

List of Figures

1.1	Typical symmetric potential energy surface for proton transfer reaction.	2
1.2	Schematics of the proton transfer in liquid water.	3
1.3	Image of the $H_5O_2^+$ cation solvated by four water molecules in a side pocket of the bacteriorhodopsin molecule. Taken from D. Marx. ¹⁵ . . .	4
2.1	Schematic of the electro-spray technique.	10
2.2	Mass spectrum of $H^+(H_2O)_n$ cations generated with the electro-spray source.	11
2.3	Typical mass spectrum of vanadium oxide cations ($V_xO_y^+$) produced with the laser vaporization source.	13
2.4	A photograph of the electron gun received form D. Neumark, University of California, Berkley, U.S.A.	14
2.5	Mass spectrum of $Br(D(H)Br)_n^-$ anions produced with the electron impact source.	15
2.6	Mass spectrum of solvated hydroxyl anions generated with the electron impact source.	16
2.7	The ion guiding tandem mass spectrometer.	17
2.8	Photograph of the hexadecapole ion trap.	19
2.9	Schematics of a multipole with a cylinder ring electrode. The lower part shows a schematic representation of the potential along the axis of the system.	20
2.10	The trapping process. The upper part of the figure shows the ion trap filled with He buffer gas and the entrance ($TEnL$) and exit ($TExL$) electrostatic lenses. In the lower part of the figure, the trapping procedure is presented. The ion trajectory shows how the ions lose kinetic energy during the collision with the He gas atoms.	22
2.11	Schematic of a free electron laser consisting of an electron gun, an accelerator and a magnetic field structure (undulator), which is placed in a resonator cavity. Figure received from FOM.)	23
2.12	Schematic of the Free Electron Laser for Infrared eXperiments (FELIX) situated at the FOM Institute for Plasma Physics, Rijnhuizen, the Netherlands. (Figure received from FOM.)	24
2.13	The pulse structure of the free electron laser FELIX. (Figure received from FOM.)	25

2.14	Typical evolution of the FELIX laser power over the scanning range used in the experiments.	26
2.15	Schematics of the measurement procedure.	28
3.1	The vibrations of a linear three atomic molecule.	33
3.2	Schematic representation of the Morse potential curve for a two atomic molecule.	34
3.3	Schematics of the "ladder climbing" mechanism.	38
3.4	The sequential incoherent absorption mechanism.	39
4.1	The first multiphoton infrared spectrum of $BrHBr^-$ anion.	44
4.2	The vibrational predissociation spectrum of $BrHBr^- \cdot Ar$	45
4.3	The VPD spectrum of $BrDBr^- \cdot Ar$	48
4.4	The IRMPD and VPD spectra of $BrHBr^-$ and $BrHBr^- \cdot Ar$	50
4.5	The IRMPD and VPD spectra of the $BrDBr^-$ and $BrDBr^- \cdot Ar$ anions.	53
4.6	The infrared photodissociation spectrum of $Br(HBr)_2^-$	54
4.7	The infrared photodissociation spectrum of the $Br(DBr)_2^-$ anion recorded at different laser pulse energies.	55
4.8	The infrared photodissociation spectrum of $Br(DBr)_2^-$ (black line) and $Br(HBr)_2^-$ (red line). The IR spectrum of $Br(HBr)_2^-$ was divided by 1.4, the harmonic isotope shift.	57
4.9	The infrared photodissociation spectrum of the $Br(HBr)_3^-$ anion recorded at a laser power of 25 mJ / macropulse.	58
4.10	The infrared photodissociation spectrum of the $Br(HBr)_3^-$ anion measured with 50 mJ/macropulse laser pulse energy.	59
4.11	The C_{2v} structure for $Br(HBr)_2^-$ (above) and the C_{3v} structure for $Br(HBr)_3^-$ (below) (B3LYP/aug-cc-pVTZ method). (calculations performed by N. Pivonka ⁷³).	61
4.12	Infrared VPD spectrum of $BrHI^- \cdot Ar$ anion.	65
4.13	Infrared VPD spectrum of $BrDI^- \cdot Ar$	66
4.14	Comparison of the experimental predissociation spectra (black line) with the calculated frequencies and intensities (vertical bars). The upper panel shows $BrDI^-$; the lower panel shows $BrHI^-$. The experimental data are normalized to the background signal and shown on a logarithmic scale. Calculated intensities are normalized to the largest intensity and plotted on a linear scale for comparison. ⁷⁵	68
4.15	IR-VPD spectrum of $BrHI^- \cdot Ar$ (closed circles, upper trace) and the IRMPD spectrum of $BrHI^-$ (open circles, lower trace). ⁷⁵	69
4.16	Infrared VPD spectrum of $BrDI^- \cdot Ar$ (closed circles, upper trace) and the IRMPD spectrum of $BrDI^-$ (open circles, lower trace). ⁷⁵	70
5.1	IRMPD spectra of the Zundel cation $H_5O_2^+$ and of the deuterated ion $D_5O_2^+$	78
5.2	IRMPD spectra of the deuterated isotopomers $D_xH_{5-x}O_2^+$ (x = 0, 1...5)	80

