

**Contents**

Preface ix

*Chapter 1 (A. Gross)***Dynamics of molecule-surface interactions from first principles**

1. Introduction	1
2. Fundamentals of molecular and dissociative adsorption	2
3. Quantum dynamics versus classical dynamics	4
4. Determination of potential energy surfaces	5
5. Dissociative adsorption and associative desorption of hydrogen at metal and semiconductor surfaces	7
6. Molecular trapping of oxygen at metal surfaces	13
7. Electronically non-adiabatic effects in the adsorption dynamics	21
8. Conclusions and outlook	23
References	23

*Chapter 2 (G.R. Darling and S. Holloway)***H<sub>2</sub> dissociation dynamics on metals: where do we stand?**

1. Introduction	27
2. Electronic structure	28
2.1. Vibrational effects in dissociation and scattering: $V(\mathbf{r})$	29
2.2. Molecular rotations: $V(\theta, \phi)$	30
2.3. The active site for reaction: $V(X, Y)$	31
2.4. Steering-dominated reactions	32
3. The potential energy surface	35
4. Classical or quantum dynamics?	35
5. Scattering hydrogen from metal surfaces	37
6. Is the surface really 'inert'?	42
7. A forward look	46
Acknowledgments	47
References	47

*Chapter 3 (B. Jackson)***Eley-Rideal and hot atom reactions between H atoms on metal and graphite surfaces**

1. Introduction	51
2. Reactions of H atoms with H adsorbed onto metal surfaces	52
2.1. Energetics: the PES	52
2.2. Dynamics: single collision quantum studies	55
2.3. Dynamics: multi-adsorbate QC studies	58
2.4. Kinetic studies	64

3. Reactions of H(g) with H adsorbed onto graphite surfaces	68
3.1. Energetics: the PES	69
3.2. Dynamics	70
4. Conclusions	73
Acknowledgments	74
References	74

*Chapter 4 (A.W. Kleyn)***Molecular beam scattering at metal surfaces**

1. Chemical dynamics and molecular beams: An introduction	79
2. Experimental procedures	81
3. Scattering studies	83
3.1. Atom scattering	83
3.2. Molecular scattering at bare surfaces, angular distributions and energy transfer	85
3.3. Molecular scattering at dissociative surfaces	87
3.4. Molecular scattering at adsorbate covered surfaces	89
3.5. Molecular scattering and rotational excitation	91
3.6. Molecular scattering and vibrational excitation	94
3.7. Molecular scattering, preparation of the internal states	95
3.7.1. Thermal manipulation of molecular beams	95
3.7.2. Optical state preparation	96
3.7.3. Electrostatic state preparation	97
4. On the way to adsorption	99
4.1. Trapping and desorption	100
5. Conclusions	104
Acknowledgments	104
References	104

*Chapter 5 (S.M. McClure, M.I. Reichman, D.C. Seets, P.D. Nolan, G.O. Sitz and C.B. Mullins)***Dynamics of precursors in activated dissociative chemisorption systems**

1. Introduction	109
2. Definition of activated and facile precursor systems	110
3. Experimental methods	111
4. Brief history of precursor-mediated chemisorption for facile systems	113
4.1. Trapping of Xe on Pt(111)	113
4.2. Trapping-mediated and direct chemisorption of N <sub>2</sub> on W(1 0 0)	115
4.3. Alkane chemisorption on Pt(111) and Ir(11 0)	116
4.4. Direct chemisorption of CH <sub>4</sub> on various surfaces	119
4.5. Summary	125
5. Precursor-mediated chemisorption for activated systems	126
5.1. Methane on Ir(11 0), Ir(111), and Pt(11 0)-(1 × 2)	126
5.2. Summary of CH <sub>4</sub> /Ir and CH <sub>4</sub> /Pt investigations	133

5.3. Oxygen (O <sub>2</sub> ) dissociation on single crystal platinum surfaces	134
5.4. Summary of O <sub>2</sub> /Pt investigations	140
References	140

