List of Figures

The interaction potential between an ion and a molecule according to the Langevin theory $(V(r))$, combined with a Lennard-Jones repulsive term (ar^{-12}) .	12
The dependence of the first-order rate constant $k_{overall}^{(1)}$ on the buffer	16
The reaction path and the activation energy for a catalyzed (grey line) and an uncatalyzed (black line) chemical reaction.	10 21
Possible mechanisms for catalytic CO oxidation reaction via deposited	07
The CO oxidation reaction enabled by small gold clusters deposited on a thin film of magnesium oxide. The carbon dioxide yield is depicted	21
as a function of the cluster size. \ldots \ldots \ldots \ldots \ldots \ldots \ldots The structure of bare gold and mixed gold-strontium clusters deposited on MgO thin films. (a) and (b) Au_8 , (c) Au_4 , (d) Au_3Sr , (e) and (f)	28
Au_8O_2 , (g) Au_4O_2 , (h) Au_3SrO_2	29 31
Schematic representation of the principle of NeNePo spectroscopy.	39
The experimental NeNePo signal for Ag_3 clusters measured at a wave- length of 415 nm ($\lambda_{Pump} = \lambda_{Probe} = 415 nm$).	41
One dimensional cut along the bending mode coordinate Q_x of the potential energy surfaces for the silver trimer	19
The normal vibrational modes of a triatomic molecule, where Q_s represents the symmetric stretching mode, Q_x the bending mode and Q_y the antisymmetric stretching mode.	42
The experimental apparatus: cluster source, triple quadrupole mass spectrometer, detector. (a) cluster source (CORDIS), (b) target cham- ber, (c) Q_0 quadrupole, (d) Q_1 quadrupole (mass filter), (e) Q_2 quadru- pole (guiding quadrupole), (f) octopole ion trap, (g) Q_3 quadrupole mass spectrometer, (h) channeltron detector.	48
	The interaction potential between an ion and a molecule according to the Langevin theory $(V(r))$, combined with a Lennard-Jones repulsive term (ar^{-12})

4.2	The cluster source, target chamber and Q_0 quadrupole	49
4.3	Softlanding: reduction of the kinetic energy distribution of clusters inside Q_2 by means of helium collision.	50
4.4	(a) Comparison between the effective potential of an octopole (black line) and of a quadrupole (grey line) ion trap as a function of the relative distance to the center of the trap. (b) A typical trajectory of an ion inside an octopole ion trap.	53
4.5	The octopole ion trap. (a) The octopole ion trap inside the gold plated housing. (b) The octopole ion trap connected to the cryostat.	54
4.6	Thermalization of Pd_{13} cluster through collisions with helium atoms. The initial cluster temperature has a value of 1500 K and the buffer gas temperature has a value of 100 K	56
4.7	The averaged ion signal after 10 trap cycles measured with a LeCroy oscilloscope.	58
4.8	Detailed view of the fs-oscillator. The geometrical arrangement of the crystal, the prism pair and the folding mirror can be observed	61
4.9	The spectrum of a fs-laser pulse generated by the oscillator (open grey circles). The gaussian function fit of the spectrum (black line) and the full width at half maximum (FWHM) are depicted on the graph	62
4.10	The geometry of the amplification stage inside the multipass amplifier where the eight passes through the Ti:Sa crystal are shown explicitly.	64
4.11	TOPAS: a schematic representation of the (a) first, second and third beam pass; (b) fourth pass; (c) fifth beam pass through the nonlinear crystal.	66
4.12	The experimental setup composed of the laser system and the triple quadrupole mass spectrometer.	69
4.13	The autocorrelation trace of the pump and probe pulses as a function of the delay time between the two laser pulses measured on the gold plate. The experimental parameters are: $\lambda_{Pump} = \lambda_{Probe} = 406 \ nm$, $P_{Pa} = -P_{Pa} + -2.3 \ mW$	71
4.14	The crosscorrelation trace of the pump and probe pulses as a function of the delay time between the two laser pulses measured on the gold plate.	11
	The experimental parameters are: $\lambda_{Pump} = 323 \ nm, \ \lambda_{Probe} = 410 \ nm, \ P_{Pump} = 2.0 \ mW, \ P_{Probe} = 10 \ mW.$	72
5.1	Typical mass spectra of gold cations. The cluster signal is depicted as a function of the cluster mass.	76
5.2	Reactivity of Au_2^+ , Au_3^+ and Au_7^+ with O_2 at room temperature.	. s 78
5.3	Reactivity of Au_2^+ clusters at low temperatures with residual amounts of carbon monoxide present in the vacuum chamber	82

