Photoionization of Rare Gas Clusters

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PHOTOIONIZATION OF RARE GAS CLUSTERS

by

Huaizhen Zhang

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Physics
Advisor: Nora Berrah, Ph.D.

Western Michigan University
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This thesis concentrates on the study of photoionization of van der Waals clusters with different cluster sizes. The goal of the experimental investigation is to understand the electronic structure of van der Waals clusters and the electronic dynamics. These studies are fundamental to understand the interaction between UV-X rays and clusters. The experiments were performed at the Advanced Light Source at Lawrence Berkeley National Laboratory. The experimental method employs angle-resolved time-of-flight photoelectron spectrometry, one of the most powerful methods for probing the electronic structure of atoms, molecules, clusters and solids.

The van der Waals cluster photoionization studies are focused on probing the evolution of the photoelectron angular distribution parameter as a function of photon energy and cluster size. The angular distribution has been known to be a sensitive probe of the electronic structure in atoms and molecules. However, it has not been used in the case of van der waals clusters.

We carried out outer-valence levels, inner-valence levels and core-levels cluster photoionization experiments. Specifically, this work reports on the first quantitative measurements of the angular distribution parameters of rare gas clusters as a function of average cluster sizes.
Our findings for xenon clusters is that the overall photon-energy-dependent behavior of the photoelectrons from the clusters is very similar to that of the corresponding free atoms. However, distinct differences in the angular distribution point at cluster-size-dependent effects were found. For krypton clusters, in the photon energy range where atomic photoelectrons have a high angular anisotropy, our measurements show considerably more isotropic angular distributions for the cluster photoelectrons, especially right above the 3d and 4p thresholds. For the valence electrons, a surprising difference between the two spin-orbit components was found. For argon clusters, we found that the angular distribution parameter values of the two-spin-orbit components from Ar 2p clusters are slightly different. When comparing the $\beta$ values for Ar between atoms and clusters, we found different results between Ar 3s atoms and clusters, and between Ar 3p atoms and clusters. Argon cluster resonance from surface and bulk were also measured. Furthermore, the angular distribution parameters of Ar cluster photoelectrons and Ar atom photoelectrons in the 3s $\rightarrow$ np ionization region were obtained.
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Huaizhen Zhang
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Chapter I

Introduction

Cluster research has received considerable attention in the past four decades. Clusters build a bridge between atoms and solids, and this characteristic allows researchers to better understand the transition between the microcosmic world and the macrocosmic world. The study of electrons, ejected by incident electromagnetic radiation, began many years ago. The photoelectric effect, a phenomenon discovered by Heinrich Herz in 1900 [1] and theoretically explained by Albert Einstein [2] in the early 20th century, occurs when electrons, impinged upon by electromagnetic radiation, are ejected from a solid; the electromagnetic radiation is made up of particles called photons. Photoelectron spectroscopy [3] continues to be very useful in physics, chemistry, biology, and many other fields. Electrons can be emitted from the interaction between the photon and atoms, molecules, clusters, and solids. This present work deals with electrons emitted from clusters.

Clusters of atoms and molecules have been studied since 1950 [4, 5, 6, 7, 8, 9, 10, 11, 12, 13], when the super sonic expansion jet was introduced by Hagen and Obert [5]. The discovery of fullerene $C_{60}$ [14], a cluster consisting of 60 carbon atoms, was another important step for cluster research. In these last decades of the twentieth century, cluster science has developed into an independent interdisciplinary field which links many areas of physics and chemistry. In general, cluster can be defined as an aggregation of many atoms. Cluster size (number of atoms per cluster) is a significant
parameter, which determines cluster properties both in physics and chemistry. Due
to the cluster’s nanometer scale size, clusters physical and chemical properties can be
totally different from a single atom, molecule or solid, thus providing a good testing
ground to investigate the transformation of structure and properties with cluster size [8,
9, 10, 15]. This special size-dependent characteristic has triggered many scientists to
investigate clusters using different experimental techniques.

Investigations of the interaction of photons with matter, such as atoms, molecules
and solids, is a fundamental research subject in astronomy, biology, chemistry and
many other scientific areas. Exploring this subject often requires probing the elec­
tronic structure of matter, the origin of all physical and chemical properties. Therefore,
the investigation of the basic light-cluster interaction, achieved through the methods of
photoionization and photoexcitation is important for gaining a better understanding of
cluster electronic structure and properties. In this dissertation, we applied the photoion­
ization method to study rare gas clusters.

Rare gas Ar, Kr and Xe clusters are important systems for investigating the develop­
ment of the electronic structure, properties and phenomena, as the cluster-size changes.
These rare gas atoms have closed shells creating a weak bond, called a van der Waals
bond, between two neighbor atoms in clusters. Therefore, rare gas average cluster sizes
can be easily controlled. Since Becker’s research breakthrough in 1950 [4], different
experimental techniques, such as x-ray absorption spectroscopy [16, 17, 18, 19, 20],
x-ray photoelectron spectroscopy [21, 22, 23, 24, 25, 26, 27] and fluorescence spec­
troscopy [28, 29], have been applied to study the rare gas clusters. For example, Fe-
dermann et al. [16] used time-of-flight ion spectrometry to determine the yield of Ne cluster ions, and reported the first resonant K-shell absorption spectra of Ne clusters with different sizes. Knop et al. [17] employed mass spectrometry and photoelectron spectroscopy to measure site-specific inner-shell excitation of Kr clusters, and determined the total electron yield spectra within the Kr 3d excitation region between 90 and 96 eV, for average cluster sizes between 2 and 1250. Ruhl et al. [19] applied x-ray absorption spectroscopy to study Ar clusters, and concluded that the spectrum of Ar clusters changes systematically from atom to solid, referring to its "solidlike" behavior increasing with increasing cluster size. Additionally, there are a few groups working on the mixed rare gas clusters [30, 31] and M. Lundwall et al. [30] is one of these groups. For example, they used the coexpansion method to produce the free heterogeneous Ar-Kr clusters and investigated them using x-ray photoelectron spectroscopy. In comparison to cluster surface and bulk binding energy shifts, relative intensities, and peak widths, they have shown that the krypton atoms favor the bulk position while the argon atoms favor the surface position in mixed Ar-Kr clusters.

Despite the advances in cluster research only a few studies used angle-resolved photoelectron spectroscopy to study the photoelectron angular distribution parameter of rare gas clusters. Ohrwall et al. [23], in their photoelectron study of free Xe clusters, noticed substantial differences in the angular dependence of the photoelectron intensity from Xe clusters compared to Xe atoms; however, there were no quantitative measurements of the angular distribution. Recently, Rolles et al. [27] corroborated these qualitative measurements by performing experiments that allowed the determination of
the angular distribution parameter $\beta$ for free Xe clusters. The measurements showed the evolution of the Xe 4d and 5p photoelectron angular distribution parameter as a function of photon energy and cluster size and revealed strong cluster-size-dependent variations, which were traced to elastic photoelectron scattering.

Knowledge about the electronic structure of rare gas clusters, however, is still limited. Most studies have been reported using the X-ray absorption spectroscopy technique. Only a few rare gas cluster studies using photoelectron spectroscopy have been reported. This dissertation is the first comprehensive work about angle resolved photoelectron studies in rare gas Ar, Kr and Xe clusters where the angular distribution parameters $\beta$ has been determined, as a function of photon energy and average cluster sizes.

The research presented in this dissertation used the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory as the source of photons. The ALS is a third-generation synchrotron radiation source featuring high intensity, high resolution and high tunability enabling the study of the interaction of light with rare gas clusters. Two time-of-flight (TOF) electron spectrometers and a two-dimensional (2D) photoelectron spectroscopy technique were used in the presented work to determine and reveal new aspects of cluster structure and dynamics. Photoelectrons subsequent to the photoionization of the inner shells and outer shells in rare gas Ar, Kr and Xe clusters have been measured. The intensity of the photoelectron profiles as a function of photon energy was studied. Particularly, the photoelectron angular distributions of Ar 2p, Ar 3s, Ar 3p, Kr 3d, Kr 4p, Xe 4d and Xe 5p have been obtained in specific photon energy ranges.
The study of the photoionization of rare gas clusters with different average cluster sizes is presented in this dissertation in the following seven chapters. This introductory chapter introduces in general the motivation and present background and status of rare gas cluster research work. Chapter two provides the fundamental physics concepts: cluster physics, dipole approximation, angular distribution, and photoionization and photoelectron spectroscopy. Chapter three presents the experimental technique, including all of the details about the experimental setup and data analysis. Chapter four reports on the electronic structures of free Ar, Kr, and Xe atoms and their corresponding clusters. The inner-shell and outer-shell photoionization experiments of Ar, Kr, and Xe clusters are separately described in chapters five and six respectively. Chapter seven focuses on the resonance study in Ar clusters. Finally, in chapter eight, a brief conclusion of this dissertation is given.
CHAPTER II

GENERAL BACKGROUND

2.1 Cluster Physics

Cluster physics [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 32], a fast-developing field, links many areas of physics and chemistry. In this field, a cluster is defined as an aggregation of a small and finite number of atoms or molecules. It bridges the gap between a free atom and an infinite solid matter, shown schematically in figure 2.1. Since clusters can change properties continuously or abruptly depending on their cluster size, it is very important to add one atom or molecule at a time when studying clusters and determining their properties. The outmost layer of a cluster is called the surface; the inner layer is called the bulk. Cluster size describes the number of atoms or molecules per cluster. The range of the cluster size can start from two atoms, called a dimer, up to several tens of thousands of atoms, called a large aggregate.

A cluster's nanometer scale size can cause the cluster's physical and chemical properties to be totally different from a single atom, molecule or the solid. The varying characteristics of clusters have led to an active and exciting research field. Some applications have been used to tailor catalysis, or the construction of novel materials. The evaluation of various physical and chemical properties from the expansion of an atom, through a cluster, to the solid state gives us a better understanding of the origin of solid properties. In simpler terms, by controlling the average cluster size, the properties of a cluster can be controlled to some degree [32].
In order to fully understand these size-dependent characteristics, it is important to study clusters’ electronic structures. The geometric structure of clusters as a function of cluster size consists of the spatial change of the atoms or molecules, as well as their arrangements. The electronic structure change of clusters corresponds to the energy change of the electronic states. The geometric structure of clusters as a function of cluster size consists of the spatial change of the atoms or molecules, as well as their arrangements.

2.2 Van der Waals Cluster Production in a Supersonic Jet

Almost 50 years ago, Becker, Bier and Henkes [4] published their work about the formation of cluster beams, beams of clusters. Then, in 1980, Hagena [5, 7] published his research, deducing the scaling laws for cluster beam parameters which make it possible to estimate the rate of cluster formation. This finding has led to many applications in cluster research. Hagena’s scaling laws were applied in our experiments.

There are several methods to produce free clusters depending on the cluster type, such as ionic clusters, covalent clusters, metal clusters, and van der Waals clusters. A
supersonic jet is employed to produce the van der Waals clusters in our experiments.

Briefly, a rare gas with low temperature and high pressure expands out of a cooled nozzle through a vacuum chamber; it passes through a supersaturation and a condensation process, leading to the formation of rare gas clusters. The atoms in the cluster interact through van der Waals forces. The average cluster size (number of atoms per cluster) depends on the temperature $T_0$ and pressure $P_0$ of the cluster source, the shape and size of the nozzle, and the type of gas used to form the cluster. In our experiments, we used liquid $N_2$ to cool the gas and a heater to control the temperature of the cluster source.

There are various common sorts of cluster nozzles with different shapes and geometries. Sonic nozzle, laval nozzle, conical nozzle [5], and small aperture are typical types used to produce the cluster. In this dissertation, a conical nozzle with diameter $d = 100 \mu m$ and a flat aperture were employed to produce the rare gas Ar, Kr and Xe clusters. In our experiments, we have measured different cluster sizes which vary from 20 atoms
up to over 8000 atoms. The average Xe cluster size varies from 60 atoms up to over 8000 atoms, with the pressure from 40 KPa to 210 KPa and the temperature 170 K to 230 K. For Kr clusters, the range of the cluster size is 50 to 6000, under the condition of the temperature $T_0 = 170 \text{ K} \sim 190 \text{ K}$ and the pressure $P_0 = 60 \text{ KPa} \sim 200 \text{ KPa}$. Argon cluster sizes vary from 20 to 700, with $T_0 = 105 \text{ K} \sim 120 \text{ K}$ and $P_0 = 95 \text{ KPa} \sim 222 \text{ KPa}$. A schematic picture of this process is shown in figure 2.2.