*Chapter 6 (A. Hodgson)*

**State-resolved measurements of surface reaction dynamics**

1. Introduction	143
2. Measuring and interpreting product state distributions	144
2.1. Surface reactions	144
2.2. Product state measurements	146
2.3. Interpreting product excitation	147
2.4. Detailed balance and the relationship of desorption to adsorption	150
2.5. Low dimensional models of desorption	153
3. Nitrogen recombination	157
3.1. Introduction	157
3.2. Angular distributions	158
3.3. Nitrogen recombination at Cu(111)	159
3.4. Nitrogen recombination on Ru(0001)	163
3.5. NO and N <sub>2</sub> O reduction to form N <sub>2</sub>	168
3.5.1. Nitrogen recombination on Pd(110)	168
3.6. N <sub>2</sub> formation during NO and NH <sub>3</sub> reduction on Pt(100)	171
3.7. Conclusion	172
References	172

*Chapter 7 (B.E. Hayden and C. Mormiche)*

**Direct and indirect channels to molecular dissociation at metal and metal alloy surfaces**

1. Introduction	177
2. Direct activated and non-activated dissociation	178
2.1. Hydrogen dissociation on copper	179
2.2. Methane dissociation on platinum	182
2.3. Hydrogen dissociation on platinum	189
3. Indirect dissociation	194
3.1. The indirect channel: accommodated precursor	194
3.1.1. Nitrogen dissociation on W(100) and W(100)-c(2 × 2)Cu	194
3.1.2. Oxygen dissociation on Pt(111) and Pt(533)	198
3.2. The indirect channel: un-accommodated precursor	205
3.2.1. Hydrogen dissociation on Pt(111) and Pt(533)	206
3.2.2. Hydrogen dissociation on W(100), W(100)-Cu and W(100)-N surfaces	210
3.2.3. The step-mediated indirect channel to hydrogen dissociation	216
4. Conclusions	217
References	217

*Chapter 8 (L. Vattuone, L. Savio and M. Rocca)*

**Chemisorption dynamics in the presence of well defined surface defects**

1. Introduction	223
2. Experimental set-up for angle and energy resolved experiments	224
2.1. Experimental set-up and spectroscopic tools	224
2.2. Measurement of the sticking coefficient	225
2.3. Surface geometry and surface preparation	226
3. O <sub>2</sub> and C <sub>2</sub> H <sub>4</sub> adsorption at low Miller Ag surfaces	227
3.1. The ethylene epoxidation reaction	227
3.2. O <sub>2</sub> /Ag	227
3.3. Evidence for the importance of kink sites	229
3.4. C <sub>2</sub> H <sub>4</sub> /Ag	230
4. O <sub>2</sub> and C <sub>2</sub> H <sub>4</sub> interaction with stepped (n 1 0) Ag surfaces	231
4.1. O <sub>2</sub> /Ag	231
4.2. C <sub>2</sub> H <sub>4</sub> /Ag	239
5. Discussion	241
6. Conclusions	243
Acknowledgments	244
References	244

*Chapter 9 (C.R. Henry)*

**Reaction dynamics on supported metal clusters**

1. Introduction	247
2. Methods and techniques	248
2.1. Methodology to study reaction kinetics on supported model catalysts	248
2.2. Experimental set-up	249
2.2.1. The CRMC2-Marseille experimental set-up	250
2.2.2. The Fritz Haber Institut experimental set-up	251
3. Preparation and structural characterization of supported model catalysts	252
3.1. Introduction	252
3.2. Nucleation and growth kinetics	252
3.2.1. Thermal energy atom scattering (TEAS)	252
3.2.2. Other techniques	254
3.3. Structure and morphology	257
4. Adsorption-desorption kinetics	258
4.1. NO	258
4.2. CO	265
4.3. Oxygen	268
5. Catalytic reactions	268
5.1. CO oxidation	268
5.1.1. Introduction	268
5.1.2. Steady state kinetics	269
5.1.3. Transient regimes	273

