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Electron Spectroscopy using Ultra Brilliant Synchrotron X-ray sources

by

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Abstract

The development of photoelectron spectroscopy since the early days of the technique is discussed. The focus is on the interaction between instrumental development and scientific achievements. In particular the opportunities provided by the increasingly brilliant synchrotron radiation sources are discussed. The contribution is focused on core level studies. The recent development is demonstrated by using selected examples obtained at today's most advanced synchrotron radiation facilities. The spectral resolution and intensity that can be reached at these facilities reveal new effects and provide detailed information on the investigated systems. The examples are mainly taken from studies of atoms and molecules where different effects can be most accurately identified and separated.

1. Introduction

Photoelectron spectroscopy is a powerful technique for studying many aspects of matter. The technique probes the electron structure in a very direct way. Angle resolved measurements of the valence electrons can be used to probe the band structure and the Fermi surface of crystalline solids. Core level photoelectron spectroscopy provides detailed element specific information about atoms, molecules, liquids, solids and surfaces. The inherent surface sensitivity of the technique has been very important for the development of surface science. As synchrotron radiation facilities become more and more powerful, enabling use of higher photon energies with higher brilliance, the technique expands towards new increasingly bulk sensitive directions, providing ways to study the bulk properties of samples, to make depth profiles and to study e.g. buried interfaces.

The first major break-through for core level photoelectron spectroscopy was the discovery of the chemical shift fifty years ago [1-4]. The technique has continued to develop and new applications have opened up continuously. There are a number of important factors that have pushed this development. There has been a dramatic development of the electron spectrometers. The energy resolution has improved by orders of magnitude over the years. Also the angular resolution has improved as new spectrometer solutions have been introduced. The sensitivity of the spectrometers has also developed dramatically, not the least due to the implementation of various multi-detection techniques. There are also opportunities to incorporate an analysis of the spin state of the photoelectrons. Much of the development can be explained by improved detectors, better electronics, more stable power supplies and the dramatic improvement of the computer technology. The most important factor in the field is the development of increasingly brilliant synchrotron radiation light sources. Today, most advanced photoelectron spectroscopy measurements are performed using synchrotron radiation. Some very high resolution band structure studies at very low photon energies are performed using laser radiation. Furthermore, laser based sources are used when performing ultra-fast time-resolved measurements.

This contribution will mainly focus on core level photoelectron spectroscopy. The long-term development of this technique can be nicely illustrated by the successive improvement of the classical C 1s photoelectron spectrum of the ethyl-trifluoroacetate molecule [4]. This

molecule was designed to demonstrate the power of the core level chemical shift for determining the chemical composition of a system. The first recording was published in the first monograph of the ESCA group in Uppsala [5]. The spectrum shown in the upper part of Fig. 1 was recorded by a magnetic spectrometer and was excited by non-monochromatized X-rays from a stationary anode. The sample was in this case frozen out on a backing. The C1s spectrum shows four clearly resolved peaks corresponding to the four chemically inequivalent carbon atoms in the molecule. The lines were found to have the same intensity within the error limits, which indicated a direct relation between stoichiometry and intensity.

Fig. 1 The C1s core level spectrum of ethyl-trifluoroacetate. The upper spectrum from Ref.[5], is obtained using a solid sample and non monochromatized MgK_{α} radiation to excite the spectrum. The lower spectrum from Ref. [6] was obtained in the gas phase using monochromatized AlK_{α} radiation for excitation.

In the lower part of Fig. 1 we show the corresponding spectrum recorded a decade later, this time from the gas phase molecule [6]. In this case a hemispherical electrostatic analyser was used. Furthermore, the spectrum was excited by monochromatized AlK_{α} X-rays from a rotating anode. The improvement in resolution is evident. The lines are now completely separated, allowing a very precise determination of the binding energy shifts. There were hints of some differences in the line profiles in these recordings. However, the resolution was not sufficient to allow any definitive conclusions in this direction at that time.

In Fig. 2 a recent recording of the same spectrum is shown [7]. The spectrum was in this case obtained at SOLEIL in Paris, which is one of the most powerful third generation synchrotron radiation facilities today. The resolution was 40 meV, i.e. more than 10 times

better than in the spectrum in the lower part of Fig. 1.

Fig. 2. The C1s core level photoelectron spectrum of ethyl-trifluoroacetate recorded at the PLEIADES beamline at SOLEIL. The energy resolution was 40 meV and it is seen that the linewidths are essentially determined by inherent effects: Lifetime broadening, presence of two conformers and vibrational broadening. Reprinted from Travnikova et al. [7], Copyright 2012, with permission from Elsevier.

In spite of this, we note that the observed overall line widths are almost the same as in the previous spectrum. However, it is now clearly seen that the line profiles are significantly different for the different carbon atoms and that they contain considerable fine structure. Each peak must consist of a number of features. In order to interpret these line profiles and extract the information they contain, it is necessary to consider the details of the photoionization process and to incorporate modern theoretical methods. It is furthermore seen that the intensity ratios are not exactly the stoichiometric 1:1:1:1 ratios. This is due to multi-electron effects and to the fact that the photoionization cross-section is not simply a property of an individual atom in the molecule but is affected by the surrounding atoms in the molecule.