Clusters are often characterized by a parameter $\Gamma^*$. This condensation parameter $\Gamma^*$ can be derived from the bimolecular collisions and unimolecular decay reactions, which correlates cluster formation in different expansions. This parameter is a dimensionless parameter, which has been defined for the rare gases as:

$$
\Gamma^* = k \frac{(P_0/mbar)(d/\mu m)^{0.85}}{(T_0/K)^{2.2875}}
$$

(2.1)

Where the gas constant $k$ have been calculated from the molar enthalpy at 0 K and the density of the solid according to Hagena [5, 7]. For the different rare gases, the parameter $k$ is given in the below table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>3.85</td>
<td>185</td>
<td>1646</td>
<td>2980</td>
<td>5554</td>
</tr>
</tbody>
</table>

Based on Hagena’s scaling laws [5, 7] for cluster formation, in our experiments, the empirical relation between size of the cluster and the initial expansion conditions is
determined by:

\[ < N > = -18.2277 + \frac{3919.04}{1 + \exp\left(\frac{4793.28 - \Gamma^*}{809.965}\right)} \]

(2.2)

Where \( < N > \) is the average size of the cluster, which can be changed by varying the nozzle diameter \( d_0 \), pressure \( P_0 \) and temperature \( T_0 \) of the rare gas cluster source.

For a conical nozzle with the half-opening angle \( \alpha \), the parameter \( \Gamma^* \) can be described as:

\[ \Gamma^* = k \frac{(P_0/\text{mbar})(d/\mu m * 0.736/tana)^{0.85}}{(T_0/K)^{2.2875}} \]

(2.3)

Then the empirical scaling laws to determine the average cluster size is defined as:

\[ < N > = \begin{cases} 33 \left( \frac{\Gamma^*}{1000} \right)^{2.35}, & \text{for } \Gamma^* > 1800 \\ \exp[-12.83 + 3.51(ln\Gamma^*)^{0.8}], & \text{otherwise} \end{cases} \]

(2.4)

In our experiments, the average cluster size \( < N > \) has the spread by \( \pm \frac{<N>}{2} \). For example, the average cluster size \( < N > = 60 \) means that the real cluster size is from 30 atoms to 90 atoms per cluster.

2.3 Photoionization and Photoexcitation Processes

Investigating photoprocesses in clusters can provide a unique outlook on the dynamics of clusters; more specifically, exploring photoprocesses could help us deepen our understanding of the electronic structures of rare gas clusters. In our experiments, two types of photoprocesses are involved: photoexcitation and photoionization. The details of these processes are described below.

2.3.1. The Photoexitation Process
Figure 2.3  Schematic of Photoexcitation and Photoionization Processes. The solid circles represent electrons; the empty circles represent the hole left by the excited electron or the emitted electron.

For an atom or a molecule, if the energy level difference between two states is equal to $h\nu$, and if a photon with energy $h\nu$ interacts with this targeted atom or molecule, this photon is absorbed by this atom or this molecule; during this process, an electron in this atom or this molecule may be excited from the lower energy level to a higher energy level. This process is called the photoexcitation process, shown in figure 2.3.

2.3.2. The Photoionization Process

If the energy of the photon is sufficiently high and an electron is emitted with kinetic energy $E_k$, this process is called photoionization [2], as shown in figure 2.3. The kinetic energy of the electron is defined as:

$$E_k = h\nu - E_b$$  \hspace{1cm} (2.5)

Where $E_b$ is the electron binding energy, the energy difference between the ground
state and the final ionic state. In this process, the energy is conserved and the emitted electron takes as kinetic energy the difference between the binding energy and the photon energy. This formula is given by A. Einstein (1905) [2]. In our experiments, we measured the kinetic energy of the emitted electrons from our rare gas clusters.

2.4 Auger Processes

The Auger decay processes usually include two types of decay processes: normal Auger decay process [33] and resonant Auger decay process [34].

![Figure 2.4 Schematic of Normal Auger Decay Process. The solid circles represent electrons; the empty circles represent the hole left by the excited electron or the emitted electron.](image)

After the inner shell ionization, the subsequent decay process, leaving the system in a doubly ionized final state configuration, is defined as the normal Auger decay process. This Auger decay was discovered by a French physicist, Pierre Auger, in 1925 [33]. In this process, two outer shell electrons interact with each other; one electron loses energy and fills the inner shell hole left by the ionized electrons, while the other outer shell electron absorbs the lost energy from the first electron, and gets ionized. Two
holes are left in this process, as shown in figure 2.4.

![Diagram of Resonant Auger Decay Process]

**Figure 2.5** Schematic of Resonant Auger Decay Process. The solid circles represent electrons; the empty circles represent the hole left by the excited electron or the emitted electron.

The resonant Auger decay process, on the other hand, is described as the following. After the inner shell excitation, the non-radiation decay process, leaving the system singly charged in either a 1-hole final state configuration or a 2-holes and 1-particle final state configuration. Depending on which electrons participate in the de-excitation decay process, this resonant Auger decay process can be divided into two groups: the
participator decay and spectator decay. For the participator decay, the excited electron participates in the process; for the spectator decay, the excited electron is a spectator. These two processes are described in figure 2.5.

In this dissertation, Ar cluster resonant Auger decay process was observed. The Ar cluster resonance is founded at photon energy $h\nu = 27.005$ eV and $h\nu = 27.674$ eV. In addition, the corresponding Ar atom resonance were observed at $h\nu = 26.66$ eV, $h\nu = 28.05$ eV, $h\nu = 28.57$ eV, $h\nu = 28.817$ eV, $h\nu = 28.957$ eV, $h\nu = 29.045$ eV, and $h\nu = 29.281$ eV.

2.5 Angular Distribution

Clusters are similar to atoms and molecules, in that all have a spatial distribution of electrons. Determining the emitted electron angular distribution from clusters is one of the fundamental observables for studying the electronic structure. The angular distribution can be obtained through measuring the intensities of photoelectrons, as a function of angle. The angular dependence arises from the dipole nature of the transition.

The assumption that the electromagnetic field of the photon beam, proportional to $\exp(ikr) = 1 + ikr + ..., is approximated to unity, is called the electronic dipole approximation. With the dipole approximation and a synchrotron photon beam with the polarization $p$, the measured ionization intensity $I(\theta)$ of the photoelectrons is given by:

$$I(\theta) = \frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left( 1 + \frac{\beta}{4}(1 + 3pcos2\theta) \right)$$

(2.6)

In this equation, $\theta$ is the angle of detection measured between the direction of the
electric field of the incoming radiation and the electron emission direction, $\beta$ is the
asymmetry parameter or the angular distribution anisotropy parameter, $\sigma$ is the pho­
toionization cross section, and $\frac{d\sigma}{d\Omega}$ is the differential cross section which is proportional
to the observed photoelectron intensity [35].

When we use linearly polarized synchrotron radiation, the polarization $p$ of the pho­
ton beam is 1. We can extract the angular distribution of the photoelectrons using [36]:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} (1 + \beta P \cos \theta)$$ \hspace{1cm} (2.7)

Where $P$ is the second order Legendre Polynomial:

$$P = \frac{(3\cos^2 \theta - 1)}{2}$$ \hspace{1cm} (2.8)

The polar plot of the angular distribution anisotropy parameter $\beta$ is shown in figure
2.6. In order to keep the cross section $\sigma$ positive, the range of the angular distribution
anisotropy parameter $\beta$ is only between -1 to 2.

From this graph, we can see that for $\beta = 0$, the differential cross section is isotropic.
For the angle $\theta = 54.7^0$, we get the same differential cross section at all beta values and
this angle is called the magic angle, where the electron emission is independent of the
$\beta$ value.

In this dissertation, the photoelectron intensity of Ar, Kr and Xe clusters with dif­
ferent cluster size were measured. In addition, the corresponding photoelectron angular
distribution parameters $\beta$ were obtained as a function of photon energy and cluster size.
Figure 2.6  The Asymmetry Parameter $\beta$ at Different Angles.
CHAPTER III

EXPERIMENTAL APPARATUS AND TECHNIQUES

3.1 Synchrotron Radiation

When charged particles like electrons are accelerated to move near the speed of light in a circular orbit, they emit energy in the form of photons. These photons are emitted in a narrow cone, at a tangent to a circular orbit. This electromagnetic radiation is called synchrotron radiation, and this radiation was first discovered in 1946 at the General Electric 70 MeV synchrotron [37]. Synchrotron Radiation is a tool to probe matter in general and in particular the structure of atoms, molecules and clusters. All the experiments included in this dissertation were carried out at the Advanced Light Source (ALS), a third synchrotron [38] at Lawrence Berkeley National Laboratory. Figure 3.1 presents the principal elements of the ALS.

The ALS consists of the following important parts, which are shown in figure 3.1.

(1) The Linac

The linac is also called the linear accelerator, which is the electromagnetic catapult that brings electrons from a standing start to a relativistic velocity (99.9948% of the speed of light).

The main three parts of the linear accelerator are:

(a) The electron gun

(b) The buncher

(c) The linac itself
Each part is responsible for a stage of the electrons acceleration. The electron gun is where the electron acceleration starts. The buncher accelerates the pulsing electrons as they come out of the electron gun and pack them into bunches. The linac is just an extension of the buncher, which receives additional radio frequency (RF) power to continue accelerating the electrons, and compacting them into tighter bunches. When the electrons leave the linac, the velocity can reach values very close to the speed of light.

(2) The Booster Synchrotron

The booster synchrotron is circular boosting the energy of the electrons to reach a speed of 99.999994% of the speed of light. Electrons will reach the target energy (usually 1.9 GeV) and be ready to enter into the storage ring.

(3) The Storage Ring
The storage ring is roughly circular, and it has 12 arc-shaped sections (about 10 meters) joined by 12 straight sections (about 6 meters). As soon as the electrons reach the target energy in the booster synchrotron, an injection system will transfer them to the storage ring where they will circulate for hours, emitting the photon beams as they pass through bending magnets as well as undulators and wigglers.

(4) The Undulators and Wigglers

The undulators are located in the straight sections of the storage ring, where the brightest synchrotron light at the ALS comes from. They have over one hundred magnetic poles lined up in rows above and below the electron beam. The magnets will force the electrons and make them move in a snake-like path when they pass through the magnets, so the photons will be added together from the entire curve, and are directed into the beamline. Wigglers are very similar to the undulators, but they have fewer magnetic poles [39].

(5) The Beamline

From the storage ring to the workstation, the beamline delivers the photon Via a series of optical devices. Beamline mirrors guide and concentrate a thin beam of light (photons) to the experimental chamber to excite and ionize our clusters. In details, the horizontal focusing mirror and the vertical condensing mirror steer and focus the beam to be horizontal and vertical respectively, at the entrance slit of the monochromator. Since the storage ring produces so many photons with a broad wavelength range, we have to use beamlines with monochromators to choose photons with specific wavelengths. Monochromators, acting like prisms, spread the thin photon beam into a spec-
trum of different wavelengths in order for the desired wavelength to be selected to ionize our sample. The monochromators have three different gratings: low 380, medium 925 and high 2100 lines/mm period, corresponding to three photon energy ranges which are (17 eV - 61 eV), (40 eV - 150 eV) and (90 eV - 340 eV) [40] respectively. The exit slit is used to control the photon energy range, which has a variable opening. The experimental measurements in this thesis were carried out using an 8 cm 55 period U8 undulator of beamline 10.0.1, which has a spherical grating monochromator to select the wavelength. Beamline 10.0.1 is shown in figure 3.2.

(6) The Sample Workstation / Experimental Station

The workstation or experimental station consists of a vacuum chamber housing detectors and is described under experimental apparatus below.

(7) The RF System

The RF system is the radio-frequency system, which supplies power to the ALS in the form of microwaves. The microwaves are the radio waves, whose wavelengths are between about one meter and one millimeter. Microwave power is used to accelerate...
electrons, keeping them whirling around the ALS storage ring at almost the speed of light. The electrons release this energy as x rays and ultraviolet light. The three basic components of the RF system are klystrons, waveguides and RF cavities.

In this thesis, all the measurements were carried out using two-bunch operation of the storage ring. In this case, only two electrons bunches are stored in the ring and are separated by 328 ns. Usually, in multibunch operation, there are 328 bunches electrons which are separated by 2 ns. The two-bunch operation is necessary for us since we use time-of-flight (TOF) spectrometry [38, 41] to perform our experiments. The two-bunch mode of operation provides the timing trigger for our electronics described below.

3.2 Experimental Apparatus

The experimental setup is shown in figure 3.3. After the photons are monochromatized by the grating monochromotor, the selected wavelength passes through the experimental chamber. In this thesis, all the experiments are performed using time-of-flight (TOF) photoelectron spectroscopy [38, 41], which was designed by Dr. Berrah’s group. Two TOF spectrometers shown in figure 3.4 are housed in a rotatable chamber. They are located at 0° and 54.7° (magic angle) with respect to the photon electric field vector. The cluster source (built by Dr. John Bozek (ALS) in collaboration with our team) is located in the space between the two spectrometers. Figure 3.4 is the cross section of the chamber viewed from the front of the chamber along the photon beam, which has two TOFs spectrometers and the cluster source with gas supply. The photon beam is perpendicular to the vacuum chamber and the photons interact with the tar-
Figure 3.3 Schematic of the Experimental Setup.

get cluster in the middle of the chamber. The star shown in figure 3.3 represents the interaction region.

