

Contents

Abstract	I
Zusammenfassung	V
List of Abbreviations	VII
1 Introduction	1
2 Fundamentals	5
2.1 Linear and Non-Linear Spectroscopy	5
2.1.1 Excitation and Following Processes	5
2.1.2 Excited State Population in a Two-Level System	6
2.1.3 Linear Absorption Spectroscopy	8
2.1.4 Saturated Laser-Induced Fluorescence	9
2.2 Temperature and Pressure Dependence of Rate Coefficients of Gas Phase Reactions	10
2.2.1 Temperature Dependence	11
2.2.2 Pressure Dependence	12
2.2.3 Statistical Rate Theory	13
2.3 Complex-Forming Bimolecular Reactions	13
2.3.1 Mechanism and Overall Kinetics	14
2.3.2 Pressure Dependence	16
2.3.3 Temperature Dependence	17
2.3.4 Quantum chemical Methods for the Description of Potential Energy Surfaces	18
3 Experimental	21
3.1 Gas Injection Methods	21
3.1.1 Original Setup	21
3.1.2 Revised Setup	22
3.1.3 Preparation of Gas Mixtures in Cylinders	23
3.1.4 Bubbler Technique for High Pressures	25

3.2	Pulsed Laser Photolysis/Laser-Induced Fluorescence	28
3.2.1	Experimental Setup	28
3.2.2	Reaction Cells	31
3.2.3	Absorption Unit	35
3.2.4	Radical Production and Detection	36
3.2.5	Error Analysis	38
3.3	UV/Vis Absorption	43
3.3.1	Static Experiments	43
3.3.2	Slow-Flow Experiments	43
4	Studies on the Purity of HNO₃ and Revision of the PLP/LIF Setup	45
4.1	Introduction	45
4.2	Identification and Quantification of Impurities	49
4.2.1	Experimental Procedure	49
4.2.2	Results and Discussion	49
4.2.3	Conclusions	51
4.3	Purity of Nitric Acid Gas Mixtures	52
4.3.1	Experimental Procedure	52
4.3.2	Results and Discussion	53
4.3.3	Conclusions and Revision of the Gas Injection Method	54
4.4	Supply of Pure Nitric Acid in the Gas Phase	56
4.4.1	Experimental Procedure	57
4.4.2	Results with Concentrated Nitric Acid	58
4.4.3	Results with a Ternary Mixture	59
4.4.4	Conclusions	63
4.5	Consequences for the PLP/LIF Experiment	64
4.5.1	Measurements with the High-Pressure Bubbler	64
4.5.2	Measurements with HNO ₃ -Containing Gas Mixtures	67
4.5.3	Measurements with Low Reactant Concentrations	68
4.6	Outlook	70
5	The Reaction DME + OH	73
5.1	Introduction	73
5.2	Experimental Procedure	78
5.3	Analysis	79
5.4	Results and Discussion	81
5.5	Conclusion and Outlook	85

6 The Reaction DEE + OH	87
6.1 Introduction	87
6.2 Experimental Procedure	93
6.3 Analysis	94
6.4 Results and Discussion	96
6.5 Conclusion and Outlook	101
7 The Reaction DMM + OH	103
7.1 Introduction	103
7.2 Experimental Procedure	105
7.3 Analysis	106
7.4 Results and Discussion	108
7.5 Conclusion and Outlook	115
A Appendices	117
A.1 Appendix to Chapter 4	117
A.2 Appendix to Chapter 5	118
A.3 Appendix to Chapter 6	122
A.4 Appendix to Chapter 7	147
Bibliography	161
List of Publications	171