell with all sites therein*
- *Draw the periodic images clockwise from N to SE*

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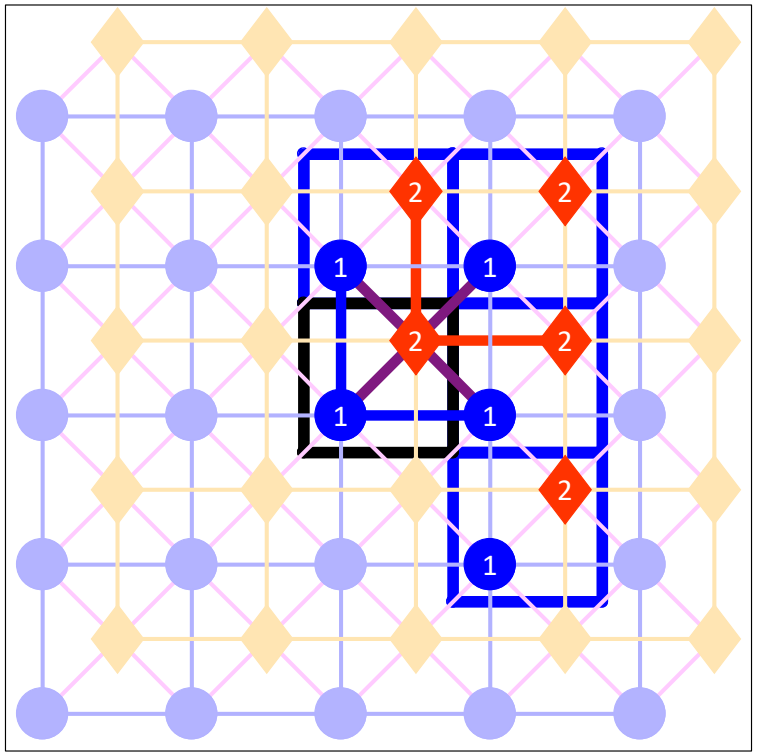


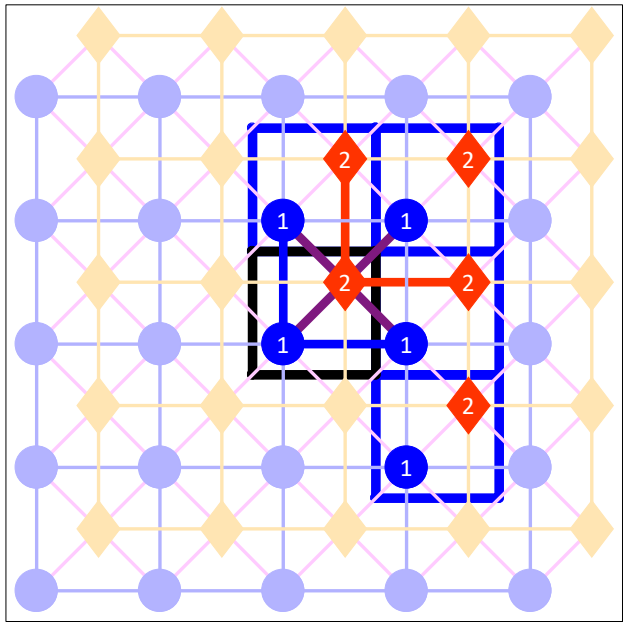
- *Draw the unit cell with all sites therein*
- *Draw the periodic images clockwise from N to SE*
- *Mark all links with neigh-bouring sites on these cells*