Figure 3.4 depicts few more details about the experimental chamber used in the experiment. The horizontal dashed line represents the photon electric field vector of the photon beam. TOF 1 is located at the magic angle, 54.7° relative to the photon electric field vector, and TOF 2 is at 0°. The magic angle corresponds to the angle where the differential cross section is independent of the beta values. The chamber shown in figure 3.3 and figure 3.4 can be rotated to allow for higher statistics data. The cluster source is between the two spectrometers, as introduced in chapter 2. Using this setup, two spectra can be measured simultaneously at these two angles. This simultaneous measurement is an essential method for the quantitative determination of the photo-electron angular distribution parameters, since it is independent of photon or cluster
The schematic diagram of one electron TOF spectrometer is shown in figure 3.5. The total flight length of the photoelectrons to travel from the interaction region to the detection plate is 689 mm, while the detection plate is a pair of microchannel plates (MCPs) [42] and an anode detection plate mounted at the end of the flight tube. This total flight length includes 20 mm of distance from the interaction region to the 2mm diameter entrance aperture of the TOF nose, 78 mm of TOF nose and 591 mm of TOF tube. Since the electron is sensitive to stray electric and magnetic fields, a layer of \( \mu \)-metal inside the TOF nose and tube sections is used to shield the outer magnetic field. The energy resolution of this spectrometer is about 1% of the photoelectron kinetic energy. In order to reach this resolution, usually a negative retarding potential is used to reduce the photoelectron energies of the higher kinetic energy photoelectrons. A
positive retarding potential is applied to accelerate the slow photoelectrons so they can be detected.

Two stacked MCPs [42] are mounted at the end of the TOF tube. They trigger a signal by producing a cascade of electrons once they are hit by one of the flying photoelectrons. In the experiment, the two MCP plates are stacked together with a bias angle (about 80°) opposite to each other, which can cause a "chevron type" shown in figure 3.6. Electrons are then collected on an anode which forms an output pulse signal. Each MCP is an array of miniature electron multipliers oriented parallel to each other. The size of each MCP is approximately 0.5 mm in thickness and 42 mm in diameters of the active area. The latter consists of 104 – 107 small holes or channels and each hole or channel is about 10 μm in diameter. In order to optimize the secondary emission characteristics of each channel, the channel matrix is usually manufactured from a lead glass, a special semiconductor material. Additionally, the front and rear surface of the
MCP1

MCP2

Anode

\[ e^- \]

\[ V1 = 500 \text{ V} \]
\[ V2 = 1500 \text{ V} \]
\[ V3 = 1600 \text{ V} \]
\[ V4 = 2600 \text{ V} \]
\[ V5 = 2700 \text{ V} \]

\[ \text{output pulse} \]

\[ R \]

**Figure 3.6** Schematic of the Two MCPs in the Chevron Configuration. The voltages on the right side of this figure is the approximate voltage values applied on the MCPs in the experiment. MCP have a metallic coating, usually Nichrome or Inconel, which can provide parallel electrical contact to each channel. In order to produce more secondary electrons to increase the signal, the higher voltage is applied at the exit of the plate. Usually under these conditions, the electron avalanche has an electron gain of about \( 2 \times 10^4 \) under an applied voltage of 1000 V.

The detail of the electron avalanche, which is called Chevron configuration, is shown in figure 3.6. In the experiment, the approximate voltages applied on the MCP are shown on the left hand side in figure 3.6. After an electronionized from the clusters hits the MCP, the anode detector provides an output pulse which is extracted from the load resistor R. The signal is then fed to the fdata acquisition system.
3.3 Data Acquisition and Analysis

The schematic diagram of the electronics that processes the signal is shown in figure 3.7, which includes the amplifier (AMP), the constant fraction discriminator (CFD), the time-to-amplitude converter (TAC), the analog-to-digital (ADC), the multichannel analyzer (MCA) and the computer (PC).

A pulsed signal is generated from the anode plate at the end of the TOF spectrometer. It is shaped and amplified with an amplifier with about an amplification of 50. Much of the unwanted background is removed by the constant fraction discriminator, which presets a threshold and improves the start time resolution by manipulation of the original input signals. The CFD output signal is the start signal from the time-to-amplitude converter, which provides a $0 \sim 10 \text{ V}$ full-scale output signal proportional to the time difference between the start and the stop signal. In the experiment, the bunch marker signal, a negative NIM pulse (-0.8 V) from the ALS storage ring, acts as the stop signal for the time-to-amplitude converter. The TAC analog-output voltage is converted into a channel number with the analog-to-digital converter, which has maximum channel resolution of 8192 and is operated in the pulse-height-analysis and anticoincidence mode. The output signal of the digital ADC is delivered into a multichannel analyzer, which supports up to 16384 channels from an external ADC and can store up to 16777215 counts per channel. The MCA acts as a channel address and increment in the corresponding channel. Finally the data from the MCA is read into the PC and stored, and the resulting counts vs channel spectrum is displayed as a graph on a PC.
The experiment has been run using two custom-made PC data acquisition software packages. One is the LabView acquisition program, the other was written in C++ programming language. The LabView acquisition program is used to collect individual time spectra and monitor the photon beam current as well as the chamber pressure. The C++ acquisition program allows us to carry out two dimensional measurements (2D scans) where the photon energy is varied and all kinetic energy electrons are recorded. This software can be used to collect the individual time spectra, change photon energy with the pre-set steps across the region of interest, and store the data information in ASCII and Binary formats, which also gives a 2D map of the photoionization process.

The data collected using Labview or the photon scans using the acquisition programs are stored in counts vs. time format. The spectra were calibrated by using known corresponding atomic photoelectron lines, such as Xe 4d, Xe 5p and Ar 3s and Ar 3p, to obtain the scaling factors for the time-to-energy conversion and to generate the electron transmission efficiency of the analyzers as a function of kinetic energy. All 2D
spectra have been converted from time to energy scale, and corrected for transmission efficiency, variation in photon flux and collection time.
CHAPTER IV

PHOTOIONIZATION EXPERIMENTS IN ARGON, KRYPTON
AND XENON CLUSTERS

In this chapter, we introduce the photoionization experiments of Ar, Kr and Xe which are described in more details in the following chapters. The angular distribution of the photoelectrons from these clusters are also introduced.

4.1 Electronic Structures of Ar, Kr, and Xe Atoms

The electronic structure is important to understand since it affects the properties of atoms, molecule, clusters and solids. The electronic structure of an atom is connected to valence electrons and core electrons [13, 43]. The valence levels can be further separated into two sub-levels: outer valence level and inner valence level. For Ar, Kr and Xe free atoms, the electronic structures are provided below:

Ar: \(1s^22s^22p_{1/2}^22p_{3/2}^23s^23p_{1/2}^23p_{3/2}^2\)

Kr: \(1s^22s^22p_{1/2}^22p_{3/2}^23s^23p_{1/2}^23p_{3/2}^23d_{5/2}^23d_{3/2}^24s^24p_{1/2}^24p_{3/2}^2\)

Xe: \(1s^22s^22p_{1/2}^22p_{3/2}^23s^23p_{1/2}^23p_{3/2}^23d_{5/2}^23d_{3/2}^24s^24p_{1/2}^24p_{3/2}^24d_{5/2}^24d_{3/2}^25s^25p_{1/2}^25p_{3/2}^2\)

These electronic structures also present the spin-orbit split components, which are due to the spin and orbit coupling. The outer valence level, inner valence level and core level of the corresponding atoms are shown in the table 4.1.

In our experiments, we measured photoelectrons from the outer valence level, inner valence level and core level of the corresponding clusters as shown in the table 4.2.
Table 4.1  Electronic Structures of Ar, Kr, and Xe Free Atoms.

<table>
<thead>
<tr>
<th>Levels</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Valence Level</td>
<td>$3p_{3/2}^23p_{3/2}^3$</td>
<td>$4p_{3/2}^24p_{3/2}^3$</td>
<td>$5p_{3/2}^25p_{3/2}^3$</td>
</tr>
<tr>
<td>Inner Valence Level</td>
<td>$3s^2$</td>
<td>$4s^2$</td>
<td>$5s^2$</td>
</tr>
<tr>
<td>Core Level</td>
<td>$1s^22s^22p_{3/2}^22p_{3/2}^3$</td>
<td>$1s^2...3d_{3/2}^33d_{5/2}^4$</td>
<td>$1s^2...4d_{3/2}^44d_{5/2}^6$</td>
</tr>
</tbody>
</table>

Table 4.2  Electronic Structures of Ar, Kr, and Xe Cluster Studied in This Thesis.

<table>
<thead>
<tr>
<th>Levels</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Valence Level</td>
<td>$3p_{3/2}^23p_{3/2}^3$</td>
<td>$4p_{3/2}^24p_{3/2}^3$</td>
<td>$5p_{3/2}^25p_{3/2}^3$</td>
</tr>
<tr>
<td>Inner Valence Level</td>
<td>$3s^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Core Level</td>
<td>$2p_{3/2}^22p_{3/2}^2$</td>
<td>$3d_{3/2}^43d_{5/2}^6$</td>
<td>$4d_{3/2}^44d_{5/2}^6$</td>
</tr>
</tbody>
</table>

As mentioned before, the clusters bridge the gap between free atoms and solids. In comparison to the atomic electronic structure based on single separate energy levels the solids have continue energy levels which are called the electronic band structure. An example of solid electronic band structure is shown in figure 4.1. The cluster electronic structures may have one or both atomic or solid behaviors [44]; the schematic evolutions of electron energy levels for free atoms, clusters and solids are shown in figure 4.2.

Figure 4.1 shows us the electronic band structure of solid. The band gap differs depending upon the type of the solid. The metal does not have a band gap. The overlap
range allows the electrons easy transfer between the two bands. The binding energy range of metals is about 0.5 ~ 3 eV. The semiconductors, which have a binding energies of about 1 ~ 4 eV, lie in the middle. The insulators have the biggest band gap, making it more difficult for electrons to escape from the valence band to the conduction band. The binding energy range for the insulator is over 4 eV.

As shown in figure 4.2, the free atoms have only single energy levels, while the solid have continuous energy levels to compose the energy band. The electronic energy structures of clusters bridge the gap between these two different types of energy levels. This characteristic of clusters can provide us with a better understanding of the origin properties of solids since we can achieve measurements as a function of average cluster size until we reach the solid state. In this figure, the smallest cluster is called a dimer, which is made of only two free atoms.
4.2 Photoionization Experiments of Ar, Kr and Xe Clusters

As mentioned in Chapter 3, our experiments were carried out with two electron TOF spectrometers, using the undulator beamlines 8.0.1 and 10.0.1 of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Our rare gas Ar, Kr and Xe clusters with variable cluster sizes were produced through the supersonic jet, which is described in Chapter 2. Note that the simultaneous measurement at two different angles, 0° and 54.7°, in our experiments is crucial for the quantitative determination of the photoelectron angular distribution parameters of rare gas clusters, since simultaneous measurement cancels count rate variations due to temperature and the density fluctuations of the cluster beams. The detection and transmission efficiency of TOF detectors were calibrated by using the known corresponding atomic photoelectrons lines. In or-
Table 4.3  Sizes of Ar, Kr and Xe Cluster Studied in the Photon Energy Ranges of Interest.

<table>
<thead>
<tr>
<th>Position</th>
<th>Clusters</th>
<th>Cluster Size</th>
<th>Photon Energy Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence Shell</td>
<td>Ar3p, Ar3s</td>
<td>50 ~ 300</td>
<td>15eV ~ 100eV</td>
</tr>
<tr>
<td>Inner Shell</td>
<td>Ar2p</td>
<td>60 ~ 280</td>
<td>260eV ~ 400eV</td>
</tr>
<tr>
<td>Valence Shell</td>
<td>Kr4p</td>
<td>70 ~ 230</td>
<td>85eV ~ 145eV</td>
</tr>
<tr>
<td>Valence Shell</td>
<td>Kr4p</td>
<td>1200, 5400</td>
<td>20eV ~ 80eV</td>
</tr>
<tr>
<td>Inner Shell</td>
<td>Kr3d</td>
<td>70 ~ 252</td>
<td>100eV ~ 200eV</td>
</tr>
<tr>
<td>Valence Shell</td>
<td>Xe5p</td>
<td>70 ~ 170</td>
<td>20eV ~ 120eV</td>
</tr>
<tr>
<td>Inner Shell</td>
<td>Xe4d</td>
<td>270</td>
<td>75eV ~ 170eV</td>
</tr>
</tbody>
</table>

der to achieve sufficient spectral resolution, we set up suitable retarding voltages to the two-stage drift tube of the TOFs. In our experiments, the photon energy ranges of interest and sizes of Ar, Kr and Xe clusters are shown in table 4.3.