For the analysis of the spectra we must consider the dynamics of the core hole states, giving rise to complex vibrational profiles of the lines. First of all we observe that the overall width is largest for the $-\text{CH}_3$ carbon, and that the lines seem to be narrower as the number of hydrogen ligands gets smaller. This is expected considering the large vibrational excitation energies for the C-H stretch mode of the core hole states. It can be noted that this splitting is much larger than the lifetime broadening of the C1s core hole state. In spite of this there are no clearly resolved lines implying that many more vibrational modes contribute to the spectra. A detailed analysis also revealed that one must consider the presence of two conformers at room temperature: anti-gauche and anti-anti. The

calculated model vibrational profiles for these two conformers are included in Fig. 2 and it is seen that the spectrum can be very well reproduced.

In order to give a more detailed view of the complexity of the line profiles we show in Fig. 3 how one of the lines is composed. The line profile is very well reproduced by calculations. First of all there is the influence of the various stretching modes. The CH stretch corresponds to an excitation energy of about 400 meV, the other modes have lower vibrational energies. In particular it is found that it is very important to consider the whole

Fig. 3. An expanded detail of Fig. 2 showing the C1s peak from the CH₂ carbon. The C-H stretch mode gives a large splitting, but it is also seen that there is a multitude of torsion modes contributing to the observed line profile. In addition, the presence of the two conformers gives additional contribution to the profile. Reprinted from Travnikova et al. [7], Copyright 2012, with permission from Elsevier.

multitude of vibrational states related to the various torsion modes. Furthermore, one must treat separately the line profiles for the two conformers of the molecule. It is found that there is a shift of around 100 meV between these two profiles. When considering all these effects, the spectral line profile can be very well reproduced by the calculations. This example shows that this type of measurements combined with a thorough theoretical analysis provides an opportunity to investigate many important properties of molecules. Not the least, this analysis reveals the importance of the torsion modes which are excited by the perturbation induced by the core hole photoionization. This type of studies may for instance be used to get insight into related types of phenomena like protein folding.

In this paper we will discuss some aspects of the development of high resolution photoelectron spectroscopy. In particular we will focus on the role of Synchrotron Radiation. We will discuss the development of the experimental facilities and the experimental equipment over the years and discuss where we stand today. We will give a few illustrating examples of effects that can now be studied with the resolution available at today's most modern facilities and beamlines. We will mainly focus on core level photoelectron spectroscopy. There has been an equally important development of valence photoelectron studies which we will only briefly comment.

2. Experimental development

Photoelectron spectroscopy has developed continuously for more than 50 years and the development continues. This is due to advances in many fields. The electron spectrometers have changed dramatically over these decades. Fig. 4 shows four types of electron spectrometers constructed in Uppsala which illustrate this development. The evolution of the X-ray sources has been even much more dramatic. The original measurements were performed with standard X-ray tubes as the excitation sources. Today, the most advanced measurements are performed with third generation synchrotron radiation facilities being more than ten orders of magnitude more brilliant than the original X-ray sources. In addition, all the other types of instrumentation included in the experimental set-ups have undergone dramatic developments.

When photoelectron spectroscopy was first developed in the 1950s and 1960s one used the type of magnetic spectrometers originally developed for nuclear physics and beta-ray spectroscopy, see Fig 4a. As the excitation sources one usually used Cr or Cu anodes, which meant that the kinetic energies of the photoelectrons were typically several keV. These high energies were required for the operation of the electron detectors used at that time. The relatively high photon energies implied that the ionization cross-sections were quite low and the spectral resolution was of the order of a few eV. In spite of this, many of the basic properties of photoelectron spectroscopy were established already at this time, like the core-level chemical shift. The spectrum in Fig.1a was obtained by a spectrometer of this type [5].

Fig 4. Four spectrometers developed in Uppsala. a) The first "iron free" magnetic electron spectrometer from Kai Siegbahn's pioneering group [5]. b) The first electrostatic gas phase electron spectrometer with x-ray monochromator and multichannel detection [6]. c) An advanced modern electrostatic electron spectrometer from VG Scienta [8]. d) The recently developed Angular Resolved Time Of Flight electron spectrometer (ARTOF) [9,10].

In the 1970s high resolution electrostatic spectrometers were developed. Furthermore, it was realized that the narrowest core levels of all elements in the Periodic Table could be reached using lower photon energies. These X-ray transitions were also intrinsically narrower, which led to improved spectral resolution. MgK_α and AlK_α radiation at 1254 eV and 1487 eV, respectively, became the most used excitation sources. At this time one also started to develop monochromators for the AlK_α radiation. In the most advanced versions these were designed to collect a very large solid angle of the emitted X-rays [11]. Another important development was the introduction of multi-detection schemes. This led to spectrometers with a much improved information rate and with an optimal resolution typically in the range of 0.4 to 1 eV. The spectrum in Fig.1b was obtained with a spectrometer in Uppsala which pioneered many of these developments and which is shown in Fig. 4b [6]. This electrostatic spectrometer was equipped with a water cooled rotating X-ray anode, it used a quartz crystal monochromator for the AlK_α radiation and it incorporated a 2D electron detector based on multichannel plates, a phosphorus screen and a TV-camera readout. At this time commercial spectrometers with similar characteristics were also developed like for instance the Hewlett Packard 5950A electron spectrometer [12]. The development of this type of spectrometers continued and in Kai Siegbahn's laboratory in Uppsala a work to optimize all different components of this type of

ESCA spectrometers started. Two spectrometers of this type were built, one for gas phase samples and one for solids and surfaces. These spectrometers became quite complicated but nevertheless produced a lot of excellent results. In fact it is only quite recently that gas phase results of higher quality around the AlK_{α} excitation energy have become available.