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
```

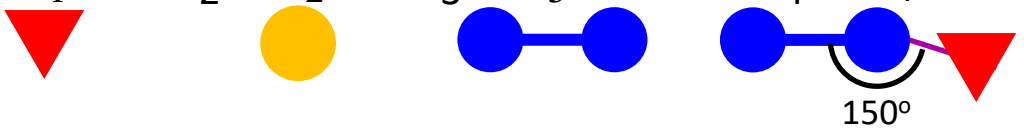


- Straightforward translation of the figure into file: `lattice_input.dat`

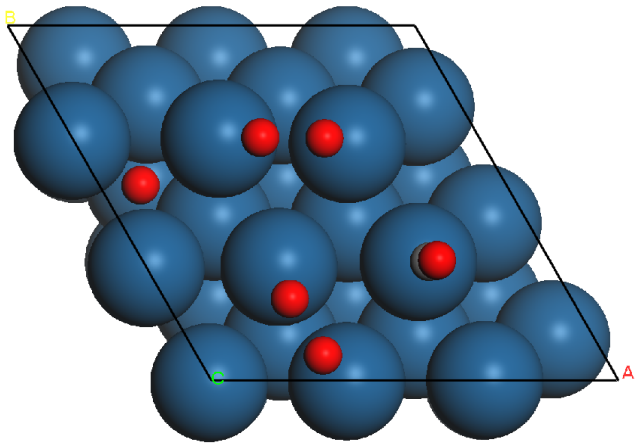
Energetics Model

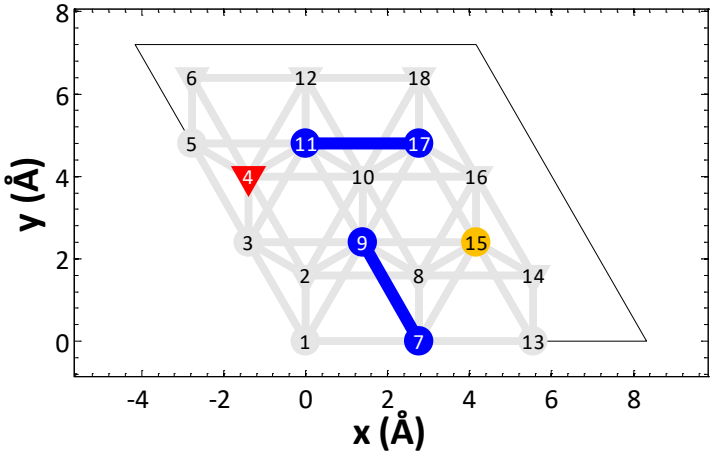
- *Zacros* incorporates cluster expansion Hamiltonians for the accurate representation of adsorbate lateral interactions