In our experiments, we measured the photoelectrons subsequent to photoionization of the Ar, Kr and Xe clusters with variable cluster sizes. We collected our data in two data formats: 1-dimensional spectrum and 2-dimensional spectrum, called the 2D map. One-dimensional format was used for Ar, Kr and Xe clusters. 2D map data format was used only for Ar and Xe clusters.
CHAPTER V

STUDY OF INNER-SHELL AND INNER-VALENCE SHELL
PHOTOIONIZATION OF ARGON, KRYPTON AND
XENON CLUSTERS

This chapter reports on the investigation of inner-shell photoionization in three different types of clusters (Ar 2p, Kr 3d, and Xe 4d). It also focuses on inner-valence shell photoionization in Ar 3s clusters. The findings of this work are published in Physical Review A by Zhang et al. [45].

5.1 Overview

The focus of this chapter is to report on the angle-resolved measurements of inner-shell photoionization of Ar, Kr and Xe rare gas clusters. The measurements have been carried out using the photon beam from an undulator beamline at the Advanced Light Source, using time of flight photoelectron spectroscopy. The photoelectron spectra following the photoionization of Ar 2p, Kr 3d, and Xe 4d clusters with different cluster sizes were measured. The intensity distributions of the photoelectrons have been measured, and the angular distribution parameters $\beta$ as a function of the photon energy were probed for variable average cluster sizes. In particular, the two spin-orbit components of the Ar 2p, Kr 3d, and Xe 4d clusters with the average cluster size $\langle N \rangle =$ 70, $\langle N \rangle =$ 250, and $\langle N \rangle =$ 270 were obtained. The results show that the angular distributions of the cluster photoelectrons are almost similar with those of the corresponding free atoms, except for the photon energy range just above the corresponding
photoionization thresholds. In addition, the angular distribution parameter of Ar 3s photoelectrons from Ar clusters with average cluster size $<N> = 230$ was also obtained. Our measurements reported the first photoelectron angular distribution parameter $\beta$ of the inner-shell Ar 2p, Ar 3s, Kr 3d, and Xe 4d rare gas clusters.

5.2 Introduction

As mentioned in chapter 1, cluster size is a key parameter for many physical and chemical properties of clusters [8, 9, 10]. Changing cluster size from the dimer to the solid can provide a good testing ground to investigate the transformation of structure and property with increasing cluster size. The closed-shell that characterizes rare gas clusters, makes it fairly easy to control the average cluster size over a very large range. A variety of experimental techniques have been used to study rare gas clusters, such as x-ray absorption spectroscopy [16, 17, 18, 19, 20] and x-ray photoelectron spectroscopy [21, 22, 23, 24, 25, 26, 27]. For example, Federmann et al. [16] used time-of-flight ion spectrometry to determine the yield of Ne cluster ions, and reported the first resonant K-shell absorption spectra of Ne clusters with different sizes. Knop et al. [17] employed mass spectrometry and photoelectron spectroscopy to measure site-specific inner-shell excitation of Kr clusters. They determined the total electron yield spectra within the Kr 3d excitation region between 90 eV and 96 eV, for average cluster sizes $<N> = 2 ~ 1250$. Additionally, there are some research groups working on the mixed rare gas clusters and their findings reported in [46, 47, 48, 49, 50]. However, only a few studies have been conducted using angle-resolved photoelectron...
spectroscopy. Ohrwall et al. [23], in their photoelectron study of free Xe clusters, noticed substantial differences in the angular dependence of the photoelectron intensity from Xe clusters compared to Xe atoms; however, there were no quantitative measurements of the angular distribution. We substantiated these quantitative measurements by performing experiments that allow the determination of the angular distribution parameter for free Ar, Kr, and Xe clusters. Especially, we have carried out inner-shell photoionization of Ar 2p, Kr 3d, and Xe 4d clusters with different cluster sizes.

For inner-shell level studies of rare gas clusters, knowledge of the electronic structure of Ar, Kr, and Xe clusters is rather limited. Feifel et al. [25] studied the photoionization of valence and core level of Ar, Kr, and Xe clusters at certain photon energies using photoelectron spectroscopy. Hatsui et al. [26] determined the Kr 3d ionization energies of small clusters with the average size \( N \leq 30 \), and provided evidence for site-specific photoemission in small Kr clusters. To the best of our knowledge, no angle-resolved measurements are reported for argon and krypton clusters, especially for the core level and inner valence level of argon, krypton, and xenon clusters. This lack of data motivated this work which reports the first measurement of the Ar, Kr and Xe photoelectron angular distribution parameter as a function of photon energy and cluster size. Specifically, the two spin orbit components of the Ar 2p, Ar 3s, Kr 3d and Xe 4d were obtained.

After the interaction of the photon beam with clusters, photoelectrons are emitted with kinetic energy, along with a positive ion cluster. The photoionization of Ar 2p, Ar 3s, Kr 3d, and Xe 4d clusters that were carried out as part of this thesis can be
schematically represented in figure 5.1.

\[ \text{Ar 2p: } 2s^2 2p^6 3s^2 3p^6 + h\nu \rightarrow 2s^2 2p^5 3s^2 3p^6 + e^- \]

\[ \text{Ar 3s: } 2s^2 2p^6 3s^2 3p^6 + h\nu \rightarrow 2s^2 2p^5 3s 3p^6 + e^- \]

\[ \text{Kr 3d: } 3p^6 3d^9 4s^2 4p^6 + h\nu \rightarrow 3p^6 3d^9 4s^2 4p^6 + e^- \]

\[ \text{Xe 4d: } 4p^6 4d^{10} 5s^2 5p^6 + h\nu \rightarrow 4p^6 4d^{10} 5s^2 5p^6 + e^- \]

**Figure 5.1**  Schematic of the Photoionization of Ar 2p, Ar 3s, Kr 3d, and Xe 4d Clusters.

### 5.3 Results and Discussion of the Photoionization of Ar 2p and Ar 3s Clusters

The experiments were performed in beamlines 8.0.1 and 10.0.1 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. In these experiments, argon gas was expanded through a 100 \( \mu \)m diameter conical nozzle with an opening angle of 14° at stagnation pressures from 120 to 200 KPa and a nozzle temperature between 126 to 130 K. With these parameters, using the empirical scaling law formulas \([27, 51, 52, 53, 54]\), the average cluster size for Ar 2p clusters ranged from 62 to 262. In addition, we used of a small pinhole with 100 \( \mu \)m diameter at stagnation pressure from 175 to 222 KPa and a pinhole temperature between 117 to 128 K, to obtain Ar 3s cluster with average cluster sizes \( <N> = 200 \sim 280 \).

The experimental set-up included two time-of-flight (TOF) spectrometers located...
at $0^\circ$ and at the magic angle $54.7^\circ$ with respect to the photon beam. The argon cluster source was mounted at $90^\circ$ with respect to the photon beam. The spectra were collected in individual time-of-flight spectrum format. In order to obtain sufficient spectral resolution, suitable retarding voltages for different photo energies were used on to the two-TOF spectrometers, as shown in the table below.

Table 5.1  Retarding Voltages Applied in Ar 2p and Ar 3s Experiments.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>Retarding Potential</th>
<th>$hv$</th>
<th>Photon Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar 2p</td>
<td>$0 \sim 120eV$ (Nose)</td>
<td>$250 \sim 410eV$</td>
<td>$150 \sim 200meV$</td>
</tr>
<tr>
<td></td>
<td>$0 \sim 100eV$ (Tube)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar 3s</td>
<td>$23 \sim 65eV$ (Nose)</td>
<td>$50 \sim 100eV$</td>
<td>$100meV$</td>
</tr>
<tr>
<td></td>
<td>$20 \sim 52eV$ (Tube)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Photoionization of Ar 2p Clusters*

The photoelectron spectra of Ar 2p clusters with cluster size $< N >= 262$ are shown in figure 5.2. These spectra were taken at the photon energy of $280$ eV at two e-TOFs angles $0^\circ$ and $54.7^\circ$. Atomic Ar 2$p_{1/2}$ and Ar 2$p_{3/2}$ photolines from the free atoms in the cluster beam, and cluster Ar 2$p_{1/2}$ and Ar 2$p_{3/2}$ structures are both presented in figure 5.2. The spectra photo energy were calibrated by using known corresponding atomic photoelectron lines, the Ar 2$p_{1/2}$ and Ar 2$p_{3/2}$ photolines shown in figure 5.2. These atomic lines allowed us to obtain the scaling factors for the time-to-energy conversion of the spectra and to generate the electron transmission efficiency of
the analyzers as a function of kinetic energy. In figure 5.2, the red and blue lines are the fitting lines. In this case, surface and bulk components of the cluster are not resolved in this spectrum due to the use of a lower photon energy resolution of 150 meV in our measurements.

Figure 5.2 Photoelectron Spectra for the Photoionization of the Ar 2p Clusters with Cluster Size $\langle N \rangle = 262$ at Photon Energy 290eV. The spectra were measured with the TOF detector at 0° in panel (A) and the magic angle (54.7°) shown in panel (B).

Since the data collected are in a counts vs. time format. In order to obtain mean-
ingful results, these data must be corrected and converted to an intensity vs. energy scale. The first step is to remove the background counts. The second step is to use the observed atomic peaks Ar $2p_{1/2}$ and Ar $2p_{3/2}$ to calibrate the photoelectron kinetic energy, using the formula $E \propto r^{-2}$ [55], where $r$ is the distance from source to detector. The result of the photoelectron kinetic energy calibration is shown in figure 5.3. The top panel in figure 5.3 shows the spectrum at TOF angle $0^0$, and the bottom panel shows the spectrum at TOF angle $54.7^0$.

![Image of photoelectron spectra](image)

**Figure 5.3** Photoelectron Spectra for the Photoionization of the Ar 2p Clusters with Cluster Size $< N > = 262$ at Photon Energy 290eV. The spectra were measured with the TOF detector at $0^0$ in panel (A) and the magic angle ($54.7^0$) shown in panel (B). In this figure, the red and blue lines are the fitting lines.
The relative cross section of each final ionic state can be found directly from the atomic photolines Ar $2p_{1/2}$ and $2p_{3/2}$ in figure 5.3. The relative efficiency of the detectors can be obtained through the below formula below.

$$E_{ff} = \frac{1}{(\beta + 1)} \frac{I_0}{I_{54.7}}$$  \hspace{1cm} (5.1)

Where $E_{ff}$ is the relative efficiency between two detectors. $I_0$ is the area of the curve fitted to the atomic peaks Ar $2p_{1/2}$ and Ar $2p_{3/2}$ measured at TOF angle $0^\circ$, shown in the top panel of figure 5.3. $I_{54.7}$ is the area of the curve fitted to the atomic peaks Ar $2p_{1/2}$ and $2p_{3/2}$ measured at the e-TOF angle $54.7^\circ$, shown in the bottom panel of figure 5.3. $\beta$ represents the atomic Ar $2p_{1/2}$ and Ar $2p_{3/2}$ angular distribution parameters.

The final and corrected Ar cluster peaks for the two fine structures $2p_{1/2}$ and $2p_{3/2}$ can be calibrated using the relative efficiency $E_{ff}$. Finally, the cluster Ar $2p_{1/2}$ and Ar $2p_{3/2}$ angular distribution parameters can be obtained through the following expression:

$$\beta' = \frac{I'_0}{I'_{54.7}} - 1$$  \hspace{1cm} (5.2)

Where $\beta'$ represents the cluster Ar $2p_{1/2}$ and Ar $2p_{3/2}$ angular distribution parameters. $I'_0$ is the area of the curve fitted to the cluster peaks Ar $2p_{1/2}$ and Ar $2p_{3/2}$ measured at TOF angle $0^\circ$, shown in the top panel of figure 5.3. $I'_{54.7}$ is the area of the curve fitted to the cluster peaks Ar $2p_{1/2}$ and Ar $2p_{3/2}$ measured at TOF angle $54.7^\circ$, shown in the bottom panel of figure 5.3.

The angular distribution parameters $\beta$ of Ar $2p_{1/2}$ and Ar $2p_{3/2}$ clusters with average size $< N > = 70$ and $< N > = 270$ were obtained and are shown in figure 5.4. As can be observed, for these two different Ar clusters, the angular distribution parameters are
found to be almost identical to the free atoms angular distribution parameters within the experimental error bars.

Figure 5.4  Schematic of the Ar 2p Cluster Angular Distribution Parameters β from Two Spin Orbit Components (Open and Closed Circles) with Two Different Cluster Sizes <N> = 70 and <N> = 250. The solid curves present the corresponding free atoms, which are the length and velocity from the random-phase approximation with exchange calculation (RRPA) used to calibrate the cluster data [56].

