# Photoionization and Photofragmentation of Fullerenes 

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## Kurzfassung (German Abstract)

Seit ihrer Entdecknug erweckten die Fullerene großes Interesse aufgrund ihrer einzigartigen hochsymmetrischen Struktur. Dabei stellen die Erforschung ihrer elektronischen Struktur sowie ihr Fragmentationsverhalten, sowohl für Theoretiker als auch für Experimentalphysiker, eine Herausforderung dar.
Wir haben präzise Messungen der emittierten Photoelektronen aus der Valenzschale von im gasförmigen und im festen Zustand befindlichen $\mathrm{C}_{60}$ und $\mathrm{C}_{70}$ durchgeführt, um verzweigungshältnisse, partielle Wirkungsquerschnitte und im Falle von $\mathrm{C}_{60}$ den Winkelanisotropieparameter der beiden äußeren Molekülorbitale HOMO (Highest Occupied Molecular Orbital) und HOMO-1 zu bestimmen. Das Verzweigungshältnis der entsprechenden HOMO und HOMO-1 Zustände weist bei $\mathrm{C}_{60}$ die selbe oszillierende Struktur für beide Phasen auf. Im Falle von $\mathrm{C}_{70}$, ergibt sich jedoch ein deutliche Unterschied von 0,5 für den nichtoszillierenden Untergrund wenn man die Daten aus der Gasphase mit denen aus der festen Phase vergleicht. In allen Fällen zeigen die partiellen Wirkungsquerschnitte der beiden äußeren Molekülorbitale eine oszillierende Struktur mit exponentiellem Abfall, wobei die Frequenz der Oszillation mit dem Durchmesser der Fullerene verknüpft ist. Die Fourier-Transformation der Wirkungsquerschnitte liefert direkte Informationen über die geometrische Struktur der Moleküle, wie Radius des Kohlenstoffhältigs oder Dicke der Elektronenhülle. Insgesamt stimmen die experimentellen Werte mit verschiedenen theoretischen Vorhersagen gut überein, abgesehen von einer theoretisch zu erwartenden, resonanzartigen Struktur in den partiellen Wirkungsquerschnitten bei kleinen Photonenergien.
Ferner untersuchten wir die Dynamik der Valenzschalen- und K-Schalen induzierteFragmentation, welche durch suksessive Emission neutraler $\mathrm{C}_{2}$-Teilchen erfolgt. Bei der Valenzschalenionisation wurden die Wirkungsquerschnitte der $\mathrm{C}_{60}^{q+}$-Ionen $(q=1,2,3)$ sowie der $\mathrm{C}_{60-2 m^{-}}^{+}(m \leq 3)$ und $\mathrm{C}_{60-2 m^{-}}^{2+}(m \leq 5)$ Fragmente bestimmt und diskutiert. Ein möglicher Anregungsmechanismus bei $\mathrm{C}_{60}$ ist das Plasmon, eine kollektive Schwingung der äußeren Valenzelektronen. Das sogenannte Volumenplasmon verursacht eine Vergrößerung des Ionisationswirkungsquerschnittes von neutralem $\mathrm{C}_{60}$, insbesondere die $\mathrm{C}_{60}^{2+}$-Produktion ist dabei erhöht. Um Genaueres über die zugrunde liegenden An- und Abregungsprozesse zu erfahren, wurden Elektronen-Ionen-Koinzidenzmessungen durchgeführt. Hierin können $\mathrm{C}_{58}^{2+}$ - oder $\mathrm{C}_{56}^{2+}$-Fragmente anhand ihrer emittierten Elektronen identifiziert werden, obwohl die Fragmentation auf einer längeren Zeitskala abläuft als die Ionisation. Oberhalb der K-SchalenIonisationsgrenze von $\mathrm{C}_{60}$ werden hauptsächlich doppelt und dreifach geladene Fullerene erzeugt. Zusätzliche Elektron-Elektron-Koinzidenzmessungen decken hierbei die Mechanismen der Mehrfach-Elektronen-Prozesse auf. So zeigen als Resultat, dass Beiträge zu den dreifach geladenen Fullerenen hauptsächlich von direkter Doppelionisation, angetrieben durch die Erzeugung eines Plasmons mit nachfolgendem Augerzerfall, stammen.
$\qquad$

## Abstract

Due to their unique geometrical structure fullerenes have attracted much attention over the years since their discovery. However, a deeper understanding of their electronic structure and fragmentation behavior is still a challenge for both theoreticians and experimentalists.
We have performed high resolution measurements of photoelectrons emitted from the valence shell of $\mathrm{C}_{60}$ and $\mathrm{C}_{70}$, for both gas phase and solid state samples, in order to obtain branching ratios, partial cross sections, and in the case of $\mathrm{C}_{60}$ angular distribution anisotropy parameters of the two highest occupied molecular orbitals, HOMO and HOMO- 1 . The ratio between the corresponding HOMO and HOMO- 1 levels, which consist of unresolved lines, exhibit the same oscillatory structure for both phases in the case of $\mathrm{C}_{60}$, but shows an nonoscillating offset of 0.5 for the gas phase measurements compared to solid state data in the case of $\mathrm{C}_{70}$. Fourier transformation of the cross section rations displays the information about the geometrical properties of the molecules; their radius and the thickness of the electronic hull. The partial cross sections of the two outermost molecular orbitals exhibit in both cases oscillations with a frequency related to the diameter of the molecule superposed on the exponential decay curve. The overall agreement between different theoretical calculations and our experiment for branching ratios, partial cross sections and beta parameters is very good except of a striking disagreement with respect to the predicted discrete resonance structure in the partial cross sections. We assume that resonances in the partial cross sections are quenched by the vibrations of the molecule. During the same measurement we recorded a new series of the K -shell photoelectron spectra of $\mathrm{C}_{60}$ with particular empahasis on the qualitative analysis of all ionization processes.
We also studied valence shell and K -shell induced fragmentation dynamics of $\mathrm{C}_{60}$ which proceeds via a subsequent emission of neutral $\mathrm{C}_{2}$ particles. In the valence region cross sections of the $\mathrm{C}_{60}^{q+}$ ions $(\mathrm{q}=1,2,3)$ and of the fragments $\left\{\mathrm{C}_{60-2 m}^{+}(m \leq\right.$ $\left.3), \mathrm{C}_{60-2 m}^{2+}(m \leq 5)\right\}$ are discussed. A possible excitation process for $\mathrm{C}_{60}$ is the creation of a plasmon, a collective motion of the outer electrons. The so-called volume plasmon causes an enhancement of the ionization cross section of neutral $\mathrm{C}_{60}$ accompanied by an increased production of $\mathrm{C}_{60}^{2+}$. To learn more about the underlying excitation and relaxation processes, we performed corresponding electron-ion coincidence measurement. Here, fragments like $\mathrm{C}_{58}^{2+}$ or $\mathrm{C}_{56}^{2+}$ can be identified by their outgoing electrons, although the fragmentation takes place on a longer time scale than the ionization. Above the carbon K-shell of $\mathrm{C}_{60}$ the main products are doubly and triply charged fullerenes. Corresponding electron-electron coincidence measurements were carried out to achive a deeper understanding about the fundamental processes causing the many-electron emission in this energy region. These results show that the main contributions to the triply charged ion yield is direct double photoionization of $\mathrm{C}_{60}$ followed by Auger decay. However, in contrast to most atoms and molecules, it is driven by the plasmon excitation associated with the K -shell photoionization of $\mathrm{C}_{60}$.

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## Introduction

### 1.1 Fundamental properties of fullerenes

Fullerenes were discovered in 1985 by Robert Curl and Richard Smalley from Rice University, USA and Harold Kroto from the University of Sussex, UK ${ }^{1}$ while doing experiments with carbon clusters in supersonic beams. In their studies of all-carbon species they formed clusters by laser ablation from a graphite target into an exchange gas of helium. Using mass spectrometry they found a rich array of even-numbered carbon clusters with sizes greater than about 32 atoms and also showed that odd-numbered carbon structures were not stable above a number of 30 atoms. Eleven years later, in 1996, they were awarded the Nobel Prize in Chemistry for their accomplishments. However, the evidence for the existence of these molecules remained indirect until 1990, when the researchers Krätschmer and Huffman at the Max Planck Institute for Nuclear Physics in Heidelberg, Germany ${ }^{2}$ used a carbon-arc plasma to produce the first macroscopic quantities of them. Since then fullerenes are among the most investigated elements and are constantly attracting great amounts of attention. In 1991, Science magazine named the $\mathrm{C}_{60}$ for the "molecule of the year" calling it "the discovery most likely to shape the course of scientific research in the years ahead"

The most abundant and the most investigated molecule from the fullerene family is the $\mathrm{C}_{60}$ molecule. It possesses a unique geometrical structure with the highest possible symmetry. The $\mathrm{C}_{60}$ molecule consists of 60 carbon atoms bounded in the nearly spherical configuration with the diameter of about 7.1 A. This shape is called a truncated icosahedron (Fig.1.1b), with 20 hexagons and 12 pentagons (it's also the shape of a soccer ball). The icosahedron is one of the five Platonic solids (3D convex shapes whose faces are identical regular polygons). The other four are the tetrahedron, the cube, the octahedron and the dodecahedron. The icosahedron has 20 faces, each one an equilateral triangle. Chopping off each vertex reveals the 12 pentagonal and 20 hexagonal faces of the truncated icosahedron, which is also one of the 7 Archimedean solids (shapes made from truncating Platonic solids in certain ways). In the truncated icosahedral structure of the $\mathrm{C}_{60}$ molecule every
carbon atom is equivalent, sharing a double bond and two single bonds with its nearest neighbours. The thirty double bonds, $1.40 \AA$ in length, are located at the shared edges of adjacent hexagons and are shorter than the $1.45 \AA$ single bonds surrounding each pentagon. All bonds are satisfied, all carbon atoms are equivalent, and the chemical and structural stability of the molecule is extraordinary high. The molecule was proposed to be also dubbed buckminsterfullerene because its shape reminiscent of the geodesic domes popularized by American architect Buckminster Fuller.



Figure 1.1: Icosahedron (a) and truncated icosahedron (b) ${ }^{3}$


Figure 1.2: Hybridization of the $\sigma$ - and $\pi$ - orbitals for $\mathrm{C}_{60}$. The angle between the $\mathrm{p}_{z}$ axis and a carbon-carbon bond vector is $101.6^{\circ}{ }^{3}$

Fullerenes differ from the other two forms of the carbon atom (diamond and graphite) in the hybridization of the atomic $s$ and $p$ levels. Carbon atoms with the kind of connectivity
present in the $\mathrm{C}_{60}$ molecule (three-connected to other carbon atoms by one double bond and two single bonds) are usually referred to as " $\mathrm{sp}^{2}$ carbons" because the orbitals used for the sigma-bond of the three adjacent carbons are hybrids of the 2 s orbital and the two 2 p orbitals ( $2 \mathrm{p}_{x}$ and $2 \mathrm{p}_{y}$ ). The remaining 2 p orbital ( $2 \mathrm{p}_{z}$ ) is responsible for the $\pi$-bond. The angle between a $\mathrm{p}_{z}$ axis and a C-C bond vector is $101.6^{\circ}$ (Fig.1.2). The bowl-shape or concavity at each $\mathrm{sp}^{2}$ carbon center introduces some strain into the molecule. However, the high symmetry distributes that strain evenly across the entire structure.
$\mathrm{C}_{70}$, the next most abundant molecule from the fullerenes family can be obtained from $\mathrm{C}_{60}$ by cutting it into two halves, rotating one half by $36^{\circ}$ and inserting a ring of 10 extra atoms between the two $\mathrm{C}_{60}$ hemispheres. The resulting structure has two pentagons at the poles, and a belt of hexagons around the equator. This structure, with a good approximation, can be represented by an ellipsoid of axes $a=b=7.3 \pm 0.1 \AA$ and $c=8.5 \pm 0.1 \AA .{ }^{4}$ Ten additional, equatorial atoms, located $3.55 \AA$ from the center, don't influence much the overall distribution of the bonds which is similar as in the case of $\mathrm{C}_{60}$.

Early ultraviolet photoemission spectroscopy studies of fullerene ions ${ }^{5}$ indicated that $\mathrm{C}_{60}$ and $\mathrm{C}_{70}$ are electronically closed shell molecules with appreciable gaps between the highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO. Fig.1.3 depicts the energy levels of $\mathrm{C}_{60}$ in the molecular state referenced to the vacuum level. Electron removal from an isolated molecule yields the ionization potential (IP) and addition yields the electron affinity level (EA). Both states are of the ion and they correspond to the $\mathrm{N}-1$ and $\mathrm{N}+1$ states. For $\mathrm{C}_{60}$ these energies are respectively, $7.6 \mathrm{eV}^{6}$ and $2.65 \mathrm{eV}^{7}{ }^{7}$


Figure 1.3: Energy-level diagram referenced to the vacuum level $\mathrm{E}_{\text {vac }}$ for isolated $\mathrm{C}_{60}$ showing the ionization potential (IP) and the electron affinity (EA) levels and for the solid showing the HOMOand LUMO-derived bands. The ground state of $\mathrm{C}_{60}$ with N electrons is depicted at the right. ${ }^{8}$

The mass spectrometry studies of O'Brien et al. ${ }^{9}$ performed in 1987. showed that the large fullerenes with 34 atoms or more, under laser irradiation, fragment by loss of $\mathrm{C}_{2}$ units. Before the fullerenes were discovered, Bloomfield et al. ${ }^{10}$ had also shown this fragmentation pattern for $\mathrm{C}_{60}$. Since the ionization threshold for $\mathrm{C}_{60}$ photofragmentation is about 7.6 eV , it was clear that the isolated molecules were highly stable. An appropriate model of this fragmentation pattern was offered by O'Brien et al. ${ }^{9}$ wherein pentagons on the excited fullerene surface are allowed to "migrate" until two of them join. In these regions of high stress, the $\mathrm{C}_{2}$ unit joining the pentagons evaporates and the fullerene shell closes, leaving a $\mathrm{C}_{n-2}$ fullerene. For fragmentation of the gas phase molecules, this process can be continued until the cage reaches 32 atoms. For small cluster sizes, the strain involved in maintaining a closed structure is apparently too great, and the structure breaks into chains and rings with both even and odd numbers of carbon atoms.

Solid fullerenes are molecular crystals which are stable at room temperature and are bound largely by van der Waals forces. $\mathrm{C}_{60}$ crystallize in a close-packed structure with a nearest neighbor spacing of $10 \AA$. The room temperature crystal structure is face-centeredcubic with a lattice constant of $14.2 \AA$. At about 260 K , a first order orientational phase transition occurs that makes the structure simple cubic. ${ }^{11}$ At the lowest temperatures (< 90 K ), an orientational glass has been postulated. ${ }^{12}$ At high temperature $\mathrm{C}_{70}$ forms an orientationally disordered face-centered-cubic lattice. ${ }^{13}$ Cooling of the $\mathrm{C}_{70}$ crystals to 345 K results in freezing two degrees of orientational motion and the resulting crystal symmetry is rhombohedral. ${ }^{14}$ Further cooling below 295 K yield to a monoclinic symmetry. ${ }^{14}$

The physical and chemical properties of $\mathrm{C}_{60}$ and other fullerenes are now being intensively studied since they have a great potential of application as new materials. Among the fullerene-related materials of special interest are metal-doped $\mathrm{C}_{60}$ crystals, which can be superconducting. Moreover, the cage-structure carbon clusters $\mathrm{C}_{N}$ can trap molecules inside and such $\mathrm{C}_{N} \mathrm{X}$ clusters (X-trapped atoms or molecules) may exhibit a variety of electronic structures which could be used not only to construct new materials but also to make small molecular devices. Isolation of one of two $\mathrm{C}_{78}$ isomers ( $\mathrm{D} 3-\mathrm{C}_{78}$ ) revealed that it exhibits chirality. Finally, fullerenes are also present in the microtubes comprising coaxial tubes of graphite sheets with fullerene end caps.

## The Experiment

### 2.1 Light sources

Synchrotron radiation is generated when charged particles, such as electrons or positrons, are forced to travel on a circular orbit with velocities close to the speed of light. In high energy electron or positron storage rings, such as DORIS III and BESSY II, which have a circumference of almost 300 meters, the particles circulate nearly one milion times per second. The particles are deflected by special magnets (undulators and wigglers) and as a result of the radial acceleration in the magnetic field (Lorentz force) they emit electromagnetic radiation.


Figure 2.1: Emission pattern of electrons in circular motion ${ }^{149}$

The emission pattern for synchrotron radiation is determined essentially by that of a single circulating electron. For a slow electron moving with velocity $v$ along a circle of radius $R$ (with orbital frequency $\omega=v / R$ ), the energy of the emitted radiation is $\hbar \omega$, and one obtains a spatial radiation distribution as shown in the Fig.2.1. $\sum$

In the storage ring, the electrons move with a relativistic velocity along a macroscopic circle. In this case one has to transform the radiation emission pattern from the Fig.2.1, which is still valid in the frame of the moving electron, into the laboratory frame. The transformation yields the radiation emission pattern shown in the Fig.2.2.


Figure 2.2: Emission pattern of the synchrotron radiation in the laboratory frame of reference ${ }^{149}$

Practically all radiation is pressed into the forward direction, tangential with respect to the circular path of the electron. The opening half-angle of the cone is equal to $1 / \gamma$ where

$$
\begin{equation*}
\gamma=\left(1-\frac{v^{2}}{c^{2}}\right)^{-1 / 2}=\left(\frac{E}{m_{0} c^{2}}\right) \tag{2.1}
\end{equation*}
$$

with $E$ being the energy and $m_{0}$ the mass of the circulating electron. The instantaneous power radiation by relativistically accelerated electron is given by:

$$
\begin{equation*}
P=\frac{e^{2} \gamma^{2} \omega^{2} p^{2}}{6 \pi \varepsilon_{0} m_{0}^{2} c^{3}} \tag{2.2}
\end{equation*}
$$

where $p$ is the momentum while the other symbols have their usual meaning. The orbital frequency, $\omega$, is approximately equal to $c / R$ for an electron with velocity $v \rightarrow c$ and energy $E$ moving over a circular orbit of radius $R$.

Synchrotron radiation is produced in the insertion devices (undulators and wigglers) which consist of a series of periodic magnetic structures with length $\lambda_{0}$ and number N (N~30-100)(Fig.2.3). They produce an oscillatory (zigzag) path of the electrons. Wigglers
and undulators are several meters long and are installed in the storage ring. Because of the many magnetic poles in succession, the electrons emit a beam of light far more intense than the light produced by an individual deflecting magnet.


Figure 2.3: Wiggler / undulator with permanent magnets ${ }^{150}$

Wigglers and undulators can be distinguished from each other according to the magnitude of the parameter K which relates the maximum deflection angle $\alpha$ of the electron path to the natural opening angle $1 / \gamma$ for the searchlight cone of the emitted synchrotron radiation:

$$
\begin{equation*}
K=\frac{\alpha}{1 / \gamma} \tag{2.3}
\end{equation*}
$$

For $\mathrm{K} \gg 1$ (typically 10-100) the searchlight cones from the individual wigglers contribute separately to the intensity available in the horizontal plane and produce a gain in intensity which is 2 N times the value of the corresponding radiation from the deflection in a single wiggler. Wigglers lead to emission of a more continuous spectrum of radiation. For $\mathrm{K}=1$ the searchlight cones from the individual undulators overlap which causes interference effects between electromagnetic waves emitted from the same electron at different places on its travel through the undulator field. As a result of this interference, a redistribution of the spatial and spectral intensity occurs. The condition for constructive interference follows from the correct timing for the movement of the electron and its emission of light. For the radiation emitted at angles $\theta$ and $\psi$ with respect to the undulator axis ( $\theta$ within the plane of the wigglers, $\psi$ perpendicular to it) one gets:

$$
\begin{equation*}
\lambda_{n}=\frac{1}{n} \frac{\lambda_{0}}{2 \gamma^{2}}\left[1+\frac{K^{2}}{2}+\gamma^{2}\left(\theta^{2}+\psi^{2}\right)\right] \tag{2.4}
\end{equation*}
$$

with $\lambda_{n}$ being the wavelength of the $\mathrm{n}_{t h}$ harmonic radiation ( $\mathrm{n}=1$ is called the fundamental radiation). The interference effects between the waves from N magnetic periods create an up to $\mathrm{N}^{2}$ times greater intensity of the single wave.

