

CONTENTS

1	Introduction	10
1.1	The infrared absorption of water	11
1.2	Vibrational pump–probe spectroscopy	13
1.2.1	Absolute magnitude of the pump–probe signals	16
1.3	Outline of this thesis	16
2	Experimental details	18
2.1	Three-wave mixing as an infrared source	18
2.1.1	Parametric generation and amplification	19
2.2	Pulse generation for pump–probe experiments	20
2.2.1	Titanium-sapphire amplifier	20
2.2.2	Topas: a BBO-based OPG/OPA device	20
2.2.3	Pulse generation ($\sim 3 \mu\text{m}$) for one-color experiments	20
2.2.4	Pulse generation ($\sim 3 \mu\text{m}$) for two-color experiments	21
2.2.5	Pulse generation at $\sim 4 \mu\text{m}$	22
2.3	Sample	22
2.4	Pump–probe setup	23
2.4.1	Two-color setup	24
2.4.2	One-color polarization-resolved setup	25
2.5	Pulse characterisation	26
2.6	Refinements of the pump–probe signal description	27
2.7	Noise suppression	30
2.7.1	Uncorrelated noise	30
2.7.2	Time-correlated noise	32
2.8	Thermal effects in the sample	33
3	Generation of mid-infrared pulses by $\chi^{(3)}$ difference frequency generation in CaF_2 and BaF_2	36
3.1	Introduction	36
3.2	Experiment	37
3.3	Results	38
3.4	Conclusions	40
4	Vibrational relaxation in HDO: D_2O	41
4.1	Introduction	41
4.2	Experiment	41
4.3	Results	42
4.4	Intermediate-state model	43

4.5	Discussion	47
4.6	Conclusions	49
5	Isotope effects on vibrational relaxation and hydrogen-bond dynamics in water	50
5.1	Introduction	50
5.2	Experiment	51
5.3	Results	51
5.4	The Brownian-oscillator model	53
5.5	Thermalization and fits	55
5.6	Discussion	56
5.7	Conclusions	58
6	Dynamics of water molecules in an alkaline environment	59
6.1	Introduction	59
6.2	Experiment	61
6.3	Results	62
6.3.1	Transient spectra	62
6.3.2	The OH band as a distribution of Brownian oscillators	63
6.3.3	Dynamics at small delays	65
6.3.4	Fit details	67
6.4	Discussion	68
6.5	Conclusions	71
7	Orientational relaxation of HDO: D₂O as an activated process	73
7.1	Introduction	73
7.2	Experiment	75
7.3	Results	75
7.4	Activated reorientation and spectral diffusion	76
7.4.1	Model	76
7.4.2	Discussion of the model	79
7.4.3	Comparison with other studies	81
7.5	Conclusions	82
7.6	Appendix: mathematical details	82
7.6.1	Rotational diffusion	82
7.6.2	Spectral diffusion	83
7.6.3	Anisotropy decay at large delays	84
7.6.4	Numerical implementation	85
8	Spectral diffusion and mechanism for autodissociation	86
8.1	Introduction	86
8.2	Experiment	87
8.3	The equilibrated transient spectrum	87
8.3.1	Quantum-mechanical Lippincott-Schroeder model	88
8.3.2	Calculation of transient spectra	91
8.4	The dynamics of the transient spectra	93
8.4.1	Spectral diffusion	93

8.4.2	Inertial dynamics	95
8.5	Autodissociation of water	97
8.5.1	Transition state	98
8.5.2	Mechanism	100
8.6	Conclusions	100
	Appendix: The cm^{-1} unit	102
	Bibliography	103
	Summary	113
	Samenvatting	115
	Nawoord	119
	Curriculum Vitae	121
	Index	122
	Colophon	125