5.2. NO reduction by CO	278
5.2.1. Reaction mechanism	278
5.2.2. Particle size and shape effects	282
6. Conclusions and perspective	285
Acknowledgments	286
References	287

*Chapter 10 (Y. Murata and K. Fukutani)*

**Laser-induced desorption from metal and oxide surfaces**

1. Introduction	291
2. General concept of the DIET process	292
3. Measuring system of laser-induced desorption for NO and CO	294
4. NO and CO desorption from Pt(1 1 1) surfaces	297
4.1. Adsorption structure of NO and CO on Pt(1 1 1)	297
4.2. Experimental results of laser-induced desorption	303
4.2.1. Desorption of NO from Pt(1 1 1)	303
4.2.1.1. Desorption from fcc hollow species	303
4.2.1.2. Desorption from on-top species	304
4.2.1.3. Desorption from hcp hollow species	305
4.2.2. Desorption of CO from Pt(1 1 1)	308
4.3. Desorption mechanism	310
4.3.1. Electronic excitation in the desorption process	310
4.3.2. Internal energy distribution of desorbed molecules	311
4.3.3. Impulse model in the DIET process	312
4.3.4. PES in the intermediate excited state for the frustrated rotation	313
4.3.5. Lifetime of the intermediate excited state	314
4.3.6. NO desorption of on-top species from Pt(1 1 1)	315
4.3.7. Angular distribution of desorbed NO from Pt(1 1 1)	317
5. NO and CO desorption from oxide surfaces	318
5.1. Experimental results	319
5.1.1. NO desorption from NiO(0 0 1)	319
5.1.2. CO desorption from Cr <sub>2</sub> O <sub>3</sub> (0 0 0 1)	320
5.2. Theoretical analysis	321
5.2.1. NO desorption from NiO(0 0 1)	321
5.2.2. CO desorption from Cr <sub>2</sub> O <sub>3</sub> (0 0 0 1)	323
6. Future prospect – selectivity in the desorption	324
6.1. NO desorption from Pt(1 1 1)–Ge surface alloy	325
References	328

*Chapter 11 (H.J.W. Zandvliet, G. Brocks and B. Poelsema)*

**Diffusion on semiconductor group IV (0 0 1) surfaces**

1. Introduction	331
2. The silicon and germanium (0 0 1) surfaces	332
3. Diffusion of adatoms and adsorption sites for dimers	336

4. Dimer diffusion pathways	340
5. Dimer rotation	344
6. Diffusion driven concerted motion of substrate atoms	345
7. Intermixing	346
8. Is there any influence of the STM tip?	347
9. Conclusions	347
References	348

*Chapter 12 (R. van Gastel, J.W.M. Frenken, B.S. Swartzentruber, E. Somfai and W. van Saarloos)*

**Diffusion of vacancies in metal surfaces: theory and experiment**

1. Introduction	351
1.1. The role of vacancies in surface diffusion	351
1.2. Can surface vacancies be important?	352
1.3. Can we see surface vacancy diffusion directly?	352
2. STM measurements of vacancy-induced diffusion	353
2.1. Qualitative observations of vacancy-induced surface diffusion	353
2.2. Direct proof for the role of vacancies	353
2.3. Statistics of vacancy-induced diffusion	356
3. Theory of two-dimensional vacancy-induced tracer diffusion	357
3.1. Tracer diffusion on an infinite system	357
3.2. Discrete model for tracer diffusion on a finite surface	358
3.3. Continuum model for tracer diffusion on a finite surface	362
4. Sources and sinks of surface vacancies	363
5. Vacancy energetics	364
5.1. Activation energy for vacancy-mediated tracer diffusion	364
5.2. Interpretation of the energetics	365
6. Vacancy-mediated self-diffusion	368
7. Summary	368
Notes	369
Acknowledgments	369
References	369

Index	371
-------	-----