Synchrotron radiation has a number of unique properties: ${ }^{15,16}$

- High brightness: synchrotron radiation is extremely intense (hundreds of thousands of times higher than conventional X-ray tubes) and highly collimated.
- Wide energy spectrum: synchrotron radiation is emitted with a wide range of energies (between infra-red to energetic-short wavelength x-rays). Monochromatic radiation of the desired wavelength can be obtained by locating a monochromator at a tangential point of the circular orbit, where the radiation is emitted.
- Synchrotron radiation is highly polarized.
- It is emitted in very short pulses. Each pulse is separated from each other by a period equal to the transit time of the electron in the circular path (a billionth of a second).

Our measurements were mainly performed at the beamline BW3 of HASYLAB (Hamburger Synchrotronstrahlungslabor) in DORIS III and partly at the beamline TGM4 of BESSY II (Berliner Speicherring Gesellschaft fr Synchrotron Strahlung).


Figure 2.4: Schematics of the beamline BW3 at HASYLAB ${ }^{17}$

The schematics of the BW3 beamline ${ }^{17}$ is presented in Fig.2.4. It has two different undulators mounted on a revolver type device and a modified SX-700 plane grating monochromator built by Zeiss. Monochromator consists of a premirror (PM), a plane grating (G), and a spherical focusing mirror (FM) which focuses the light into the exit slit (ES). It covers the spectral energy range from $20 \mathrm{eV}-2000 \mathrm{eV}$ with excellent spectral resolution
of 0.1 eV and high photon flux of $10^{12}$ photons/s. Monochromatized light from the exit slit is refocused by an ellipsoidal mirror (BW3.2) into a spot of about $150 \mu \mathrm{~m}$ in diameter at the sample position. According to the SX-700 design, the position of the exit slit is fixed by keeping $\mathrm{c}=\cos \alpha / \cos \beta=$ const., where $\alpha$ and $\beta$ are the angle of incidence and diffraction at the plane grating, respectively. ${ }^{18}$ In the standard SX-700 mode $(c=2.25)$ the size of the exit slit is about $80 \mu \mathrm{~m}$.

TGM4 ${ }^{19}$ (Fig.2.5) is a medium-resolution dipole beamline at the electron storage ring BESSY II. The schematics of the beamline is shown in Fig.2.5.


Figure 2.5: Schematics of the beamline TGM4 at BESSY ${ }^{19}$

It consists of toroidal grating monochromator which has 2 gratings with vertical deflection $2 \theta=146^{\circ}$. It covers the photon energy range between 20 and 130 eV with the resolution of 158 meV (with grating slits of $100 \mu \mathrm{~m}$ ).


Figure 2.6: Photon flux from the TGM4 monochromator at BESSY $\mathrm{II}^{20}$

Photon flux of the TGM4 monochromator is presented at the Fig.2.6. Most of the total intensity represents first-order light. In addition to the spectral light of interest, a monochromator delivers a certain amount of higher-order and stray light. The minor intensity contributions of second- and third-order light for the TGM4 monochromator are plotted against the nominal first-order setting of the monochromator, i.e. if the monochromator is set at 40 eV , one obtains a relative intensity of $0.88,0.05$ and 0.07 for 40,80 and 120 eV , respectively. Our detailed analysis of the photoion spectra recorded at this beamline showed that they indeed don't have considerable influence on the obtained results.

### 2.2 The Experimental set-up

Our photoelectron and photoion spectroscopy measurements have to be carried out under high vacuum conditions because ejected electrons and created ions cannot propagate under atmospheric pressure due to collisions with the gas molecules. Another reason for requiring good vacuum conditions is to prevent surface contamination when experiments on solid samples are carried out. Also, the micro channel plates, as parts of the time-of-flight detectors, require pressure conditions of about $10^{-6} \mathrm{mbar}$. Therefore our experiments were performed with a background pressure of about $10^{-7} \mathrm{mbar}$ which we produced by turbomolecular-pumps, basically metal propellers rotating very fast ( 1000 rps ) and hitting all gas molecules out of the region to be pumped.


Figure 2.7: The experimental set-up showing two time-of-flight (TOF) electron spectrometers mounted to a rotatable chamber ${ }^{150}$

Fig.2.7 shows the experimental set-up used to perform photoelectron spectroscopy measurements. It consists of two TOF spectrometers positioned at different angles, in conjuction with synchrotron radiation from DORIS III and BESSY II storage rings. The TOF spectrometers are mounted in a plane perpendicular to the photon beam propagation direction. The effect of the Earth's magnetic field within the spectrometers is minimized with

Helmholtz coils. A special feature of this experiment is the possible rotation of the whole vacuum chamber with the differentially pumped time-of-flight analyzers during normal operating conditions. This was made possible by using a differentially pumped rotational feedthrough and turbomolecular pumps operating in any installation position. For the photoion measurements one of the spectrometers was replaced with the ion TOF detector. The photon beam crosses an effusive beam of $\mathrm{C}_{60}$ molecules, provided by an oven resistively heated to $\approx 500^{\circ} \mathrm{C}$. The size of the interaction region is determined by the intersection of the monochromatic photon beam (focal size $\approx 1 \mathrm{~mm}$ ) with the molecular beam (beam size $\approx 5 \mathrm{~mm}$ at about 5 mm above the outlet aperture). For the solid state measurements, the $\mathrm{C}_{60}$ vapor was collected on a stainless-copper plate which could be moved into the interaction region after termination of the gas-phase measurement. The effusive gas jet of constant density for the calibration measurements is controlled by an MKS Baratron. The chamber is separated from the beam-line vacuum of the monochromator by a multiple-stage differential pumping unit with a typical pressure of $10^{-9} \mathrm{mbar}$.

### 2.3 The Detectors

### 2.3.1 The Electron time-of-flight (TOF) Detector

Fig. 2.8 shows one of the electron analyzers in detail. Each TOF spectrometer consists of a pair of microchannel plates mounted at the end of the field-free drift tube. After ionization of the target molecules in the interaction region (IR), electrons are flying in the direction of the spectrometer and are detected via a stuck of micro-channel plates (MCP).


Figure 2.8: Schematic model of an electron time-of-flight spectrometer ${ }^{151}$

The main part of the analyzer is a micro-channel plate. That is a thin ( 0.5 mm ) glass plate with capillaries in it. A voltage of $800-1000 \mathrm{~V}$ is applied along the plate. Electrons hitting the inside of the capillaries may trigger a cascade of secondary electrons, which amplifies itself and is collected on an anode behind the plate. The signal is amplified and fed into a constant fraction discriminator (CFD), then to the start of a time-to-amplitude
converter (TAC). The stop signal of the TAC is provided by the bunch marker signal from the storage ring. The analog pulse from the TAC is digitized by the analog-to-digital converter (ADC) and accumulated in a multichannel analyzer (MCA). The resulting counts versus time spectrum is then stored and displayed on a PC using a Labview data acquisition program which was developed in our group. The acquisition program, in addition to recording spectra, monitors flux of the synchrotron radiation and the chamber pressure. In order to improve the resolution of our spectra when it was necessary, we applied different retarding potentials at the retarding cage and the inner nose of the spectrometer. In order to measure the flight time of the electrons the photoelectron spectroscopy measurements were taken when HASYLAB at DESY III was operating in a two bunch mode in which only two positron bunches circle in the storage ring with an interval of roughly 480 ns in between them. By measuring the arrival times of the ejected electrons relative to the photon pulse, complete photoelectron spectra could be obtained.

Obtained time spectra are not linear in energy and thus simple Gaussian line shapes are asymmetric, especially at low kinetic energies. Therefore they have to be converted to the energy scale. The relationship between the flight time t and the kinetic energy $\mathrm{E}_{k i n}$ of an electron under field-free conditions is given by:

$$
\begin{equation*}
E_{k i n}=\frac{1}{2} m v^{2}=\frac{m l^{2}}{2} \times \frac{1}{t^{2}} \tag{2.5}
\end{equation*}
$$

with $m$ being the electron mass and $l$ being the distance from the interaction region to the detector. Channel positions of photolines are measured at different photon energies to get a data set of few points. By energy conservation, differences between photon energies and binding energies are the final electron kinetic energies and can be assigned to appropriate channels. Connection between a channel in the time spectrum (ch) and flight-time $(t)$ is accomplished using channel position of the prompt. It is defined as the position of the fastest photoline corresponding to the scattering of the light. Eq. 2.5 can be rewritten as:

$$
\begin{equation*}
E_{\text {kin }}(\text { ch }) \sim \frac{1}{(\text { prompt }-c h)^{2}} \tag{2.6}
\end{equation*}
$$

This is illustrated in Fig. 2.9 for two sets of our $\mathrm{C}_{60}$ gas phase data. The next step is to linearize this data set by plotting the square root of $1 /\left(\right.$ prompt-ch) ${ }^{2}$ (which is equal to $\mathrm{F}_{\text {lin }}$ on the graph) with respect to the kinetic energy $\left(\mathrm{E}_{\text {kin }}\right)$ and fitting a straight line through the points. If the prompt peak is not visible in the spectrum, it is possible to determine its position by trying different channel numbers where the prompt is expected. Because there is just one straight line possible through the measured data set, the prompt position can be determined to better than 0.1 channel. The linear fit function is then transformed back, assigning every channel an energy value (Fig.2.9). Time to energy conversion gets more complicated for energies below 5 eV because the electrons are strongly influenced by magnetic field, and the kinetic energy axis cannot be determined accurately with a linear
fit. It is necessary to use several quadratic fit functions in small steps and to smoothly add it to the linear fit to obtain a complete and accurate time-to-energy conversion.

Our spectra were converted from the time to energy scale by using photoelectron spectra of the Ne 2 s and 2 p photoelectron lines, of well-known binding energy, for a range of photon energy such that the kinetic energies of the $2 s$ and $2 p$ lines cover the kinetic energy of interest. In order to obtain the detector transmission we also used Ne 2 s 2 p lines which have known photoionization cross sections and angular distributions. ${ }^{21}$ For possible differences in the detection efficiency they have to be normalized with respect to each other. Transmission functions for two TOF detectors positioned at different angles in the case of our $\mathrm{C}_{60}$ gas phase measurement are presented at Fig.2.11 and Fig.2.12.


Figure 2.9: Time to Energy curve for the photon energy range (a) $20-40 \mathrm{eV}$ and (b) $40-70 \mathrm{eV}$ for the $\mathrm{C}_{60}$ gas phase measurement. The position of the $\mathrm{C}_{60}$ 's HOMO line was used for which the binding energy is 7.6 eV .


Figure 2.10: Linearization of Time-to-Energy Conversion for the photon energy range (a) 20-40 eV and (b) $40-70 \mathrm{eV}$ for the $\mathrm{C}_{60}$ gas phase measurement. The position of the $\mathrm{C}_{60}$ 's HOMO line was used for which the binding energy is 7.6 eV .


Figure 2.11: Transmission curves for the photon energy range from $20-40 \mathrm{eV}$ for TOF spectrometers positioned at two different angles (a) $\theta=54.7^{\circ}$ and (b) $\theta=0^{\circ}$ for the $\mathrm{C}_{60}$ gas phase measurement. Ne 2s 2 p photolines were used which have known photoionization cross sections and angular distributions.


Figure 2.12: Transmission curves for the photon energy range from $40-70 \mathrm{eV}$ for TOF spectrometers positioned at two different angles (a) $\theta=54.7^{\circ}$ and (b) $\theta=0^{\circ}$ for the $\mathrm{C}_{60}$ gas phase measurement. Ne 2 s 2 p photolines were used which have known photoionization cross sections and angular distributions.

### 2.3.2 The Ion time-of-flight (TOF) Detector

Figure 2.13 presents the schematic of a position sensitive ion TOF spectrometer, the Angular Resolved Fixed Molecule Angular Distribution Spectrometer (ARFMADS) developed in the Becker group ${ }^{22}$ which was used for the fragmentation and coincidence studies of the fullerene. The ions are produced in the interaction region (IR) which is situated in between the pusher and the extractor electrodes. A pulsed high voltage applied to these electrodes accelerates the ions into the drift tube, where they travel in a constant electric potential until they hit a stack of multi-channel plates. The length of the drift tube is 200 mm .


Figure 2.13: Ion time-of-flight spectrometer ${ }^{152}$

The ion impact produces a cloud of secondary electrons in the MCPs which is detected on the position sensitive anode. A reflection mesh above the MCPs prevents secondary electrons from leaving the detection zone and being accelerated by the drift tube potential back into the IR. The detector consists of a stack of three micro-channel plates. A ion that is hitting the surface of the first MCP sets free one or more electrons which trigger the release of a charged cloud in the MCPs by secondary electron amplification. The timing pulses are sent to the data acquisition module, that determines the time difference to a reference signal with a resolution of 120 ps . To determine the time of flight a positive pulse is taken from the output side of the last MCP. It is passed through a capacitor and sent to potential signal line. Typical values for timing pulses are: amplitude +100 mV , FWHM 1.5 ns , rise time $<800 \mathrm{ps}$. The signal line for the timing pulse has an impedance of $50 \Omega$. The timing signal is sent through an inverting pre-amplifier to a constant-fraction-discriminator (CFD), as the CFD can only process negative pulses. The position of the falling edge of the NIM-pulse is independent of the height of the timing pulse.


Figure 2.14: Schematics of the electronics set-up using a TDC module for an experiment with ion time-of-flight spectrometer

Fig.2.14 shows a sketch of the electronics that is used in time of flight measurement. HV Pulser produces HV for the Pusher of the Ion Detector. HV Pulser also has Monitor Out signal which after some level translation of the signal goes to the ion TDC producing a Start Signal and Fast Multihit Gate Signal. The difference between these two signals should be larger than 60 ns . After some level transformation it will set a gate for the ion signal (at the Ion CFD). This CFD gets signal from the Ion MCP after certain preamplification and inversion. It then can produce Multihit Stop Signal at the Ion TDC.

### 2.3.3 The Oven

The oven which was used in our experiments is a result of several improvements of the original result of the study. ${ }^{23}$ The main part of the oven is crucible containing the sample and being surrounded by a system of wires (Fig.2.15). The crucible and the nozzle are made of steel. The crucible is fixed to a long rod and can be removed for refilling without changing the alignment of the oven. The hole on the crucible and on the nozzle should be in the same line pointing to the interaction region. The oven is installed on a xyz manipulator and can be adjusted in such a way that the spectrometer register maximal signal. Commercial bifilar heating cables (Philips,Thermocoax) are bent around the main body of the oven. A bifilar wiring is applied in order to minimize the magnetic fields created by the heating current. Typical value for the current in our experiment was 1.05 A in order to get a temperature of about $450^{\circ} \mathrm{C}$. The hot core of the oven is surrounded by the metal shields which reduce the radiative heat losses. Before beginning of measurements the sample has to be baked for few hours at the temperature of about $300^{\circ} \mathrm{C}$ in the vacuum, otherwise there would be remainders of organic solvents, e.g. toluene (methyl benzene) which would influence the spectra. The powder of $\mathrm{C}_{60}$ also should not be heated in the presence of oxygen because it decomposes at $200^{\circ} \mathrm{C}$ into an amorphous carbon-oxygen compound. The
vapor density of the target during the measurement was about $1.5 \times 10^{18} \mathrm{~cm}^{-3}$ for $\mathrm{C}_{60}$ and about $3.1 \times 10^{17} \mathrm{~cm}^{-3}$ for $\mathrm{C}_{70}$. Temperature measurement is performed with the installed Chromium-Aluminium Termoelement. For the calibration purposes the oven can be used as a gas inlet at any time since it is connected with the gas inlet system for that. For the solid state measurements, the $\mathrm{C}_{60}$ and $\mathrm{C}_{70}$ vapor was sublimed on a stainless-copper plate which could be moved into the interaction region of the chamber.


Figure 2.15: Resistively heated oven

## Photoionization of fullerenes

### 3.1 The photoelectric effect

The photoeffect is the emission of electrons of matter under the influence of electromagnetic radiation. ${ }^{24}$ This phenomenon was discovered by Hertz in 1887. and first explained correctly in 1905. by Einstein, who suggested that light propagates and is absorbed in fixed amounts, or quanta, called photons. The photoeffect was explained as a process of photon absorption in a metal by an electron with a consequent increase in the electron's kinetic energy. If it became sufficiently high, the electron could leave the metal. Naturally, the same process may take place in an isolated atom or molecule (Fig.3.1). The basic photoeffect equation, which links the photon energy $h v$ and the energy $E_{k i n}$ of the ejected electron is:

$$
\begin{equation*}
h v=E_{k i n}+E_{b i n} \tag{3.1}
\end{equation*}
$$

Here $h$ is Planck's constant and $E_{\text {bin }}$ is the atomic ionization potential, defined as the minimum energy necessary to remove an electron from the atom and leave the ion in some particular state (also called electron binding energy). The magnitude of $E_{\text {bin }}$ is thus lowest when the ion is left in its ground state. After the interaction, if one electron has been released, the system consists of an atomic ion and a free electron, the photoelectron.


Figure 3.1: Photoionization ${ }^{149}$

The process can be summarized simply as:

$$
\begin{equation*}
h v+A \rightarrow A^{+}+e^{-} \tag{3.2}
\end{equation*}
$$

where $A$ is the atom in his ground state, $A^{+}$is the atomic ion and $e^{-}$is the ejected electron.

The study of photoionization provides important information about the electronic structure of the atoms and molecules. This includes not only the investigation of the cross section for the process, but also the energy and angular distributions of electrons ejected from the atom or molecule.

### 3.2 Many electron processes. Auger processes

Direct photoionization is not the only process possible after the interaction of the atoms and molecules with electromagnetic radiation. There are other, so called, many electron processes in which more than one electron participate in the transition. A special situation in the photoionization process occurs when one of the electrons from the inner-shell is ejected. The ionized atom that remains after the ejection of the core hole electron is in a highly excited state and will rapidly relax back to a lower energy state by one of the two processes:
(1) Radiative process (x-ray fluorescence)
(2) Non-radiative process (Auger emission)

In the case of the carbon atom (or molecules which consist of carbon atoms) Auger processes are more probable than fluorescence.

The production of a core hole in the target atom A is performed by photoionization:

$$
\begin{equation*}
A+h \nu \rightarrow A^{+*}+e_{p} \tag{3.3}
\end{equation*}
$$

where $A^{+*}$ is the atom in a highly excited state, $e_{p}$ is the primary emitted electron. In the case of radiative process, the vacancy transfers to a higher shell under emission of characterisctic x-rays:

$$
\begin{equation*}
A^{+*} \rightarrow A^{+}+h v \tag{3.4}
\end{equation*}
$$

If the vacancy is filled via Auger emission this is resulting in two vacancies in the higher shell in atom:

$$
\begin{equation*}
A^{+*} \rightarrow A^{2+}+e_{\text {Auger }} \tag{3.5}
\end{equation*}
$$



Figure 3.2: Photoionization and associated processes ${ }^{149}$
where $A^{2+}$ is a doubly ionized atom. In this case, one electron falls from a higher level to fill an initial core hole and the energy liberated in this process is simultaneously transferred to a second electron; a fraction of this energy is required to overcome the binding energy of this second electron. In the Auger process, the final state is a doubly-ionized atom with core hole in the higher subshell. These new vacancies could be transferred into the ground state via a cascade of successive radiative and Auger processes. These sequent processes lead to charged ions. The kinetic energy of the Auger electron can be estimated from the binding energies of the various levels involved in the trasition. For example: if K-shell vacancy is filled by electron from $L_{I}$, with electrons from $L_{I I, I I I}$ leaving: $E_{k i n}=E_{K}$ - ( $\left.E_{L I}-E_{L I I, I I I}\right)$. This type of transition is referred to in general as a $K L_{I} L_{I I, I I I}$ transition. If the first two letters are the same, the transition is called Coster-Krönig transition.