Photoionization of Ar 3s Clusters

We present in figure 5.5 the Ar 3s cluster photoelectron spectrum, which was taken at photon energy $h\nu = 70eV$ from the e-TOF detector located at $0^\circ$ with respect to the electric field vector of the photon beam. This spectrum is presented as a function of kinetic energy. The average cluster size of this Ar 3s cluster spectrum is <N> = 230. The spectrum in this figure shows the atomic Ar 3s photoline and two cluster
components structures: the surface and bulk components. In this figure, the red and blue lines are the least-squares fitting lines. For this small cluster size, since the ratio of surface to bulk atoms is high, the surface component should have a higher intensity than the bulk component, and this is well displayed in figure 5.5.

![Figure 5.5](image_url)  

**Figure 5.5** Schematic of the Ar 3s Photoelectron Spectrum Measured at Photon Energy $h\nu = 70$ eV with Cluster Size $<N> = 230$. The red and blue lines show the fitting result to separate the atom, cluster surface and cluster bulk components.

The photoelectron angular distribution of Ar 3s cluster $<N> = 230$, as a function of photon energy is depicted in figure 5.6. In this case, the atomic photoelectron angular distribution parameter in the investigated photon energy range is exactly equal to 2.0 [57]. However, as can be seen from this figure, Ar 3s cluster angular distribution parameter is only about 1.25. Furthermore, a large difference in $\beta$ values between the surface and bulk components is found to be 0.6 $\beta$ unit. This observed difference is attributed to the electron elastic scattering effects [27, 58]. The explanation is that an
increased elastic scattering cross section for lower electron kinetic energies leads to an increased randomization of the emission directions of the cluster photoelectron. The photoelectrons emitted from the inner-valence level of the cluster bulk could be scattered from neighboring atoms, and their angular distribution will be hence much less anisotropic than that of the electrons emitted from the cluster surface.

Figure 5.6 Schematic of the Ar 3s Cluster Angular Distribution Parameters $\beta$ from Two Cluster Components: Surface and Bulk with Cluster Size $< N > = 230$. The solid curves present the corresponding free atoms, which is used to calibrate the cluster data [57].

5.4 Results and Discussion of the Photoionization of Kr 3d Clusters

The measurements of the photoionization of Kr 3d cluster were carried out using undulator beamlines 8.0.1 and 10.0.1 of ALS in the same manner at the photoionization experiments conducted on Ar 2p and Ar 3s clusters. In order to obtain sufficient spec-
Table 5.2 Retarding Voltages Applied in Kr 3d Measurements.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>Retarding Potential</th>
<th>hv</th>
<th>Photon Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr 3d</td>
<td>0 ~ 100eV (Nose)</td>
<td>98 ~ 200eV</td>
<td>50meV</td>
</tr>
<tr>
<td></td>
<td>0 ~ 90eV (Tube)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With central resolution from the two time-of-flight electron spectrometers, suitable retarding voltages for different photon energies were used as shown in the table below.

In this experiment, krypton gas was expanded through a small pinhole (flat nozzle, diameter 100 μm with a full opening angle of 14° at stagnation pressures from 120 to 200 KPa and a nozzle temperature between 163 to 175 K. With these parameters and applying the same empirical scaling law formulas [27, 51, 52, 53, 54] as the above mentioned previously, the average cluster sizes obtained for Kr were 70 and 232.

We used a photon resolution of 50 meV for the photoionization of Kr 3d cluster size $<N>=66$ and $<N>=211$, and we measured the photoelectron spectra at two angles for at least 300 s. Figure 5.7 depicts the photoelectron spectra of the Kr 3d cluster photoelectron for size around $<N>=250$ clusters which were taken at different photon energies. The spectra show atomic Kr $3d_{3/2}, 3d_{5/2}$, peaks from uncondensed atoms present in the beam, and the corresponding cluster peaks Kr $3d_{3/2}$ and Kr $3d_{5/2}$, which include cluster surface and bulk peaks. Based on the known atomic ionization thresholds and the theoretical atomic angular distribution parameters, the atomic peaks can be used to calibrate the photoelectron kinetic energy and extract the
relative efficiencies of the TOF detectors.

Figure 5.7  Schematic of the Kr 3d Core Level Photoelectron Spectrum Measured at Photon Energy $h\nu = 150eV$ with Cluster Sizes $< N > = 66$ and $< N > = 211$. The spectra were measured with the TOF detector at the magic angle. The red and blue lines show the fitting result to separate the atom, cluster surface and cluster bulk components.

As for the case of Ar 2p clusters, the angular distribution of the Kr 3d photoelectron as a function of photon energy for cluster sizes $< N > = 70$ and $< N > = 252$ have been obtained. The result is shown in figure 5.8. In this figure, the solid curves from reference [59] represents the free atomic angular distribution parameters, which were used to calibrate the Kr 3d clusters photolines. Clearly, for these cluster sizes, the
photoelectron angular distributions from the Kr 3d clusters are nearly the same as for the atoms, with the exception of the photon energies just above the Kr 3d threshold.

![Graph showing angular distribution parameters β vs photon energy for Kr 3d clusters and atoms.]

**Figure 5.8** Schematic of the Kr 3d Cluster Angular Distribution Parameters β from Two Cluster Components: Surface and Bulk with Cluster Sizes <N> = 70 and <N> = 252. The solid curves present the corresponding free atoms, which is used to calibrate the cluster data [59].

### 5.5 Results and Discussion of the Photoionization of Xe 4d Clusters

Similarly to the photoionization of Ar 2p, Ar 3s and Kr 3d clusters, the measurements of the photoionization of Xe 4d clusters were carried out using undulator beamlines 8.0.1 of ALS to cover the photon energy range of interest. The details of the methodology were described in last two sections. In order to obtain sufficient spectral resolution, suitable retarding voltages for different photo energies were used on the
Table 5.3  Retarding Voltages Applied in Xe 4d Measurements.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>Retarding Potential</th>
<th>hv</th>
<th>Photon Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe 4d</td>
<td>0 ~ 90eV (Nose)</td>
<td>75 ~ 175eV</td>
<td>50meV</td>
</tr>
<tr>
<td></td>
<td>0 ~ 80eV (Tube)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

two-TOF spectrometers, as described in the table below.

In this experiment, a beam of rare-gas van der Waals cluster was produced by an adiabatic expansion cluster source and crossed with a photon bandwidth of 50 meV synchrotron radiation. For this present experiment, xenon gas with a stagnation pressure, \( P_0 = 60 \) to 200 Kpa, and nozzle temperature 170 K to 240 K was expanded through a 100 \( \mu \)m with a full opening angle of 14° to produce clusters with average sizes \( < N > = 270 \).

Setting the photon resolution to 50 meV for Xe 4d cluster size of \( < N > = 270 \), the photoelectron spectra were accumulated simultaneously at two angles for at least 300 s. Figure 5.9 depicts the spectra of the Xe 4d cluster photoelectron taken at different photon energies. The spectra show atomic Xe 4d\( _{3/2} \), 4d\( _{5/2} \), peaks from uncondensed atoms present in the beam, and the corresponding cluster peaks Xe 4d\( _{3/2} \) and Xe 4d\( _{5/2} \), which include cluster surface and bulk peaks. Based on the known atomic ionization thresholds and the theoretical atomic angular distribution parameters, the atomic peaks can be used to calibrate the photoelectron kinetic energy and the relative efficiencies of the TOF detectors.
Figure 5.9 Schematic of the Xe 4d Core Level Photoelectron Spectrum Measured at Photon Energy \( hv = 150eV \) with Cluster Sizes \( < N > = 270 \). The spectra were measured with the TOF detector at the magic angle. The red and blue lines show the fitting result to separate the atom, cluster surface and cluster bulk components.

Like for the case of Ar 2p and Kr 3d clusters, we have also studied the angular distribution of the Xe 4d photoelectron as a function of photon energy for cluster sizes \( < N > = 270 \). The result is shown in figure 5.10. Clearly, for these cluster sizes, the photoelectron angular distributions from the Xe 4d clusters are nearly the same as for the atoms, with the exception of the photon energies just above the Xe 4d threshold.

5.6 Comparison and Conclusions

The photoelectron angular distribution parameter \( \beta \) for inner-shell ionization of Ar, Kr, and Xe clusters has been obtained from the simultaneous measurements of photoelectron spectra at two different angles. We have also compared the \( \beta \) values to the corresponding atomic values. Overall, inner-shell Ar 2p, Kr 3d and Xe 4d clusters pho-
Figure 5.10  Schematic of the Xe 4d Cluster Angular Distribution Parameters $\beta$ from Two Cluster Components: Surface and Bulk with Cluster Sizes $N \geq 270$. The solid curves present the corresponding free atoms, which is used to calibrate the cluster data [27, 35, 60, 61, 62].

to electron angular distribution are similar with the corresponding free atoms. Furthermore, we found no significant difference between two Kr 3d cluster sizes $N \geq 70$ and $N \geq 250$, and no noticeable difference between two fine structure in Xe 4d clusters. However, in the first 10 to 15 eV above the ionization thresholds, Ar 2p, Kr 3d and Xe 4d cluster photoelectron angular distributions are distinctly less anisotropic than the corresponding free atoms. This effect is attributed to a high elastic-scattering cross section for electrons with low kinetic energies. This is because the electrons are scattering off of as they leave the cluster so that the angular distribution effect gets smeared out. Elastic scattering typical formula is [63]:

\begin{align*}
\text{Elastic Scattering} & = \frac{1}{2} \left( 1 + \frac{\sin^2 \theta}{2} \right)
\end{align*}
\[ \frac{d\sigma}{d\Omega} = \left[ \frac{z_1 z_2 e^2}{4E} \right]^2 \frac{4}{\sin^2 \theta} \frac{\sqrt{1 - \left[ \frac{M_1 \sin \theta}{M_2} \right]^2} + \cos \theta}{\sqrt{1 - \left[ \frac{M_1 \sin \theta}{M_2} \right]^2}} \]  

(5.3)

Where \( \frac{d\sigma}{d\Omega} \) is the differential cross section, \( z_1 \) is the atomic number of incident ion, \( z_2 \) is the atomic number of the target atom, \( E \) is the energy of incident ion, \( M_1 \) is the mass of incident ion, \( M_2 \) is the mass of target atom, and \( \theta \) is the angle of incidence.

This formula shows that strong elastic scattering of the photoelectrons, as they leave the clusters, leads to a randomization of the electron emission direction; hence causes an isotropy of the angular distribution. This effect is particularly visible when the atomic angular distribution is just above the threshold. For higher photon energy, elastic scattering can affect only very big cluster size.

In the case of Ar 3s clusters, the average cluster angular distribution parameter of is found to be 1.25, while the theoretical value of the free atom is equal to 2.0. This is a big difference of \( \beta \) values between clusters and atoms, since the difference is around 0.75 \( \beta \) units. There is also a big difference of about 0.6 \( \beta \) unit between the cluster surface and bulk components. In low photon energy range just above 65 eV, the angular distribution profile is noticeably higher for both the surface and bulk components. This is due to the increased elastic-scattering cross section for lower electron kinetic energies which leads to an increased randomization of the emission directions of the cluster photoelectrons. In addition, the photoelectrons from the cluster bulk component are more likely to scatter from the neighboring atoms; hence the angular distribution is much less anisotropic than those from the cluster surface component.
factor for the difference is that Ar 3s inner-valence level seems to be more "localized",
and thus more similar to inner-shell electrons than to outer-valence electrons.
CHAPTER VI

STUDY OF VALENCE-SHELL PHOTOIONIZATION OF ARGON, KRYPTON AND XENON CLUSTERS

This chapter reports on the investigation of valence-shell photoionization in Ar 3p, Kr 4p and Xe 5p clusters and represents the findings which will be published in Physical Review A by Zhang et al [64].

6.1 Overview

This chapter gives particular emphasis to report on the measurements and the findings concerning the outer-valence photonionization of variable-size argon, krypton, and xenon rare gas clusters. The experiments has been conducted using angle-resolved time of flight photoelectron spectroscopy. In particular, the photoelectrons subsequent to photoionization of the Ar 3p, Kr 4p, and Xe 5p outer valence levels were measured and the corresponding spectra were observed in single time of flight spectra and in two-dimensional map (electron kinetic energy as a function of photon energy) spectra. Photoelectron angular distributions as a function of photon energy were probed for Ar 3p, Kr 4p, and Xe 5p clusters for with various cluster sizes. This work reports the first exploration of the photoelectron angular distribution parameters $\beta$ from different Ar, Kr, and Xe van der Waals cluster sizes. Specifically, we found that the angular distribution parameter $\beta$ values of clusters are more isotropic than the corresponding free atoms, in the photon energy ranges just above the photoionization thresholds. Further-
more, a surprising difference between the two spin-orbit components was found, for the valence electrons which we can not explain.

