

CONTENTS

1	Introduction	11
1.1	Water	11
1.2	Phase diagram	12
1.3	Ice I _H	13
1.4	Absorption spectrum	15
1.5	Proton transfer	16
1.6	Energy transfer	18
1.7	Heavy water	19
1.8	Outline	20
2	Spectroscopy	21
2.1	Light-matter interaction	21
2.2	Equation of motion	22
2.3	Linear response	23
2.3.1	Susceptibility and refractive Index	23
2.3.2	Resonant versus off-resonant	24
2.3.3	Wave propagation	25
2.3.4	Inhomogeneous broadening	26
2.4	Non-linear response	27
2.4.1	Different orders	27
2.4.2	Frequency mixing	28
2.4.3	Pump-probe spectroscopy	30
2.4.4	Spectral diffusion	32
2.5	Quantum mechanical systems	34
2.5.1	Transition rate	34
2.5.2	Oscillation	35
2.5.3	Line width	36
2.5.4	Quantum anharmonic oscillator	37
3	Experimental	39
3.1	Pulse generation	39
3.2	Pump-probe setup	41
3.3	Sample cell	41
3.4	Detector	43

4	Analysis and Modeling	45
4.1	Transient Absorption and Anisotropy	45
4.2	Multi-component Analysis	47
4.2.1	Singular value decomposition	48
4.2.2	Least-squares fitting	49
4.2.3	Spectral decomposition	50
4.2.4	Temporal decomposition	50
4.2.5	Anisotropic decomposition	51
4.3	Spectral signatures	52
4.4	Unimolecular reactions	54
4.4.1	Rate matrix	54
4.4.2	Parallel model	55
4.4.3	Cascade model	56
4.5	Pseudo-unimolecular reactions	57
4.5.1	Survival probability	57
4.5.2	Concentration dependence	59
4.5.3	Continuum limit	60
4.5.4	Diffusion	62
4.6	Förster transfer	62
5	Molecular Reorientation of Liquid Water	65
5.1	Introduction	65
5.2	Experimental	67
5.3	Results	68
5.4	Interpretation	72
5.5	Model	74
5.6	Discussion	76
5.7	Conclusions	77
5.8	Appendix: Jumping model	78
6	Water as a Molecular Hinge	81
6.1	Introduction	81
6.2	Experiment	82
6.3	Results	83
6.3.1	Linear spectra	83
6.3.2	Nonlinear spectra	85
6.3.3	Kinetic model	89
6.3.4	Anisotropy modeling	90
6.3.5	Spectral shapes	91
6.3.6	Fit results	92
6.4	Discussion	95
6.4.1	Relaxation	95
6.4.2	Intramolecular energy transfer	96
6.4.3	Rotational diffusion	96
6.4.4	Implications	97
6.5	Conclusion	98

6.6	Appendix: Anisotropy of a hinge	98
7	Spectral Diffusion of Water near Bromide Ions	101
7.1	Introduction	101
7.2	Experimental	102
7.3	Results	103
7.4	Interpretation	109
7.5	Discussion	111
7.6	Conclusions	113
8	Proton Transfer in Liquid Water	115
8.1	Introduction	115
8.2	Theory	118
8.3	Experimental	120
8.4	Results	121
8.5	Discussion	129
8.6	Conclusions	131
8.7	Appendix: Diffusion coefficient	132
9	Proton Transfer in Ice	135
9.1	Introduction	135
9.2	Experimental	137
9.3	Results	140
9.3.1	Decomposition	140
9.3.2	Temperature dependence	142
9.3.3	Concentration scaling	144
9.3.4	Quantitative model	147
9.3.5	Global fit	149
9.4	Discussion	152
9.5	Conclusion	155
10	Förster Transfer to Hydrated Protons	157
10.1	Introduction	157
10.2	Experiment	158
10.3	Results and discussion	161
10.3.1	Transient spectra	161
10.3.2	Energy relaxation	163
10.3.3	Förster transfer	166
10.3.4	Implications	169
10.3.5	Rotational diffusion	169
10.4	Conclusion	171
11	Förster Transfer in Ice	173
11.1	Introduction	173
11.2	Experimental section	174
11.3	Results	177

11.3.1	Linear spectrum	177
11.3.2	Transient spectra	177
11.3.3	Heat correction	178
11.3.4	Temperature dependence	179
11.3.5	Concentration dependence	180
11.3.6	Ice structure	181
11.3.7	Förster rate	183
11.3.8	Limited transfer range	184
11.3.9	Model	184
11.3.10	Förster radius	185
11.3.11	Cluster simulation	187
11.3.12	Vibrational relaxation rate	188
11.4	Conclusion	189
	Bibliography	191
	Summary	203
	Samenvatting	207
	Dankwoord	215