However, already in the 1970s but particularly in the 1980s the power of synchrotron radiation as an excitation source for photoelectron spectroscopy started to become evident. The pioneering facilities, such as DORIS in Hamburg and SPEAR at Stanford, were so called first generation storage rings. These were facilities, originally designed for nuclear and particle physics experiments, but that could also deliver synchrotron radiation from the bending magnets. Following the success of these facilities, second generation storage rings started to appear. These were optimized for delivering synchrotron radiation of highest possible brilliance from the bending magnets. Among facilities which made important contributions we note SRS at Daresbury, Tantalus in Madison, Wisconsin, SUPER-ACO in Paris, Photon Factory in Tsukuba and NSLS at Brookhaven.

Synchrotron radiation provided a large number of new opportunities. The exciting radiation could be fully tuned in the range from a few eV to several keV. Many beamlines also allowed a full variation of the polarization state of the photons. The tunability of the photon energy made it possible to vary the cross-section of different photoemission lines. In some cases very large cross-section variations could be obtained by resonant photoemission. The tunability also made it possible to vary the surface sensitivity for solid samples. It was also possible to perform measurements at quite a good spectral resolution, for example for shallow core levels a resolution of the order of 100 meV could be reached. Already the early use of synchrotron radiation implied a very large boost for the electron spectroscopy field.

The development of insertion devices like undulators initiated the construction of third generation storage rings. These facilities are optimized to provide optimum electron beam conditions in the straight sections of the storage ring where the insertion devices are placed. In the 1990s such facilities started to come in operation, the first ones directed towards spectroscopy work being ALS at Berkeley, ELETTRA in Trieste, MAX II in Lund and BESSY II in Berlin. At the same time new and improved monochromator solutions were developed. Furthermore, new generations of electron spectrometers were designed

to utilize the properties of the synchrotron radiation in the best possible way. Such an example is the Scienta SES-200 electron spectrometer [8]. The principles behind this instrument have been further developed and VG Scienta today produces the advanced version R-4000 which is seen in Fig. 4c. The results from SOLEIL in this report were obtained using such an instrument.

With the third generation facilities one reached experimental conditions where the resolution in photoelectron spectroscopy experiments are typically only a few tens of meV, in some cases even a resolution of about 1 meV can be achieved. The third generation facilities are still developing. Especially a number of facilities with electron energies around 3 GeV have more recently been constructed which give excellent opportunities for advanced spectroscopic measurements in the soft X-ray regime. Such facilities are SLS in Villigen, SOLEIL in Paris and DIAMOND in Didcot, Oxfordshire. These are excellent sources for high resolution photoelectron spectroscopy experiments. There are two beamlines at SOLEIL, which have contributed significantly to the topic of this review: PLEIADES and GALAXIES. The PLEIADES beamline is dedicated to soft X-ray studies (9 - 1000 eV) of gas-phase atoms, molecules, clusters, and nanoparticles and their ions [13]. GALAXIES is a tender X-ray beamline (2.3 - 12 keV) hosting a resonant-inelastic X-ray scattering (RIXS) as well as a high energy X-ray photoelectron spectroscopy (HAXPES) end-stations [14].

With the higher electron energies and with the much improved brilliance of the most recent synchrotron radiation facilities, the field of high resolution photoelectron spectroscopy is furthermore extended to higher photon energies. Excellent conditions can now be reached also in the range of several keV. This opens up the field of bulk studies and investigations of buried interfaces. This development also provides better opportunities to study samples related to applied and industrial projects and for investigating *in situ* processes.

It is now also possible to build synchrotron radiation sources that approach the diffraction limit. PETRA III in Hamburg has reached an emittance of 1 nmrad. NSLS II at Brookhaven will soon be commissioned with an electron beam emittance below 1 nmrad. MAX IV, which is presently under construction in Lund, has defined a new step in this development with its multibend achromat lattice. The 3 GeV ring with a circumference of 528 m will reach an electron beam emittance of only 0.2-0.3 nmrad. In addition to this, the MAX IV

facility will also contain a smaller 1.5 GeV storage ring which will host a number of VUV and soft X-ray beamlines. The MAX IV concept is now adopted at some other leading facilities in the world which will be upgraded according to these concepts, e.g ESRF and APS.

Another line of development, where storage ring facilities will play an important role, is related to time resolved studies. Free Electron Lasers are the ideal sources for producing ultra-short X-ray pulses in the femtosecond range and with extreme peak brilliance. However, this type of source is not evidently ideal for high resolution photoelectron spectroscopy. A major limitation for such measurements is the Coulomb interaction between the emitted electrons. This will spread the emitted electrons both in terms of energy and angle. The magnitude of the Coulomb repulsion effects depends on parameters like photon flux, pulse length and on the size of the illuminated spot. This sets an upper limit for what photon density on the sample can be used for a certain spectral resolution. These effects are important already at present third generation facilities as shown experimentally by Zhou et al. [15]. These effects have also been accurately modeled by Hellmann et al. [16] In order to increase the information rate, for high resolution measurements, it is therefore an advantage to use a photon source which operates at a high repetition rate, such as a storage ring facility. In this way one can reduce the number of photons per pulse and still maintain a good signal. The pulse length is in this case usually limited to the picosecond (ps) regime. When a storage ring is operated in the so called low-alpha mode one may also reach a little below one ps. However, the ps regime is very relevant for many important processes. An interesting proposal is the BESSY VSR (Variable pulse length Storage Ring) project [17] where the BESSY II facility will be upgraded to a high repetition rate, variable pulse length, source operating in the ps regime.

