

# Chapter 1

## Introduction and Motivation

Gold as an element in its bulk form is known to be synonymous with noble chemical behavior and it is considered to be the least reactive metal in the periodic table. However, when its size is reduced to the nanometer range, gold loses its nobleness and exhibits a striking reactive behavior.<sup>1</sup> The unique properties of nanometer gold particles are currently an important research area of nanoscience and nanotechnology. The special optical properties of gold colloids and nanoparticles were used since ancient times for coloring ceramics and glasses, as well as dyeing textiles. One famous example is represented by the Lycurgus Cup (4th-5th century B.C.) which shows a red color in transmitted light and appears green in reflected light.<sup>2</sup> In the Middle Ages, gold nanoparticles were used for manufacturing the colored windows of Gothic churches. Nowadays, a well known example is represented by the photographic process where the presence of gold particles significantly enhances the sensitivity of the photographic film.

Despite these fascinating optical properties, gold was considered for a long time to be catalytically inactive. The interest in the potential catalytic properties of gold nanoparticles was awakened two decades ago when Haruta *et al.* reported on the low-temperature catalytic activity of supported gold nanoparticles towards the carbon monoxide combustion.<sup>3-5</sup> Moreover, it was found that gold nanoparticles deposited on metal oxide surfaces also show a surprisingly high catalytic activity in the partial oxidation of hydrocarbons, hydrogenation of carbon oxides and reduction of nitrogen oxides.<sup>6</sup> These unexpected catalytic properties of gold nanoparticles have a significant importance in current and future applications in the field of chemical and biological

sensors, imaging of cells and biomolecules, chemical industry as well as environmental protection and maintenance.<sup>2,6</sup>

Although the catalytic properties of nanoscale gold were intensively studied during the past decades,<sup>7</sup> the intrinsic mechanisms of the heterogenous catalysis at atomic and molecular level are still unknown. Therefore, model systems were searched for, which have similar properties to the real catalysts and, at the same time, are simple enough to be described theoretically. With respect to this, clusters<sup>a</sup>, which contain between a few atoms and a few thousands of atoms, are well suited model systems for the study of the elementary mechanisms of heterogenous catalysis. “Small is different” was postulated a few years ago by U. Landman, referring to the physical and chemical properties of clusters, which can differ completely from those of the corresponding bulk materials.<sup>9</sup> In this non-scalable regime (a few atoms to a few tens of atoms) the electronic structure still has a discrete, quantified character and thus, every cluster with a specific number of atoms and electrons has its own intrinsic, characteristic electronic structure. Due to this, by adding or removing a single atom from a cluster of a certain size, drastic changes in the physical and chemical properties can be obtained.

Recently, it was found that small, mass-selected gold clusters which contain at least eight atoms ( $Au_8$ ), deposited on a thin film of magnesium oxide  $MgO(100)$ , enable the oxidation reaction of carbon monoxide ( $CO$ ) to carbon dioxide ( $CO_2$ ). Theoretical calculations revealed that a charge transfer between the  $MgO$  surface and the cluster plays a significant role in the catalytic process by loosening the oxygen-oxygen bond and thus making the  $CO$  oxidation reaction possible.<sup>10</sup> In order to fully understand this mechanism, the study of mass-selected, charged gold clusters in the gas-phase presents substantial advantages: the influence of a surface is eliminated and the intrinsic catalytic properties of the clusters can be investigated. In the case of gas-phase investigations on charged clusters, the control of the cluster size can be easily achieved. This is in contrast to surface studies, where the coalescence of the deposited clusters is difficult to avoid. Furthermore, the influence of the cluster charge on the reactivity towards different gases can be systematically studied in the gas-phase.

Due to this, the efforts in this work are focused on the study of the catalytic prop-

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<sup>a</sup>The origin of the word cluster comes from the germanic word “Klustro” which represents a pile of material or nonmaterial things.<sup>8</sup>

erties of small, gas-phase, mass-selected, charged gold clusters towards the oxidation reaction of carbon monoxide. The production of mass-selected charged metal clusters began in the late 1970's<sup>11-15</sup> and since then, the experimental techniques have been developed continuously. In the experiments presented here, the combination of a tandem quadrupole mass spectrometer with a temperature variable octopole ion trap allows the study of the reactivity of gold clusters towards molecular oxygen and carbon monoxide under thermodynamically controlled conditions.

The development of femtosecond (fs) laser technology in combination with pump-probe spectroscopic techniques enables the study of the nuclear dynamics of a molecular system in real time<sup>16-18</sup> and represents the birth of a new scientific field referred to as femtochemistry. In a pump-probe scenario, a pump laser pulse populates a transient state which is interrogated *via* a time delayed probe laser pulse that projects the transient state into a defined, final signal state. Information about the time evolution of the transient state is obtained by monitoring the signal from the final state as a function of the delay time between the pump and probe laser pulses.

In the experiments presented in this work, the negative-to-neutral-to-positive (NeNePo) spectroscopy was applied in order to investigate the dynamics of gold clusters on the femtosecond time-scale. This pump-probe technique, developed in the group of Prof. L. Wöste, allows for the study of the nuclear dynamics of a system on the neutral potential energy surface of the electronic ground state and it was successfully applied to the study of the fs-dynamics of silver clusters.<sup>19</sup> The advantage of the NeNePo spectroscopy relies on the mass selection of the system prior to and after the interaction with the ultrashort laser pulses. For the study of the reaction products which are usually cluster-adsorbate complexes, the NeNePo method was extended to a new spectroscopic method referred to as *reactive NeNePo* which combines the methodology of the cluster reactivity measurements with the "classical" NeNePo fs-dynamics experiments. With this approach, the sequential processes involved in a chemical reaction can be monitored in real time.

The systematic investigation of the reaction kinetics and fs-dynamics of small gold clusters presented in this work is structured as follows: in chapter 2, the theoretical concepts of the reaction kinetics will be described, where a special accent will be set on ion-molecule reactions. The general theory of catalysis and an introduction into the field of nanocatalysis of deposited gold nanoparticles and clusters will be presented in

chapter 2 as well. In chapter 3, the theoretical basis applied to the characterization of the nuclear dynamics of the molecular systems relevant to this work will be outlined. The NeNePo method will be presented and its principle will be illustrated with the description of previously performed NeNePo experiments. The experimental setup utilized for the investigation of the reaction kinetics and femtosecond time-resolved dynamics of small, mass-selected gold clusters will be presented in chapter 4. The experimental results obtained from the systematic study of the reactivity of gold clusters towards molecular oxygen and carbon monoxide will be shown in chapter 5. In these studies, the influence of the cluster charge as well as the cluster chemical composition on their reactive behavior will be emphasized. It will be shown that relativistic effects play a significant role in the reactivity of gold clusters. The first experimental evidence of a catalytic cycle for the  $CO$  oxidation reaction carried out by  $Au_2^-$  clusters will be presented in chapter 5 as well. The investigation of the fs-dynamics of neutral gold dimers and trimers by applying the NeNePo spectroscopy will be shown in chapter 6. The first steps for the implementation of the reactive NeNePo spectroscopy for the study of the molecular dynamics of gold cluster-adsorbate complexes will be shown in chapter 6 as well. The conclusion and the new perspectives opened by the experimental investigations described in this work will be presented in chapter 7.