6.2 Introduction

As mentioned in chapter 2 and chapter 5, due to cluster nanometer scale size, cluster physical and chemical properties can vary as a function of cluster size. Our motivations to carry out the reported work stems from the fact that this characteristic led to this active and exciting field in need of further thorough experimental and theoretical investigations. In simpler terms, by controlling the average cluster size, the property of the cluster can be controlled to some degree [4, 5]. For example, some chemical properties, like the catalytic property, are strongly dependent on the cluster size. The physical properties such as the geometric and electronic structures can vary substantially when adding an atom to the cluster. For example, copper clusters become semi-conducting and silicon clusters become metallic respectively at certain cluster sizes [65, 66]. Many researchers have investigated rare gas clusters using different experimental techniques, such as x-ray photoelectron spectroscopy [20, 22, 23, 24, 25, 26, 27, 28, 30, 31, 67, 68, 69, 70, 71, 72], which is one of the few feasible methods to study the free pure rare gas clusters and the mixed rare gas clusters. For free van der Waals clusters, many studies have been reported. For instance, using x-ray electron spectroscopy, Lundwall et al [30] examined two mean argon cluster sizes \(< N >= 2100\) and \(< N >= 60\). They observed the photon energy dependent intensity variations in \(L_{2,3}M_{2,3}M_{2,3}\) Auger spectra of argon clusters, and concluded that the extrinsic scattering effects involving
the photoelectron can explain the Auger signal variations. Murakami et al. [31] used x-ray photoelectron spectroscopy to carry out electron-ion-coincidence measurements for K shell excited Ne, Ar, and Kr clusters with the cluster size ranging from 1 atom to about 3000 atoms. They observed the multiple-charged ions and single-charged ions as cluster fragments, and concluded that the charges generated on the cluster surface are strongly delocalized and that charges generated inside the cluster are more localized. Rühl et al. [28] carried out several experiments on free Ar clusters. They investigated the fluorescence of argon clusters in the Ar 2p excitation regime (240 eV - 310 eV) using fluorescence excitation spectroscopy, which shows a different evolution as a function of the mass-selected cluster ions.

The existing work provided a strong motivation for our investigations, specially since there is no systematic study using angle-resolved photoelectron spectroscopy for free van der Waals clusters to generate the angular distribution parameters $\beta$ as a function of photon energy. One of the reasons is the difficulty to extract this information unless one carries out the measurements at two different angles simultaneously to avoid changes in cluster characteristics or photon variations. Only Ohrwall et al. [23] made use of the angle-resolved photoelectron spectroscopy to study the free Xe clusters, without quantitative measurements of the angular distribution. They reported qualitatively the differences in the angular dependence of the photoelectron intensity from Xe clusters compared to Xe atoms. Our group recently corroborated these qualitative measurements by reporting the angular distribution parameters for free Xe and Kr clusters [27, 64]. The measurements allowed us to obtain the evolution of the Xe 4d and
5p, Kr 3d and 4p photoelectron angular distribution parameters as a function of photon energy and cluster size. These investigations exposed the strong cluster-size-dependent variation due to elastic photoelectron scattering. In the present study, we used the same experimental technique as for the inner-valence investigations in Ar, Kr, and Xe clusters [27, 64] to study the outer-valence photoelectron angular distribution for different cluster sizes to probe possible systematic effects among different van der Waals clusters.

Like for the case of inner-shell photoionization of argon, krypton, and xenon clusters, knowledge of the electronic structure of outer-valence shell of clusters is still limited. Feifel et al. [25] have researched this subject by employing photoelectron spectroscopy to study qualitatively the photoionization of the inner valence and outer valence level of argon clusters. This work reports on the first measurements of the angular distribution parameters \( \beta \) as a function of photon energy and cluster sizes in the case of the outer-valence electrons in argon, krypton, and xenon clusters.

After the interaction of the photon with clusters, photoelectrons from the outer-valence levels are emitted with kinetic energy which we measure. The process of the photoionization of Ar 3p, Kr 4p, and Xe 5d cluster is shown in figure 6.1.

6.3 Results and Discussion of the Photoionization of Ar 3p Clusters

The outer-valence photoionization experiments for Ar, Kr and Xe clusters were carried out using synchrotron radiation from the undulator beamlines 8.0.1, 9.0.1 and 10.0.1 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.
Figure 6.1  Schematic of The Photoionization of Ar 3p, Kr 4p, and Xe 5p Clusters.

In the case of Ar 3p clusters photoionization of argon gas was expanded through a pinhole at a stagnation pressure from 175 to 222 KPa and a pinhole temperature between 117 to 128 K. With these parameters, using the empirical scaling law formulas [27, 51, 52, 53, 54, 64], Ar 3p cluster with the average cluster size of \(< N > = 280\) was produced.

The experimental set-up included two TOF spectrometers located at 0° and the magic angle 54.7° with respect to the photon beam; and the argon cluster source was mounted at 90° with respect to the photon beam as well. The Ar 3p cluster spectra were collected in 2-dimensional (2D) measurements (as described in details in chapter 3). In order to obtain sufficient spectral resolution, suitable retarding voltages for different photon energies were used to the two TOF spectrometers. The spectra were calibrated by using the known corresponding atomic photoelectron lines, In particular the Ar 3p photolines was used to obtain the scaling factors for the time-to-energy conversion of the spectra and to generate the electron transmission efficiency of the analyzers as a
function of kinetic energy. 2D spectra were converted from time to energy scale, and corrected for transmission efficiency, variation in photon flux and collection time. A typical argon 3p excitation cluster 2D map is shown in figure 6.2, which was measured with one TOF detector at the magic angle. This 2D map was constructed through the accumulation of photoelectron spectra at the magic angle for at least 100 s for each spectrum, and then the photon energy was increased by 100 meV in the case of argon.

![Figure 6.2](image)

**Figure 6.2** Two-dimensional Map of the Excitation of the 3p Shell in Ar Clusters Measured at Magic Angle 54.7°. In this 2D map, the cluster size $<N> = 220$ atoms. The top and bottom panels show the spectra taken at $h\nu = 30$ eV and $h\nu = 35$ eV respectively. The color bar at the right top of this 2D map shows the different intensity.

In this 2D map, Ar clusters with an average size of $<N> = 220$ was ionized in the photon energy range 29 eV to 40 eV. The photoelectron kinetic energy from 13 eV to
Figure 6.3  Schematic of the Angular Distribution Parameter $\beta$ of Ar 3p Cluster. Dots presents the clusters, compared to single atoms (solid curves) from reference [57]. The solid curves are the theoretical calculations to calibrate the corresponding cluster data.

24.2 eV was recored. Figure 6.2 top panel displays a spectrum measured at $h\nu = 30eV$, and the bottom panel shows a spectrum measured at $h\nu = 35eV$. A color bar shows the intensity gradient. In this 2D map, two atomic components were clearly resolved, while for the cluster components, only two split components Ar $3p_{1/2}$ and Ar $3p_{3/2}$ were slightly resolved.

The photoelectron angular distribution parameters $\beta$ of the Ar 3p valence shell clusters for cluster size $< N >= 210$ and those of the atoms are shown in figure 6.3, in the photon energy range between 17 eV to 100 eV. The atomic photoelectron angular distribution parameter values are theoretical calculation values from reference [57], which
were used to calibrate the Ar 3p clusters. Comparing these Ar 3p clusters with Ar 3p atoms, the angular distributions are almost identical within the experimental error bars, with the exception of a slight difference up to 40 eV photon energy. In this first 30 eV above the threshold, the atomic angular distributions are much more anisotropic than that of the clusters. We attribute this difference to the elastic electron scattering. When the elastic electron scattering cross sections are high, the emission directions of the cluster photoelectrons are partially randomized through elastic scattering events, thus leading to lower values of their $\beta$ parameters.

### 6.4 Results and Discussion of the Photoionization of Kr 4p Clusters

The photoionization experiments of Kr 4p cluster were carried out using undulator beamlines 8.0.1 and 10.0.1 of the ALS, similarly to the Ar 3p clusters. Two time-of-flight (TOF) electron spectrometers were used to carry out the simultaneous measurement. In order to obtain sufficient spectral resolution, suitable retarding voltages for different photo energies were used on the two-TOF spectrometers, as specified in the table below.

In the Kr 4p cluster experiments, krypton gas was expanded through a 100 $\mu$m
Figure 6.4  Photoelectron Spectra from the Photoionization of the Outer Valence Level 4p from Kr Clusters. These spectra were measured with the TOF detector located at the "magic angle". The clusters with size (a) \( <N> = 1200 \) and (b) \( <N> = 5400 \) were measured at photon energies \( h\nu = 30 \text{ eV} \) and 30.8 eV respectively.

An example of Kr 4p cluster spectra is shown in figure 6.4, which were measured at photon energies \( h\nu = 30 \text{ eV} \) and \( h\nu = 30.8 \text{ eV} \). In this figure, cluster Kr \( 4p_{1/2} \) and Kr
Figure 6.5  Schematic of the Angular Distribution Parameter $\beta$ of Kr 4p Cluster. Dots presents the clusters, compared to single atoms (solid curves) [57]. The solid curves are the theoretical calculations to calibrate the corresponding cluster data.

$4p_{3/2}$ components are clearly separated and resolved. The top panel shows a spectrum measured at 30 eV with cluster size $<N>=1200$. The bottom panel presents a spectrum of cluster size $<N>=5400$, measured at photon energy 30.8 eV. In this figure, two atomic lines are also observed due to the uncondensed cluster beam. They were used to calibrated cluster components.

The angular distribution parameters $\beta$ for Kr 4p clusters with cluster sizes $<N>=70 \sim 230, 1200$ and 5400, are shown in figure 6.5 along with those of the Kr 4p free atoms. As in the case of Ar 3p clusters, the angular distributions for Kr 4p clusters with different cluster sizes are similar to the corresponding atoms within the experimental
error bars, with the exception of a slight difference up to 50 eV photon energy. In this figure, two spin orbit components of cluster Kr 4p are also presented. We note a surprising difference between the two cluster spin orbit components which we can’t explain. In particular, the difference is around 0.5 $\beta$ unit. The figure also compares the angular distributions of the atoms and the clusters. We attribute the different angular distributions of Kr 4p to valence band structure formation in the clusters. Similar effects were seen in reference [73]. In the first 40 eV above threshold, the atomic Kr 4p angular distributions are more isotropic than that of Kr 4p cluster. This is due to the elastic electron scattering effects [27], similar to the Ar 3p clusters.

6.5 Results and Discussion of the Photoionization of Xe 5p Clusters

Similarly to the Ar 3p and Kr 4p clusters, the measurements of the photoionization of Xe 5p cluster were carried out using undulator beamlines 8.0.1 of the ALS to cover the photon energy range of interest. The details of the methodology were already described in the last two sections. In these Xe 5p experiments, Xe cluster beams were generated using a supersonic expansion jet. Xenon gas was expanded through a 100 $\mu$m diameter conical nozzle with an opening angle of 14° at stagnation pressures from 170 to 240 KPa and a nozzle temperature between 170 to 240 K. This resulted in producing Xe cluster size between 60 and 8000.

Xe 5p cluster spectra were collected in two dimensional measurements. A typical 2D spectrum of Xe 5p is shown in figure 6.6. In order to obtain sufficient spectral resolution, suitable retarding voltages for different photo energies were used to the
The photoelectron angular distribution parameters $\beta$ from the Xe 5p valence shell
Figure 6.7  Schematic of the Angular Distribution Parameter $\beta$ of Xe 5p Cluster. Dots presents the clusters, compared to single atoms (solid curves) [35, 60, 61, 62]. The solid curves are the theoretical calculations to calibrate the corresponding cluster data.

clusters with cluster size $<N>$ = 70 ~ 170 and those of the atoms are shown in figure 6.7, in the photon energy range between 17 eV to 100 eV. As for the case of Ar 3p and Kr 4p clusters, the angular distribution parameters of Xe 5p clusters is approximately the same as the corresponding atoms within the experimental error bars, with the exception of the low energy range 15 eV to 60 eV. In this figure, two spin orbit components of cluster Xe 5p are also presented. The solid curves [35, 60, 61, 62] are the theoretical calculations used to calibrate the corresponding data. In the first 40 eV above threshold, the atomic angular distribution is much more anisotropic than that of the clusters, similarly to the Ar 3p and Kr 4p cluster cases. This is due to the elastic electron scattering effects discussed previously [27]. However, the cluster angular distribution of the fine
structure components in the case of Xe, ie Xe $5p_{1/2}$ and $5p_{3/2}$, is less different than the Ar 3p, Kr 4p and Xe 5p cluster cases. We do not understand the reason, despite many efforts and discussions with many theorists [74]. All theorists have told us that it is very hard to carry out calculation of cluster angular distributions.