In order to improve the conditions for very high resolution time resolved photoelectron spectroscopy it is also important to optimize the transmission of the electron spectrometer. Fig. 4d shows a new type of time-of-flight electron spectrometers (ArTOF) that has been developed in a collaboration between the Department of Physics in Uppsala and VG Scienta [9,10]. This type of spectrometer uses the same type of electron lenses as the modern hemispherical spectrometers. However, in this case the energy analysis is based on the time of flight of the electrons in the electron lens which means that it has to be

optimized in a slightly different way. Under certain conditions an optimum resolution of well below 1 meV can be reached with this type of spectrometer. A major advantage is that the acceptance angle is very large. All electrons, entering the spectrometer in a cone of opening angle of up to $\pm 30^\circ$ and in a certain energy window, are detected. In this way photoelectron spectra can be recorded at a much lower photon flux than with a conventional setup, thereby providing opportunities for minimizing space charge broadening. The high transmission is also very favorable for time-resolved studies and for coincidence measurements.

The time-of-flight scheme requires a pulsed photon source. In the case of the ArTOF spectrometer it can operate at a repetition rate of up to a few MHz. This is well matched to a storage ring operated in the single bunch mode. Since this mode of operation implies a major restriction in terms of available beam time for the general users, a set of developments have been initiated in order to be able to use the ArTOF spectrometer during so-called hybrid mode operation. This mode, where one electron bunch is isolated in the storage ring within a sufficiently large window where there are no other stored electrons, is normally available at many storage ring facilities. In this way it is possible to arrange a certain beamline such that it only sees this single bunch. All other experiments can then still benefit from the high total current of the storage ring. One way to select the radiation from this isolated electron bunch is to use a mechanical chopper. Such a solution is under development at HZB/BESSY II. Another possibility is to modify the path or the extension of the hybrid electron bunch in the storage ring. In this way it is possible to arrange a beamline in such a way that the X-rays from this bunch can be separated from the X-rays from the main bunch train [18,19]. A detector gating technique has also been developed where it is possible to block the electrons originating from the general bunch from reaching the detector [20].

3. Broadening effects in photoelectron spectroscopy

Since the start of photoelectron spectroscopy there has been a continuous development of the instrumentation which has led to dramatic improvements of the quality of the data. At the same time new theoretical approaches have been developed and it has been possible to model the spectra with increasing accuracy. This has led to new understanding of the

basic concepts and photoelectron spectroscopy has developed into a widely used technique in physics, chemistry, technology and industrial applications.

In order to extract the relevant information from the spectra it is necessary to have a detailed understanding of the photoionization process itself. The level of understanding will always be related to the level at which the experiments can be performed. Without appropriate instruments and measurements, the theoretical approaches cannot be validated.

The basics of photoelectron spectroscopy is that an X-ray or UV source is used to excite the electrons in the system to the continuum and that an electron energy analyzer is used to disperse the kinetic energies. In the simplest system, the hydrogen atom, the electron will, at reasonably low temperatures, be in the ground state and after photoionization the electron will have a well-defined energy. For more complex systems - already the case of the He atom is in this respect a complex three body system - the concept of a precisely defined energy is modified due to the interaction between the particles. In the simplest case of the hydrogen atom the electron spectrum would consist of electrons with one single energy. However, we will never observe this. There will be a distribution of excitation energies from the photon source. There will also be a finite resolution of the electron spectrometer. This implies that also in the ideal case of hydrogen we would see a peak in the electron spectrum with a characteristic profile.

We usually refer to all effects that broaden a spectrum as *line broadening effects*. Some of these effects are due to the limitations in the experimental setup, and some are due to *inherent broadening effects* related to the excitation process and to the investigated system. At several stages of the development of photoelectron spectroscopy it has been discussed whether new improvements of the resolution will really provide new information. The basis for these discussions has been that there are certain intrinsic broadening effects which will anyway mask all finer details in the spectra. However, in the end it has been found that when the resolution is improved new information appears. What has been considered to be unavoidable broadening effects at a certain resolution level can be investigated and modeled in detail at higher resolution, whereby important new information can be extracted.

For the modeling and interpretation of the spectral shapes it is often useful to separate these effects into different contributions and to treat these separately. In this way the understanding of the spectroscopic process and about how to extract the important information from the spectra develops in the best way. In principle, it is possible to simulate the full spectrum using a so called *spectral function*. However, such an overall description is very rarely useful for relating the electron spectrum to other physical and chemical properties. The most used approach is instead to start with the notation of very precise states also for more complex systems and then to add the influence of different effects. This may be done by adding these one by one. However, in some cases different effects cannot be well separated and a detailed analysis requires that they are treated together.

For solid samples there are some unavoidable broadening mechanisms, which will mask other contributions and which will make it impossible to fully separate these. Such an example is the presence of the continuum of low lying electronic excitations for metallic solids which will create asymmetrically broadened core electron lines due to shake-up processes [21].

Furthermore, for solids one will usually probe chemically different sites. The presence of the surface will for instance lead to different chemical surroundings for the atoms located at different depth in the sample [22]. In some metallic solids well separated peaks are found for the outermost surface layer [23]. However, if the surface core level shift is small this will simply lead to broadened peaks. Furthermore, also deeper layers may be slightly shifted due to the presence of the surface. In the case of Be distinct peaks have in fact been seen for the first four atomic layers [24], see Fig. 5.

Due to these solid state broadening effects we will, to a large extent, use examples for atoms and molecules when discussing *the different types of broadening mechanisms*. These different contributions are, however, as important for all other types samples and the knowledge achieved by studying atoms and molecules give important insight into the interpretation of photoelectron spectra in general.