Fig.3.2 shows an overall of different electronic excitation and deexcitation channels, with and without resonant excitation. Without going in details for each of them here we mention only situations which are of further interest for our experimental results. One possibility is excitation of a valence electron, creating a vacancy and a +1 charge state of a molecule which was already mentioned (Fig.3.1(b)). A similar excitation of a core electron to an unbound final state is presented (Fig.3.1(a)). Fig.3.1(e) shows Auger transitions leaving a system in a +2 charge state. On the other hand, if a core electron is photoexcited to a resonant bound state, the system remains charge neutral until deexcitation, and again Auger-like transitions will dominate. This leads to two new possibilities: the participant and spectator (Fig.3.1(i,j,k)). Another example is when a single, energetic photon is absorbed by an atom or molecule and part of its energy is transferred via Coulomb interaction to a second electron. One possibility is that this second electron is excited to a certain, unoccupied molecular orbital (Fig.3.1(c)). As a result, the photoelectron spectrum contains additional (shake-up) satellite lines which are (generally) weaker than the main line which represents the direct single photoionization. This process can also result in the simultaneous emission of two electrons (Fig.3.1(d)) and it's called shake-off or direct double photoionization.

Fig.3.3 illustrates some of the excitation processes mentioned above. It represents our photoelectron spectrum of solid $\mathrm{C}_{60}$ taken at the photon energy of 284.09 eV . It is obtained after time-to energy conversion and without the subtraction of the background. The origin of this background is in the scattering of the photoelectrons in the solid. More precisely, the spectrum belongs to the group of the so-called resonant photoelectron spectra (RPES) where a core electron (in this case C 1 s electron) is photoexcited to a resonant bound state and the further decay is observed.


Figure 3.3: Resonant photoelectron spectrum of solid $\mathrm{C}_{60}$

In order to study this resonant spectrum one may first consider the x-ray absorption spectrum of $\mathrm{C}_{60}$. The result of one such measurement ${ }^{25}$ for the solid $\mathrm{C}_{60}$ and the photon energy of interest is presented at Fig.3.4. The peaks in the spectrum are different molecular orbitals where only the first component (indicated as LUMO) has significant weight. That means that for this particular photon energy C1s electron is photoexcited to the LUMO orbital.


Figure 3.4: X-ray absorption spectrum of solid $\mathrm{C}_{60}{ }^{25}$

The identification of the photolines at Fig. 3.3 can be obtained by the comparison of this resonant photoelectron spectrum, for excitation at the LUMO resonance, to the valence photoelectron spectrum on the binding energy scale. This is presented at Fig.3.5 where the valence spectrum for the solid $\mathrm{C}_{60}$ was taken at the photon energy of 110.12 eV and the resonant spectrum contains second-order light C 1 s line which has not been subtracted. Comparing these two spectra reveals that only the first three bands in the resonant spectrum represents participant channels (because they are equivalent of the valence PES). For higher binding energies they start to mix with the spectator contribution (which is a valence-
excited state equivalent of shake-up in PES).


Figure 3.5: Resonant photoelectron spectrum of the solid state $\mathrm{C}_{60}$ compared with the valence photoelectron spectrum on the binding energy scale

Actually, similar measurement have already been performed by Brühwiler et al. ${ }^{26}$ where they found that only the band derived from the highest occupied molecular orbital (HOMO) at 282.5 eV (on the kinetic energy scale) has a pure participant origin, whereas the band below may contain slight contributions from other transitions, and the next band at 279 eV is degenerate with a noticeable background of spectator contributions. According to the authors, distinction between the participant and the spectator contribution in such large systems is very difficult due to the correlation effects. Also, their spectrum shows a great similarity between Auger (which is not determined for our measurement) and spectator autoionization which is again the consequence of great size of the system. In such cases the perturbation caused by a single valence electron is relatively small and therefore Auger and spectator contribution overlap.

### 3.3 Molecules and molecular spectra

The properties of molecules are determined by their electron configurations. The fundamental physics of electrons in molecules is identical to electrons in atoms, however, the
detailed form of the electromagnetic potential is different. Molecular binding is caused by electromagnetic interactions of electrons and protons in atoms. A molecular bond occurs when it is energetically favorable for two or more atoms to be close to each other, which means that a certain energy is required to separate the atoms. The molecular bond length is defined to be the distance between the nuclei of the atoms. A molecule is a configuration of atoms that are sufficiently close together such that the probability densities of the outer electrons overlap. This causes the energy levels to be perturbed because the electrons of a given atom interact with the electrons and nuclei of the neighboring atoms.

When an atom or molecule absorbs energy electrons are ejected from thir ground state $\left(\mathrm{E}_{0}\right)$ to some excited state $\left(\mathrm{E}^{*}\right)$ (Fig.3.6). The energy levels of electrons in molecules are quantized so that molecules have electronic excitations similar to atoms. In addition to electronic excitations, molecules have degrees of freedom not available in single atoms. These additional degrees of freedom arise from the fact that the nuclei in a molecule may have a relative motion even though the center of mass of the molecule is fixed. One of these degrees of freedom is vibrational motion of the nuclei. Molecules may also rotate about an axis through the center of the mass and therefore they have additional rotational energy. Vibrational and rotational levels also have discrete energy, which can be considered as being on the top of each electronic level (Fig.3.6).


Figure 3.6: Electronic levels in the molecule

Table 3.1 illustrates the differences between different energies in the molecule.

Table 3.1: Comparison of the electronic, vibrational and rotational molecular energy spectra

| Excitation | Energy estimate | Typical Energy |
| :--- | :--- | :--- |
| Electronic | $\frac{h^{2}}{8 m d_{d a m}^{2}}$ | 4 eV |
| Vibrational | $\frac{h^{2}}{\pi d_{\text {atam }}^{2}} \sqrt{\sqrt{m M}}$ | $10^{-1} \mathrm{eV}$ |
| Rotational | $\frac{h^{2}}{4 \pi^{2} M d_{\text {dom }}^{2}}$ | $10^{-3} \mathrm{eV}$ |

In the energy estimation $m$ is the mass of the electron, $M$ is the mass of the molecule, and $d_{\text {atom }}$ is the diameter of an atom. ${ }^{27}$ Due to the present resolution in our experiments we were able to observe only electronic transitions in fullerenes, although some more advanced recent measurements with $\mathrm{C}_{60}$ showed additional, vibrational structure. ${ }^{28}$

### 3.3.1 Born-Oppenheimer approximation

As we've already mentioned, in a molecule, the nuclei can move as a whole in translational and rotational motion or with respect to each other in a vibrational motion. Because of the large mass of the nuclei relative to electrons, they move much more slowly than electrons and this justifies Born-Oppenheimer adiabatic separation of electronic and nuclear motion. In other words, one should normally expect that ionization is much faster than dissociation. When a molecule is photoexcited into an electronic excited state (or relaxes from an excited state), the dipole electric transition probability is determined with a matrix element with an electronic and nuclear term. Usually, one can separate the electronic from nuclear terms, the letter being called the Franck-Condon factors and the transition is called "vertical".

### 3.3.2 Molecular Orbitals

A molecular orbital $\psi$ gives, through the value $\psi^{2}$, the distribution of the electron in the molecule. A molecular orbital is like an atomic orbital, but spreads throughout the molecule. A molecular orbital is usually approximated as a linear combination of atomic orbitals (LCAO).

Electrons accumulate in regions where atomic orbitals overlap and interfere constructively. This kind of orbital is called bonding orbital, an orbital which, if occupied, contributes to a lowering of the energy of a molecule. If the atomic orbital interfere destructively, i.e. if they are combined with opposite signs, the resulting orbital is called antibonding, an orbital which, if it is occupied raises the energy of the molecule relative to the separated atoms.

The molecular orbitals, as the atomic orbitals, can be divided into the core orbitals, those of the inner, closed shells, the valence orbitals, those of the valence shells, and the virtual orbitals, those of the molecule which are unoccupied in its ground state.

The molecular orbitals of homonuclear molecules are labelled with a subscript $g$ or $u$ that specifies their parity, their behavior under inversion. If the orbital doesn't change the sign under the operation of inversion it has even parity and is denoted as $g$ (gerade). If the orbital has an opposite sign, it has odd parity and is denoted as $u$ (ungerade).

The molecular orbitals are denoted as $\sigma, \pi \ldots$ as the analogue of $\mathrm{s}, \mathrm{p} \ldots$ orbitals in atoms.

### 3.3.3 Symmetry of molecules

An action that leaves an object looking the same after it has been carried out is called a symmetry operation. For each symmetry operation there is a corresponding symmetry element; this can be the point, line or plane with respect to which the symmetry operation is performed. Symmetry operations that may leave a structure unchanged are:

- Exchange, E
- Rotation by $2 \pi / \mathrm{n}, \mathrm{n} \varepsilon \mathrm{Z}$
- Inversion, I
- Reflection through a plane, $\sigma$

Molecules are classified according to their symmetries, i.e. according to their symmetry elements and point groups. For example, $I_{h}$ symmetry group, which is the point group of $\mathrm{C}_{60}$ molecule, contains the inversion and it is formed by 120 different symmetry operations. $\mathrm{C}_{70}$ molecule possesses a lower symmetry, $\mathrm{D}_{5 h}$.

### 3.4 Partial and differential cross sections. Beta parameter

The photoionization process is determined by several quantities which are functions of the photon frequency $\omega$ (energy) : the total $\sigma(\omega)$, the partial $\sigma_{i}(\omega)$ photoionization cross sections and angular distribution asymmetry parameters $\beta_{i}(\omega)$ where index $i$ is denoting the quantum numbers of the ionized shell. ${ }^{29}$

The total photoionization cross section gives the total probability of ionization of a system by electromagnetic radiation of a given energy and is given as the sum of intensities from several subshells:

$$
\begin{equation*}
\sigma(\omega)=\sum_{i} \sigma_{i}(\omega) \tag{3.6}
\end{equation*}
$$

It can be obtained experimentally, for example from the ion yield measurements. ${ }^{30} \mathrm{~A}$ more specific and informative quantity about a particular subshell ionization process is the partial cross section which is expressed via a photoionization amplitude, which is a matrix element of the operator $\widehat{H}_{e}$ describing the interaction of an electron with the electromagnetic field. In the dipole approximation the partial cross section is given by:

$$
\begin{equation*}
\left.\sigma_{i}(\omega)=\frac{4 \pi^{2}}{\omega c}\left|\left\langle\psi_{i}\right| \widehat{H}_{e}\right| \psi_{f}\right\rangle\left.\right|^{2} \tag{3.7}
\end{equation*}
$$

where $\left\langle\psi_{i}\right|$ and $\left|\psi_{f}\right\rangle \mid$ are the electron's initial and final state wave functions, respectively. The photoelectron angular distribution $d \sigma / d \Omega$ (Fig.3.7) indicates the probability that an electron is emitted in a certain direction in space (i.e. in a certain solid angle element $d \Omega$ ).


Figure 3.7: Geometry for dipole angular distributions ${ }^{152}$

In the dipole approximation it is given by the following expression:

$$
\begin{equation*}
\frac{d \sigma_{i}(\omega, \theta)}{d \Omega}=\frac{\sigma_{i}(\omega)}{4 \pi}\left[1+\beta_{i}(\omega) P_{2}(\cos \theta)\right] \tag{3.8}
\end{equation*}
$$



Figure 3.8: Electron angular distribution for different values of the asymmetry parameter $\beta^{151}$

Here, $\Omega$ is the solid angle, $P_{2}(\cos \theta)$ is the second order Legendre polynomial, and $\theta$ is the photoelectron emission angle which is measured with respect to the electric vector of the light. At the so-called "magic angle" $\theta=54.7^{\circ}$ this polynomial becomes zero and therefore the differential cross section becomes proportional to the integral partial cross
section. The so-called angular distribution asymmetry parameter, $\beta$ (Fig.3.8), ranges from $\beta=2\left(\frac{d \sigma}{d \Omega} \approx \cos ^{2} \theta\right)$ to $\beta=-1\left(\frac{d \sigma}{d \Omega} \approx \sin ^{2} \theta\right)$. From the energy dependence of the asymmetry parameter $\beta$, we can obtain certain informations about the dynamical behaviour of the different partial waves.

### 3.5 Photoionization of the Valence shell of $\mathrm{C}_{60}$

### 3.5.1 Electronic structure of $\mathbf{C}_{60}$

Electronic structure of $\mathrm{C}_{60}$, which is important for the understanding of its many imporant properties, was computed and investigated by a large number of authors. ${ }^{31-41}$ Many of the basic features of the electronic structure of $\mathrm{C}_{60}$, in particular the closed-shell electronic configuration and the symmetry of the electronic levels, were predicted well before the first optical absorption ${ }^{42}$ and photoemission ${ }^{43,44}$ measurements yielded some insight into the electronic structure. The measurements of the electronic and optical properties by direct ${ }^{45}$ and inverse ${ }^{46}$ photoemission, absorption ${ }^{47-49}$ and electron energy loss ${ }^{50,51}$ spectroscopy allowed to test and to refine the theoretical descriptions of the energy levels. The early calculations and other simple models ${ }^{52,53}$ using the independent particle approximation, were found to give a good qualitative picture of the energy levels. The experimental electron distribution curves and the observed elementary excitations revealed however the importance of electron correlation effects ${ }^{54}$ so that more sophisticated calculations using $a b$ initio ${ }^{55}$ and density functional treatments ${ }^{56,57}$ were used in order to provide a more accurate description. Some of the most important results are presented below.

The least energetically bound electron states are sixty $\pi$ electrons which determine the way how $\mathrm{C}_{60}$ bonds to other atoms or molecules in the solid state since the $\pi$ bond spreads outside the molecule more than the $\sigma$ bond and has larger intermolecular overlap. Fig.3.9 presents an overview of $\pi$ electronic levels for an isolated $\mathrm{C}_{60}$ molecule and for $\mathrm{C}_{60}$ in the solid state. The distribution in energy of these sixty $\pi$ electrons of an isolated $\mathrm{C}_{60}$ molecule (left) was obtained from Hückel calculations performed by Haddon et al.. ${ }^{58}$ The $\pi$ electrons pair up with opposite spins to fill thirty energy states. The degeneracies and the symmetries of these states are indicated in the figure. The $a, t, g$ and $h$ labels correspond to degeneracies of $1,2,4$ and 5 , whereas the $g$ and $u$ subscripts correspond to even (gerade) and odd (ungerade) symmetry. The highest occupied $h_{u}$ molecular orbital (HOMO) contains ten electrons. Electron removal from this orbital in an isolated molecule yields the ionization potential (IP) level at $7.6 \mathrm{eV} .{ }^{7}$ The lowest unoccupied $t_{1 u}$ molecular orbital (LUMO) can contain six electrons. HOMO to LUMO ( $h_{u} \rightarrow t_{1 u}$ ) transitions are dipole forbidden.


Figure 3.9: The distribution in energy of the sixty $\pi$ electrons of $C_{60}$. The left part represents the result of the Hückel energy calculation of the molecular orbitals in an isolated $\mathrm{C}_{60}$ molecule. The right part of the figure represents the result of the local density approximation calculation for fcc $\mathrm{C}_{60}{ }^{59}$

For the solid state $\mathrm{C}_{60}$ Saito and Oshiyama ${ }^{56}$ used the local density approximation LDA to calculate the band structure of the fcc $\mathrm{C}_{60}$ crystal. The calculation indicates that the fcc $\mathrm{C}_{60}$ crystal is a direct semiconductor with an energy gap of 1.5 eV . Band structure of fcc $\mathrm{C}_{60}$ around energy gap is depicted in the right part of the Fig.3.9. Here the independentparticle energy bands derived from the $h_{u}$ and $t_{1 u}$ levels in the molecular $\mathrm{C}_{60}$ are shown as a function of crystal momentum in the Brillouin zone of fcc $\mathrm{C}_{60}$. These bands are broadened in the solid and show a dispersion. The valence band derived from the $h_{u}$ level is fivefold degenerate and the conduction band derived from the $t_{1 u}$ level is threefold degenerate. The calculation also shows that these two bands are relatively narrow ( 0.4 eV ) indicating the similarities in the electronic properties between molecular and solid $\mathrm{C}_{60}$. The derived energy gap between them is about 1.9 eV . Transitions between the valence band top and the conduction band bottom are, for symmetry reasons, optically forbidden.

HOMO-LUMO gap can also be experimentally determined from the photoemission spectroscopy and inverse photoemission spectroscopy measurements by probing the density of occupied and unoccupied states. The result of such measurement for the solid state $\mathrm{C}_{60}{ }^{60}$ is presented in Fig. 3.10 where both spectra are referenced to the Fermi level. For the separation in energy between the centers and the edges of the HOMO and LUMO band the authors obtained values of 3.7 eV and 2.6 eV , respectively. The latter one corresponds to the minimum energy needed to crate a separated electron and hole (which is equal to the

HOMO-LUMO gap).


Figure 3.10: Experimantal determination of the HOMO-LUMO gap in the solid state $\mathrm{C}_{60}$ by means of photoemission spectroscopy (left) and inverse photoemission spectroscopy (right) ${ }^{59}$

### 3.5.2 Photoelectron spectra of $\mathbf{C}_{60}$

We have performed high-resolution measurements of photoelectrons emitted from the valence shell of $\mathrm{C}_{60}$, for both gas phase and solid state, in order to obtain branching ratio, partial cross sections and the angular distribution anisotropy parameters of the two highest occupied molecular orbitals, HOMO and HOMO-1. ${ }^{61}$ Our measurements were performed at the undulator beamline BW3 of the Hamburg Synchrotron Radiation Laboratory HASYLAB at DESY. ${ }^{17}$ The experimental setup is sketched at Fig.2.7. Outgoing electrons were detected in time-of-flight (TOF) electron spectrometers at two different angles with respect to the electric vector of the ionizing radiation in order to derive the partial cross sections and the angular distribution asymmetry parameters. For that purpose one of the detectors was positioned at $0^{\circ}$ and the other at the so-called 'magic angle' (54.7 ${ }^{\circ}$. The effect of the angular distribution at this angle is, in principle, eliminated and the relative partial cross sections can be directly determined. Obtained spectra were also normalized to the beamline flux profile which was determined from the Neon data and the photocurrent measured on a gold mesh placed in the beamline in front of the analysis chamber. In our study, the photon energy dependence of the photoelectron spectra of $\mathrm{C}_{60}$ was recorded in the range
of $\mathrm{h} v=20-70 \mathrm{eV}$ for the gas phase, and in the range from $\mathrm{h} v=20 \mathrm{eV}$ up to carbon K-edge for the solid state.


