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## Hydrogen dissociation on metal surfaces

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# Hydrogen dissociation on metal surfaces

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volgens besluit van het College voor Promoties  
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door

Mark Wijzenbroek  
geboren te Vlaardingen in 1988

# Promotiecommissie

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# List of acronyms

|          |                                          |
|----------|------------------------------------------|
| AIMD     | <i>ab initio</i> molecular dynamics.     |
| BOSS     | Born–Oppenheimer static surface.         |
| BtH      | bridge-to-hollow.                        |
| CRP      | corrugation reducing procedure.          |
| CT       | classical trajectory.                    |
| DFT      | density functional theory.               |
| DVR      | discrete variable representation.        |
| DW       | Debye–Waller.                            |
| FBR      | finite base representation.              |
| FCC      | face-centered cubic.                     |
| FFT      | fast Fourier transform.                  |
| GGA      | generalized gradient approximation.      |
| HCP      | hexagonal close packed.                  |
| HEG      | homogeneous electron gas.                |
| LDA      | local density approximation.             |
| meta-GGA | meta-generalized gradient approximation. |
| ML       | monolayer.                               |
| MSO      | modified surface oscillator.             |

|        |                                           |
|--------|-------------------------------------------|
| NEB    | nudged elastic band.                      |
| PAW    | projector augmented wave.                 |
| PES    | potential energy surface.                 |
| QCT    | quasi-classical trajectory.               |
| QD     | quantum dynamics.                         |
| RMSE   | root mean square error.                   |
| SCM    | static corrugation model.                 |
| SM     | surface mass.                             |
| SO     | surface oscillator.                       |
| SRP    | specific reaction parameter.              |
| TD-DFT | time-dependent density functional theory. |
| TDWP   | time-dependent wave packet.               |
| TOF    | time-of-flight.                           |
| TtB    | top-to-bridge.                            |
| USPP   | ultrasoft pseudopotential.                |
| XC     | exchange–correlation.                     |
| ZPE    | zero-point energy.                        |

# List of symbols

## Coordinates of a diatomic molecule

|             |                                                                                                                    |
|-------------|--------------------------------------------------------------------------------------------------------------------|
| $U$         | Lateral position of the center of mass of a diatomic molecule with respect to the surface (skewed coordinates).    |
| $V$         | Lateral position of the center of mass of a diatomic molecule with respect to the surface (skewed coordinates).    |
| $X$         | Lateral position of the center of mass of a diatomic molecule with respect to the surface (Cartesian coordinates). |
| $Y$         | Lateral position of the center of mass of a diatomic molecule with respect to the surface (Cartesian coordinates). |
| $Z$         | Distance of the center of mass of a diatomic molecule to the surface.                                              |
| $\varphi$   | Azimuthal angle of a diatomic molecule.                                                                            |
| $\vartheta$ | Polar angle of a diatomic molecule.                                                                                |
| $\vec{r}$   | Collection of $U, V, Z, r, \vartheta, \varphi$ .                                                                   |
| $r$         | Bond length of a diatomic molecule.                                                                                |

## Coordinates of an atom

|              |                                                                               |
|--------------|-------------------------------------------------------------------------------|
| $\vec{\rho}$ | Collection of $u, v, z$ .                                                     |
| $u$          | Lateral position of an atom with respect to the surface (skewed coordinates). |

|     |                                                                               |
|-----|-------------------------------------------------------------------------------|
| $v$ | Lateral position of an atom with respect to the surface (skewed coordinates). |
| $z$ | Distance of an atom to the surface.                                           |

**Corrugation reducing procedure**

|          |                                                                 |
|----------|-----------------------------------------------------------------|
| $I^{3D}$ | Three-dimensional interpolation function.                       |
| $I^{6D}$ | Six-dimensional interpolation function.                         |
| $V^{1D}$ | Repulsive pair potential used for the calculation of $I^{3D}$ . |
| $V^{3D}$ | Three-dimensional potential energy surface.                     |
| $V^{6D}$ | Six-dimensional potential energy surface.                       |