Fig. 5. Be 1s spectra from Be(0001) recorded at different photon energies . Separated peaks are seen for the first four surface layers, with the deeper layers at higher binding energies. The peak at the highest binding energy corresponds to the bulk. The insert shows the model line shape used for fitting of all the peaks except the one corresponding to the top surface layer. The model line is constructed assuming multiple excitations of phonons. Reprinted with permission from Andersen et al. [24]. Copyright 2001 by the American Physical Society.

3.1 Lifetime broadening

As soon as an atom contains more than three electrons, the inner electron photoionization process will be followed by a decay of the remaining electrons to a lower state. In this process a photon can be emitted or another electron may be emitted in an Auger process. Since the time for the decay is uncertain due to the Heisenberg principle, also the notion of an exact energy will be modified. We will instead observe a peak with a certain *lifetime broadening*. In this way we start out from the concept of an "ideal" process and we add the effects of what happens to the final state by a decomposition of the problem. It can be added that also the lines in an electron spectrum from the hydrogen atom will be lifetime broadened. The final state of the system contains one continuum electron and the remaining proton. But this system is not alone in the universe. **Even the vacuum contains fluctuations that may de-excite the system with an (extremely small) contribution to the line width. Such a deexcitation is of course more or less impossible to measure, but this is**

Fig. 6. The $4p_{3/2}$ core photoelectron spectrum of Hg in the gas phase [25,26]. The FWHM is 5.4 eV and the profile is almost 100% Lorentzian. Reprinted from Martensson et al. [26], Copyright 2015, with permission from Elsevier.

interesting since it highlights the importance of how we partition the studied system. In order not to get lost in very minor effects we restrict the studied system to a particular sample and we disregard the rest of the universe. In the case of atomic and molecular physics, such a separation can be made in practice by using dilute samples where we can disregard the interaction with other atoms or molecules in the sample. For solids or liquids this type of partitioning demands much more consideration. In such systems the theoretical treatment may for instance involve a separation between the part of the system where the core ionization occurs and where the calculations are performed at a certain level. The effects of the remaining system is then treated as modifications of these results. In this section, however, we mainly discuss the case of free atoms or molecules where it is more straight-forward to separately discuss the different contributions.

The photoionization of the outermost valence electrons leads to states which cannot decay via Coulombic decay since this process is energetically impossible. The only possible decay mechanism is via photon emission which is a slow process in this case. The lifetime broadenings are then in the sub meV range and we can normally disregard this contribution to the line widths in a photoelectron spectrum. For the inner valence levels and for core levels, Coulombic decay processes are allowed leading to *autoionization* or *Auger electron emission*.

The finite lifetime of a core level usually gives rise to a Lorentzian line profile. The lifetime broadenings for the narrowest core levels for most elements in the Periodic Table lie in the

range 0.1 - 1 eV. However, it anyway pays off to have a resolution much better than that. The Lorentzian contribution can usually be accurately extracted by fitting procedures. Due to the long tails of the Lorentzian shape this contribution to the overall broadening can often be well taken care of. In Fig. 6 we give an example of an almost purely Lorentzian profile.

A Lorentzian profile is produced when a core level interacts with one or several weak, structure-less and flat continua. In this case the decay process of the vacancy is exponential, and the intrinsic line shape can be described by one parameter, the Lorentzian line-width. The latter is related to the decay time by the Heisenberg formula.

Sometimes the interaction involves discrete states or structured continua. In such cases the line profiles are much more complex and the concept of a single lifetime parameter that describes the line profile breaks down. In the inner valence electron region (20-40 eV) this occurs frequently. In these cases one must consider more explicitly the Configuration Interaction (CI) between these different states. However, in the core region the levels are much more separated in energy, whereby the energy matchings which are necessary for these effects to occur become rather rare. In a few cases, strong CI-resonances have been seen also in core level spectra. For Xe and the neighboring elements in the Periodic Table there is a strong interaction between the 4p and $4d^{-2}nl$ states which are very close in energy [27]. This effect is particularly strong since all the main vacancies involved are located in the same main shell with a principal quantum number of 4. A similar energy matching of the 3p single and $3d^{-2}$ double hole states occurs for Kr and its neighboring elements [27,28], see Fig. 7. For studying these effects and the resulting line shapes in detail it is clear that high resolution is important.

Another case, where clearly non-Lorentzian line profiles are seen, concerns *retarded post collision interaction* [29]. In the case of exciting close to the threshold, the outgoing Auger electron interacts with the slow photoelectron giving rise to an asymmetric *post collision line profile*. Again, it is important to have the best possible resolution in order to determine these profiles.

Fig. 7. The Kr 3p photoelectron spectrum obtained using monochromatized AlK α X-rays for excitation. The lines show a multiplet structure due to configuration interaction. Reprinted from Svensson et al. [28], Copyright 1988, with permission from Elsevier.

3.2 Vibrational broadening

The final state of the photoionization process or of the Auger process can be vibrationally excited. If the individual vibrational states can be resolved, electron spectroscopy provides a very interesting tool to study the dynamics of the ionized states. If the instrument broadening and/or the lifetime broadening is larger than the typical splitting of the individual vibrational states, the vibrational bands will be observed as broadened peaks. Even in the cases when the vibrational splitting is so small that we cannot observe the individual states it pays off to use the highest possible resolution, since vibrational envelopes can be calculated and can be fitted to the measured profiles, as was demonstrated in Fig. 3. In the case of direct single photoionization it is often possible to use the Franck-Condon principle and then the line profiles follow a *Franck-Condon distribution*. If many vibrational states are populated the Franck-Condon distribution will be almost the same as a *Poisson* distribution which can be easily fitted to the data. If more than one mode is excited the analysis can be quite involved and a detailed theoretical analysis may be required. Such an example was given in Fig. 3 above.