6.6 Comparison and Conclusions

The photoelectron angular distribution parameters $\beta$ of the valence Ar 3p clusters for cluster size $<N> = 210$, Kr 4p cluster with sizes $<N> = 70 \sim 230$, 1200 and 5400 and Xe 5p cluster with size $<N> = 70 \sim 170$ are shown in panel (c), (b) and (a) respectively, along with those of the atoms in figure 6.8.

The comparison of the Ar 3p, Kr 4p and Xe 5p clusters, leads to the conclusion that the angular distribution parameters for the cluster outer valence levels are more isotropic than in the case of free atoms. The scattering of the photoelectron after photoionization can be one of the reasons to explain the behavior of the angular distribution being more isotropic in clusters than in free atoms. The sites of electrons in clusters, localized or delocalized, can affect the angular distribution of the clusters and thus their relationship to the atoms. Outer valence electrons in the atomic clusters are more delocalized than the inner valence levels, which are localized and do not overlap with the neighboring atoms.
Figure 6.8  Schematic of the Angular Distribution Parameter $\beta$ of Ar 3p Cluster in Panel (c) Compared to the Angular Distribution Parameters $\beta$ of Kr 4p and Xe 5p in Panel (a) and (b), Respectively. Dots presents the clusters, compared to single atoms (solid curves) [35, 57, 60, 61, 62]. The solid curves are the theoretical calculations to calibrate the corresponding cluster data.
CHAPTER VII

RESONANCE STUDY OF ARGON CLUSTERS IN THE 3s→np IONIZATION REGION

The electronic structure of Ar, Kr, and Xe clusters, can be divided into valence levels and core levels, similarly to the cases of atoms and molecules. We have investigated and studied the electronic valence shells and the electronic core shells of Ar, Kr, and Xe clusters in chapter 5 and chapter 6, using angle resolved photoelectron spectroscopy technique. In order to further understand the electronic structures of rare gas clusters and how these cluster models compare to free atoms and infinite solids, this chapter investigates the Rydberg resonances in Ar cluster with cluster size \(< N > = 270\) in the 3s→np ionization region. These findings are published in Journal Physics B by Zhang et al. [75].

7.1 Overview

The photoionization of argon clusters with an average cluster size \(< N > = 270\) has been investigated and studied in the vicinity of the Ar 3s→np autoionizing resonances using angle-resolved time-of-flight photoelectron spectroscopy. The Ar 3p outer-valence photoelectron spectra were measured using two-dimensional maps that show the resonance profiles for free atoms as well as for the surface and bulk components of the cluster. For the first time, photoelectron yields and photoelectron angular distributions of the two spin-orbit components from argon clusters are reported as a
function of the photon energy. Moreover, the photoelectron angular distribution parameters of the two spin-orbit components of free argon atoms are also obtained.

7.2 Introduction

We will introduce here the notion of excitons since we will use this terminology in the chapter. A fundamental quantum electronic excitation consists of a negatively charged electron and a positively charged hole bound to each other by the electrostatic attraction. In general, an exciton is an electrically neutral excited state of an insulator or a semiconductor, and it is usually a quasiparticle of the solid [76]. Excitons can be treated in two limiting cases: Mott-Wannier exciton which has a radius much larger than the lattice space, and Fenkel exciton which has a radius smaller than the lattice space. Wannier exciton, named for Sir Nevill Francis Mott and Gregory Wannier, usually exist in semiconductors. Fenkel exciton, named after Yakov Frenkel, exists in insulator [77].

Valence shell resonances in clusters were first studied below the ionization thresholds by fluorescence spectroscopy [78, 79, 80, 81, 82]. Wörmer et al [78, 79, 80, 81, 82] investigated the systematic evolution of the Rydberg resonances leading to the first ionization threshold in Ar, Kr, and Xe clusters from the atom to the bulk and recognized the occurrence of surface excitations as well as transverse and longitudinal bulk excitons in the cluster. For example, in reference [78], Stapelfeldt et al deduced the evolution of electronic excitations in Kr clusters with cluster size $<N> = 2 - 3000$ from fluorescence excitation spectroscopy. In reference [82], Wörmer et al. investigated the evolution of Wannier excitons in free argon clusters. Later, Wörmer et al. [83, 84]
extended this work to the Rydberg transition above threshold, which were linked to "Frenkel" or "intermediate type" excitons [77]. For example, Müller et al. [83] reported and analyzed the excitation and decay processes of neutral and ionized Ar clusters using fluorescence spectroscopy. Except for the fluorescence spectroscopy techniques, coincident threshold photoelectron - photoion spectroscopy [85, 86, 87, 88], electron spectroscopy [27, 45, 73] and photoabsorption spectroscopy [89] were also used to study the Rydberg resonances and exciton formation in rare gas clusters. Pavlychev and Rühl studied the 3s—>np window resonances in Ar clusters with cluster sizes 80, 270 and 750, using total electron yield measurements [89]. Through the comparison of experimental results with calculations, a splitting of surface resonances in tangential and normal components could be observed. However, no partial cross sections and angular distributions were reported.

This chapter reports on the first measurement of the spin-orbit resolved partial photoelectron yields and the photoelectron angular distribution parameters $\beta$ of the Ar 3p photoelectrons in the region of the $3s^23p^6 \rightarrow 3s3p^5np(n = 4 - 9)$ resonant excitations in Ar clusters with cluster average size $< N > = 270$.

Free atom Ar $3s^23p^6 \rightarrow 3s3p^5np$ autoionization resonances have been studied and reported in references [90, 91, 92, 93, 94, 95, 96], using experimental technique [90, 91, 92, 93, 94] and theoretical calculations [95]. There into, $3s^23p^6 \rightarrow 3s3p^5np(n = 4 - 16)$ autoionization resonances in the energy range between 26 and 29.3 eV was studied by high resolution did photoelectron spectroscopy and reported in [96]. Berrah et al [96] investigated the systematic evolution of the Ar $3s^23p^6 \rightarrow 3s3p^5np(n =$
Rydberg resonances, analyzed the cross section shape for the first six resonance, and obtained the Ar 3p photoelectron angular distribution parameters $\beta$. Their results, which did not separate the fine structure components, are in good agreement with the findings reported in this chapter. However, up to now, the the angular distribution of the two spin-orbit components of Ar 3p$_{1/2}$ and Ar 3p$_{3/2}$ have not been studied.

The first measurement of the spin orbit partial photoelectron yield and photoelectron angular distribution parameters of the free atom Ar 3p is also reported in this chapter.

### 7.3 Results and Discussion

Ar cluster resonance experiments were carried out at Lawrence Berkeley National Laboratory, using synchrotron radiation from the undulator beamline 10.0.1 of the ALS. 2D map photoelectron spectroscopy methodology [41, 97] was applied in these measurements. The experimental set-up is the same as the one used in chapter 5 and chapter 6. In order to obtain sufficient spectral resolution, retarding voltages of $-4.5V/ -6.0V$ were applied to the two-TOF spectrometers. The spectra were calibrated using the known cross sections and angular distributions of the atomic 3p photoelectron lines in order to obtain the scaling factors for the time-to-energy conversion and the electron transmission efficiency of the analyzers as a function of photoelectron kinetic energy. 2D spectra were converted from time to energy scale, and corrected for transmission efficiency, variation in photon flux and collection time. A typical 2D map of the argon 3p excitation region is shown in figure 7.1. This 2D map was constructed through the accumulation of photoelectron spectra in 10 meV intervals in the magic angle TOF an-
alyzers (at 54.7° with respect to the light polarization direction) for 100 s per spectrum. Simultaneously, the corresponding spectra were also measured at 0°, thus compiling another 2D spectrum at this angle. Argon clusters were generated using a supersonic jet expansion, which can produce a cluster beam including some uncondensed free atoms. The average argon cluster size $< N >$ was 270 atoms, which was determined using the expansion pressure $P_0 = 175$ KPa, a pinhole diameter $d = 100 \, \mu m$, and the temperature $T_0 = 122$ K.

The partial electron yield as a function of photon energy for the photoionization of Ar 3p atoms and clusters are shown in figure 7.2 and figure 7.3 respectively. The partial electron yield of the two Ar 3p spin-orbit components were measured a photon energy resolution of 47 meV at 26 eV to 58.5 meV at 29.1 eV. The partial electron yields of the two Ar 3p spin-orbit components were obtained, with this high resolution. As mentioned in the previous section, the cluster beam contained both uncondensed free atoms and rare-gas clusters. The partial electron yield and the photoelectron angular distribution parameters $\beta$ of the free Ar atoms, as a function of photon energy, are shown in figure 7.2. The top panel shows the partial electron yield and the bottom panel show the angular distribution parameters $\beta$. In the top panel, both spin-orbit components show the pronounced structure of the Ar $3s^23p^6 \rightarrow 3s3p^5np (n = 4 - 9)$ autoionizing resonances, which agrees well to the previous, unresolved measurement [96], albeit with slightly less resolution. In the bottom panel, the corresponding angular distribution parameters of the atomic photoelectrons for the two spin-orbit components $3p_{1/2}$ and $3p_{3/2}$ are presented. Their overall structure reproduces well the unresolved measure-
Figure 7.1 Two-dimensional Photoelectron Map of the 3s→np Autoionizing Resonance Region in Ar Clusters (Average Size $N \gtrsim 270$ Atoms) Measured at the Magic Angle (54.7° with Respect to the Light Polarization Direction). The photoelectron intensity is shown on a color scale with blue representing the lowest and red the highest count rate. The panel on the top shows the Ar 3p photoelectron spectra at 26 eV and 27 eV, while the panel on the right shows the total electron yield across the resonance region.
Table 7.1  Comparison of Experimental and Theoretical Data for the Atomic Ar 3s<sup>2</sup>3p<sup>6</sup> → 3s3p<sup>6</sup>n<sup>p</sup> Resonance Positions. The photon energy scale in the present measurement was calibrated so that the first resonance positions coincide with the measured energies in Electron Loss.

<table>
<thead>
<tr>
<th></th>
<th>3s → 4p</th>
<th>3s → 5p</th>
<th>3s → 6p</th>
<th>3s → 7p</th>
<th>3s → 8p</th>
<th>3s → 9p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs</td>
<td>26.614</td>
<td>27.996</td>
<td>28.509</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron Loss</td>
<td>26.605</td>
<td>27.994</td>
<td>28.509</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ment, but with the β-values of the 3p<sub>3/2</sub> component being slightly higher than those of the 3p<sub>1/2</sub>, as predicted by R-matrix calculations [57], which did not take into account the resonances. A comparison of the resonance positions with other references is shown in table 1. Our results values are about 50 meV lower than the atomic resonance positions reported in reference [96].

For Ar clusters, the partial electron yield and the photoelectron angular distribution parameters β, as a function of photon energy, are shown in figure 7.3. The average cluster size presented in figure 7.3 is <N> = 270. In figure 7.3, the top panel shows the partial electron yields of the two split-orbit components from the clusters compared to the same cluster size measured by Pavlychev and Rühl [89]. The figure also shows the total electron yield from solid Ar, and the bottom panel shows two spin-orbit component angular distribution parameter β values for Ar clusters.
Figure 7.2  Spin-orbit Resolved Partial Electron Yield Across the $3s^23p^6 \rightarrow 3s3p^6np (n = 4 - 9)$ Resonances in Ar Atoms (Top Panel), and Corresponding Photoelectron Angular Distribution Parameters $\beta$ (Bottom Panel). The blue dotted lines in both panels show the results of an unresolved measurement with better photon energy resolution, while the green and purple solid lines show a theoretical prediction for the angular distributions without the resonances. A typical error bar is shown at $h\nu = 27.5\text{eV}$ in both panels.
The resonances in the cluster appear as broad features that can be identified as surface and bulk excitations. While atomic spectra show pure atomic Rydberg transitions and condensed phase spectra are dominated by bulk excitations, cluster spectra, as a bridge between atoms and solids, are governed by both bulk and surface excitations that vary with cluster size and asymptotically turn into excitons in the solid. Particularly, our measurements also have a good agreement with Pavlychev and Rühl [89] that confirm the splitting of the surface resonances into a normal component $3s^{-1}np_{\text{norm}}$ at lower energy and a tangential component $3s^{-1}np_{\text{tang}}$ at higher energy. Table 2 shows a comparison of the resonance positions between our present results and Pavlychev and Rühl [89] findings. The comparison confirms our interpretation of the data.

