

Contents

Introduction	1
1 Coherence and wave packet interferometry	4
1.1 Wave packets	4
1.1.1 Franck - Condon principle	5
1.2 Coherence	6
Absorption and wave packet interferometry in the time dependent framework	11
1.2.1 Auto - correlation with ns excitation	12
1.2.2 Cross - correlation with fs pulse train excitation	14
2 System: Br₂/Ar	15
2.1 Gas phase properties	15
2.1.1 Physical and chemical properties	15
2.1.2 Electronic structure	15
2.1.3 Spectroscopic properties of free Br ₂ molecules	16
2.1.4 Selection rules	16
2.2 Properties of halogens in the cage: State of the art	17
2.2.1 Cage effect	18
2.2.2 Electronic and vibrational coupling with the lattice	19
2.2.3 Absorption and excitation spectra of Br ₂ /Ar	21
2.2.4 Emission spectroscopy of Br ₂ /Ar	22
2.2.5 Predissociation	24
2.2.6 Vibrational energy relaxation	26
2.2.7 Coherence times	28
3 Experimental technique	29
3.1 Experimental basics	29
3.1.1 Sample preparation	29
3.1.2 Fluorescence detection	29
3.2 Frequency resolved spectroscopy	30
3.3 Time resolved spectroscopy	31
3.3.1 Experimental overview	31
3.3.2 Ultrashort laser pulses	33
3.3.3 Single pump - probe experiment	39
3.4 Control instruments for the generation of pulse sequences	42
3.4.1 Michelson interferometer	42
3.4.2 Pulse shaper	43
3.4.3 Double pump experiment	49

3.4.4	Multiple pump - probe experiment	51
4	Analysis 1: Frequency resolved spectroscopy	53
4.1	Results	54
4.1.1	Emission spectra from covalent excited states B, A and A'	54
4.1.2	Excitation of covalent states	58
4.1.3	Temperature dependence	65
4.1.4	Polarisation dependence	65
4.1.5	Bleaching experiments	67
4.2	Discussion	72
5	Analysis 2: Time resolved spectroscopy	80
5.1	Pump - probe spectroscopy results	80
5.1.1	Polarisation dependence	80
5.1.2	Intensity dependence	84
5.2	Discussion of pump - probe spectroscopy	86
5.2.1	Simulation of wave packet dynamics on the B-state of free Br ₂	87
5.2.2	Open questions	89
6	Control: Interference with phase controlled pulse sequences	93
6.1	Tutorial solution: Michelson interferometer	93
6.1.1	Double pulse experiment	93
6.1.2	Electronic coherence in the PLPP spectra	97
6.2	Advanced solution : Pulse shaper	99
6.2.1	Pulse train excitation	99
6.2.2	Double pump - probe experiment – time resolved	102
6.2.3	Pulse train pump - probe experiment	106
6.3	Discussion of control experiments	112
6.3.1	Phase reconstruction	113
6.3.2	Predissociation	122
6.3.3	Wave packet interferometry	126
6.3.4	Electronic coherence	130
	Summary	132
	Bibliography	135
	Appendix A	150