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



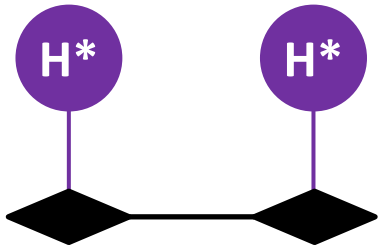
Energy = -5.191008 eV



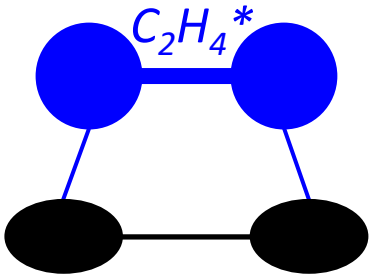


Energetics Input

- 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*

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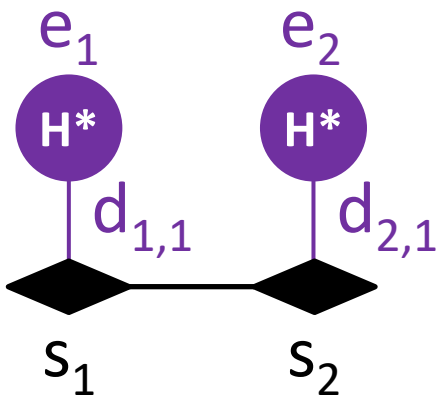