5.4	Typical mass spectra for negatively charged gold clusters measured after mass selection in Q_1 (see chapter 4, Fig. 4.1). The cluster signal	
	intensity is depicted as a function of cluster mass.	85
5.5	Reactivity of Au_1^- , Au_2^- and Au_3^- clusters with oxygen.	86
5.6	The experimental values of the electron affinity (EA) for gold clusters	
	$(Au_n^-, n = 1 - 70)$.	88
5.7	Kinetic traces for the reaction of Au_2^- with O_2 at an ion trap tempera- ture of 300 K. The ion signals (open symbols) and the summed signal (filled squares) are depicted as a function of the reaction time	89
5.8	Kinetic traces for the reaction of Au_2^- with O_2 at different tempera- tures. The normalized cluster ion signals (open symbols) and the sim- ulated signals (solid lines) are depicted as a function of the reaction time.	91
5.9	Double logarithmic representation of the temperature dependence for the decomposition metric of finite h of the A O^{-} metric metric based on the second se	0.6
5.10	Structure of the $Au_2O_2^-$ complex, predicted by DFT theoretical calcu-	90
	lations. The bond lengths are given in \mathring{A}	97
5.11	Reactivity of negatively charged gold clusters Au_1^- , Au_2^- and Au_3^- with $CO. \ldots \ldots$	99
5.12	Kinetic traces of the reaction of Au_2^- clusters with CO at different temperatures. The normalized ion signals (open symbols) and the simulated signals (solid lines) are shown as a function of the reaction time	101
5.13	Kinetic traces of the reaction of Au_3^- clusters with CO at different temperatures. The normalized ion signals (open symbols) and the simulated signals (solid lines) are shown as a function of the reaction time.	101
5.14	Kinetic traces (open symbols) for the reaction of Au_3^- clusters with CO at 100 K. The fitting procedure consists of purely consecutive CO adsorption processes, without the final equilibrium step.	103
5.15	Double logarithmic representation of the temperature dependence of the decomposition rate coefficients in the case of (a) Au_2CO^- and (b) Au_2CO^- reaction products	112
5.16	The calculated structure of Au_3CO^- (a) and Au_2CO^- (b). The bond	114
2	lengths are given in \mathring{A} .	114
5.17	Mass spectra for the reaction of Au_1^- , Au_2^- and Au_3^- clusters with O_2 and CO at different temperatures.	117
5.18	Kinetic traces of the reaction of Au_2^- clusters with O_2 and CO at different temperatures. The normalized ion signals (open symbols) and the simulated signals (solid lines) are shown as a function of the reaction time.	121