Figure 3.11: The electron yield for the gas phase $\mathrm{C}_{60}$ at the magic angle ( $54.7^{\circ}$ ), which is proportioned to the partial cross section, as a function of the binding energy for three different photon energies ${ }^{61}$

Typical gas-phase spectra for different photon energies are shown in Fig.3.11. They show numerous and sharp features, which is consistent with the predicted high symmetry of the molecule and the large degeneracy of the corresponding orbital levels. The comparison of these spectra with a solid state spectra (Fig.3.12), taken at the same experiment, reveals a close similarity indicating the weakness of the interaction (which is of the van der Waals type) between molecules in the molecular solid. However, relative intensities of the valence photoemission lines of solid and gaseous $\mathrm{C}_{60}$ are different, probably because of inelastic scattering effects and differences in the corresponding transition matrix elements. We also compared our results with the theoretical calculations for the electronic structure of $\mathrm{C}_{60}{ }^{62}$ (Fig.3.13) performed with the plane wave pseudopotential local density method. This approach employs the Ceperley and Adler form of exchange correlation. The shape of the theoretical density of states is in very good agreement with the experimental data. The agreement between the theory and experiment is particularly good in the low binding
energy part of the spectrum, whereas it becomes worse in the second part of the spectrum where the two-electron emission processes give rise to the continuous electron distribution.


Figure 3.12: The electron yield for the solid $\mathrm{C}_{60}$ at the magic angle $\left(54.7^{\circ}\right)$, which is proportioned to the partial cross section, as a function of the binding energy for three different photon energies ${ }^{61}$

The general characteristic of the valence spectrum of $\mathrm{C}_{60}$ is that the orbitals of the same type are close in energy and that the orbitals with increasing values of $\ell$ have increasing energies. The first two peaks in the spectrum correspond to two highest occupied molecular orbitals (HOMO and HOMO-1), which both have $\pi$ character. ${ }^{32}$ However, these states have different symmetries: HOMO band arises from the single odd $6 h_{u}-\pi_{5}$ orbital and HOMO-1 is a mixture of the even $6 \mathrm{~g}_{g}-\pi_{4}$ and $10 \mathrm{~h}_{g}-\pi_{4}$ orbitals. They have fivefold and ninefold degeneracy, respectively and both are dipole allowed. Features with higher binding energies (labeled as A, B, C in Fig.3.11, 3.12 and 3.13) contain states of both $\sigma$ and $\pi$ character with even and odd symmetry. The deeper valence features are almost entirely $\sigma$ derived. Calculations based on a pseudopotential plane-wave local LDA mechanism ${ }^{63}$ reveal the similar results allowing us to identify the orbital character and symmetry of each
of the valence lines.
Furthermore, our results show oscillations in the intensity of these two outermost molecular orbitals as a function of the photon energy. Each maximum in intensity of HOMO is matched by a minimum of HOMO-1. These oscillations are well known and have been the subject of several investigations with simplified theoretical models ${ }^{63-65}$ and the same behaviour is actually measured both in the gas phase ${ }^{66,67}$ and the solid state. ${ }^{68}$

Benninig et al. ${ }^{68}$ have first observed these oscillations for condensed phase $\mathrm{C}_{60}$. They showed relative intensity modulations of these lines with photon energy up to 100 eV and interpreted these effects in terms of final-state symmetries and parity selection rules. These intensity modulations provide evidence for the existence of high-lying final states that are not plane-wave like. However, this interpretation regards the existence of these states basically as a solid state effect which should not appear in the ionization of the free molecule, at least not so pronounced. According to our data, the solid-state interactions play only a minor role and the origin of the observed oscillations in the partial cross sections of the two highest molecular orbitals should basically be the same and caused by the molecule itself. That is in a way not unusual because if a molecule has a nearly spherical structure with a large radius, certain oscillations will be expected.


Figure 3.13: (a) calculated density of states (DOS) for the valence states of solid $\mathrm{C}_{60}$ at $65 \mathrm{eV}^{62}$ (b) our experimental data for the same photon energy

The importance of the sherical structure of $\mathrm{C}_{60}$ for the intensity oscillations was for the first time pointed out by Xu, Tan and Becker. ${ }^{64}$ They approximated the initial and final state wave functions as a product of radial and angular part in the spherically symmetric potential of $\mathrm{C}_{60}$, and calculated the energy positions of the cross section minima by using one of the dipole allowed states. Their explanation attributes the variation of the photoionization cross section to the possible formation of spherical standing waves of the final state electrons inside the molecule. An incoming spherical electron wave moving towards the center of the molecule may be virtually reflected there, producing an outgoing wave which then forms a standing wave. This effect may be considered as intramolecular interference. The amplitude of the final state wave function at the spherical shell changes periodically with the wave number and thus with the final energy. Since the initial wave function of the delocalized valence electrons is distributed mainly around the radius of the molecule, the
photoionization matrix element must also change periodically. This is reflected on the corresponding partial cross section.

The calculations of Hasagewa et al. ${ }^{63}$ also showed that these oscillations originate from the interference of photoelectron waves emanating from the 60 carbon atoms. In the first approach they used the single-scattering approximation for the final state with the result of the STO-56 molecular orbital calculation for the initial state. It showed out that the accuracy of the final state has little effect on the oscilations. That is a specific character of the initial state. The simplified analytical calculations using plane-wave final state and the spherical-shell-like initial state gave the equal oscillations as obtained by more sophisticated method.


Figure 3.14: The jellium potential for $\mathrm{C}_{60}$ from ${ }^{69}$ (solid) and its derivative $\mathrm{dV}(\mathrm{r}) / \mathrm{dr}$ (dashed) ${ }^{65}$

Further theoretical model of Frank et al. ${ }^{65}$ showed that this diffraction effect in the photoionization cross section is caused by the sharp edge of the molecule potential and that it is directly related to the geometrical properties of the electron cloud, such as its thickness and the diameter of the molecule. This approach is based on the jellium approximation for the potential of $\mathrm{C}_{60}{ }^{69}$ (Fig.3.14) in combination with a density-functional theory (DFT) description of the delocalized electron cloud. ${ }^{70}$ The carbon atoms of $\mathrm{C}_{60}$ form the surface of a sphere on which they are distributed uniformly. Since each C atom supplies 4 valence electrons there is a cloud of 240 electrons in a hollow sphere centered around the cage of the carbon ions.

The diffraction effect is best understood if the dipole operator is presented in the socalled acceleration form:

$$
\begin{equation*}
D_{a}=\frac{1}{i \omega} \nabla_{r} V(r)=\frac{1}{i \omega} \frac{d V(r)}{d r} \tag{3.9}
\end{equation*}
$$

As it can be seen from the Fig. 3.14 it is zero in regions where the potential is flat (e.g. inside the molecule). Therefore, the ionized electron is only created at the edges of the potential where its gradient $d V / d r$ is large. Under these assumptions it is easy to understand the interference pattern by the difference of the path lengths of electron waves coming from the molecule edges.


Figure 3.15: Partial cross-section ratio HOMO/HOMO-1 for gas and solid $\mathrm{C}_{60}$ for different photon energies. The lines show the results of different theoretical models: theoretical curves with a Jellium model (-----) and with LDA calculations ( $-\cdot-\cdot-$ ); semiempirical curves with a Shell model ( $\cdots \cdots \cdot$ ) and with a Shell+Cage model (- ). The experimental data of ref. ${ }^{67}$ are shown by open rhombs, whereas the data of the present work are given by open circles for the gas phase data and crosses for the solid state measurements. ${ }^{61}$

The branching ratio of the two outermost molecular orbitals HOMO and HOMO-1, for the gas and condensed phase, is displayed in Fig.3.15 togather with two different theoretical calculations and semiempirical fit (Appendix A). It is independent of the photon flux and target density variations. These new measurements of the partial cross section data over a large energy range made it possible to analyze the observed oscillations in terms of structural information of the fullerene. The Fourier transformed cross section data (Fig.3.16) can be used to determine the radius of the fullerene (R) and the thickness of the delocalized electron cloud $(\Delta)$. One has to keep in mind that these geometrical properties
of the $\mathrm{C}_{60}$ molecule are not directly displayed by the peak positions in the plotted Fourier spectrum; they correspond rather to the asymptotic frequencies $f_{\ll}^{-1}$ being proportional to the energy window dependant spectral frequency $f^{-1}$. The photoelectron cutoff energy of 280 eV used in this study corresponds to a proportionality factor of 1.085 , giving a radius $\mathrm{R}=3.55 \AA$, which is in good agreement with the electron scattering results of Vos et al. ${ }^{71}$ and most other theoretical calculations. It is interesting to note that the agreement with the jellium calculation is improved compared to the former less densely measured data set, ${ }^{67}$ particularly concerning the low frequency beating peak.


Figure 3.16: Fourier transform of the cross section ratio in Fig. 3.15 for the experimental data for the solid state (filled circles) and the LDA calculation using a spherical jellium potential (dashed line) ${ }^{61}$

### 3.5.3 Partial cross sections of the two highest occupied molecular orbitals, HOMO and HOMO-1 of $\mathrm{C}_{60}$

Figure 3.17 shows partial cross sections of $\mathrm{C}_{60}$ 's two outermost orbitals for the gas phase. The photon energy was increased in small steps of 0.1 eV in the photon energy range from 19 to 50 eV , and in larger steps of 1 eV from 50 to 70 eV . The experimental results are compared with two different theoretical calculations. The first theoretical ab initio calculation ${ }^{72}$ employed a convergent one-center expansion and a local density approximation (LDA) Hamiltonian, which explicitly included the nonspherical nature of the potential. The results of this calculation for the individual HOMO and HOMO-1 cross-section show, along with the steady decrease, the out of phase oscillations which persist up to high energy with almost constant amplitude in relative terms.


Figure 3.17: Partial cross sections for the two outermost orbitals of gas phase $\mathrm{C}_{60}$ (a) HOMO and (b) HOMO-1. ${ }^{61}$ The experimental data are shown by open circles. The theoretical curves are from ref. ${ }^{72}$ (dashed line) and ref. ${ }^{73}$ (solid line), respectively.

The high icosahedral symmetry makes a rather strong selection of the angular momenta which are compatible with each ireducibile representation. Therefore, most of the dipole allowed final continuum states contain actually only high angular momenta components: the consequent strong centrifugal barrier may create a typical double-well effective potential, where virtual valence antibonding states can be confined or the continuum waves can be trapped. These quasibond states have strong overlap with respect to the initial (ionized) orbitals, and therefore very intense and sharp resonances are observed in the calculation.

The second theory is using Hartree-Fock (HF) molecular orbitals and is solving the coupled scattering equations for the ejected electron in the field of the molecular ion within a polyatomic Schwinger variational method. ${ }^{73}$ The computed partial cross section shows a very rich structure and the presence of a similar narrow peak superimposed over a highly oscillatory background. It is suggested that such pronounced structure is the result of resonant electronic state in the field of the residual molecular ion.


Figure 3.18: Three-dimensional representations of the resonant wave functions. In both views of the resonances, one-eight of the carbon cage of $\mathrm{C}_{60}$ is represented ${ }^{73}$

As a conclusion, the general behavior of the partial cross section is very well described by the theory. Also, the quantitative agreement is quite satisfactory considering the scat-
tering of the experimental data points. At low energies the photoionization cross section is dominated by the well known plasmon peak resulting from collective electron behavior. For higher energies the ionization cross sections for HOMO and HOMO-1 exhibit out of phase oscillations, with a frequency related to the diameter of the molecule, superposed on the exponential decay. The only discrepancy between theory and experiment is the predicted existence of the pronounced resonant structures in the partial cross sections.


Figure 3.19: Partial cross sections for the two outermost orbitals of solid $\mathrm{C}_{60}$ (a) HOMO and (b) HOMO-1. ${ }^{61}$ The theoretical curves are from ref. ${ }^{72}$

Both theories show such structures in their calculations, found however at different positions, while no sharp structures are found in the experimental data. Because of the
present measurement it seems reasonable to assume that the resonances in the partial cross sections are probably quenched by the vibrations of the molecule. The complex resonant wave functions of the resonantly excited states are in delicate balance between stabilization and decay forced by the different vibrational modes, such as the breathing mode of $\mathrm{C}_{60}{ }^{3}$ . In most cases the excited states are probably unstable and therefore do not appear in the partial cross section.

Figure 3.19 represents partial cross section for HOMO and HOMO-1 for the solid state measurements in the same energy range from $20-70 \mathrm{eV}$ measured with the step of 1 eV . As it can be seen, they exhibit the similar kind of behaviour as in the case of gas phase. This is another confirmation that the origin of the oscillations is in the molecule itself.

### 3.5.4 Beta parameter of the two highest occupied molecular orbitals, HOMO and HOMO-1 of $\mathrm{C}_{60}$

We also determined the angular distribution asymmetry parameter, $\beta$, of the HOMO and the HOMO-1 for the same photon energies and compared our results with theoretical calculations ${ }^{72,73}$ (Fig.3.20). As it was already mentioned, in atomic and molecular photoionization, the $\beta$ parameter ${ }^{74}$ reflects the photoelectron's angular momentum information. ${ }^{75,76}$ The angular momentum may be influenced by scattering of the photoelectron on other atoms in the molecule giving rise to additional components and shifts in their relative phases. This phenomenon is in particular pronounced in shape resonances in molecular photoionization. ${ }^{77}$ The theoretical curves for the $\beta$ values of $\mathrm{C}_{60}$ 's HOMO and HOMO1 are very structured, especially in the low energy region, while the experimental results show much smoother and wider structures. This is in accordance with the interpretation of the cross section oscillations as a quantum state effect of a three-dimensional box potential with no significant effect on the phase of the outgoing photoelectron wave. For both HOMO and HOMO-1, the asymmetry parameters $\beta$ change very fast from zero to positive values over a very narrow photon energy range. They are both increasing after a minimum at about 25 eV , although this is shifted by a few eV with respect to each other. This behavior reflects the effect, that the ejected electrons are emitted with increasing kinetic energy away from the isotropic distribution more towards the direction of the electric field of the light.

The agreement between theory and experiment is, concerning the general trend, also satisfactory for the $\beta$ values, however to a lower extend than for the partial cross sections. Even in the nonresonant regime the different theories deviate in the $\beta$ values from each other up to about half of an unit.


Figure 3.20: The angular distribution asymmetry parameter $\beta$ for the two outermost orbitals of $\mathrm{C}_{60}$ (a) HOMO and (b) HOMO-1 as a function of the photon energy. The figure shows experimental results (open circles) ${ }^{61}$ and theoretical curves from ref. ${ }^{73}$ (solid line) and ref. ${ }^{78}$ (dashed line), respectively.

### 3.6 K-Shell Photoionization of $\mathbf{C}_{60}$

### 3.6.1 Plasmon excitation of $\mathrm{C}_{60}$ molecules

During the same measurement we also recorded K -shell photoelectron spectra of $\mathrm{C}_{60}$. These spectra, besides the main line, posses a variety of satellite lines and higher lying plasmon excitations. Fig. 3.21 shows an example of such spectrum taken at 390 eV , cover-
ing the whole range of kinetic energies down to zero kinetic energy.


Figure 3.21: A recorded spectrum of the $54.7^{\circ}$-analyzer for a photon energy of $390 \mathrm{eV} .{ }^{153}$ In (a) the time-of-flight(TOF) spectrum is shown, in (b) the spectrum is converted to the binding energy. In (c) a part of the spectrum is given after the substraction of this background. The broad peak on the right side is caused by several plasmon excitations. The positions of the plasmons are marked and have been taken from, ${ }^{79}$ the intensity of Gauss-functions and the width, about 10 eV (FWHM), have been fitted to the experimental spectrum.

The nearest features to the main $\mathrm{C}(1 \mathrm{~s})$ line consist of $\pi$ type shake-up satellites. They
are all already well known and well described, both in theory ${ }^{80,81}$ and experiment. ${ }^{82,83}$ In the energy region between 10 and 20 eV there are no discrete dipole transitions for free molecules and collective resonances are the dominating effects here. ${ }^{81}$ This is in accordance with our result showing a broader satellite, characteristic for plasmon like excitations, at 12.6 eV . The high energy satellites start with the feature at about 18 eV from the main line. It is mainly ascribed to a dipole like collective $(\sigma+\rho)$ resonance which is characteristic for $\mathrm{C}_{60}$ molecule. ${ }^{84}$ It has already been predicted by theoretical calculations ${ }^{81,85}$ and also found in electron energy loss ${ }^{86}$ and x-ray photoemission spectra. The next feature on the high energy side is positioned at an energy of about 23.1 eV . Östling et al. ${ }^{86}$ and Vasvàri ${ }^{87}$ obtained theoretically a collective excitation for the $\mathrm{C}_{60}$ molecule at about 22.0 eV and for the solid fullerene at 21.2 eV , respectively. These calculations are in good agreement to the observed one. The large peak at about 27.3 eV is also well known and it is attributed to the $\sigma+\pi$ plasmon (caused by all valence electrons) for solid $\mathrm{C}_{60}{ }^{86-88}$ since the corresponding feature is difficult to observe in the case of the free molecule. ${ }^{66,89,90}$ The feature having an energy of 32.0 eV may be explained by a dipole active plasmon mode that has been predicted to occur at about 33 eV by Lambin et al. ${ }^{91}$ using a dielectric shell model. The weaker satellite at about 37.4 eV is more difficult to identify. However, Puska and Nieminen ${ }^{69}$ have suggested a plasmon like excitation for the molecule to appear at about 35 eV from the main line.


Figure 3.22: Spectra as function of the binding energy of the $180^{\circ}$-analyser are shown for different photon energies. ${ }^{153}$ The background of the low kinetic energy electrons from Auger processes is already subtracted.

The dependence of the plasmon excitation on the photon energy is illustrated in

Fig.3.22. With increasing photon energy broad peak referred as plasmon is increasing in intensity. We have performed a more detailed quantitative analysis of this feature. Figure 3.23 shows the yield of the plasmon peak relative to the yield of the $\mathrm{C}(1 \mathrm{~s})$ line as a function of the photon energy. Plasmon yield starts to rise suddenly and then slower reaches a plato and stays constant till very high photon energy. This kind of behavior corresponds to the model of T. D. Thomas, ${ }^{92}$ a rather general description of excitation processes, described in more detail in the Appendix B, which in principle requires only some basic quantities:

$$
\begin{equation*}
\mu=\mu_{\infty} \exp \left\{-(r \Delta E)^{2} /\left(15.32 E_{\mathrm{ex}}\right)\right\} \tag{3.10}
\end{equation*}
$$

$\mu$ : intensity ratio of the "shake-up" process and the $\mathrm{C}(1 \mathrm{~s})$ main line, $\mu_{\infty}$ : asymptotic value of $\mu$ (taken from ${ }^{92}$ ),
$r$ : the distance until the electrons are separated from the molecule given in $\AA, r \approx 0.4 \AA$ (note $\mathrm{r} \ll \mathrm{r}\left(\mathrm{C}_{60}\right)$ ),
$\Delta \mathrm{E}$ : the excitation energy of the "shake-up" process given in eV,
$\mathrm{E}_{e x}$ : the kinetic energy of the outgoing electrons also given in eV .


Figure 3.23: Experimental (filled circles) ${ }^{153}$ and calculated (full line) values of the ratio of the intensity of all plasmon peaks and the intensity of the $\mathrm{C}(1 \mathrm{~s})$ main line as function of the excitation energy. The calculation is based on the model of Thomas, ${ }^{92}$ with $r=0.4 \AA$ and have been normalized to the value at 1487 eV from ${ }^{79}$

The comparison with the Thomas model also reveals that the excitation process is localized (because $r \ll \mathrm{r}\left(\mathrm{C}_{60}\right)$, e.g. the distance untill the electrons are separated is much smaller than the dimensions of the molecule rather than a delocalized relaxation in respond to core-hole creation. The sudden limit intensity is as large as $30 \%$ of the total K-shell ionization events.

We also determinated the angular distribution asymmetry parameter of the $\mathrm{C}(1 \mathrm{~s})$ line (Fig.3.24) and compared it with the previous measurements of Liebsch et al. ${ }^{66}$ and the measurements of CO performed in our group, as well as with the theoretical calculation of Zimmermann. ${ }^{93}$ Our measurements reveal that the $\beta$ parameter is increasing with increasing photon energy towards its maximum value of 2 . Our measurements are in good agreement with the theoretical calculation. The small deviation of asymmetry parameter from $\beta=2$ can be attributed to the molecular effects. In this photon energy region, the photoelectron may be scattered by the atoms in the molecule and thereby pick up additional angular momentum before it finally leaves the molecule.