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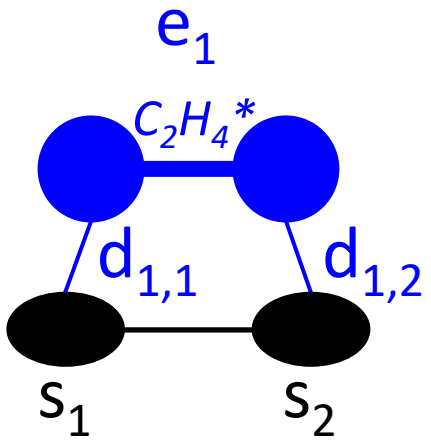
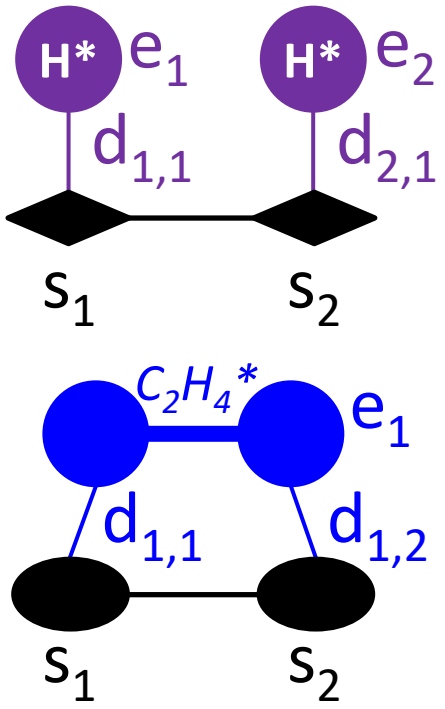


Bidentate ethylene binding

- *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

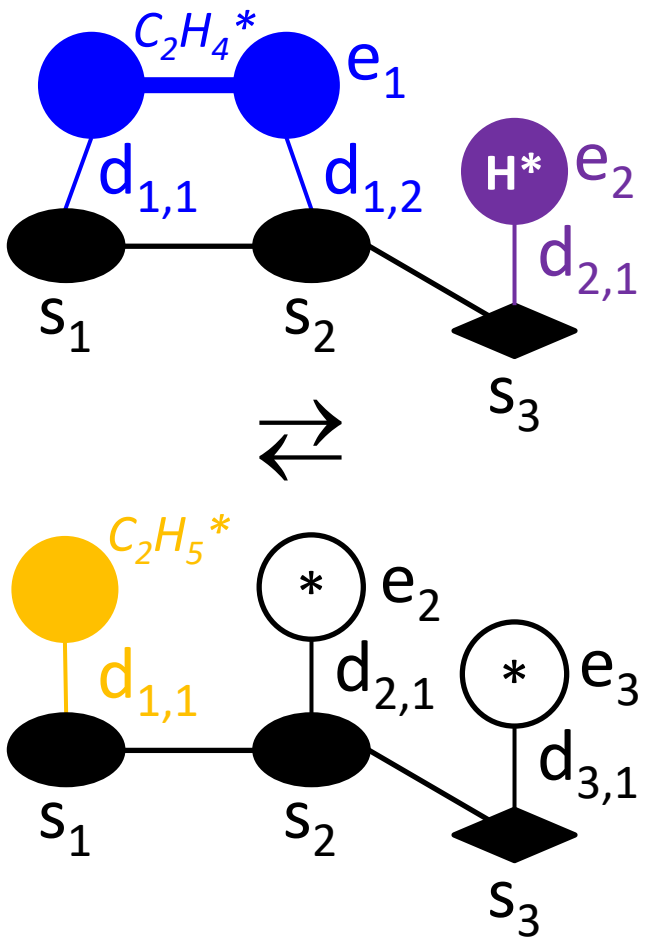
Mechanism Input

```
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
```

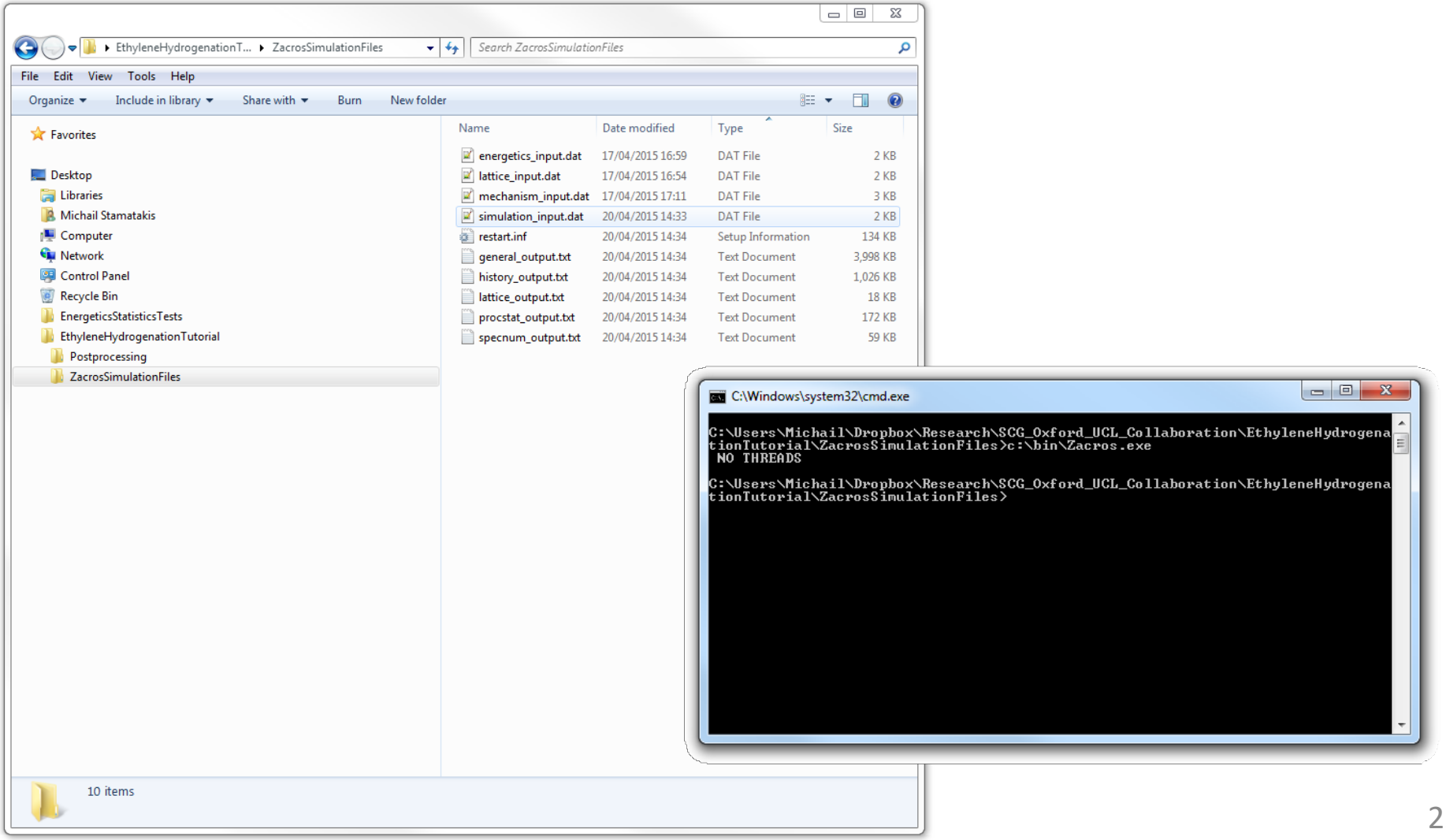


