# Reactivity of Organic Molecules on Semiconductor Surfaces Revealed by Density Functional Theory

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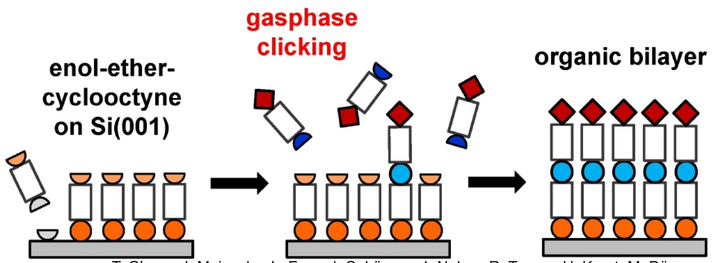
GRK 1782 Functionalization of Semiconductors

SFB 1083 Structure and Dynamics of Internal Intefaces

## Introduction

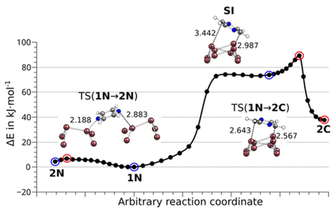
Recipe - Organic functionalization of semiconductor surfaces:

- Start with a well established semiconductor like Si or Ge
- Combine it with organic molecules
  - Use a bifunctional molecule designed to tackle the high reactivity of semiconductor surfaces
  - Use a second organic molecule to introduce new functionalities
- Aim for functionalities in the field of solar cells, OLED, sensing or molecular electronics



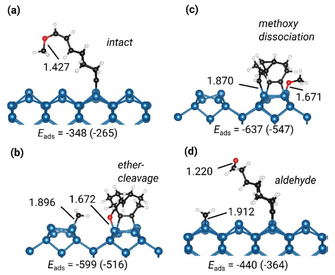

T. Glaser, J. Meinecke, L. Freund, C. Länger, J.-N. Luy, R. Tonner, U. Koert, M. Dürr, Chem. Eur. J. 2021, 27, 8082 - 8087.

## Organic molecules on Si(001) & Ge(001)



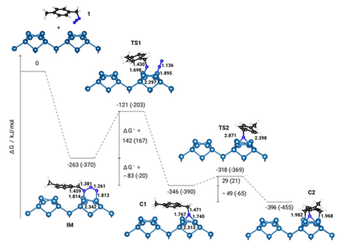

Pyrazine on Ge(001)

- Model system to study reactivity of heteroaromatic molecules
- Most stabel structures show dative bonding by N atoms or covalent bonding by C atoms
- High coverages & low temperatures preffer singly bonded structures via N atoms
- Loss of aromaticity for doubly bonded structures




Bifunctional cylcooctyne on Si(001)

- Building block for the first organic layer
- Selective adsorption via cyclooctyne group
- Ether as second functional group
- Problematic: Reactivity of the ether towards the Si(001) surface
- Reaction barrier large enough to prevent reactions at 150 K



Methyl-substituted Benzylazide on Si(001)

- Model system to study formation of the second organic layer (click chemistry)
- The molecule strongly reacts directly with Si(001)
- Stable adsorption (IM) at low temperatures
- Release of $N_2$ at 300 K observed
- Experimentally confirmed

## Scaling

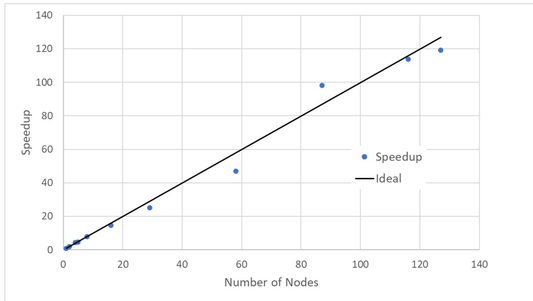
### System & Computational details

$GaH_3$ on GaP(001)

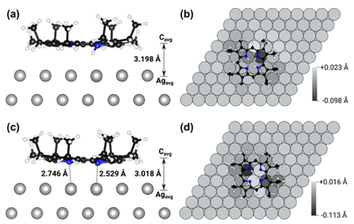
- $H_{32}Ga_{50}P_{34}$ - $GaH_3$ (366 electrons)

Periodic DFT calculations with VASP 5.4.4:

- PBE-D3(BJ)
- 5 k-points (gamma centered)
- 107.000 plane waves
- 10 min runtime for every benchmark calculation

