



Universiteit
Leiden
The Netherlands

Semi-empirical approach to the simulation of molecule-surface reaction dynamcis

Migliorini, D.

Citation

Migliorini, D. (2019, March 14). *Semi-empirical approach to the simulation of molecule-surface reaction dynamcis*. Retrieved from <https://hdl.handle.net/1887/69724>

Version: Not Applicable (or Unknown)

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/69724>

Note: To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The handle <http://hdl.handle.net/1887/69724> holds various files of this Leiden University dissertation.

Author: Migliorini, D.

Title: Semi-empirical approach to the simulation of molecule-surface reaction dynamics

Issue Date: 2019-03-14

Semi-Empirical Approach to the Simulation of Molecule-Surface Reaction Dynamics

PROEFSCHRIFT

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden,
op gezag van Rector Magnificus prof. mr. C. J. J. M. Stolker,
volgens besluit van het College voor Promoties
te verdedigen op donderdag 14 maart 2019
klokke 15:00 uur

door

Davide Migliorini
geboren te Crema, Italië, 1990

Promotiecommissie

Promoter: Prof. dr. G. J. Kroes

Overige leden: Prof. dr. H. S. Overkleeft

Prof. dr. M. T. M. Koper

Prof. dr. C. Fonseca Guerra

Prof. dr. A. L. Utz
Tufts University,
Medford, MA, USA

Prof. dr. R. D. Beck
École Polytechnique Fédérale de Lausanne,
Lausanne, CH

Dr. M. Alducin
Centro de Física de Materiales,
Donostia - San Sebastián, ES

Dr. J. Meyer

ISBN: 978-94-028-1392-0

The research reported in this thesis has been performed in the Theoretical Chemistry Group at the Leiden Institute of Chemistry (Einsteinweg 55, 2333 CC, Leiden NL). This work has been made possible by financial support by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and by the European Research Council through an ERC-2013 advanced grant (Nr. 338580), and with computer time granted by NWO Exacte Wetenschappen, EW (NWO Physical Sciences Division).

In the beginning the Universe was created.
This had made a lot of people very angry
and been widely regarded as a bad move.

– Douglas Adams.

On the cover are reported the bond lenghts of the laser-off trajectory number 0059 for CHD₃ on Pt(211) and $\langle E_i \rangle = 58$ kJ/mol.

Contents

1 General Introduction	1
1.1 Heterogeneous Catalysis	1
1.2 From Heterogeneous Catalysis to Surface Science (and Back)	3
1.3 Molecules on surfaces: Possibilities and Challenges	5
1.4 Aim of this Thesis	7
1.5 Main Results	9
1.6 Outlook	13
2 Methods and Theory:	
A Semi-Empirical Approach to Density Functional Theory	23
2.1 Introduction	23
2.2 SRP Approach to DFT	25
2.2.1 Density Functional Theory	25
2.2.2 Plane Wave DFT	28
2.2.3 Exchange-Correlation Functional	29
2.2.4 Specific Reaction Parameter Functional	32
2.3 Semi-Empirical Strategy	34
2.4 Initial Condition Sampling	37
2.4.1 Molecular Beam	38
2.4.2 van der Waals Functionals and Residual Energy	43

2.4.3	Metal Surface Temperature	46
3	Application of van der Waals Functionals to the Calculation of Dissociative Adsorption of N₂ on W(110) for Static and Dynamic Systems	55
3.1	Introduction	56
3.2	Method	61
3.3	Results and Discussion	67
3.3.1	Static Results	67
3.3.2	AIMD Results	81
3.4	Summary and Conclusions	97
4	Surface Reaction Barriometry: Methane Dissociation on Flat and Stepped Transition Metal Surfaces	105
4.1	Introduction	106
4.2	Method	108
4.3	Results and Discussion	110
4.3.1	Theory-Experiment Comparison	110
4.3.2	Implications for Simulating Heterogeneous Catalysis	117
4.4	Summary and Conclusions	121
5	Methane on a Stepped Surface: Dynamical Insights on the Dissociation of CHD₃ on Pt(111) and Pt(211)	129
5.1	Introduction	130
5.2	Method	132
5.3	Results and Discussion	134
5.3.1	Transition States	136
5.3.2	Energy Transfer to Parallel Motion	141
5.3.3	Energy Transfer to Surface Phonons	148
5.3.4	Reaction Site and Dissociation Geometry	151
5.4	Summary and Conclusions	159

6 CHD₃ Dissociation on Pt(111): A Comparison of the Reaction Dynamics Based on the PBE Functional and on a Specific Reaction Parameter Functional	167
6.1 Introduction	168
6.2 Method	171
6.3 Results and Discussion	173
6.3.1 Surface Motion and Effective Barriers	177
6.3.2 Motion Across the Potential Energy Surface and the Minimum Energy Path	180
6.3.3 Molecule-Surface Interaction Times	185
6.3.4 Energy Transfer to the Surface	185
6.4 Summary and Conclusions	187
7 HOD on Ni(111): <i>Ab Initio</i> Molecular Dynamics Prediction of Molecular Beam Experiments	197
7.1 Introduction	198
7.2 Method	201
7.2.1 Electronic Structure Method	201
7.2.2 Dynamics Calculations	203
7.3 Results and Discussion	209
7.4 Summary and Conclusions	222
Samenvatting	233
Curriculum Vitae	239
List of Publications	241