Figure 3.24: Angular distribution asymmetry parameter of the $\mathrm{C}(1 \mathrm{~s})$ line

### 3.6.2 Strong enhancement of double Auger decay following plasmon excitation in $\mathbf{C}_{60}$

We also performed a spectral analysis of the whole electron spectrum which takes into account all primary and secondary ionization processes. Primary processes which include: $\mathrm{C}(1 \mathrm{~s})$, satellites, plasmon and shake-off electrons are the result of the direct K-shell ionization. Secondary processes which include both single and double Auger processes are the result of the relaxation process after the K-shell ionization.


Figure 3.25: Photoelectron spectrum recorded with a photon energy of 390 eV . Different types of contributions are marked with colours. The intensity of the single and double Auger processes can be deduced from the coloured areas. ${ }^{153}$

Contributions from different excitation processes in such "complete electron spectrum" (Fig.3.25) can be presented by the following equation:

$$
\begin{equation*}
\text { Auger }_{\text {total }}=\text { Auger }_{\text {single }}+\text { Auger }_{\text {double }}=\mathrm{C}(1 \mathrm{~s})+\text { Satellites }+ \text { Plasmons }+\mathrm{e}_{\text {shake-off }} \tag{3.11}
\end{equation*}
$$

Of course, mentioned approximation of the processes is pretty simplified and therefore gives certain discrepancies with our electron-ion coincidence measurements discussed latter in the text. The analysis yields the rate of double Auger as high as $60 \%$ of the total Auger yield (Fig.3.26). This is extremely high value, rising the question of its origin. Assuming that the main line and the related shake-off emission result predominantly in single

Auger decay, K-shell photoionization associated with satellite and plasmon excitations remains as the only possible source for such a high double Auger rate.


Figure 3.26: The yield of single (filled circles) and double (filled triangles) Auger processes as a function of the photon energy (a). ${ }^{153}$ Open symbols have been taken from. ${ }^{66,99}$ The yield is normalized with the intensity of the $\mathrm{C}(1 \mathrm{~s})$-main line, the electron shake-off processes and the intensity of satellites and plasmons. The yields of these primary processes are shown in (b)

The only reason for this highly unusual behavior may be the fact that satellite and plasmon excitations both populate LUMO states which are strongly delocalized and may be completely in the continuum for the double charged $\mathrm{C}_{60}^{2+}$ ion resulting from the K shell ionization and the subsequent core-hole refilling process. The excited electron cannot survive in this unstable situation and will consequently leave the $\mathrm{C}_{60}$ ion along with the

Auger electron in form of an Auger shake-off transition. These arguments, however, have to be validated by more sophisticated calculations.

### 3.7 Valence shell Photoionization of $\mathbf{C}_{70}$

### 3.7.1 Electronic structure and Photoelectron Spectra of $\mathbf{C}_{70}$

The electronic structure of $\mathrm{C}_{70}$ molecule, up to now, has not been so extensively investigated as in the case of $\mathrm{C}_{60}$. Yet, certain informations about it are available from the photoelectron spectroscopy measurements of the gas phase $\mathrm{C}_{70}$ using synchrotron radiation ${ }^{94,95}$ and from several calculations which have been reported. ${ }^{4,96-98}$ The addition of 10 carbon atoms around the equator of $\mathrm{C}_{60}$ to produce $\mathrm{C}_{70}$ introduces $10 \pi$ electrons and $30 \sigma$ electrons. Molecular elongation for $\mathrm{C}_{70}$ has little effect on the overall distribution of bands, but lowering of molecular symmetry results in lower degeneracies of molecular orbitals. In order to learn more about its electronic structure we have performed the same kind of high resolution measurements of the emitted photoelectrons from the valence shell of solid state $\mathrm{C}_{70}$. We derived the branching ratio and partial cross sections of the two highest occupied molecular orbitals HOMO and HOMO-1. These measurements were also carried out at the undulator beamline BW3 of HASYLAB at DESY. The experimental set-up is, in principle, the same as it was for the $\mathrm{C}_{60}$ measurements (Fig.2.7) except that for the detection of the outgoing electrons we used only one time-of-flight (TOF) electron spectrometer positioned at the angle of $54.7^{\circ}$ with respect to the electric vector of the ionizing radiation. For the solid state measurements the angle between the copper substrate with respect to the direction of the incoming light was $\sim 45^{\circ}$ (Fig.3.27). The angle between the surface normal and photoelectron emission as well as the angle between the surface normal and the polarization plane were $\sim 19^{\circ}$ and $\sim 51^{\circ}$, respectively. The spectra were recorded in the photon energy range from 25 eV up to carbon K edge with the steps of 1 eV . We compared our results with theoretical calculations ${ }^{78}$ and our previous results for the gas phase $\mathrm{C}_{70}$ performed at the same beamline. ${ }^{100}$

Typical spectra for three different photon energies, for both gas and condensed phase, are presented in Fig.3.28 and Fig.3.29 and are in good agreement with theoretical calculations. ${ }^{96}$ Their results show 16 features in the valence band and 10 in the conduction band. The most pronounced difference between $\mathrm{C}_{60}$ and $\mathrm{C}_{70}$ lies in the splitting and broadening of the two highest occupied molecular orbitals HOMO and HOMO-1. In $\mathrm{C}_{60}$, the $\mathrm{p}_{\pi}$ bands have no discernible underlying structure. In $\mathrm{C}_{70}$, the corresponding features are split into three resolvable photoemission features in the first peak and two in the second. That means that for $\mathrm{C}_{70}$ there will be five additional $\mathrm{p}_{\pi}$-derived bands in the vicinity of HOMO. The greater complexity of the $\mathrm{C}_{70}$ spectrum compared to that of $\mathrm{C}_{60}$ is expected due to the lower symmetry of $\mathrm{C}_{70}$ (which results in lower degeneracies of the energy levels) and the ten additional $\pi$ electrons from the additional carbon atoms. Our results reveal a corre-
spodence of the electronic structure of gas and solid phase, as in the case of $\mathrm{C}_{60}$, because molecules in the molecular crystal behave in many respects like free molecules.


Figure 3.27: The geometry of the experimental set-up for the solid state measurement


Figure 3.28: The electron yield (at $54.7^{\circ}$ ) for the gas phase $\mathrm{C}_{70}$ as a function of the binding energy for three different photon energies. ${ }^{154}$

Our photoelectron spectra of $\mathrm{C}_{70}$ also show energy dependant oscillations in the partial cross sections of the two highest occupied molecular orbitals, HOMO and HOMO-1, although less pronounced than in the case of $\mathrm{C}_{60}$. The branching ratio of these two photolines is shown in Fig. 3.30 in the photon energy region from 25 to 200 eV . Using this ratio one avoids uncertainties produced by photon beam intensity fluctuations. We also compared our results with the previous measurements for the gas phase performed in our group and compared them with the theoretical calculations of Decleva. ${ }^{78}$ The comparison between the two phases shows interesting and unexpected difference. The ratio between the corresponding HOMO and HOMO-1 shows an offset of 0.5 for the gas phase compared to solid state data. The latter one are constantly lower for all energies between 25 and 200 eV . Theoretical calculations performed within the LCAO approximation show good agreement for both data sets, if one assumes, that in the gas phase the (+16a')-orbital is unoccupied, which means, that it is a part of the LUMO structure. We assume, that this orbital becomes filled from the substrate due to the smaller HOMO-LUMO gap in $\mathrm{C}_{70}$ (photoemission from the negative $\mathrm{C}_{70}$ ion gives the value of $1.2 \mathrm{eV}^{5}$ which is considerably lower than in the case of $\mathrm{C}_{60}$ ) . This result demonstrates how strong substrate-fullerene interaction can become, if electron transfer becomes energetically possible.


Figure 3.29: The electron yield (at $54.7^{\circ}$ ) for the solid state $\mathrm{C}_{70}$ as a function of the binding energy for three different photon energies. ${ }^{154}$


Figure 3.30: Partial cross section ratio HOMO/HOMO-1 for gas and solid $\mathrm{C}_{70}$ for different photon energies. ${ }^{154}$ The results are compared with LDA calculations from ref. ${ }^{78}$


Figure 3.31: Partial cross-section ratio $\mathrm{HOMO} / \mathrm{HOMO}-1$ of solid $\mathrm{C}_{70}$ for different photon energies. Experimental data $(\bullet)$ and the results of a semiempirical fit ( -

The solid line in Fig. 3.31 is the result of a simple model (Appendix A). Herein, the data are approximated by an exponentially decaying set of spherical Bessel functions, including electronic and geometric properties of $\mathrm{C}_{70}$. Using a Levenberg-Marquardt algorithm for an estimation of the fitted parameters we obtained values close to the known ones. Fourier
transform of the relative cross section data (Fig.3.32) directly display the geometric properties of the molecule, like cage radius-R (in this case the mean value of the two elipsoid axis) and the thickness of the electronic hull ( $\Delta$ ).


Figure 3.32: Fourier transforms of the cross-section ratios for solid $\mathrm{C}_{60}(\square)^{61}$ and for solid $\mathrm{C}_{70}$, taken from Fig. 3.31 (exp. data: •, model: -—).

The transformed experimental data show more structures at larger distances than the simple model and the shape of the $\mathrm{C}_{70}$ experimental curve is more broad than in the case of $\mathrm{C}_{60}$. This is in a way expected, since the $\mathrm{C}_{70}$ molecule is shaped ellipsoidally and has lower symmetry than the $\mathrm{C}_{60}$ molecule which is fully spherically shaped.

Figure 3.33 shows partial cross section of the $\mathrm{C}_{70}$ 's two outermost orbitals. The overall agreement between theory and experiment is very good. As in the case of $\mathrm{C}_{60}$, the ionization cross sections exhibit the same kind of oscillations with a frequency related to the diameter of the fullerene molecule superposed on the exponential decay. We believe that the sudden drop of the partial cross sections at the end of the photon energy range comes rather from the variations of the beamline's flux than the molecule itself.


Figure 3.33: Partial cross sections of the two highest occupied molecular orbitals, HOMO and HOMO-1, for both solid and the gas phase of $\mathrm{C}_{70}$. The results are compared with LDA calculatios from ref. ${ }^{78}$

## Valence-Shell Photofragmentation of C 60

### 4.1 Photofragmentation of fullerenes

Fragmentation dynamics of the fullerene clusters was first studied by O'Brien and coworkers ${ }^{9}$ with the laser induced fragmentation of the jet-cooled fullerene molecules up to 80 atoms in size by time of flight technique. They found two different photophysical regimes. The first applies to clusters with 34 atoms or more which all dissociate producing even numbered fragments. Large even clusters fragment by the loss of the high energy species $\mathrm{C}_{2}$ (with dissociation energy of about 9.8 eV ) while odd ones lose a C atom. The second regime applies to clusters composed of 31 or less atoms, all of which fragment by the loss of $\mathrm{C}_{3}$. These photophysical results are interpreted as consequences that the large even clusters have edgeless, spheroidal cage structures while the small ones have linear chain or ring structures. For spheroidal shells, only the even numbered clusters can close. Shells containing an odd number of atoms are possible, but all such structures must have several dangling bonds. This explains why the even clusters would be so much more stable.

Fragmentation dynamics of $\mathrm{C}_{60}$ has also been extensively studied . ${ }^{6,9,101-110}$ The first studies on the stability of $\mathrm{C}_{60}^{+}$fullerene ions were carried out with $\mathrm{C}_{60}^{+}$ions produced by laser ablation of graphite . ${ }^{9}$ O'Brien and co-workers were the first to conclude that at least three (and possibly more) photons of ArF laser radiation (i.e. at least 19.2 eV ) have to be absorbed by cold $\mathrm{C}_{60}^{+}$ions to cause fragmentation observable in the microsecond time regime. Yoo et al. ${ }^{6}$ produced $\mathrm{C}_{60}^{+}$ions by vacuum ultraviolet (VUV) single-photon ionization of pure $\mathrm{C}_{60}$ and studied fragmentation of $\mathrm{C}_{60}^{+}$ions so produced for photon energies of $16.84,19.8,21.2,23.1,26.95$, and 40.8 eV . No $\mathrm{C}_{58}^{+}$fragment ions were observable at the photon energy of 26.95 eV , while "with a considerable struggle", a weak signal of $\mathrm{C}_{58}^{+}$(with a ratio between the $\mathrm{C}_{58}^{+}$fragment ion current and the $\mathrm{C}_{60}^{+}$parent ion current of $0.07 \pm 0.04$ ) was observed at a photon energy of 40.8 eV . In this experiment this corresponded to an
internal energy of the decaying $\mathrm{C}_{60}^{+}$ion of approximately 39 eV .
It is now well accepted that the main fragmentation channel of the $\mathrm{C}_{60}^{+}$fullerene ion is the sequential loss of $\mathrm{C}_{2}$ units. From an energetic point of view, the fission-like process of splitting the fullerene into two fragments is less likely and also the statistical arguments are in favor of the first type of decay.

### 4.2 The Experimental Details

We studied the photofragmentation dynamics of $\mathrm{C}_{60}$ by means of synchrotron radiation. ${ }^{111}$ Gaseous fullerene were provided from a resistively heated oven, ionized by irradiation of monochromatized synchrotron radiation, and detected after analysis with ion time-of-flight mass spectrometer. The experiment has been carried out at the dipole beamline TGM4 of BESSYII. Measurements of Ne/Ar resonances were carried out to check the accuracy of the monochromator settings. The photon energy was changed in 1 eV steps from 26 to 130 eV . In this way, seven scans have been measured, each scan taking about 3 h .

We were using $\mathrm{C}_{60}$ with $99.98 \%$ purity. The sample was purchased and further purified by eliminating the organic solvent such as benzene or toluene through heating the sample 18 h in a vacuum at $250^{\circ} \mathrm{C}$. Regulating the temperature of the oven enabled us to attain the optimum experimental conditions that kept a stable flow of the $\mathrm{C}_{60}$ vapor.

It has been reported ${ }^{112,113}$ that an oven temperature between 535 and $655^{\circ} \mathrm{C}$ affects the $\mathrm{C}_{60}^{2+} / \mathrm{C}_{60}^{+}$ratio after excitation with 41 eV photons. In order to prove a possible temperature dependence we recorded $\mathrm{C}_{60}^{2+} / \mathrm{C}_{60}^{+}$ratio between 420 and $500^{\circ} \mathrm{C}$ for photon energies of 41,65 and 90 eV (Fig.4.1). Merely C ${ }_{60}^{q+}$ ionization takes places with the 41 eV photons, whereas additional fragmentation occurs with the higher photon energies. In all cases a temperature dependence was not observed.

A periodically pulsed extraction field has been used to extract the ions at right angles to the molecular and light beams. In this experiment the extraction pulse starts the time of flight measurement, which is stopped when the ions are detected at the end of the flight tube. The duration and the repetition rate of this pulse voltage were $10 \mu \mathrm{~s}$ and 12 kHz , respectively with pulse amplitude of 820 V . For each selected wavelength, TOF spectra were accumulated until a satisfactory signal-noise ratio was achived. The ion signal intensities were obtained by integrating the area of the respective peaks while subtracting background contributions.


Figure 4.1: Temperature dependence of the $\mathrm{C}_{60}^{++} / \mathrm{C}_{60}^{+}$ratio for three different photon energies

### 4.3 The Spectra

Figure 4.2 shows a typical TOF mass spectra observed for three different photon energies. For presentation the TOF spectra have been converted to the ion mass-per-charge m by $\mathrm{m}=\mathrm{a}(\mathrm{TOF}+\mathrm{b})^{2}$ with appropriate chosen constants a and b . We see $\mathrm{C}_{60}^{+}$and $\mathrm{C}_{60}^{2+}$ peaks accompanied by a number of peaks due to fragment ions as well as a series of peaks. In the energy interval between 65 and 90 eV , the doubly charged species $\mathrm{C}_{56}^{2+}$ and $\mathrm{C}_{58}^{2+}$ were detected efficiently, as well as the triply charged $\mathrm{C}_{60}^{3+}$. Measurements were repeated several times for given parameters.


Figure 4.2: Parts of spectra (converted to a mass-per-charge scale) for photon energies of $h v=41$, 65 , and 90 eV . The inset shows the low-mass region of the spectrum taken with 90 eV . Contributions of small fragment ions from the $\mathrm{C}_{60}^{q+}$ ion break-up (like $\mathrm{C}_{60}^{q+{ }^{*}} \rightarrow \mathrm{C}_{2}^{+}+\ldots$ ) are negligible in this mass region. ${ }^{111}$

### 4.4 The Photoionization Cross Section

We derived the photoionization cross section $\sigma(\mathrm{X})$ for producing the fullerene type X from the following formula:

$$
\begin{equation*}
\sigma(X) \equiv N \frac{Y(X)}{Y\left(A r^{+}\right)} \sigma\left(A r^{+}\right) \tag{4.1}
\end{equation*}
$$

Here $\mathrm{Y}(\ldots)$ stands for the observed yield of the fullerene or argon ions. The total cross sections of argon ions $\sigma\left(A r^{+}\right)$were taken from . ${ }^{29}$ A normalization factor was chosen in a way that our total cross section corresponds to the total $\mathrm{C}_{60}$ photoionization cross section reported by Berkowitz for 40.8 eV photons . ${ }^{114}$


Figure 4.3: Photoionization cross section for producing $\mathrm{C}_{60}^{+}(\bullet)$ and $\mathrm{C}_{60}^{2+}(\curvearrowleft)^{111}$ derived from equation (4.1). Error bars are the one-sigma deviation. The solid line (-) marks the cross section of all charged fullerene ions. The dashed line ( ---- ) gives 60 times the total photoabsorption cross section of a single C-atom. ${ }^{115}$

We compared so derived cross section of fullerene ions with the total photoabsorption cross section of a singly carbon atom multiplied by $60{ }^{115}$ (Fig.4.3, dashed line). For photon energies higher than $\approx 60 \mathrm{eV}$ the total photoabsorption cross section of a singly carbon atom multiplied by 60 runs nearly parallel to the cross sections of $\mathrm{C}_{60}^{+, 2+}$ showing fast decreasing with increasing photon energy and is close to the total cross section of the fullerene ions. For photon energies lower than $\approx 60 \mathrm{eV}$ some deviations are found probably due to the molecular-like features of $\mathrm{C}_{60}$, such as shape resonances or the giant plasmon resonance, whose high energy side lies in the beginning of our analysed energy region.

Hertel et al. ${ }^{116}$ have explained the steep increase in single ionization cross-section
above 15 eV by the collective excitation of the valence electrons of $\mathrm{C}_{60}$ ( $\sigma+\pi$ plasmon) and compared their results with the excitation of a dipole plasmon as calculated in.$^{84}$ Those plasmon excitations have a large degree of correlations. In contrast to the singly charged fullerene ions where a plasmon excitation plays a significant role for the total ion yield, this does not seem to apply to the doubly charged ions. Formation of these ions requires a minimum energy of 19 eV which is very close to the plasmon resonance energy. The doubly charged ions might be produced even exclusively through direct ionization. In contrast to the decrease of the singly charged fullerene ions, the $\mathrm{C}_{60}^{2+}$ cross-section curve stays flat until 60 eV and exhibits a shallow dip around 50 eV .


