

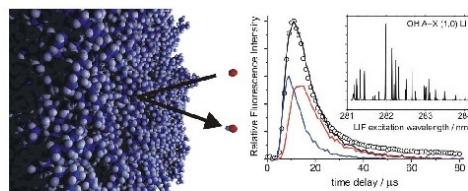


Sven Philipp Kurt Köhler (Autor)

Dynamics of the Gas-Liquid Interfacial Reaction of O(³P) Atoms with Squalane

Sven Philipp Kurt Köhler

DYNAMICS OF THE GAS-LIQUID INTERFACIAL REACTION OF O(³P) ATOMS WITH SQUALANE



 Cuvillier Verlag Göttingen

<https://cuvillier.de/de/shop/publications/2163>

Copyright:

Cuvillier Verlag, Inhaberin Annette Jentzsch-Cuvillier, Nonnenstieg 8, 37075 Göttingen,
Germany

Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

Contents

| | |
|---|-----------|
| Abstract | iii |
| Acknowledgements | vi |
| Declaration | ix |
| 1 Introduction | 1 |
| 1.1 Reaction Dynamics | 1 |
| 1.1.1 Conceptual Formulation | 2 |
| 1.1.2 Objectives | 2 |
| 1.2 Motivation | 3 |
| 1.3 Previous Experimental Work | 5 |
| 1.3.1 Reaction Dynamics of O(3P) and Gas-phase Hydrocarbons . | 5 |
| 1.3.2 Reaction Dynamics of O(1D) and Gas-phase Hydrocarbons . | 9 |
| 1.3.3 Dynamics of O(3P) and Liquid Hydrocarbons | 9 |
| 1.3.4 Reactions with Self-Assembled Monolayers | 11 |
| 1.3.5 Scattering Experiments with Spectroscopic Detection Methods | 13 |
| 1.4 Previous Theoretical Work | 14 |
| 1.4.1 Reactions between O(3P) Atoms and Gas-phase Hydrocarbons | 14 |
| 1.4.2 Simulations of a Free, Liquid Hydrocarbon Surface | 17 |
| 1.4.3 QM/MM Studies of O(3P) and Self-Assembled Monolayers . | 18 |
| 1.5 Procedure and Structure | 20 |
| 2 Experimental | 21 |
| 2.1 Liquid Surface | 21 |
| 2.2 Optical System | 23 |

| | |
|---|-----------|
| 3 Spectroscopy | 27 |
| 3.1 Electron Configuration and Term Symbols | 27 |
| 3.2 Hund's Cases | 28 |
| 3.2.1 Hund's Case (a) | 29 |
| 3.2.1.1 Λ -type doubling | 30 |
| 3.2.2 Hund's Case (b) | 30 |
| 3.2.2.1 ρ -type doubling | 30 |
| 3.3 Energy Levels | 32 |
| 3.4 Selection Rules and Allowed Transitions | 32 |
| 3.5 Laser-Induced Fluorescence | 34 |
| 4 Experimental Results | 37 |
| 4.1 Verification of the Authenticity of the Reactive Hydroxyl Radical | 37 |
| 4.1.1 Deuterium labelling | 37 |
| 4.1.2 Confirmation that Hydroxyl Radicals are Nascent | 38 |
| 4.1.3 Appearance Profiles of Hydroxyl Radicals | 39 |
| 4.2 Monte-Carlo Simulations of Time-of-Flight Profiles | 41 |
| 4.2.1 Monte Carlo Selector Steps | 43 |
| 4.2.2 Results of the Monte Carlo Simulations | 48 |
| 4.3 Rotationally Resolved Spectra of Nascent Hydroxyl Radicals | 49 |
| 4.3.1 Relative Calibration Scheme | 50 |
| 4.3.2 Rotational Distributions | 51 |
| 4.4 Vibrational Branching Ratio | 60 |
| 4.5 Λ -Doubling and Spin-Orbit Effects | 61 |
| 5 Molecular Dynamics Simulations | 65 |
| 5.1 The Molecular Dynamics Technique | 65 |
| 5.2 Methodology | 66 |
| 5.2.1 Force Field | 67 |
| 5.2.2 Starting Configurations | 70 |
| 5.2.3 Simulation Procedure | 72 |
| 5.3 Results of MD Simulations | 73 |
| 5.3.1 Confirmation of Equilibrium | 73 |

| | | |
|------------------------|---|------------|
| 5.3.2 | End-to-end Distance Distribution | 76 |
| 5.3.3 | Surface Structure | 77 |
| 5.4 | Flight Path Tracking Simulations | 82 |
| 5.4.1 | Collision Probability | 82 |
| 5.4.2 | Reactive Geometry | 83 |
| 5.4.2.1 | Collinear Transition State | 84 |
| 5.4.3 | Successful Collisions | 90 |
| 5.4.4 | Secondary Collisions with Surface Molecules | 92 |
| Appendix: | INPUT Files | 94 |
| | FIELD File | 94 |
| | CONFIG File | 95 |
| 6 | Discussion | 96 |
| 6.1 | Relationship between Internal and External Energy Distributions | 96 |
| 6.2 | Information about the Transition State | 101 |
| 6.3 | Comparison with Model Calculations | 103 |
| 6.4 | Discussion of the Vibrational Branching Ratio | 104 |
| 6.5 | Discussion of the Molecular Dynamics Simulations | 105 |
| 6.6 | Implications of the Oxygen Atom Tracking Simulations | 107 |
| 7 | Conclusion | 111 |
| 7.1 | Conclusions from Experimental Studies | 111 |
| 7.2 | Conclusions from Theoretical Studies | 113 |
| 7.3 | Future Work | 114 |
| 7.3.1 | Partially Deuterated Squalane | 114 |
| 7.3.2 | Self-assembled Monolayers | 115 |
| 7.3.3 | Future Theoretical Works | 116 |
| Bibliography | | 119 |
| List of figures | | 127 |
| List of tables | | 129 |
| Appendix A | | 131 |

| | |
|----------------------|-----|
| Appendix B | 132 |
| Appendix C | 134 |