5.3	VPD spectrum of $H_5O_2^+ \cdot Ar$ ^{97,98} (a)) and IRMPD spectra of $H_5O_2^+$ measured at FELIX ¹⁰⁰ (b)) and at CLIO ⁹⁶ (c))	83
5.4	The structures of the $H_9O_4^+$ cation predicted by Ojamäe <i>et al.</i> ¹⁰⁷ at the MP2/TZ2P level of theory. Oxygen atoms are displayed by dark spheres; hydrogen atoms by white spheres.	87
5.5	The harmonic vibrational spectra for the monomers H_3O^+ and H_2O , for $H_5O_2^+$ in C_2 symmetry and for $H_9O_4^+$ in C_2 and C_3 symmetries. Taken from Ojamäe <i>et al.</i> ¹¹³	88
5.6	IRMPD spectrum of $H_9O_4^+$ measured at FELIX energy of 28 mJ/macropulse at 15 μm	89
5.7	IRMPD spectrum of $H_9O_4^+$ measured at FELIX pulse energy of 60 mJ/macropulse at 15 μm	90
5.8	The VPD spectrum of $H_9O_4^+$. Taken from Headrick <i>et al.</i> ¹²³	91
5.9	IRMPD spectrum of the $H_7O_3^+$ cation.	95
5.10	Potential energy curve of $H_3O_2^-$ along the proton displacement coordinate. Taken from Dicken <i>et al.</i> ⁹⁹	99
5.11	Argon predissociation spectrum of the $H_3O_2^- \cdot Ar$ complex. Taken from Dicken <i>et al.</i> ⁹⁷	100
5.12	The IRMPD spectrum of $H_3O_2^-$	101
6.1	CASPT2 / cc-pV5Z structures for VO^+ , $VO^+ \cdot He$ and $VO^+ \cdot Ar$. (O in blue, V in light gray, He in black and Ar in green)	111
6.2	CASPT2 / cc-pVTZ structures for $VO^+ \cdot Ar_2$. (V - light gray sphere, O - blue sphere, Ar - green spheres.)	116
6.3	The gas phase IRMPD spectrum of the $V_4O_{10}^+$ cation.	119
6.4	The IRMPD spectrum of the $V_4O_{12}^+$ cation.	122
6.5	The IRMPD spectrum of O_2 and $2O_2$ -loss fragmentation channels of $V_4O_{12}^+$	123
6.6	The VPD and the IRMPD spectra of $V_3O_8^+$	125
6.7	The IRMPD spectrum of the $V_6O_{15}^+$ cation.	127
6.8	The IRMPD spectrum of the $V_6O_{13}^+$ cation.	128
7.1	Schematic representation of the few cycle IR + UV bond selective dissociation scheme for the control of the branching ratio of different dissociation channels when the saddle point is reached by photodetachment. Received from N. Elghobashi. ¹⁷¹	135
B.1	Korth Kristalle GmbH ¹⁷²	158
C.1	The gas phase IRMPD spectrum of $V_2O_3^+$	162
C.2	Simulated IR absorption spectra based on scaled B3LYP/TZVP frequencies and relative intensities of the ground state (middle row) and an energetically low-lying isomer (top row) of $V_2O_3^+$. The lower panel shows the gas phase VPD spectrum of $V_2O_3^+ \cdot He_3$. Taken from Asmis <i>et al.</i> ³⁹	163
C.3	The IRMPD spectrum of $V_3O_2^+$	165