- File: `mechanism_input.dat`

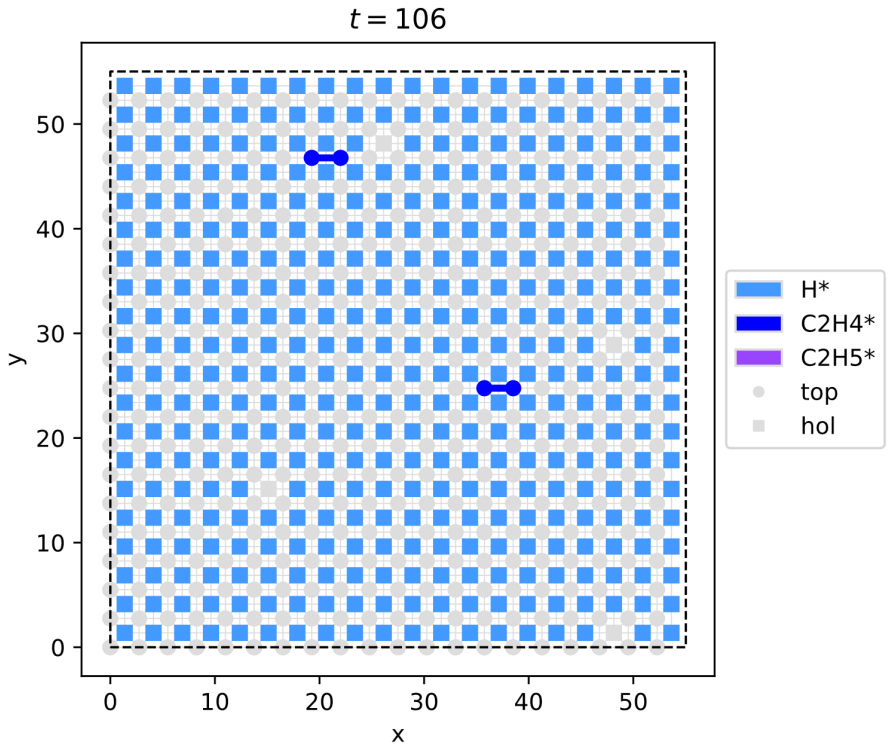
Running a Simulation

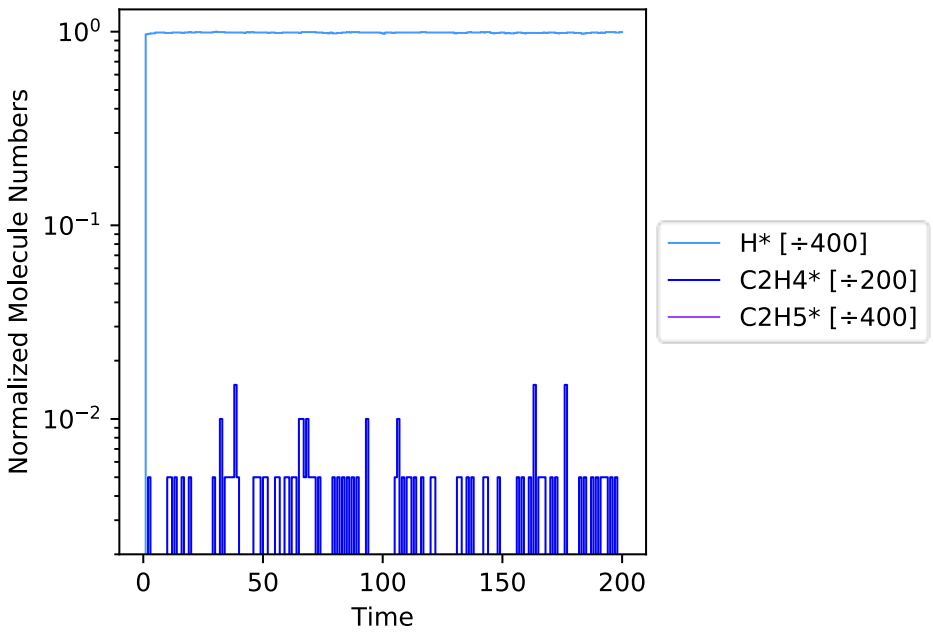
Running *Zacros*

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



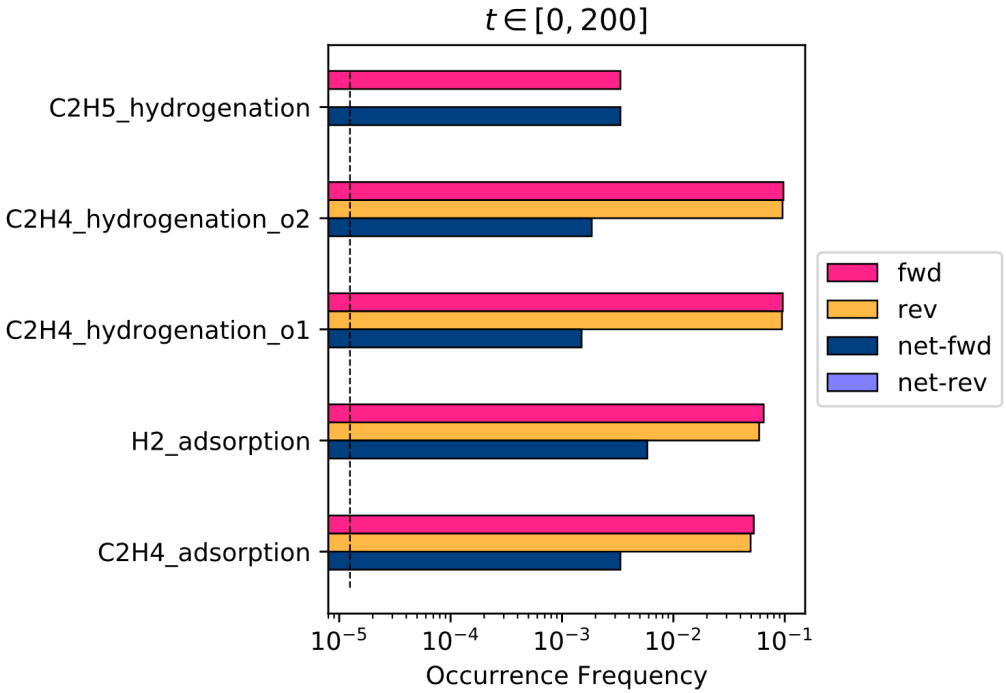
Post-processing the Results



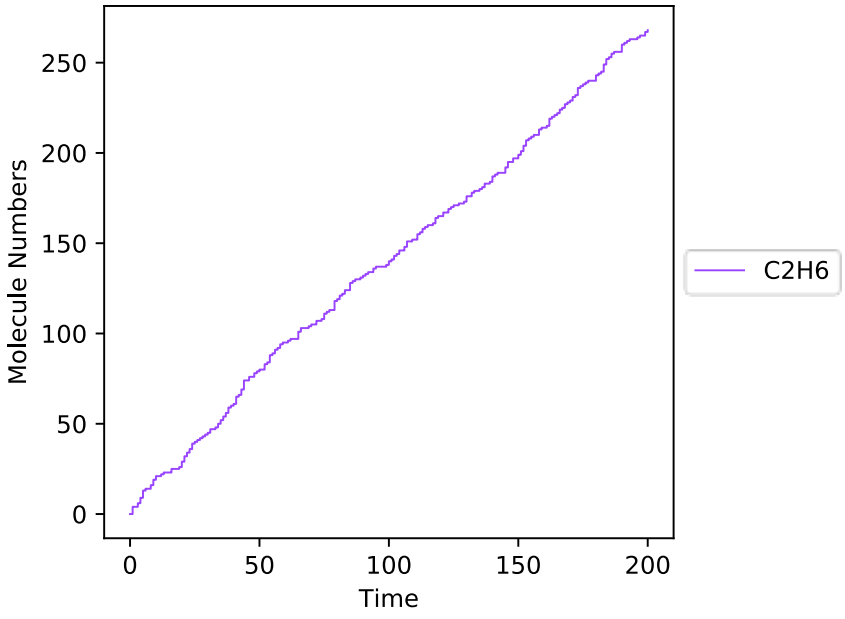


- "*Zacros*-post" tool available for post-processing output (standalone GUI and Python importable libraries)
- Surface coverages can be investigated and most abundant species identified

Post-processing the Results



Turnover Frequency:
268 molecules / 200 s / 400 sites = 0.003 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...

- 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).