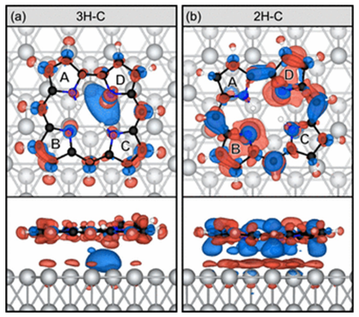



## Electronic properties



Corroles on Ag(111)

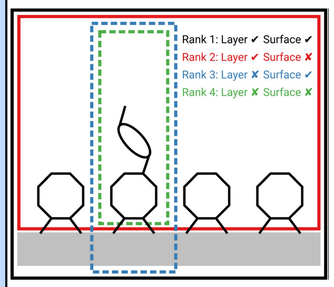
- Sytem to study charge transfer effects
- Corroles are studied due to their aromaticity and possibility to coordinate metal atoms
- Non planer adsorption structure
- Bonding by dispersion interactions
- H atom can be transfered (180 K) to the Ag(111) surface resulting in a planar structure




Charge transfer

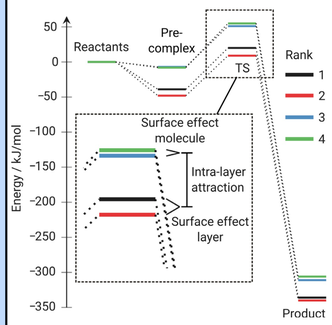
- After H transfer: Electronic interactions are present
- Charge density difference plots show strong donations from the surface to the molecule
- Charge transfer of -0.08e for 3H-C and -0.43e for 2H-C
- Charge transfer enhanced the aromaticity of the corrole

## Improving computational models




Hierarchical model systems

- Tested for the formation of the second organic layer
- 4 cylcooctyne derivates and their click-reaction with a second organic molecule
- Rank 1: Complete system
- Rank 2: Removing the substrate
- Rank 3: Removing all organic adsorbates
- Rank 4: Removing substrate & organic adsorbates

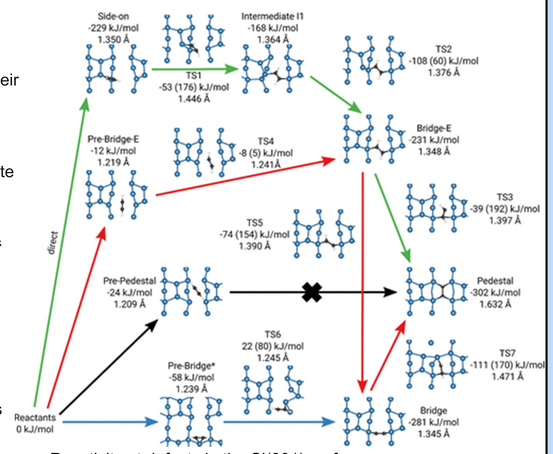



Reaction benchmark

- Total energie change by 40 kJ·mol$^{-1}$
- Reaction energies and barriers show minor differences
- Dominant effects: Intra-layer effects and substrate effects

Conclusion

- Rank 1 for high accuracy
- Rank 2 for formation of the second organic layer
- Rank 3 adsorption to the surface
- Rank 4 for screening




Reactivity at defects in the Si(001) surface

- Dimer vacancy most common defect
- Defect state in the formed bandgap
- Strong structural relaxation
- Acetylene and ethylene directy bond to defect atoms
- Cyclooctyne avoids the defect
- No direct adsorption to the thermodynamically most stable state
- Several reaction steps necessary to reach the "Pedestal" state

## Outlook

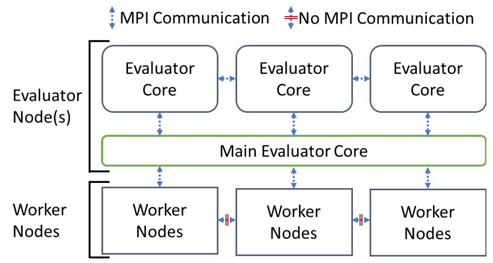
### Automated exploration of reaction networks

Research question

- Screening of organic molecules for the organic functionalization
- Exploring complex reaction networks for the CVD & ALD process

Our approach:

- Focus on elemental steps (adsorption, diffusion, decomposition)
- Combination of grid-based structure generation (minma) and reaction path optimization (NEB)
- Separation of QC calculation to enable efficient scaling

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