Figure 4.4: Experimental and theoretical cross sections for the photoionization of $\mathrm{C}_{60}^{+}$taken from the ref. ${ }^{117}$ The experimental values can be explained by two underlying processes: the excitation of a surface plasmon and, at higher energies, the creation of a volume plasmon

Just recently, it has been shown ${ }^{117}$ that the experimental values for the photoionization cross section can be explained by two underlying processes: the excitation of a surface
plasmon and the creation of a volume plasmon on higher energies (Fig 4.4).
Time-dependant density functional calculations (TDLDA) confirm that the both giant resonances in the photoionization spectrum are of collective character since they are clearly present in TDLDA while they are absent in the effective single-particle LDA approximation. Moreover, TDLDA calculation also reveals that both $\sigma$ and $\pi$ electrons contribute to the giant resonance near 22 eV (surface plasmon) while $\sigma$ electrons contribute dominantly to the plasmon near 38 eV (volume plasmon).

The origin and nature of these collective resonances may be understood in purely classical terms. ${ }^{91}$ If we imagine $\mathrm{C}_{60}$ molecule as a classical dielectric sphere it exhibits two types of excitation modes, namely, surface plasmons and volume plasmons. The volume plasmon mode, with a frequency $\omega_{p}$ determined by the electron density only, corresponds to a local radial compression of the electron density. The (dipole) surface plasmon with frequency $\omega_{s}=\omega_{p} / \sqrt{3}$ represents a collective oscillation of an incompressible electron density relative to the ionic background. Classical theory forbids the dipole excitation of the volume plasmon. Quantum mechanically, however, the photon-induced electrondensity fluctuations of the delocalized electron cloud are of non-local character and break this symmetry rule, so that surface and volume plasmon excitations are coupled and shifted with respect to their classical frequencies. ${ }^{118}$

### 4.5 The Relative Cross Sections of Fullerene Ions

The mass spectra in Fig.4.2 are dominated by $\mathrm{C}_{60}^{+}$which has the largest cross section. Although this is in contrast to the situation in ordinary polyatomic molecules ${ }^{119}$ where the parent ion is usually almost nonexistent; it is nevertheless in accordance with previous mass spectrometric studies and theoretical considerations (RRKM calculations) of the ionization and fragmentation of $\mathrm{C}_{60} .{ }^{120}$


Figure 4.5: The relative cross section of $\mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$ (normalized to the $\mathrm{C}_{60}^{+}$cross section). Some measurements recorded with a longer accumulation time are marked by big symbols. The lines are calculated according to equation (4.2). All values for $\mathrm{C}_{60}^{3+}$ are multiplied by 5 . The error bars reflect the one-sigma deviation calculated from the statistical uncertainties only. The experimental values of Fieber-Erdmann et al ${ }^{112}$ (hollow symbols with a line, scaled down by $1 / 3$ ) and Karvonen et al ${ }^{121}$ (taken with a photon energy of 280 eV ) are also shown. ${ }^{111}$

The relative cross sections of $\mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$ are presented in Fig.4.5. The ratio of the $\mathrm{C}_{60}^{2+}$ ions increases with increasing photon energy until about 62 eV and rises faster for photon energies higher than 45 eV . For photon energies beyond 62 eV a saturation for the $\mathrm{C}_{60}^{2+}$ ratio is reached. The ratio of $\mathrm{C}_{60}^{3+}$ increases until about 100 eV and stays nearly constant for higher photon energies. Both ratios of $\mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$ at high photon energies are quite similar to the values taken from the work of Karvonen et al. ${ }^{121}$ for photon energies of 280 eV . This suggests that nothing will change in the ratios of $\mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$ until the photon energy is sufficient $(\approx 284 \mathrm{eV})$ to excite an electron from the inner K -shells of the carbon atoms, which will be illustrated later in the text. An interesting feature is that the ratio values for the production of doubly and triply charged parent ions, relative to that of the singly charged parent ion, are larger than that for any fragment ion. Whereas here the ratio for doubly to singly charged ion is more than $50 \%$, for ordinary molecules or atoms this ratio seldom is more than a few percent (even in the case of the rare gases this value is considerably lower, ${ }^{122}$ for example in the case of Ne it is in the range of $15 \%$ ). The reason for these enhanced cross sections lies, on the one hand, in the fact that the production of doubly and triply charged ions is energetically more favorable than the production of fragment ions (the appearance energy of $\mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$ lies below that of any fragment ion of $\mathrm{C}_{60}{ }^{123}$ ). In addition, the sheer size of $\mathrm{C}_{60}$ and the fact that secondary electrons from an initial single-ionization process may be ejected into the empty center of the cage and subsequently interact anew with the electron cloud of the $\mathrm{C}_{60}$ enhances the chance for the occurrence of inelastic multiple-electron collisions within this quantum system, thereby increasing the probability for the production of multiply charged ions. Similar effects have been observed for the production of multiply ionized van der Waals clusters ${ }^{124}$ and metal clusters . ${ }^{125}$ The shapes of the curves for the relative cross section of $\mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$ (normalized to the $\mathrm{C}_{60}^{+}$cross section) are in the agreement with the expectations of a model developed by T. D. Thomas ${ }^{92}$ which is describing the transition from the adiabatic to the sudden regime concerning two-electron emission (Appendix B). Following this model the relative cross section is given by the formula already mentioned in the text:

$$
\begin{equation*}
\mu=\mu_{\infty} \exp \left\{-(r \Delta E)^{2} /\left(15.32 E_{\text {ex }}\right)\right\} . \tag{4.2}
\end{equation*}
$$

$\mu$ is the relative cross section concerned and $\mu_{\infty}$ corresponds to the asymptotic value at infinite photon energy. $\Delta \mathrm{E}$ is the excitation energy required, which in our case is related to the ionization potentials ( 11.4 eV for $\mathrm{C}_{60}^{2+}{ }^{126}$ and $11.4+16.6 \mathrm{eV}$ for $\mathrm{C}_{60}^{3+127}$ ) and $\mathrm{E}_{e x}$ is the kinetic energy of the outgoing electrons. The distance r that electrons travel through before they are separated from the molecule has been fitted to our experimental values with the result: $\mathrm{r}=1.76 \AA$ for $\mathrm{C}_{60}^{2+}$ and $0.8 \AA$ for $\mathrm{C}_{60}^{3+}$. Note that the parameter r is close to the radius of a single carbon atom ( $\approx 1.5 \AA$ ). The lines calculated in this way shown in Fig.4.4 satisfactory describe the experimental values, indicating that the doubly and triply charged fullerene ions are probably formed via shake-off processes in excited $\mathrm{C}_{60}^{+}$ion.

### 4.6 Fragmentation dynamics

Fig.4.6 and Fig.4.7 show the relative cross section of singly and doubly charged fullerene fragments as a function of the photon energy. Several aspects of the $\mathrm{C}_{60}$ fragmentation are apparent. For both charge states $(\mathrm{q}=1,2)$, the maxima of the $\mathrm{C}_{60-2 m}^{q+}$ curves reduce with decreasing $\mathrm{C}_{60-2 m}^{q+}$ fragment size. This can be a signature of the successive emission of $\mathrm{C}_{2}$ units. The appearance energies for fullerene fragments are given in Table 4.1. The curves for $\mathrm{C}_{60-2 m}^{+}(\mathrm{m}=1,2)$ exhibit a special feature: they pass through a maximum before they reach a lower final value. Interestingly, the decrease beyond the maximum coincides with the beginning of an enhanced formation of:


Figure 4.6: The relative cross section of singly charged fullerene fragments for different photon energies. ${ }^{111}$ Some measurements recorded with a longer accumulation time are marked by big symbols. The error bars reflect the one-sigma deviation calculated from the statistical uncertainties only. The vertical lines indicate the appearance energies of the fragments as listed in table 4.1.
(i) a smaller fragment with the same charge state $\left(\mathrm{C}_{60-2 m-2}^{+}\right)$and/or
(ii) a fragment with the same size and with a higher charge state $\left(\mathrm{C}_{60-2 m}^{2+}\right)$

For doubly charged fragments the appearance energies are increasing with the decreasing of the fragment size. This means that, for example, $\mathrm{C}_{56}^{2+}$ has its maximum at larger photon energies than $\mathrm{C}_{58}^{2+}$ and confirms the fact that the loss of $2 \mathrm{C}_{2}$ fragments requires a higher energy than that of a single $\mathrm{C}_{2}$. In addition, $\mathrm{C}_{60}^{3+}$, for which an ionization threshold of 36.9 eV has been measured ${ }^{128}$ is found in the same photon energy range as these fragment ions (Fig.4.5). This suggests a fragmentation of $\mathrm{C}_{60}^{3+}$ into $\mathrm{C}_{58}^{2+}$ and $\mathrm{C}_{2}^{+}$, which would produce $\mathrm{C}_{2}^{+}$with a high kinetic energy. However, we didn't observe any $\mathrm{C}_{2}^{+}$, since

Table 4.1: Observed appearance energies (in eV ) for $\mathrm{C}_{60-2 m}^{q+}$ fragment ions. For comparison, experimental values observed in $e^{-}+\mathrm{C}_{60}$-collisions are given in brackets. ${ }^{127}$

|  | $m=1$ | $m=2$ | $m=3$ | $m=4$ | $m=5$ |
| :--- | :--- | :--- | :--- | :---: | :--- |
| $\mathrm{C}_{60-2 m}^{+}$ | $47(43.7)$ | $51(48.8)$ | $60(54.3)$ | $-(59.9)$ | $-(65)$ |
| $\mathrm{C}_{60-2 m}^{2+}$ | $59(53.9)$ | $67(59.8)$ | $74(65.1)$ | $77(71.8)$ | $86(75.8)$ |

a large kinetic energy increases the probability of removing the ion out of the range of the detector.


Figure 4.7: The relative cross section of doubly charged fullerene fragments for different photon energies. ${ }^{111}$ Some measurements recorded with a longer accumulation time are marked by big symbols. The error bars reflect the one-sigma deviation calculated from the statistical uncertainties only. The vertical lines indicate the appearance energies of the fragments as listed in table 4.1. The experimental values of Fieber-Erdmann et al ${ }^{112}$ (hollow symbols with a line, scaled down by $1 / 3$ ) are also shown for the first two fragments.

An overview of corresponding photoelectron spectra with photon energy similar to the formation of $\mathrm{C}_{60-2 m}^{+}$fragments is given in Fig.4.8. Herein clear counterparts of the different fragments or the source of $\mathrm{C}_{60}^{2+}$ can not be identified. Therefore, we have perform electron-ion coincidence measurement to get an additional information about fragmenta-
tion dynamics in this energy region (Chapter 7). The reasons for the oscillations in the photoelectron yields of the HOMO and lower lying valence shell have already been explained in Chapter 3.


Figure 4.8: The intensity of electron spectra as a function of the binding energy taken with different photon enrgies ( $\mathrm{h} v=40-70 \mathrm{eV}$ ) Each spectrum is normalized to its own maximum and the normalized intensity increases from blue to red on linear scale. ${ }^{111}$

## K-Shell Photofragmentation of $\mathbf{C}_{60}$

### 5.1 The Experimental Details

Besides studying valence shell photofragmentation we also obtained a new set of experimental data which shows the electronic dynamics and the dissociation pathways of $\mathrm{C}_{60}$ in core-hole decay process. For that, the carbon 1s electron was excited to different bound unoccupied valence levels or to the continuum and the resulting photoion spectra were recorded. The measurements were performed at the HASYLAB (DESY) undulator beamline BW3 in Hamburg. Neutral $\mathrm{C}_{60}$ molecules, provided by an oven heated to $\approx 500^{\circ} \mathrm{C}$, were ionized with the photon beam from the dedicated synchrotron radiation facility. The photon energy was changed from 90 to 440 eV ; first in larger steps of 10 eV and than in smaller steps of 1 eV in the vicinity of $\pi *$ preedge and above 1 s ionization threshold. Several scans were taken during the measurement in different photon energy regions. For the energy calibration purpose we used Ar resonances. The measurements were carried out using ion time-of-flight (TOF) technique. The operating parameters of the ion spectrometer were as follows. The positively charged $\mathrm{C}_{60}$ ions or fragments were separated according to their mass-per-charge ratio by a pulsed field (pulse amplitude $=820 \mathrm{~V}$, duration $=10 \mu \mathrm{~s}$, repetition rate $=12 \mathrm{kHz}$, rise time $<15 \mathrm{~ns}$, field length $=5 \mathrm{~mm}$ ). The ions were accelerated into a potential of -2900 V (field length $=4 \mathrm{~mm}$ ) followed by a 200 mm long field-free drift tube. After passing the drift tube the ions hit the detector surface which was held at a constant voltage of -3300 V . The distance from the drift tube to the detector was 5 mm . For a chosen set of physical dimensions of the spectrometer, the voltages were selected so that the space focusing condition is satisfied. ${ }^{129}$ For each event the start of the extraction pulse served as the start signal, the stop signals are provided from the multihit capable ion detector. With this set-up the total time-of-flight (TOF) was about $8 \mu$ s for a $\mathrm{C}_{60}^{+}$ion.

### 5.2 The spectra

As mentioned above, TOF ion spectra were collected for photon energies of the resonant excitation and above the C1s ionization threshold. A typical spectrum for a photon energy of 390 eV is shown on Fig.5.1. For presentation the TOF have been converted to the ion mass-per-charge by $\mathrm{m}=\mathrm{a}(\mathrm{TOF}+\mathrm{b})^{2}$ with appropriate chosen constants a and b . The peak width is caused by the kinetic energy of the produced ions and slightly depends on the size of the interaction region (beam diameter $\sim 1 \mathrm{~mm}$ ).


Figure 5.1: Part of time-of-flight ion spectra (converted to a mass-per-charge scale) for a photon energy of $h v=390 \mathrm{eV}$. The inset shows the low-mass-region of the spectrum. Contributions of small fragment ions from the $\mathrm{C}_{60}^{q+}$ ion break-up (like $\mathrm{C}_{60}^{q+} \rightarrow \mathrm{C}_{2+}+\ldots$ ) are negligible in this mass region. ${ }^{153}$

The spectrum is characterized by separate line groups due to multiply charged $\mathrm{C}_{60}^{q+}$ $(q=1, \ldots, 4)$ ions, and associated mass-loss peaks separated by the mass of $\mathrm{C}_{2}$. The lines of lighter fragments are separated by a single $\mathrm{m} / \mathrm{q}$ unit and they belong to light singly charged clusters. The identification of $\mathrm{C}_{60}^{5+}$ and $\mathrm{C}_{60}^{6+}$ and their loss peaks is uncertain because many clusters with intermediate mass and higher charge state also coincide with these lines. The important feature in this spectrum is the very negligible intensity of the lightest fragments $\left(\mathrm{C}^{+}, \mathrm{C}_{2}^{2+}, \mathrm{C}_{2}^{+}, \mathrm{C}_{4}^{2+}\right)$ from the cage break-ups and fission processes. This clearly indicates that the main fragmentation mechanism is neutral $\mathrm{C}_{2}$ and $\mathrm{C}_{4}$ emission from multiplycharged $\mathrm{C}_{60}$ ions.

An overview of all spectra taken from (270-390) eV is presented in Fig.5.2. $\mathrm{C}_{60}^{+}$is the most abundant in the low energy region below the C 1 s edge. The intensity of $\mathrm{C}_{60}^{2+}$ is almost constant in the whole energy region and it is the most abundant ion above the C1s edge.
$\mathrm{C}_{60}^{3+}$ is only slightly present below C1s edge and then its intensity is slowly increasing with increasing the photon energy. Singly charged fragments are barely visible whereas different doubly and triply charged fragments are quite pronounced especially above C1s edge.


Figure 5.2: The ion yields of converted spectra as a function of the ion mass-per-charge for different photon energies (270-450) eV. Each spectrum is normalized to its own maximum and the normalized yield increases from blue to red on a linear scale. ${ }^{153}$

### 5.3 The Photoionization Cross Sections and The Ion Yields

Yield of different ions normalized to the He+ intensity for the photon energy region (270390) eV is given in Fig.5.3, and zoomed in the vicinity of the carbon K edge in Fig.5.4. A total ion yield is given in the inset of Fig.5.5 (black line). They are quite similar to the published solid and vapor phase absorption spectra ${ }^{130,131}$ and the previous results of Aksela et al. ${ }^{99,121}$ The sharpest features A, B, and C in the spectrum are due to the excitation of the 1 s electron to the $5 \mathrm{t}_{1 u}, 2 \mathrm{t}_{2 g}, 5 \mathrm{t}_{2 u}$ and $4 \mathrm{a}_{g}$ orbitals of the $\pi *$ character. In the presence of a core hole, the $\mathrm{I}_{h}$ ground state symmetry is broken resulting in $\mathrm{C}_{s}$ symmetry 131 producing a splitting of the ground -state orbital energies . The ionization threshold ( 290 eV ) is followed by intense $\sigma *$ resonance structures up to around 310 eV as shown in detail by Terminello et al. ${ }^{130}$

The photoionization cross section for producing singly, doubly and triply charged $\mathrm{C}_{60}$ ions is depicted in Fig.5.5, together with photoionization cross section of all charged ions. They all show steady increase and maximum in the vicinity of $\sigma *$ resonance and slower decrease above it until they reach a certain plato and stay constant for a wide energy region. The total photoionization cross section is in good agreement with the total photoabsorption cross section of a single C atom multiplied with 60 (blue squares).


Figure 5.3: Yield of different ions normalized to the $\mathrm{He}^{+}$intensity for the photon energy region (270-390) eV. ${ }^{153}$


Figure 5.4: Yield of different ions normalized to the $\mathrm{He}^{+}$intensity for the photon energy region (283-296) eV. ${ }^{153}$


Figure 5.5: Photoionization cross section for producing $\mathrm{C}_{60}^{+}, \mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$. The solid black line give the cross section of all charged fullerene ions, blue squares show the total photoabsorption cross section of a single C atom multiplied with 60 . The total ion yield spectrum is shown in the inset. ${ }^{153}$

### 5.4 Energy Level Diagram

A schematic energy level diagram of $\mathrm{C}_{60}$ which is illustrating the fragmentation dynamics in the vicinity of the K-edge is depicted in Fig.5.6. The diagram is based on NEXAFS, photoelectron ${ }^{132}$ and Auger electron data. ${ }^{133}$ Resonant excitation below and ionization above the C 1 s ionization threshold leads to core-hole state. As the fluorescence yield is very low in both cases, the core excitation (transition (a) on figure) is practically always followed by a resonant Auger process (c) or in the case of core ionization (b) by a normal Auger process (d) in which a fast Auger electron is accompanied with a slow photoelectron. Thus, a resonant Auger process gives rise to a singly ionized molecule while a normal Auger process produces a doubly-ionized molecule. Above the ionization threshold the decay of the core excited state gives rise to the KVV Auger group.

Fast Auger electrons carry the released transition energy but can lose part of it in multielectron processes (shake up, plasmon excitation) to the remaining ionic system. As depicted on figure the intensity distribution of the KVV group extends well above the valence hole states, thus suggesting that a large part of final states of $\mathrm{C}_{60}^{+}$lie above the double ionization limit. Hence, for some final states of Auger transitions (c) it is energetically possible to further relax towards the energy-minimized final state via second-step Auger processes (e). In these secondary processes subsequent electrons and/or $\mathrm{C}_{n}$ fragments are
emitted giving rise to multiply-charged $\mathrm{C}_{60}^{q+}$ ions or to different $\mathrm{C}_{60-n}^{q+}$ fragment ions. As the relative kinetic energy difference between the fast electrons emitted in resonant or normal Auger process in the energy region of $(280-440) \mathrm{eV}$ is negligible, they can be considered to interact very similarly with the residual ion. The slow photoelectrons, however, can cause excitation of giant plasmon resonance which strongly increases the fragmentation yield. In addition, the different character of ionic states created below and above the 1 s edge is seen in the dissociation dynamics of the $\mathrm{C}_{60}$ molecule. Experimentaly this appears as a different fragmentation distribution which will be shown further in the text.