5.19	Kinetic traces for the reaction of Au_2^- clusters with: (a) O_2 only; (b), (c) with O_2 and CO at 300 K.	122
5.20	Test of the fit quality for the reaction of Au_2^- clusters with O_2 and CO . The kinetic traces (open symbols) and the simulated signals (solid lines) are depicted as a function of the reaction time	125
5.21	The dependence of the unimolecular reaction rate constants $k_1^{(1)}$, $k_2^{(1)}$ and $k_3^{(1)}$ on the reactive gases partial pressure at different reaction temperatures.	128
5.22	Double logarithmic representation of the temperature dependence of $k_1^{(3)}$, $k_2^{(3)}$, $k_{-2}^{(2)}$ and $k_3^{(2)}$ reaction rate constants. The dashed line represents a linear fit of the experimental data.	134
5.23	Simulation of the catalytic CO oxidation cycle on Au_2^- clusters given by the equations 5.29 - 5.31 at a reaction temperature of 300 K, by using the CKS 1.0 software.	135
5.24	The catalytic cycle for the CO oxidation reaction on Au_2^- clusters, derived from the experimental data, according to the equations 5.29 - 5.31.	137
5.25	Calculated structures for the $Au_2(CO)O_2^-$ reaction product. The bond lengths are given in \mathring{A}	138
5.26	Energetics along the reaction path for the catalytic CO oxidation containing structure C , which corresponds to the peroxyformate-like $Au_2(CO)O_2^-$ species as intermediate complex	140
5.27	Energetics along the reaction path for the catalytic CO oxidation containing structure D, which corresponds to the carbonate species $Au_2CO_3^-$ as intermediate complex	141
5.28	The full catalytic cycle for the CO oxidation reaction on negatively charged gold dimers based on the experimental and theoretical results.	142
5.29	Mass spectra for the reaction of Au_2^- , $AuAg^-$ and Ag_2^- clusters with O_2 and CO at a reaction temperature of 300 K ((a), (c), (e)) and 100 K ((b), (d), (f)), respectively.	144
5.30	(a) Termolecular rate constants for the reaction of Au_2^- , $AuAg^-$ and Ag_2^- clusters with oxygen at 300 K reaction temperature.(b) Termolecular rate constants for the reaction of Au_2^- , $AuAg^-$ and Ag_2^- clusters with carbon monoxide at 100 K reaction temperature	145
5.31	Mass spectra for the reaction of Au_3^- , Au_2Ag^- , $AuAg_2^-$ and Ag_3^- clusters with O_2 and CO at 300 K ((a), (c), (e), (g)) and 100 K ((b), (d), (f), (h)) reaction temperature, respectively.	149

5.32	(a) Termolecular rate constants for the reaction of Au_3^- , Au_2Ag^- , $AuAg_2^-$ and Ag_3^- clusters with oxygen at 300 K reaction temperature. (b) Termolecular rate constants for the reaction of Au_3^- , Au_2Ag^- , $AuAg_2^-$ and Ag_3^- clusters with carbon monoxide at 100 K reaction temperature.	150
6.1	NeNePo spectra for Au_2^- clusters measured at a temperature of 100 K. (a) and (b): the signal of the Au_2^+ clusters is depicted as a function of the delay time between the pump and the probe laser pulses	155
6.2	Morse-potential energy curves of the negative, neutral and positive gold dimers $(Au_2^-/Au_2/Au_2^+)$ with all experimentally observed electronic ex-	100
6.3	cited states of the neutral Au_2 clusters	159
6.4	pump and the probe laser pulses $(t_d > 0)$	161
	ters corresponding to negative values of the delay time between the pump and the probe laser pulses $(t_d < 0)$.	163
6.5	(a) The NeNePo spectrum of Au_3 clusters. (b) The NeNePo spectrum of Au_2^+ -fragment clusters. The measured spectra are normalized to the	100
6.6	maximum of the Au_3 signal (peak B)	166
	cationic gold trimers.	170
6.7	The NeNePo spectra of Au_3 clusters measured at different ion trap temperatures: (a) $T_{octopole} = 20 K$, (b) $T_{octopole} = 100 K$, (c) $T_{octopole} =$	
6.8	200 K and (d) $T_{octopole} = 300$ K	173
C O	NeNePo spectroscopy.	176
6.9	Mass spectrum for the reaction of Au_2 clusters with O_2 and CO (grey line). The photodepletion mass spectrum (black line) is measured after $t_1 = -2000 \text{ ms}$ at a wavelength of $\lambda = 400 \text{ nm}$ and a laser power of	
	$P_{laser} = 30 \ mW$	179