

Chapter 1

Introduction

"Then God said, "Let there be light"; and there was light"

The Holy Bible, Genesis 1:3

The discovery of the photoelectric effect in 1887-1888 [1, 2] and its theoretical formulation [3] were probably two of the most powerful forces that drew the technical evolution train in the 20th century. They have led to a vast series of investigations of light interacting with matter which continues to the day and has the effect of today's understanding of the atomic and nuclear world.

Another big step in the evolution of science of the 20th century was the discovery of synchrotron radiation, in 1947. The development of the synchrotron radiation facilities for investigating the interaction of soft X-rays with matter helped science bloom in the second half of the past century.

In the 1980's the basis have been set for a new science, that was supposed to close the gap between the solid state and the gas phase: cluster physics. Structural and electronic properties of clusters have been ever since investigated, revealing size- and material-dependent properties [4, 5]. This also includes fragmentation of clusters, where size-dependent fragmentation mechanisms have been explored before [6, 7, 8]. However, cluster investigations in the core level regime have mostly focused on van der Waals clusters, with little attention being given to covalently bound clusters. This is the motivation for the present work, where the emphasis is put on investigating the ionization and fragmentation of chalcogene clusters.

Experimental studies employing neutral van der Waals clusters have the inherent disadvantage that the cluster size distribution is broad, so that size dependent fission pathways cannot be easily inferred from experimental work. In contrast, covalently bound clusters can often be prepared in well defined sizes via the evaporation from the solid phase [9, 10, 11, 12, 13]. As a result, covalently bound clusters are suitable model systems to experimentally investigate fragmentation and fission properties of ionized clusters. The mechanisms leading to the formation of stable

products have proven to be sensitive to the primary excitation process. Depending on the cluster material, charge equilibration or charge localization is observed upon multiple ionization, the latter being important in the context of multiple ionization of van der Waals clusters [8].

Chalcogene clusters have been previously investigated in the 2p and the 1s-excitation regimes [9, 10, 11, 12, 13]. Fission mechanisms of doubly and multiply charged sulfur clusters, occurring after core hole relaxation and the emission of Auger electrons, have been derived for S 2p-excited sulfur clusters using photoelectron-photoion-photoion coincidence (PEPIPICO) spectroscopy [11].

This approach provides shapes of coincidence signals by plotting in 2D the flight time of the second recorded ion versus the time of flight of the first recorded ion. From the analysis of the time of flight distribution of the ions recorded in coincidence one can draw important conclusions regarding the dynamics of the fragmentation process involved in the occurrence of the ion pairs. The fragmentation of clusters can take place in one or more steps, each different process being visible through a different correlation plot pattern. Thus it is possible to differentiate between two-, three- or four-body fragmentation processes.

One of the aims of the present work is to study the ionization of sulfur clusters via highly charged ion beams (HCI) by means of mass spectrometry and coincidence spectroscopy. Also, the investigation of the fragmentation of sulfur clusters in the S-2p and S-2s regime with the help of a position sensitive coincidence technique (COLTRIMS) is intended.

Another goal of the present work is to investigate the ionization and fragmentation of selenium clusters in the 3d regime. The study is intended to make use of various spectroscopic techniques, such as mass spectrometry, NEXAFS spectroscopy and PEPIPICO spectroscopy.

This work begins in Chapter 2. with the description of the theoretical basis on which the experiments performed are based on. Chapter 3. introduces the experimental setup as well as the ionization means used. In Chapter 4. the obtained results are discussed, while conclusions are drawn in Chapter 5.