It should be pointed out that there was initially some misunderstanding concerning the vibrational contribution to the line profile in core level spectra. In the second of the two monographs on ESCA by Siegbahn's group the general opinion in the end of the 1960's was expressed [30]: "For a molecule with a core shell vacancy the equilibrium internuclear

distance is almost the same as for the neutral molecule since the core electrons are essentially non-bonding... Thus the first vibrational level will dominate the spectrum so that the adiabatic and the vertical ionization energies are almost the same.” There was a general misunderstanding at the time when Ref. [30] was produced. For valence photoionization the bonding or non-bonding properties of a bond can be reasonably well described by the degree of overlap between the atomic orbitals involved in the bond. Since core levels are not overlapping it was thought that these should be non-bonding. However, core photoionization leads to a large reorganization of the valence electrons in the final state and thus to a reordering of the bonds. The misunderstanding was resolved only a few years later when the instrumental development in the same group made it possible to directly observe the dynamics of core hole photoionization. Clear vibrational substructure was observed in the C1s core photoelectron spectrum of the CH₄ molecule, see Fig. 8.

With the further improvements achieved at third generation facilities the analysis of core level spectra can be very detailed, providing important information about the studied systems. It should also be mentioned that the analysis is not possible using only the Born Oppenheimer approximation. The spectrum in Fig 8 has been studied many times with increasing resolution and it has been shown that the theoretical description of core level vibrational structure should involve vibronic coupling [31], as well as more subtle effects such as Fermi resonances [32].

Fig. 8. The C1s core photoelectron spectrum of CH₄ in the gas phase. Reprinted from Gelius et al. [33], Copyright 1974, with permission from Elsevier.

In the case of solid samples the vibrational excitations can be described in terms of phonon processes. Temperature dependent broadening effects have been identified since

long. The first attempt to model the phonon broadening of peaks in an electron spectrum was made by Citrin in the 1970's [34]. In certain cases, the phonon spectrum is such that the phonon excitations create distinct structures in the core level spectra. One such case is the 1s core level spectrum of Be [24]. See Fig. 5. In this case resolved peaks are seen for the four first surface layers and for the bulk and it is furthermore seen that each peak consists of a set of phonon replicas.

For adsorbates it is often found that the core electron lines are quite broad. This is a case where it was discussed if improved spectral resolution would yield much better data. However, when the resolution of the experiments improved it was seen that these profiles provide very important information about the adsorbate systems [35,36]. For a number of adsorbate systems it was at first found that the line profiles were strongly temperature dependent. For CO adsorbed on Ni(100) it was shown that this was due to the presence of frustrated translation and rotation adsorbate modes. The initial state potential energy surfaces for these modes are very shallow and many modes are excited already at room temperature. After core ionization the potential energy surfaces are much steeper and the core ionization therefore leads to large temperature dependent vibrational broadenings. When the spectral resolution was further improved it was shown that well resolved vibrational peaks could also be seen, corresponding to the excitation of CO-stretch vibrations [37]. Furthermore, the vibrational excitation spectrum was found to be characteristic of a particular adsorption site and the line shapes therefore provide important information on the details of the adsorbate systems, especially when ordered adsorbate structures are not produced [38].

Rather recently it has been realized that the phonon broadening of core electron lines using high energy excitation of the spectra is larger than at lower energies [39,40]. The mechanism behind this is the *recoil effect*. At low excitation energies the kinetic energy of the remaining ion in the photoionization process is very small and can often be neglected. At higher energies the recoil energy is larger and it will be distributed to phonons in the case of solid samples and to vibrational states in the case of free molecules. This means that the distribution of states will be markedly different from a Poisson distribution and furthermore that it changes with the excitation energy. The recoil energy is not only influencing the excitation of vibrational states. It has also been demonstrated that the rotational recoil plays an important role [41]. This will be further discussed below.

The influence of the recoil effect can only be studied if there is very high resolving power $E/\Delta E$ in the experiment. The necessary resolution is about 0.1 eV at 5-10 keV primary energy. It can be noted that modern Hard X-ray Photo Electron Spectrometers (HAXPES) today can achieve a resolving power of around 100 000. Also modern hard X-ray monochromators have a similar resolving power. With the latest developments in the field these effects can now be studied in quite some detail.

3.3 Rotational broadening

Using very high resolution at relatively low kinetic energies it is possible to disentangle rotationally excited final states in photoionization of relatively light molecules [42]. The effect is smaller than 0.1 eV and is normally observed only as a rotational contribution to the broadening of the lines. In a few cases of diatomic molecules individual rotational levels have been resolved [43]. The modeling is in this case reasonably straightforward. For multi-atomic molecules one has to make rather drastic simplifications in the analysis.

