

---

## CONTENTS

---

<b>I</b>	<b>INTRODUCTION</b>	<b>1</b>
<b>1</b>	<b>THE COLD AND ULTRACOLD REGIME</b>	<b>3</b>
1.1	General consideration . . . . .	3
1.2	Interest and range of application . . . . .	5
<b>2</b>	<b>COOLING AND TRAPPING ATOMS AND MOLECULES</b>	<b>7</b>
2.1	Experimental and theoretical achievements . . . . .	7
2.2	Ion-atom hybrid traps . . . . .	11
2.2.1	The Heidelberg experiment . . . . .	14
<b>3</b>	<b>ANIONS</b>	<b>19</b>
3.1	Anions in the cold and ultracold domain . . . . .	19
3.2	Definition and properties . . . . .	20
3.3	Reactivity: detachment processes . . . . .	24
<b>II</b>	<b>THEORETICAL BACKGROUND</b>	<b>31</b>
<b>4</b>	<b>ELECTRONIC STRUCTURE</b>	<b>33</b>
4.1	The molecular Schrödinger equation . . . . .	33
4.2	The Born Oppenheimer approximation . . . . .	34
4.3	The independent electron approximation . . . . .	37
4.4	The Hartree Fock method . . . . .	38
4.4.1	The mean field approach . . . . .	38
4.4.2	The Roothan equation . . . . .	40
4.5	Electron correlation and post-HF methods . . . . .	41
4.5.1	Configuration interaction (CI) . . . . .	42
4.5.2	Multi-configuration self consistent field (MCSCF) .	45
4.5.3	Multi-reference configuration interaction (MRCI) .	47
4.5.4	Perturbation methods (MPn) . . . . .	49
4.5.5	Coupled cluster approach (CC) . . . . .	50
4.6	The basis set . . . . .	52
4.6.1	Tempered diffuse functions . . . . .	54
4.6.2	Basis set superposition error . . . . .	54
4.7	Spin orbit coupling and relativistic effects . . . . .	56
4.8	Group theory . . . . .	59
<b>5</b>	<b>NUCLEAR DYNAMICS</b>	<b>67</b>
5.1	Capture model . . . . .	68
5.2	The close coupling method . . . . .	71
5.3	The Landau-Zener and Rosen-Zener-Demkov model .	75

<b>III RESULTS</b>	<b>77</b>
<b>6 THE MOH<sup>-</sup> MOLECULAR SYSTEM</b>	<b>79</b>
6.1 Molecular structure . . . . .	79
6.2 Vibrational frequencies . . . . .	92
6.3 The Rb-OH <sup>-</sup> case . . . . .	96
6.3.1 Ground state collision: Rb( <sup>2</sup> S)+OH <sup>-</sup> . . . . .	98
6.3.2 Excited state collision: Rb( <sup>2</sup> P)+OH <sup>-</sup> . . . . .	113
6.3.3 Total loss rate and comparison with experiment .	133
6.4 Excited states of alkaline earth hydroxide anions . . . . .	136
6.5 Conclusion and outlook . . . . .	139
<b>7 HYDRATED HYDROXIDE ANION CLUSTERS: OH(H<sub>2</sub>O)<sub>n</sub><sup>-</sup></b>	<b>143</b>
7.1 Generalities and motivation . . . . .	143
7.2 The hydrated hydroxide anion . . . . .	145
7.3 Reactivity . . . . .	150
7.3.1 Collision with H atoms . . . . .	150
7.3.2 Collision with Rb atoms . . . . .	163
7.4 Conclusion and outlook . . . . .	177
<b>8 THE RB-C<sub>2</sub><sup>-</sup> AND LI-C<sub>2</sub><sup>-</sup> MOLECULAR SYSTEMS</b>	<b>181</b>
8.1 Motivations . . . . .	181
8.2 Potential energy surfaces . . . . .	182
8.3 Reactive collisions . . . . .	186
8.4 Inelastic cross sections . . . . .	190
8.5 Conclusion and outlook . . . . .	196
<b>IV GENERAL CONCLUSION AND PERSPECTIVES</b>	<b>199</b>
<b>V APPENDIX</b>	<b>207</b>
<b>A APPENDIX A</b>	<b>209</b>
A.1 Non adiabatic coupling matrix element for Rb+OH <sup>-</sup> . . .	209
A.2 Spin orbit coupling in the Rb-C <sub>2</sub> <sup>-</sup> complex . . . . .	210
A.3 Harmonic frequencies . . . . .	212
<b>B APPENDIX B</b>	<b>217</b>
<b>BIBLIOGRAPHY</b>	<b>229</b>