Figure 5.6: Schematic energy level diagram of $\mathrm{C}_{60}$ molecule ${ }^{99,121}$

### 5.5 Relative Fragmentation

Figure 5.7 presents yield of differently charged ions (area of the main $\mathrm{C}_{60}^{q+}$ lines and their fragments) relative to the total area of $q=1,2,3$ groups. An interesting characteristic in the spectra is the relatively high intensity of the $2+$ group at $\pi^{*}$ pre-edge resonances, where the resonant Auger process leads to production of singly-ionized molecules. Thus, it seems that second step processes are energetically possible for a large fraction of the resonant Auger final states. This observation is supported by the energy level diagram, as discussed
above. Another channel for the production of multiply-charged ions could also be the shake-off process during the resonant Auger transition. Above the ionization threshold KVV normal Auger process is taking place instead of resonant Auger processes. The direct photoionization of valence electrons works as the principal mechanism for producing $\mathrm{C}_{60}^{+}$ ions, although it has relatively low cross section. This is shown in figure as the yield of $1+$ ions decrease when the photon energy crosses the ionization energy of 1 s electrons. It can be seen, however, that the relative intensity of the singly charged $\mathrm{C}_{60}$ ions and associated fragments does not drop abruptly above the threshold from $52 \%$ at 285 eV to $4 \%$ at 330 eV . The relative yield of singly charged ions decreases gradually with increasing photon energy untill it becomes saturated around 330 eV . A similar effect was observed by Eberhardt et al. ${ }^{134}$ with the yield of $\mathrm{Ar}^{+}$ions above the $\mathrm{L}_{2}$ photoionization threshold. In their paper this behavior was interpreted as the recapture of the slow photoelectron, predicted by both semiclassical and quantum theories of post-collision interaction (PCI). Thus, our results could be explained as an analogous process to the recapture seen in free atoms. In the results given by Eberhardt et al., however, the yield of $1+$ ions falls rapidly down within about 1 eV , while in our data the corresponding fall off is spread out over a range of about 20 eV . This could be explained due to the immediate vicinity of the giant plasmon resonance.


Figure 5.7: Intensities of differently charged ions relative to the sum of states ( $q=1-3$ ) lines as a function of photon energy. ${ }^{153}$ Different symbols represent different scans.

Russek and Mehlhorn ${ }^{135}$ provided quite accurate semiclassical model of Auger transitions following ionization of an inner-shell electron. In their original paper they considered an molecular electron that is bound in the molecule with energy $-\mathrm{E}_{B}$ and is ionized by a photon of energy $\omega$ (if we use atomic units $\hbar=\mathrm{m}=\mathrm{e}=1$ ) or by the impact of another elec-
tron. The energy with which the photoelectron (if we restrict ourselves only to the first case which is of interest for us) leaves the molecule after the ionization is $\mathrm{E}=\omega-\mathrm{E}_{B}=(1 / 2) \mathrm{v}^{2}-1 / \mathrm{r}$ (Fig.5.8). The inner shell vacancy left by the photoelectron is then filled with a fast Auger electron. This Auger electron overtakes a slow photoelectron at some distance R. The slow photoelectron suddenly loses the electrostatic sceening that the Auger electron had provided and the potential seen by the photoelectron changes suddenly from $-1 / \mathrm{r}$ to $-2 / \mathrm{r}$. The photoelectron consequently loses energy $1 / \mathrm{R}$ that is transferred to the Auger electron. Because the loss of the energy of the slow electron is accompanied by a corresponding energy gain by the Auger electron the energy exchange can be regarded as a post-collision interaction (PCI). It follows from the figure that the photoelectron will be recaptured and become bound again if $1 / R \geq E$, i.e. if the Auger electron catches the photoelectron at a distance $\mathrm{R} \leq\left(\omega-\mathrm{E}_{B}\right)^{-1}$.


Figure 5.8: Energy level diagram illustrating post-collision interaction. The total energy of the photoelectron is E before and E' after the Auger decay ${ }^{134}$

Figure 5.9 presents area of loss patterns $\mathrm{C}_{60-n}^{q+}$ relative to the area of main $\mathrm{C}_{60}^{q+}$ $(q=1, \ldots, 3)$ lines as a function of photon energy. In the case of doubly- and triply-ionized parent ions the loss series gain about $6 \%$ and $18 \%$ of the intensity of the corresponding main line at $\pi^{*}$ resonances, respectively, while the singly-ionized molecules give rise to
only a very weak fragmentation pattern below the ionization threshold. In addition, the relative fragmentation of the multiple ionized molecules resonates strongly at pre-edge resonances. This clearly indicates that the $2+$ and $3+$ ions originate from the resonant Auger decay followed by second step processes.


Figure 5.9: Area of loss patterns $\mathrm{C}_{60-n}^{q+}$ relative to the area of main $\mathrm{C}_{60}^{q+}(\mathrm{q}=1,2,3)$ lines as a function of photon energy. ${ }^{153}$ Different symbols represent different scans.

Very interesting characteristics of this figure is the behavior of the relative fragmentation of $\mathrm{C}_{60}^{+}$ions above the 1 s threshold. The relative fragmentation yield reaches ( 0.8 ) level at the energy of $(320 \mathrm{eV})$. Our data show explicitely the existence of the giant resonance. This enhanced fragmentation yield can be interpreted as a similar process to the excitation of giant plasmon resonance observed by Hertel et al. ${ }^{116}$ In their photofragmentation studies by UV-radiation they observed a strong resonance around a photon energy of 20 eV , interpreted as the giant plasmon resonance predicted theoretically by Bertsch et al. ${ }^{84}$ Our results are consistent with this observation as the kinetic energy of the C 1 s photoelectrons is also around 20 eV . The photoelectrons most probably have a very high probability to lose their kinetic energy to the creation of plasmon excitation and the photoelectron is "recaptured" to the ion. The created plasma oscillation then breaks the molecule by consecutive $\mathrm{C}_{2}$ emissions to $\mathrm{C}_{58}^{+}, \mathrm{C}_{56}^{+}, \mathrm{C}_{54}^{+} \ldots$ fragments.

As a conclusion from the present results obtained by the ion yield spectroscopy, above the carbon K-edge the main products of $\mathrm{C}_{60}$ are doubly and triply charged fullerenes. The next step would be to compare these results with the results of corresponding photoelectron measurements (Chapter 3.6). They reveal that the continuous intensity distribution in the
photoelectron spectra can be either the result of direct double photoionization or doubleAuger decay. The disentanglement of these two processes on the basis of normal ion or electron spectroscopy is not possible. One way to overcome this problem was performing electron-electron coincidence spectroscopy measurements (Chapter 6).

## K-Shell Photoelectron-Photoelectron Coincidence Study of $\mathrm{C}_{60}$

Coincidence spectroscopy is a powerful tool for investigating the fragmentation dynamics of molecules in the gas phase following their single photon ionization. Coincidence spectroscopies can provide important information, unavailable from conventional spectroscopic techniques, regarding the identity and energetics of reactive species, the correlation of product states, the nature of repulsive electronic states and insights into product angular distributions in the molecular frame. The main idea of these experiments is the simultaneous detection of two or more products formed in the same photoionization event.

In order to deeper understand the fundamental processes causing the many-electron emission after K -shell ionization of $\mathrm{C}_{60}$ molecule our previous photoelectron and photoion measurements were accomplished by the electron-electron coincidence measurement. In this kind of experiment we used two electron time-of-flight (TOF) spectrometers positioned at two different angles.


Figure 6.1: Electronics set-up for electron-electron coincidence measurement


Figure 6.2: Electron-electron coincidences as function of the kinetic energy of the two detected electrons. The coincidence map was recorded with a photon energy of 380 eV . Some types of processes are specified. ${ }^{153}$

Figure 6.1 shows the electronic set-up used for our electron-electron coincidence measurements, which includes a special interface added to the standard TAC and ADC modules. This set-up allows the measurement of the coincidence between a pair of electrons emitted in two different direction for all possible sharings of the excess energy. Since all kinetic energies can be measured simultaneously, a coincidence spectrum is in fact a two-dimensional coincidence map.

Figure 6.2 shows the time-to-energy converted coincidence map taken at a photon energy of 380 eV which is higher than the $\mathrm{C}(1 \mathrm{~s})$ binding energy ( 280 eV ). Some types of processes are marked. Shake-off electrons are abundant at low-kinetic energies. Therefore, even at such high photon energies, shake off processes are important to understand the yields of the multiply charged $\mathrm{C}_{60}$ ions in photoion spectra besides the Auger and double Auger processes. In the case that two shake-off electrons leave the $\mathrm{C}_{60}$ molecule, the energy sharing is very asymmetric. The faster of the two shake-off electrons contributes significantly to the broad plasmon peak besides the $\mathrm{C}(1 \mathrm{~s})$ main line.

This leads to the conclusion that the major contributions to the triply charged ion yield is direct double photoionization of $\mathrm{C}_{60}$. However, in contrast to most atoms and molecules, it is driven by the plasmon excitation associated with the K-shell photoionization of the fullerenes which is at higher binding energies already in the double electron emission continuum. This causes a specific intensity distribution and explains the origin of the broad resonant features in the continuum part of the spectrum and the unusual high amount of triply charged fullerenes of $\approx 39 \%$.

## Valence-Shell <br> Photoelectron-Photoion Coincidence Study of $\mathbf{C}_{60}$

In order to get deeper insight in the valence shell photofragmentation dynamics of $\mathrm{C}_{60}$ we also performed photoelectron-photoion coincidence measurement (PEPICO) in this energy region. The principle of recording these coincidence spectra is that after the detection of an electron a pulse is applied to extract ions from the source region and push them into the mass spectrometer. Setting up the technique for detecting the two different types of particles such that neither measurement affects the other is not such an easy task. One of the requirements, as mentioned, is that a permanent electric ion extraction field cannot be used for the detection since it would obviously affect the electron trajectories and the ion fragmentation pattern would be distorted. Instead, a voltage pulse must be applied which has "clean" rising edge, on a ns time scale, and must be triggered after the electron has be detected, but before the fragment ions have moved out of the interaction region. Consequently, the coincidence count rate is limited mainly by the electron detection efficiency. The data acquisition hardware in our measurements was based on the use of dual-chip TDC module for the electrons (resolution 60 ps , multi-hit dead-time $<20 \mathrm{~ns}$ ) and fast multi-hit TDC modules (resolution 120 ps , multi-hit dead-time $<10 \mathrm{~ns}$ ) for the ion time. The time measurement is started by the bunch marker and stopped by constant fraction discriminator (CFD). The schematics of the signal timing is presented in the Fig. 7.1. The full set-up used in the actual experiment which includes some additional elements to prevent a possible time-stamp mismatch between electron and ion TDC is shown in Appendix C.


Figure 7.1: Schematics of the timing of a photoelectron-photoion coincidence experiments with synchrotron radiation using the ARFMADS and one electron time-of-flight spectrometer

When an ion is detected following the detection of an electron the event is recorded as a coincidence. If the electron and ion detected were formed in the same photoionization event it is a true coincidence, but if the ion and electron come from different photoionization events it is a false coincidence. Thus a sum of true and false (or "accidental") coincidences is recorded when collecting data. False coincidences can be subtracted from the raw data either after the data gathering stage ("off-line") or almost simultaneously, since the spectrum of false coincidences can be obtained either by calculation or by direct measurement. Direct measurement, using random pulses instead of electron signals to trigger pulses is preferable because many random pulses may be used to generate the background spectra of false coincidences with very good statistics and because many such spectra can be taken during the period of data collection to monitor any change in the rate of false coincidences which varies with sample gas pressure. Although in theory false coincidences can be subtracted whatever their abundance, in practice it is necessary to reduce the rate of false coincidences by periodically applying electric field pulses to remove unwanted from the source region. Because the light source runs continuously these ions would otherwise accumulate in the source region between drawout pulses.

Figure 7.2 shows the electron-ion coincidence map taken with a photon energy of 93.5 eV . On the vertical axis is given electron time-of-flight and on the horizontal ion time-of-flight. The right panel (black line) represents a projection of all electron events and the upper panel is a projection of ion events. Blue line on the right panel represents a projection of all electron events from $\mathrm{C}_{60}^{+}$while the red one corresponds to the electron events from $\mathrm{C}_{60}^{2+}$. Besides the $\mathrm{C}_{60}^{q+}$ ions ( $\mathrm{q}=1-3$ ) also coincidences with $\mathrm{C}_{60-2 m}^{2+}$ fragments are clearly discernible. Coincidences with the ions are stronger than coincidences with the fragments,
but on the other hand the intensity of the ions is stronger than the intensity of the fragments. One also has to keep in mind that the intensity of $\mathrm{C}_{60}^{+}$in absolute terms is smaller than the intensity of $\mathrm{C}_{60}^{2+}$ because in the case of $\mathrm{C}_{60}^{2+}$ and $\mathrm{C}_{60}^{3+}$ one or more additional electrons are detected by the spectrometer.


Figure 7.2: Electron-ion coincidence map taken with a photon energy of 93.5 eV .

Ions are appearing at higher binding energies with increasing the charge state which is understandable because for the creation of $\mathrm{C}_{60}^{+}$a smaller energy is required ( $\approx 8 \mathrm{eV}$ ) than, for example, in the case of $\mathrm{C}_{60}^{2+}$ ion $(\approx 8 \mathrm{eV}+11 \mathrm{eV}=19 \mathrm{eV})$. Also, $\mathrm{C}_{60}^{2+}$ fragments which are present on the map appear on higher binding energies with decreasing the number of the carbon molecules. The appearing energies of these fragments are marked on the map and they are similar to the appearance energies observed while scanning with different photon energies. ${ }^{111}$ The present results indicate that in the case of doubly charged ion if we assume that the energy sharing of the two outgoing electrons is asymmetric, than the minimum energy which is required for the fragmentation, i.e. for the creation of $\mathrm{C}_{58}^{2+}$ is about $(60 \mathrm{eV}-20 \mathrm{eV})=40 \mathrm{eV}$. If the energy sharing is not asymmetric this value is even higher. In order to gain information about fragmentation dynamics of the singly charged ion additional measurements at lower energies are required where we can expect fragmentation of $\mathrm{C}_{60}^{+}$.

## Conclusion

Because of the unique molecular structure of $\mathrm{C}_{60}$ like a spherical shell much theoretical and experimental effort was devoted to study the electronic structure and the electron correlation effects of this interesting molecule. Although a large variety of techniques have been employed, there still remain many questions related to the electronic and fragmentation dynamics of $\mathrm{C}_{60}$. Tunable synchrotron radiation covering a wide energy range from VUV to X-rays provides a unique tool to study these questions for valence as well for core electrons.

We have recorded angle-resolved photoelectron spectra of gaseous and solid $\mathrm{C}_{60}$ and $\mathrm{C}_{70}$ in the valence and, in the case of $\mathrm{C}_{60}$, in the K-shell photon energy region. One of the exciting properties of these molecules are the strong oscillations in the partial cross sections of the two highest occupied molecular orbitals, HOMO and HOMO-1. The physical reason for this phenomenon lies in the molecular geometry and the electronic charge distribution. Partial cross sections and the angular distribution asymmetry parameters vary significantly with the photon energy, particularly in the near-threshold region of the valence and core ionization. Some of these effects may be attributed to scattering of the outgoing photoelectron by the atoms of the ionized $\mathrm{C}_{60}$ molecule. Our results indicate that the observed satellites of the $\mathrm{C}(1 \mathrm{~s})$ main line are most likely of shake-up character. $\mathrm{C}(1 \mathrm{~s})$ photoelectron spectra are also characterized by a broad satellite peak named plasmon excitation. This plasmon is supposed to originate from a collective motion of the delocalized electrons in the electronic hull of $\mathrm{C}_{60}$ following the ionization of a K -shell electron. Low energy electrons emitted below the shake-off threshold indicate the occurrence of K-shell vacancy filling double Auger decay. Total C(1s) photoelectron and Auger intensities are approximately equal, assuming a double Auger rate of approximately 20\%.

We also measured the distribution of $\mathrm{C}_{60}$ ions and fragments after removing electrons from the valence region. A photon energy of more than 47 eV is required in order to observe any single charged fragment ions and more than 59 eV is needed to produce doubly charged fragments. The experimental values for the photoionization cross section of $\mathrm{C}_{60}^{+}$ can be explained by two underlying processes: The excitation of a surface plasmon and the creation of a volume plasmon on higher energies. For the first time the energy dependance
of singly charged fullerene fragment ions was measured in this energy region. Normalized to the $\mathrm{C}_{60}^{+}$yield, their yields pass through a maximum before they reach their asymptotic value, while the doubly charged fragment ions increase nearly monotonically to a final value. The observed asymptotic values are similar to those reported for photon energies just below the $\mathrm{C}(1 \mathrm{~s})$ threshold. This is an indication that for the ions considered, no new ionization or fragmentation feature exists in the energy region in between. Furthermore, highly charged $\mathrm{C}_{60}^{q+}$ ions ( $\mathrm{q}=2,3$ ) are probably the result of shake-off processes, since their relative cross sections follow the expectations of the shake-off model by T.D. Thomas. In addition to the "normal" (non-coincident) electron and ion time-of-flight spectroscopy we investigated this topic with the help of an electron-ion-coincidence measurement. Most intense are coincidences between electrons and intact $\mathrm{C}_{60}^{q+}$ ions ( $\mathrm{q}=1-3$ ). Our results also indicate for the majority of the events the following mechanism: a fast electronic excitation followed by an energy transfer to the vibrational modes and a subsequent (successive) evaporation of $\mathrm{C}_{2}$ fragment(s). Since the lack of the second, non-detected electron causes some ambiguity, the measurements in the future should be extended for a lower photon energy. In this case the production of singly charged $\mathrm{C}_{60-2 m}^{+}$fragments is enhanced and a complete electron-fragment-ion-coincidence study would become feasible.