3.4 Thermal broadening

High resolution studies of gas phase samples require special considerations when it comes to the line profiles. This is due to the fact that the atoms or molecules in a gas phase sample have initial kinetic energies and momenta corresponding to their thermal motion. Even if the thermal energies are small as such, there will be a cross term in the expression for the energy of the photoelectrons which in the case of photoionization of an atom amounts to

$$\mathbf{p}_e \cdot \mathbf{P}_{\text{ion}}$$

This cross term gives the so called translational Doppler broadening and it falls out when the kinetics is worked out for the system of the ionized atom and the photoelectron. In this expression $\mathbf{p}_e$ and $\mathbf{P}_{\text{ion}}$ are the momenta of the outgoing electron and the remaining ion, respectively. Since the electron and ion in a gas phase sample move in any direction with respect to the spectrometer lens axis, one has to integrate this expression over all possible angles which will result in a Doppler broadening of the observed electron peaks. This broadening can be described by a Gaussian curve with the Full Width at Half Maximum

(FWHM) proportional to the square root of the absolute temperature of the sample gas and proportional to the kinetic energy of the photoelectron divided by the molecular mass of the final state ion. The existence of Doppler broadening was considered already in Ref. [30]. As an example, the translational Doppler broadening of the He1s electron peak at room temperature is 62 meV for 100 eV kinetic energy of the photoelectrons.

For a molecule the situation is more complex, since the recoil energy will also be distributed to internal motion, both rotational and vibrational. The recoil itself changes the envelope of the rotational and vibrational bands and it causes a shift in the vertical ionization energy. This effect is dependent on the kinetic energy of the outgoing photoelectron. The thermal Doppler broadening is due to the translational, vibrational and rotational kinetic energies of the ground state and is therefore dependent of the temperature of the sample gas [44]. For very high resolution studies the Doppler effect (rotational, vibrational and translational) defines the ultimate limit of the resolution .

Finally, it can be noted that the post-collision broadening decreases with the kinetic energy of the outgoing photoelectron, whereas the Doppler broadening increases. Therefore, there is a minimum for the photoelectron line-width which depends i.e. on the lifetime of the studied core-level and of the mass of the ion.

3.5 Broadening due to partial core hole delocalization

Core orbitals are characterized by a very small (almost zero) overlap with the orbitals of neighboring atoms. In fact, the wave functions of core levels can be very nicely described by the atomic wave functions. However, for very strong bonds, the distance between the atoms can be so small that there is an overlap between the core orbitals. This also implies that the core hole state will be split into sub-levels due to the interaction of the core electrons. The first indication that this was possible to observe was made by Kempgens et al. [45]. They found a *gerade-ungerade* (g-u) splitting of the C1s core level of about 0.1 eV for one of the most clear cases, namely the C₂H₂ and C₂D₂ molecules. As long as the experimental resolution was worse than 100 meV this effect could only be analyzed in terms of some small effects on the line broadenings. However, with the third generation storage rings the resolution was pushed to a level where the σ_g and σ_u states of the C1s ionization in C₂H₂ could be fully resolved, see Fig.9. Similar splittings have recently been seen for N1s in N₂ [46] and in a few other cases.

Fig. 9. The $C1s$ photoelectron spectrum of C_2H_2 and C_2D_2 . In addition to the vibrational splitting it is possible to observe the (partial) delocalization of the $C1s$ core orbitals in terms of a $g-u$ splitting. This splitting is strongly dependent of the interatomic distance and is by an order of magnitude smaller for ethene and practically unobservable for ethane. Reprinted with permission from Borge et al. [47]. Copyright 2000 by the American Physical Society.

3.6 Molecular and crystal field splittings

It is well known that atomic levels with angular momentum ≥ 1 are split into doublets due to spin-orbit interaction, for example a $2p$ level is split into two components, $2p_{1/2}$ and $2p_{3/2}$. The latter level is degenerate and can be further split by external fields. For solids, such strong fields can be generated by the neighboring atoms in the crystals. Such a splitting may be quite large and crystal field splittings have been known since many decades.

For molecules like H_2S or HCl the situation is quite different. The two $S2p$ spin-orbit split core levels in H_2S were not observed to have different line shapes until the resolution in the spectra became better than 100 meV. It was then seen that the $2p_{3/2}$ line could be resolved into two components with equal intensity [48]. This splitting is caused by the so called molecular fields, created by the two hydrogen ligands. The splitting between the two components is about 100 meV but curiously enough no corresponding splitting was observed in the Auger spectrum. This latter observation was actually made earlier [49] using much worse resolution than in the SR based experiment. In this study a small shift of

50 meV of the spin orbit splitting was observed when comparing the Auger and photoelectron spectra. The explanation of this effect is that the core orbitals are modified by the molecular field and that we have states of different symmetry in the molecule for the different modified orbitals [50]. The Auger process is usually very insensitive to orbital symmetry. However, in this case it turns out that the transitions to the molecular field split component with the next largest kinetic energy are strongly quenched for symmetry reasons.

4. Resonant photoemission

Resonant photoemission is a powerful tool to investigate many systems in atoms, molecules and solids. At a core edge, there may be two routes leading to the same ionized final state: the direct photoemission and a process where a core electron is excited to an unoccupied orbital, whereafter this state decays via a Coulomb mechanism. Resonant photoemission enables detailed studies of valence electron features at core edges. The emission from a particular atomic species can be highlighted and certain symmetries of the final states can be enhanced. This is frequently used to enhance the 4f and 5f emission in lanthanides and actinides, respectively.

The same type of process was identified when studying X-ray excited Auger spectra. When exciting near to a core ionization threshold, strong resonant emission of autoionization electrons was observed. When the resolution was improved it was found that the observed line widths for these processes were not limited by the lifetime of the core hole state. In analogy to optical anomalous scattering the term Auger Resonant Raman effect was introduced. In such a case also the energy of the observed electrons disperse with the photon energy, in contrast to the regular Auger process, where the outgoing electrons have constant kinetic energies. In a simple picture this is a mere consequence of the fact that there is only one outgoing electron and one ion in the final state. Therefore, the kinetic energy must be linear dependent of the photon energy of the exciting radiation.