**Density functional theory**

|                 |                                           |
|-----------------|-------------------------------------------|
| $E_{XC}$        | Exchange–correlation functional.          |
| $V_H$           | Hartree potential.                        |
| $V_{KS}$        | Kohn–Sham potential.                      |
| $V_{XC}$        | Exchange–correlation potential.           |
| $V_{ext}$       | External potential.                       |
| $\epsilon_C$    | Correlation energy per particle.          |
| $\epsilon_{XC}$ | Exchange–correlation energy per particle. |
| $\epsilon_X$    | Exchange energy per particle.             |
| $n$             | Electron density.                         |

**Geometry of the surface**

|                |                                                                     |
|----------------|---------------------------------------------------------------------|
| $\vec{q}_{id}$ | Collection of all surfaces degrees of freedom for an ideal surface. |
| $\vec{q}$      | Collection of all surface degrees of freedom.                       |
| $d_{a-b}$      | Distance between layers $a$ and $b$ .                               |

**Initial conditions**

|             |                                                   |
|-------------|---------------------------------------------------|
| $E_{\perp}$ | Perpendicular translational energy of a molecule. |
| $E_{rot}$   | Rotational energy of a molecule.                  |
| $E_{trans}$ | Translational energy of a molecule.               |
| $E_{vib}$   | Vibrational energy of a molecule.                 |

|                  |                                                                                                                                  |
|------------------|----------------------------------------------------------------------------------------------------------------------------------|
| $E_{\parallel}$  | Parallel translational energy of a molecule.                                                                                     |
| $L$              | Magnitude of the angular momentum vector.                                                                                        |
| $T_n$            | Nozzle temperature.                                                                                                              |
| $T_{\text{rot}}$ | Rotational temperature.                                                                                                          |
| $T_s$            | Surface temperature.                                                                                                             |
| $\alpha$         | Width of the velocity distribution of a molecular beam.                                                                          |
| $\varphi_i$      | Angle of incidence of the molecule (angle between the projection of the velocity vector on the $(U, V)$ plane and the $U$ axis). |
| $\vartheta_L$    | Angle between the angular momentum vector and the surface normal.                                                                |
| $\vartheta_i$    | Angle of incidence of the molecule (angle between the velocity vector and the surface normal).                                   |
| $v_0$            | Stream velocity of a molecular beam.                                                                                             |
| $v_i$            | Incident velocity of a molecule.                                                                                                 |

### Observables

|                   |                                                                  |
|-------------------|------------------------------------------------------------------|
| $A_0^{(2)}$       | Rotational quadrupole alignment parameter.                       |
| $P_{\text{deg}}$  | Degeneracy averaged initial state-resolved reaction probability. |
| $P_{\text{scat}}$ | State-to-state scattering probability.                           |
| $P_r$             | Fully initial state-resolved reaction probability.               |
| $\chi_\nu$        | Vibrational efficacy.                                            |

### Physical constants

|         |                          |
|---------|--------------------------|
| $k_B$   | Boltzmann constant.      |
| $\hbar$ | Reduced Planck constant. |

### Properties of the potential

|       |                              |
|-------|------------------------------|
| $E_b$ | Height of a barrier.         |
| $Z_b$ | $Z$ coordinate at a barrier. |
| $\xi$ | Energetic corrugation.       |
| $r_b$ | $r$ coordinate at a barrier. |

**Quantum numbers**

|        |                                                                                 |
|--------|---------------------------------------------------------------------------------|
| $J'$   | Final rotational quantum number of a diatomic molecule.                         |
| $J$    | Initial rotational quantum number of a diatomic molecule.                       |
| $\nu'$ | Final vibrational quantum number of a diatomic molecule.                        |
| $\nu$  | Initial vibrational quantum number of a diatomic molecule.                      |
| $m'_J$ | Final magnetic rotational quantum number of a diatomic molecule.                |
| $m_J$  | Initial magnetic rotational quantum number of a diatomic molecule.              |
| $m$    | A diffraction quantum number of a diatomic molecule interacting with a surface. |
| $n$    | A diffraction quantum number of a diatomic molecule interacting with a surface. |

**Reaction probability curve parameters**

|       |                                                   |
|-------|---------------------------------------------------|
| $A$   | Saturation value of a reaction probability curve. |
| $E_0$ | Dynamical barrier height.                         |
| $W$   | Width of a reaction probability curve.            |

**Static corrugation model**

|                     |                     |
|---------------------|---------------------|
| $V_{\text{coup}}$   | Coupling potential. |
| $V_{\text{strain}}$ | Strain potential.   |