Photoionization and photofragmentation dynamics of the gas-phase $\mathrm{C}_{60}$ molecule has also been studied by recording ion time-of-flight spectra after selective 1s excitation and ionization with monochromatized synchrotron radiation. The present results stress the importance of the specific character of electronic transitions in the production of fragments. At the vicinity of $\pi^{*}$ pre-edge resonances the fragmentation of multiply-charged ions varies strongly as a function of photon energy. The $\mathrm{C}_{60}^{+}$ion yield decreases slowly after 1 s threshold indicating that the slow photoelectrons can be recaptured. Somewhat further above the threshold the enhanced relative fragmentation of the parent $\mathrm{C}_{60}^{+}$ions suggests excitation of the giant plasmon resonance due to 20 eV photoelectrons. The non-coincident ion spectra were corroborated with the appropriate electron-electron coincident measurements in order to reveal the origin of doubly and triply charged $\mathrm{C}_{60}$ ions which are dominant for photon energies above the $\mathrm{C}(1 \mathrm{~s})$ threshold. Here, strong contributions come from single and double Auger processes, but also traces of electron shake-off and plasmon excitation processes can be found.
$\square$
Appendix A

## Semiempirical Model

We compared our measurements for $\mathrm{C}_{70}$ with the model of Xu et al. ${ }^{64}$ The branching ratio HOMO/HOMO-1 was determined semiempiricaly according to their model (Fig.3.31, Chapter 3). As it was already pointed out in Chapter 3, the diffraction effect in the photoionization cross section of fullerenes may be visualized by the formation of the spherical "standing wave" within the inner part of the molecule. The amplitude of this photoelectron standing wave at the spherical shell $\mathrm{r}=\mathrm{R}$ changes periodically with its "wave number" and thus with photon energy. The partial photoionization cross section is proportional to the square of the photoionization matrix element between the initial and the oscillating final state:

$$
\begin{equation*}
\sigma_{i f}(h v)=\frac{4 \pi^{2} \alpha a_{0}^{2}}{3} h v\left|<\Psi_{f}\right| \sum_{\mu} \vec{r}_{\mu}\left|\Psi_{i}>\right|^{2} \tag{A.1}
\end{equation*}
$$

and the initial state, in the roughest approximation, can be assumed proportional to $\delta(\mathrm{r}-$ R). Therefore, the partial photoionization cross section also oscillates because it is after this approximation proportional to the final state wave function:

$$
\begin{equation*}
\sigma_{i f}(h v) \sim\left|\Psi_{f}(h v,|\vec{r}|=R)\right|^{2} \tag{A.2}
\end{equation*}
$$

If we, further, suppose, that the potential of the electron is spherical symmetric (Figure A.2, dashed line), e.g. it is equal to contstant $-\mathrm{U}_{m}$ inside the molecule and vanishes outside:

$$
U(r)=\left\{\begin{array}{cl}
-U_{m} & , \forall|\vec{r}| \leq R  \tag{A.3}\\
0 & , \text { other }
\end{array}\right.
$$

and if we present the final state wave function as a product of radial and angular part:

$$
\begin{equation*}
\Psi_{f}(h v, \vec{r})=\frac{1}{r} R_{\ell}(h v, r) Y_{\ell, m}(h v, \theta, \phi) \tag{A.4}
\end{equation*}
$$

the radial part of the Schrödinger equation $(\hat{H} \Psi=E \Psi)$ has the following form:

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m_{e}}\left(\frac{d^{2}}{d r^{2}} R_{\ell}-\frac{\ell(\ell+1)}{r^{2}} R_{\ell}\right)+U(r) R_{\ell}=E R_{\ell} \tag{A.5}
\end{equation*}
$$

Here $E$ is the kinetic energy of the electron and $\mathrm{m}_{e}$ is its mass. The solution of this eigenvalue problem are $\ell$-dependent spherical Bessel functions, forming quasi standing waves inside the molecule:

$$
\begin{equation*}
R_{\ell}(h v, r)=A j_{\ell}(k r), \quad A=\text { const } . \tag{A.6}
\end{equation*}
$$

where

$$
\begin{equation*}
k^{2}=\frac{2 m_{e} E}{\hbar^{2}} \tag{A.7}
\end{equation*}
$$

Spherical Bessel function of the first kind has a general form:

$$
\begin{equation*}
j_{n}(x)=(-1)^{n} x^{n}\left(\frac{d}{x d x}\right)^{n} \frac{\sin x}{x} \tag{A.8}
\end{equation*}
$$

Several first terms are presented at Figure A.1.


Figure A.1: Spherical Bessel function of the first kind ${ }^{148}$


Figure A.2: Potential energy of the final state electron as a function of $r^{64}$

The zeros and the maxima of the squares of these functions (at the sphere of the indtaal charge distribution $r \approx R$ ) determine the positions of the maxima and the minima of the partial cross section. The order of the Bessel function depends on the angular momentum quantum number $\ell_{f}$ in the final state which is connected with the angular momentum quantum number in the initial state with the dipole selection rule: $\ell_{f}=\ell_{i} \pm 1$. Unfortunately, the effective angular momenta for $\mathrm{C}_{70}$ 's molecular orbitals HOMO and HOMO-1 are not known so far, and therefore we used the corresponding values for $\mathrm{C}_{60}$ 's molecular orbitals. The angular momentum quantum number of the initial HOMO-1 state $\left(\mathrm{G}_{g}+\mathrm{H}_{g}\right)$ of $\mathrm{C}_{60}$ is $\ell_{i}=4{ }^{32,57}$ and that of HOMO state $\left(\mathrm{H}_{u}\right)$ is $\ell_{i}=5$ mixed with 7. For very large $\ell_{f}$, the amplitude of the final state wave function at $\mathrm{r}=\mathrm{R}$ should always be small due to the high centrifugal barrier. Such final states will not contribute significantly to the photoelectron spectra. Therefore, we took the least possible $\ell_{f}$, i.e. $\ell_{f}=4$ (excited from HOMO) and $\ell_{f}=3$ (excited from HOMO-1). A more realistic description of the phenomenon which considers the localization of the electrons on the edge of the potential well with the mean radius leads to a potential of the form (Figure A.2, solid line) which is known in the literature as jellium potential : ${ }^{62,65,69,71,136-141}$

$$
U(r)=\left\{\begin{array}{cl}
-U_{00} & \forall r<R-\delta  \tag{A.9}\\
-U_{0} & \forall R-\delta \leq r \leq R+\delta \\
0 & \forall r>R+\delta
\end{array}\right.
$$

Here $\Delta=2 \delta$ is a thickness of the barrier. The exact meaning of the $\Delta$ is that it represents the thickness of the valence electron cloud. The main characteristics of this potential are:
(1) The potential energy $U$ of the final electron state in the $C_{60}$ molecule is still spherical symmetric, so that the final electron state has a definite angular momentum
(2) The centrifugal potential changes rapidly only inside the hollow molecule $(\forall r<$ $R-\delta)$ and can be approximated as a constant within the shell $(\forall R-\delta \leq r \leq R+\delta)$ and as a zero outside the shell $(\forall r>R+\delta)$.

The crutial in this model are two barrier jumps. This leads to a coherent superposition of two wave functions for the final state, and for the partial cross section now we have:

$$
\begin{align*}
\sigma_{i f}^{m o d}(h v) \sim & A \left\lvert\, j_{\ell}\left(\frac{R-\delta}{\hbar} \sqrt{2 m_{e}\left(h v-E_{b i n}+U_{0}\right)}-P\right)\right. \\
& +\left.j_{\ell}\left(\frac{R+\delta}{\hbar} \sqrt{2 m_{e}\left(h v-E_{b i n}+U_{0}\right)}+P\right)\right|^{2}  \tag{A.10}\\
= & A\left|j_{\ell}^{R-\delta}(h v)+j_{\ell}^{R+\delta}(h v)\right|^{2}
\end{align*}
$$

Such a cross section exhibits a beating apart from the oscillations. Since coherence, in principle, can be destroyed via the interaction with environment ${ }^{142}$ (which in this case refers to the scattering of the outgoing electron wave on the fullerene cage ${ }^{143}$ ), the equation for the partial cross section must be modified by the additional incoherent term:

$$
\begin{equation*}
\sigma_{i f}^{m o d}(h v) \sim A\left|j_{\ell}^{R-\delta}(h v)+j_{\ell}^{R+\delta}(h v)\right|^{2}+B\left|j_{\ell}^{R}(h v)\right|^{2}, \quad A, B=\mathrm{const} \tag{A.11}
\end{equation*}
$$

Since the partial cross section does not only exhibit oscillations, but also the amplitude of these oscillations decrease with the photon energy, the model function for $\sigma_{i f}$ must be multiplied by a damping function. After some elementary shapings the complete semiempirical model functions for $\sigma_{i f}$ of HOMO and HOMO-1 are given by:

$$
\begin{gather*}
\sigma_{\mathrm{HOMO}}^{\text {mod }}(h v) \sim N_{\mathrm{HOMO}} e^{-M_{\mathrm{HOмO}} \cdot h v}\left(\left|j_{\ell}^{R-\delta}(h v)+j_{\ell}^{R+\delta}(h v)\right|^{2}+B\left|j_{\ell}^{R}(h v)\right|^{2}\right) \\
\sigma_{\mathrm{HOMO}-1}^{\text {mod }}(h v) \sim N_{\mathrm{HOMO}-1} e^{-M_{\mathrm{HOMO}-1} \cdot h v}\left(\left|j_{\ell}^{R-\delta}(h v)+j_{\ell}^{R+\delta}(h v)\right|^{2}+B\left|j_{\ell}^{R}(h v)\right|^{2}\right) \tag{A.12}
\end{gather*}
$$

where $\mathrm{B} 0=\mathrm{B} 1=\mathrm{B}$ because the relative intensities of the coherent and incoherent part don't depend on the angular momentum and therefore are the same for both lines. In order to adjust these functions to the experimental partial cross sections of HOMO and HOMO$1, \sigma_{\mathrm{HOMO}}^{\text {exp }}, \sigma_{\mathrm{HOMO}-1}^{\text {exp }}$, we have to take into account the influence of the total cross section as well as one empirical background function $\mathrm{f}_{\mathrm{U}, \mathrm{HOMO}}(h v)$ (for which we used a constant value in our calculations) in order to correct the minima in the experimental data. Therefore we have:

$$
\begin{align*}
\sigma_{\mathrm{HOMO}}^{\text {mod }}(h v) & \sim \frac{\sigma_{\mathrm{HOMO}}^{e x p}(h v)}{\sigma_{\text {total }}(h v)}-f_{\mathrm{U}, \mathrm{HOMO}}(h v), \\
\sigma_{\mathrm{HOMO}-1}^{\text {mod }}(h v) & \sim \frac{\sigma_{\mathrm{HOMO}}^{\text {ex }}(h v)}{\sigma_{\text {total }}(h v)}-f_{\mathrm{U}, \mathrm{HOMO}-1}(h v) \tag{A.13}
\end{align*}
$$

For the adjustment of the fit function to the experimental data for HOMO/HOMO-1 ratio we used the following model function:

$$
\begin{equation*}
R_{\mathrm{HOMO} / \mathrm{HOMO}-1}^{\text {mod }}(h v)=\frac{\sigma_{\mathrm{HOMO}}^{\text {mod }}(h v)+f_{\mathrm{U}, \mathrm{HOMO}}(h v)}{\sigma_{\mathrm{HOMO}-1}^{\text {mod }}(h v)+f_{\mathrm{U}, \mathrm{HOMO}-1}(h v)} \tag{A.14}
\end{equation*}
$$

Here, fiting parameters are: $\mathrm{R}, \boldsymbol{\delta}, \mathrm{U}_{0}, \mathrm{P}, \mathrm{N}_{\text {номо }}, \mathrm{N}_{\text {номо-1 }}, \mathrm{M}_{\text {номо }}$ and $\mathrm{M}_{\text {номо-1 }}$. Using a well-known Levenberg-Marquardt algorithm for an estimation of the fitted parameters we got values for the HOMO/HOMO-1 ratio close to the known ones (Fig.3.31).

|  |
| :---: |
| Appendix |

## Transition from Adiabatic to Sudden Excitation of Core Electrons

Creation of a localized core hole in atoms or molecules causes relaxation process of the remaining electrons that respond with some sort of rearrangement. The time scale by which they respond to the deficiency of an electron charge (a positive hole) is determined by the kinetic energy of the excited electron. If the kinetic energy of the excited electron approaches zero (the photoionization threshold) it is moving very slowly from the ion core and the electrons in the ion lower their energy by slowly relaxing around the extra positive charge. Therefore, the resulting hole potential can be imagined to be turned on adiabatically. In a sudden removal the system will be shattered. In quantum machanical terms, other particles are "shaken" into the continuum (shake-off) or previously unoccupied bound states (shake-up). There is no time to rearange. In the other limit, the particle is dragged out and the remaining system adjusts at each stage.

It has been shown ${ }^{146}$ that the adiabatic limit is obtained when the switching-on time of the hole potential is $t \gg \hbar / E_{e x}$, with $E_{e x}$ a typical ion excitation energy. On the other hand, the sudden limit is valid when $t \ll \hbar / E_{e x}$.

Stöhr et al. ${ }^{147}$ first estimate energy dependence of the shake-up intensity based on a simplified version of the Hartree-Fock approximation. Within the Hartree-Fock approximation the shake-up intensity is given by Fermi's golden rule:

$$
\begin{equation*}
\left.\mu \sim\left|\left\langle\psi_{i}\right| D\right| \psi_{f}\right\rangle\left.\right|^{2} \tag{B.1}
\end{equation*}
$$

where $D=\sum_{i} d_{i}$ is the dipole operator. The most important contributions for deep corelevel absorption (Fig B.1) are of direct term and an exchange term. At high energies the exchange term becomes negligible and the shake-up cross section is:

$$
\begin{equation*}
\mu=\mu_{\infty}\left|1-\left(\frac{\Delta E}{E_{e x}}\right)^{2}\right|^{2} \tag{B.2}
\end{equation*}
$$

This result implies that the sudden limit $\left(E_{e x} \gg \Delta E\right)$ is reached faster if the main multielectron excitations are of low energy.


Figure B.1: Processes contributing to the shake-up intensity: direct (solid line) and exchange (dashed line). ${ }^{147} \mathrm{~K}$ corresponds to the inner shell state and $a$ to the valence shell state.

Thomas ${ }^{92}$ improved this model by taking into account correlation between the outgoing electron and the remaining atomic electrons when the transition is adiabatic. Using timedependant quantum mechanics approach his estimation gives for the shake-up intensity in the final state:

$$
\begin{equation*}
\mu^{f}=\left|V_{i f} / \Delta E_{i f}\right|^{2} \exp \left(-\frac{t_{0}^{2} \Delta E_{i f}^{2}}{\hbar^{2}}\right) \tag{B.3}
\end{equation*}
$$

where $V_{i f}$ is the matrix element of the potential $V$ due to the ejected core electron between initial state $i$ and final state $f . \Delta E_{i f}$ is shake-up transition energy. The quantity $t_{0}$ is the time for the ejected electron to move a distance comparable to atomic dimensions. If this distance is $r$ and if the velocity of the ejected electron is supposed to be constant then the shake-up intensity is:

$$
\begin{equation*}
\mu=\mu_{\infty} \exp \left(-\frac{m r^{2} \Delta E^{2}}{2 \hbar^{2} E_{e x}}\right)=\mu_{\infty} \exp \left(-\frac{r^{2} \Delta E^{2}}{15.32 E_{e x}}\right) \tag{B.4}
\end{equation*}
$$

## Electron-Ion Coincidence Set-up

In the electron-ion coincidence measurement when an electron is detected, the ion measurements circle is started and a high voltage ion extraction pulse is triggered by the next bunch marker. This enables that the ion time-of-flight and the time between the extraction pulse and the creation of the ions (so called insertion delay) are independent of the electron arrival time. The characteristic value of the extraction pulse provided by pulse generator (GPTA HVC-1000) are: maximum delay of 120 ns and rise/fall time of 15 ns . The gate for the ion detection opens only after the high voltage pulse is fully applied and closes before it starts to fall again. The electron detection is also inhibited until the full coincidence measurement cycle is finished. This is done with the combination of TAC and anti-coincidence unit which creates a gate for the electron CFD that closes very fast after an electron signal arrives. The electron time-of-flight information and the time-of-flight of each detected ion in the corresponding ion cycle are recorded in an event file from which coincidence events of any type, even a single-electron events, can later be extracted for the analysis. In order to prevent a possible time-stamp mismatch between electron and ion TDC, at least one ion event has to be detected per time stamp, which corresponds to roughly $1-2 \mathrm{~Hz}$ for the experiments in the reduced-bunch modes at BESSY or HASYLAB. This is enabled by inducing an additional signal input of so-called "fake ions" created by a 50 Hz pulse generator. In that way the "fake ions" are constantly generated and added into the signal pathway. They initialize their own ion cycle which is done at the logic OR unit in front of the ion TDC. The delay for the fake ions makes it possible to move them into a position in the ion spectrum of no physical importance (for example, at the very end of the spectrum where there are no real ions).


Figure C.1: Schematics of the electronics and signal pathways for an experiment with one electron time-of-flight spectrometer.

## List of Symbols and Abbreviations

## Symbols

| $a_{0}$ | the Bohr radius, $a_{0}=5.29177 \times 10^{-11} \mathrm{~m}$ |
| :---: | :---: |
| $A^{*}$ | (electronically) excited state of atom A |
| $A^{+}$ | singly charge ion of atom A |
| $\alpha$ | fine structure constant, $\alpha=137.0359895$ |
| $\beta$ | photoelectron angular distribution asymmetry parameter |
| $c$ | (vacuum) speed of light, $c=2.99792458 \times 10^{8} \frac{\mathrm{~m}}{\mathrm{~s}}$ |
| $e$ | the elementary charge, $e=1.60217733 \times 10^{-19} \mathrm{C}$ |
| $e^{-}$ | photo (or Auger) electron |
| $E_{\text {kin }}$ | kinetic energy of the photoelectron |
| $E_{\text {bin }}$ | binding energy of the photoelectron |
| $\hat{\boldsymbol{\varepsilon}}$ | polarization (unit) vector of the light |
| $h$ | Planck's constant, $h=6.6260755 \times 10^{-34} \mathrm{Js}$, $\hbar=\frac{h}{2 \pi}=1.05457266 \times 10^{-34} \mathrm{Js}$ |
| $h \nu$ | photon energy |
| $\hat{H}_{0}$ | free electron Hamilton operator |
| $i$ | imaginary unit, $i^{2}=-1$ |
| k | momentum vector; $k=\left(\sqrt{2 m_{0} E}\right) / \hbar$ |
| $l$ | orbital angular momentum quantum number/angular momentum (in atomic units) |
| $m_{0}$ | the rest mass of the electron, $m_{0}=9.1093897 \times 10^{-31} \mathrm{~kg}$ |
| $v$ | frequency of the electromagnetic radiation |
| $\Omega$ | solid angle |
| $p$ | momentum of the photoelectron, $p=m v_{0}$ |
| $P_{l}(\cos \theta)$ | $l^{\text {th }}$-order Legendre polynomial |
| $\Psi_{i}$ | wave function of (a general) initial state |
| $<\Psi_{f}\left\|\sum_{\mu} \mathbf{r}_{\mu}\right\| \Psi_{i}>$ dipole matrix element (in length form) |  |
| $\sigma_{i f}$ | partial cross section |
| $d \sigma_{i f}(h v) / d \Omega$ | differential cross section/angular distribution |

$\sigma_{g} \quad$ molecular $\sigma$-orbital with gerade symmetry
$\sigma_{u} \quad$ molecular $\sigma$-orbital with ungerade symmetry
$\theta \quad$ photoelectron emission angle (measured with respect to the polarization vector of the light
$v \quad$ velocity of the electron
$\varepsilon_{0} \quad$ dielectric constant
$\omega \quad$ orbital frequency
$\gamma \quad$ relativistic constant, $\gamma=\left(1-\frac{v^{2}}{c^{2}}\right)^{-1 / 2}$

[^0]RPA Random Phase Approximation
RRKM Rice-Ramsperger-Kassel-Marcus Theory
TAC Time to Amplitude Converter
TDC Time to Digital Converter
TDLDA Time Dependent Local Density Approximation
TOF Time-of-Flight
TGM Toroidal Grating Monochromator
TTL Transistor-Transistor Logic
HV High Vacuum
VUV Vacuum Ultra Violet (radiation)
XAS X-ray-Absorption Spectroscopy

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[^0]:    Abbreviations

    ADC Analogue to Digital Converter
    ARFMADS Angular Resolved Fixed Molecule Angular Distribution Spectrometer
    BESSY Berliner Speicherring Gesellschaft für Synchrotronstrahlung
    CFD Constant Fraction Discriminator
    DFT Density Functional Theory
    DOS Density of States
    EA Electron Affinity
    EXAFS Extended X-ray-Absorption Fine Structure
    FCC Face-Centered-Cubic Lattice

    FT Fourier Transformation

    FWHM Full Width at the Half Maximum

    HASYLAB Hamburger Synchrotronstrahlungslabor
    HF Hartree-Fock
    HOMO Highest Occupied Molecular Orbital
    HV High Voltage
    IP Ionization Potential
    IR Interaction Region
    LCAO Linear Combination of Atomic Orbitals
    LDA Local Density Approximation
    LUMO Lowest Unoccupied Molecular Orbital
    MCA Multichannel Analyzer
    MCP Multichannel Plate
    NEXAFS Near Edge X-ray-Absorption Fine Structure
    NIM Nuclear Instruments Module
    PES Photoelectron Spectroscopy
    RPES Resonant Photoelectron Spectroscopy