In figure 7.3, the bottom panel shows the angular distribution parameters of photoelectron from Ar clusters with cluster size $< N > = 270$ for the two spin-orbit components $3p_{1/2}$ and Ar $3p_{3/2}$. Compared to these two spin-orbit components, the angular distribution parameter of Ar $3p_{1/2}$ is on average about 0.25 $\beta$ units higher than that of the Ar $3p_{3/2}$, confirming our previous measurement for a similar cluster size in [73]. In the process of valence band structure formation in the clusters, the $3p_{3/2}$ component splits into two bands due to valence-orbital overlap between neighboring atoms in the atoms. This effect leads the different angular distribution of the two spin-orbit components in the clusters to have different values. Similar effects were also observed in the valence photoemission of Kr and Xe clusters [73]. An additional reason contributing to the general decrease in the angular anisotropy of the cluster photoelectrons can also be traced to elastic scattering of the photoelectrons on their way out of the cluster. A
comparison of multiple scattering calculations with experimental data for Xe clusters has been achieved in ref. [27]. In general, the cluster valence photoelectron angular distribution parameters behaves similarly to the corresponding atomic parameters. However, in the first 30eV above the threshold, the angular distributions of free atoms are very anisotropic. The elastic electron scattering cross sections are high, affecting the emission directions of the cluster photoelectrons which becomes partially randomized through elastic scattering events, which leads to the lower values of $\beta$ parameters.

As in the electron angular distribution of the atomic resonances, the landscape of the $\beta$ mimics the photoelectron spectra by also displaying window resonances. The photoelectron angular distribution changes at the resonance positions, with a clear dip at the $3s^{-1} \rightarrow 4p_{\text{surf}}$ and $3s^{-1} \rightarrow 5p_{\text{surf}}$ resonances around $h\nu = 27\text{eV}$ and $27.8\text{ eV}$, respectively. An increased angular distribution parameter at the $3s^{-1} \rightarrow 4p_{\text{bulk}}$ resonance is also clearly observed at $27.64\text{ eV}$. We attribute this increase at the position of the bulk excitation to the photoelectrons emitted from the bulk, which exhibits a decreased angular anisotropy as compared to photoelectrons emitted from the cluster surface [73].

In this figure, due to the limited resolution, the surface and bulk components of clusters weren't resolved, hence the observed angular distribution parameter of Ar clusters is an average value for the two spin-orbit components. However, since the $3s \rightarrow np$ resonances are window resonances, the bulk contribution to the photoelectron spectrum cluster peak is decreased at the position of the bulk excitation, and the remaining cluster signal is dominated by surface electrons, which have a more anisotropic angular distribution. In this sense, our measurement of the photoelectron angular distributions
Table 7.2  Experimental Data for Cluster $\text{Ar } 3s^23p^6 \rightarrow 3s3p^6np (n = 4 \sim 5)$ Resonance Position. (Unit: eV).

<table>
<thead>
<tr>
<th>$3s \rightarrow 4p$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>$3s$ $\rightarrow$ $4p_{\text{sur.(norm.)}}$</td>
<td>$3s^{-1} \rightarrow 4p_{\text{sur.(tang.)}}$</td>
<td>$3s^{-1} \rightarrow 4p_{\text{bulk}}$</td>
</tr>
<tr>
<td>$&lt; N &gt;= 80$</td>
<td>26.71</td>
<td>26.96</td>
<td>27.64</td>
</tr>
<tr>
<td>$&lt; N &gt;= 270$ (present)</td>
<td>26.71</td>
<td>26.96</td>
<td>27.64</td>
</tr>
<tr>
<td>$&lt; N &gt;= 270$</td>
<td>26.64</td>
<td>26.94</td>
<td>27.63</td>
</tr>
<tr>
<td>$&lt; N &gt;= 750$</td>
<td>26.64</td>
<td>26.96</td>
<td>27.61</td>
</tr>
<tr>
<td>Solid</td>
<td>27.51</td>
<td>27.75</td>
<td>28.12</td>
</tr>
<tr>
<td>$3s \rightarrow 5p$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atom</td>
<td>$3s$ $\rightarrow$ $5p_{\text{sur.(norm.)}}$</td>
<td>$3s^{-1} \rightarrow 5p_{\text{sur.(tang.)}}$</td>
<td>$3s^{-1} \rightarrow 5p_{\text{bulk}}$</td>
</tr>
<tr>
<td>$&lt; N &gt;= 80$</td>
<td>27.75</td>
<td>27.88</td>
<td>28.07</td>
</tr>
<tr>
<td>$&lt; N &gt;= 270$ (present)</td>
<td>27.76</td>
<td>27.88</td>
<td>28.1</td>
</tr>
<tr>
<td>$&lt; N &gt;= 270$</td>
<td>27.72</td>
<td>27.88</td>
<td>28.07</td>
</tr>
<tr>
<td>$&lt; N &gt;= 750$</td>
<td>28.05</td>
<td>27.88</td>
<td>28.05</td>
</tr>
<tr>
<td>Solid</td>
<td>28.01</td>
<td>27.88</td>
<td>28.05</td>
</tr>
</tbody>
</table>

therefore provides an independent confirmation of the spectral assignment of surface and bulk excitations in clusters.

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7.4 Conclusions

Ar $3s^{-1} \rightarrow np$ Rydberg Resonances in free atoms and clusters with cluster size $< N > = 270$ have been investigated and studied, using angle-resolved photoelectron spectroscopy and 2-dimensional photoelectron spectra technique. In Ar cluster, $3s^{-1} \rightarrow np, (n = 4 - 5)$ resonances have broad features in the total and partial electron yield that can be further separated into surface and bulk excitations. The surface excitations can be additionally split into tangential and normal components. Moreover, the first measurements of the photoelectron angular distribution parameters of the two spin-orbit components Ar $3p_{1/2}$ and $3p_{3/2}$ in free atoms and in Ar clusters with cluster size $< N > = 270$ have been reported, in the resonant region of Ar $3s^23p^6 \rightarrow 3s3p^6np$ excitations.

The difference of angular distribution between the two spin-orbit components was found by about 0.25 $\beta$ units and the effect of the difference was attributed to valence band structure formation in the cluster. However, both of them follow a similar resonance profile, with a decrease of the angular distribution parameter at the position of the surface excitations and an increase at the position of the bulk excitations due to the influence of elastic electron scattering.

Our measurements and results show some of the transition between few particle quantum effects which dominate atomic and molecular photoionization, and collective phenomena which are characteristic for solid state systems. More different cluster sizes from dimer up to thousands of atoms need to be measured and studied in order to obtain
details in transition between free atoms and the solids. More studies will lead us to better understand the valence band structure of rare gas clusters, which are of interest as fundamental model systems.
Figure 7.3  Spin-orbit Resolved Partial Electron Yield Across the Ar $3s^23p^6 \rightarrow 3s3p^6np (n = 4 – 9)$ Resonances in Ar Clusters with Average Size $\langle N \rangle = 270$ (Top Panel), and Corresponding Photoelectron Angular Distribution Parameters $\beta$ (Bottom Panel). A typical error bar for the angular distribution measurement is shown at $h\nu = 27.5 \text{eV}$. The blue dash-dotted line shows the corresponding unresolved electron yield from Ar cluster from reference, and the blue dotted line in the top panels represent the 3p partial electron yield from solid Ar.
CHAPTER VIII

SUMMARY

Xenon, krypton, and argon van der Waals clusters with different cluster sizes have been studied at the Advanced Light Source at Lawrence Berkeley National Laboratory using angle resolved time-of-flight photoelectron spectrometry technique, in combination with the two-dimensional technique (recording all electron kinetic energies as a function of photon energies).

In the case of Ar clusters, we have presented 1) outer valence level Ar $3p_{1/2}$ and Ar $3p_{3/2}$ photoelectron spectra in 2D format for an average cluster size $\langle N \rangle = 210$, 2) inner-shell Ar 3s photoelectron individual spectra for an average cluster size of $\langle N \rangle = 230$, and 3) core level Ar $2p_{1/2}$ as well as $2p_{3/2}$ photoelectron spectra of average cluster sizes $\langle N \rangle = 70$ as well as $\langle N \rangle = 250$. The 2D map technique reveals a comprehensive picture of atomic photoionization and cluster photoionization in this richly structured spectral region. From the 2D maps, the atomic two-spin-orbit split components can be totally resolved as well as the cluster two-spin orbit components. From the 2D maps, the total photoelectron yield can be easily shown for both atoms and clusters. This is the first time that a quantitative study of van der Waals clusters has been undertaken. Photoelectron angular distribution parameter $\beta$ of Ar $3p_{1/2}$ and Ar $3p_{3/2}$ cluster with cluster size of $\langle N \rangle = 210$, Ar 3s cluster with cluster size $\langle N \rangle = 230$, and Ar $2p_{1/2}$ as well as $2p_{3/2}$ clusters with cluster sizes 70 and 250 have been obtained. Photoelectron angular distribution parameter $\beta$ of inner shell Ar $2p_{1/2}$
and $2p_{3/2}$ was found to be similar to the corresponding atomic angular distribution, except just a few eV above the threshold. Photoelectron angular distribution parameter of Ar $3p_{1/2}$ and Ar $3p_{3/2}$ clusters has been obtained, as a function of photon energy between 15 eV through 100 eV. In comparison with Ar 3p atoms, the angular distribution parameters for Ar 3p clusters are more isotropic than the free atoms. This is due to photoelectrons scattering after photoionization. In the case of Ar 3s clusters, the angular distribution parameters of the surface and the bulk for the two cluster components was also obtained. The average of angular distribution parameter of Ar 3s clusters is 1.25, less than 2.0, which is the atomic angular distribution parameter. In addition, the photoionization of the 3p outer-valence electrons in free Ar atoms and Ar cluster with average cluster size $<N> = 270$ in the range of the Ar $3s^{-1} \rightarrow np$ window resonances using angle-resolved photoelectron spectroscopy was also studied. In Ar cluster, the resonances occur as broad features in the total and partial electron yield. These can be further separated into surface and bulk excitations, the former with an additional splitting into tangential and normal components.

In the case of Kr clusters, the outer valence level Kr $4p_{1/2}$ and $4p_{3/2}$ photoelectron spectra in 2D format with average cluster size $<N> = 70 \sim 230, 1200$, as well as 5400 were measured. Furthermore inner-shell Kr $3d_{3/2}$ and Kr $3d_{5/2}$ photoelectron spectra of average cluster sizes $<N> = 70$ and $<N> = 250$ have been studied. The 2D map technique reveals a comprehensive picture of atomic photoionization and cluster photoionization in this richly structured spectral region. From this 2D map, the atomic spin-orbit components can be totally resolved as well as the cluster spin-
orbit components. From the 2D map, the total photoelectron yield can be easily shown both for atoms and clusters. This is the first time a quantitative and comprehensive study of van der Waals clusters has been undertaken. Photoelectron angular distribution parameter $\beta$ of Kr $4p_{1/2}$ and $4p_{3/2}$ cluster with cluster size $< N >= 70 \sim 230$, 1200, and 5400, and Kr $3d_{3/2}$ as well as $3d_{5/2}$ clusters of cluster sizes 70 and 250 have been obtained. Photoelectron angular distribution parameter $\beta$ of inner shell Kr $3d_{3/2}$ and $3d_{5/2}$ is similar to the corresponding atomic angular distribution, except just a few eV above the threshold. The angular distribution parameter of the photoelectrons from Kr $4p_{1/2}$ and Kr $4p_{3/2}$ cluster has been obtained, as a function of photon energy. In comparison with Kr $3p$ atoms, the angular distribution parameters for Kr $3p$ cluster is more isotropic than the one for free atoms. This is due to photoelectron scattering after photoionization. The photoelectron angular distribution parameter of the Kr $4p_{1/2}$ and $4p_{3/2}$, spin-orbit components in krypton clusters have been obtained.

In the case of Xe clusters, the outer valence level Xe $5p_{1/2}$ and $5p_{3/2}$ photoelectron spectra in 2D format for the average cluster size $< N >= 70 \sim 170$, and inner-shell Xe $4d_{3/2}$ and Xe $4d_{5/2}$ photoelectron individual spectra of average cluster sizes $< N >= 270$ has been studied using both the 2D map and individual spectra. Photoelectron angular distribution parameter $\beta$ of Xe $5p_{1/2}$ and $5p_{3/2}$ cluster with cluster size $< N >= 70 \sim 170$, and Xe $4d_{3/2}$ as well as $4d_{5/2}$ clusters with cluster sizes 270 were obtained. The photoelectron angular distribution parameter $\beta$ of inner shell Xe $4d_{3/2}$ and $4d_{5/2}$ is found to be similar to the corresponding atomic angular distribution, except just a few eV above the threshold. Angular distribution parameters of photoelec-
tron from Xe $5p_{1/2}$ and Xe $5p_{3/2}$ cluster have been obtained, as a function of photon energy. In comparison with atoms, the angular distribution parameters $\beta$ for Xe clusters are more isotropic than the $\beta$ for free atoms. This result is also due to the photoelectron scattering after photoionization. In particular, photoelectron angular distribution parameter $\beta$ of the Xe $5p_{1/2}$ and $5p_{3/2}$, spin-orbit components in xenon clusters were obtained.

These results show our understanding of rare gas cluster electronic structures and how rare gas clusters bridge the gap between the free rare gas atoms and the corresponding solid. We hope this work will stimulate further theoretical and experimental investigations in the cluster study.
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74. For example, S. T. Manson, Private Communication