When studying a system under resonant Raman conditions [51] the exciting radiation contributes to the spectral broadening as in direct photoemission, opening a possibility to probe core level decay processes with "sub-natural" spectroscopic resolution [52,53].

Fig.10 gives an example of recent advances of high resolution resonant photoelectron spectroscopy. It presents a comparison between the $4d^{-1}6p$ resonant Auger spectrum of Xe measured at SOLEIL [54] and at the MAX I storage ring at MAX-lab [55]. Subtracting the contribution from translational Doppler broadening of 7 meV gives an instrument resolution of 11 meV and 31 meV for the two recordings, respectively. The improved resolution was made possible by the large increase of brilliance when going from a second to a third generation SR-facility. The earlier measurements were pioneering, since they

Fig. 10. An example of the Xe $4d_{5/2}^{-1}6p$ resonant Auger spectrum measured with 65.110 eV photons. Spectrum (a) is from Ref. [55] and (b) from Ref. [54], both recorded with an electron emission angle of 90° with respect to the polarization vector of the x-rays. Reprinted figure (a) with permission from Aksela et al. [55]. Copyright 1996 by the American Physical Society.

proved the existence of the the Raman conditions in the soft x-ray regime. In the latter study new states became visible and it was possible to increase the precision in the determination of the transition energies, intensities and angular anisotropy parameters.

"Sub-natural" line-widths have also been observed in Auger-photoelectron coincidence spectroscopy [56].

Some of the final states obtained by the de-excitation process are also accessible via direct ionization. Often the cross-section of the non-resonant process is much smaller than of the core-assisted process, especially when exciting deep core levels. However, in many cases the contributions from both pathways have to be taken into account. This leads to Fano-type profiles in the photoionization cross-section. Furthermore, the lifetime of the core-excited state may be so short that several vibrational or electronic states are simultaneously excited in the intermediate state, leading to a similar situation with multiple pathways to the same final state. A full description of these kind of resonant processes requires that all cross-terms are taken into account. Recently, interferences between the direct and resonant channels were seen in a study of the photoemission anisotropy parameter β of the resonant Auger spectrum ($O\ 1s \rightarrow \sigma^*$ excitation) of the O_2 molecule [57]. This Vibrational Scattering Anisotropy (VSA) was seen also in the acetylene molecule [58], where the full description of the spectral shapes required inclusion of two other pathways, scattering through the core-excited bending states with orthogonal orientation of the molecular orbitals, and scattering through two wells of the double-well bending mode potential.

Resonant measurements may also be used to obtain important information on the dynamics of the core excited system. The resonant spectra are sensitive to the evolution of the system on the time scale of the core hole decay. The typical time scale of core hole decay is a few fs, for deeper levels this extends to the attosecond regime. This is sometimes referred to as the “core hole clock” [59,60]. By detuning the excitation energy away from the core resonance it is furthermore possible to shorten the effective excitation-deexcitation time [61]. The “core hole clock” can be applied in numerous ways. A recent study of this kind can be found in Ref. [62]. In this paper the Cl 1s core level of CH_3Cl molecule was used, giving a time reference of about 1 fs. This time is long enough for the nuclei to start to rearrange. Resonant Inelastic X-ray Spectra (RIXS) and Resonant Photo Electron spectra (RPE) [62] were studied after excitation of a Cl 1s electron to the $8a_1$ lowest unoccupied molecular orbital (LUMO). By following the behavior (energy dispersion and broadening) of the RIXS and RPE lines as function of the photon energy detuning it was possible to unravel subtle changes in the forms of the final state potential energy surfaces. In the case of RIXS, the final state has a $Cl\ 2p^{-1}8a_1^1$ configuration while the RPE

final state is $\text{Cl } 2p^{-2}8a_1^1$, both being dissociative states, but with slightly different shapes of the potential energy surfaces.

By using a very narrow bandwidth for the excitation it is possible to selectively excite a single vibrational level of an excited state of a molecule. The instantaneous electronic excitation is followed by an evolution of the nuclear wave-packet on the potential energy surface of the excited state. Under certain conditions the excited system can develop towards a geometry far from the original equilibrium. Hence, the excitation and de-excitation processes take place in different geometries. In this way, final state geometries can be probed, which are not accessible with direct photoionization. This provides a powerful technique to map potential energy surfaces [61,63].

The excited states are not always bound. The molecule may start to dissociate upon the excitation, and if the lifetime is long enough, it might happen that de-excitation takes place in such a way that strong lines corresponding to decay in free atoms are observed. This phenomenon was reported 1986 by Morin and Nenner in [64]. Nowadays the acronym *Ultra-Fast Dissociation* (UFD) is commonly used to describe the dissociation taking place before the electronic de-excitation. A recent review by Morin and Miron [65] gives a historical perspective on the topic and summarizes a number of recent advances.

Another experiment where the core level widths are not limiting the final resolution of the spectral profiles is when measuring Auger electrons in coincidence with the corresponding photoelectron. In this case, any shift of the kinetic energy of the photoelectron away from the “ideal” energy due to the finite lifetime of the core hole state will give an identical displacement of the energy of the Auger electron, but in the opposite direction. Using coincidence techniques we can thus measure normal Auger spectra without the inherent broadening from the finite lifetime of the core hole state. This is another case where improvements of the resolution pays off. An important aspect of coincidence measurements is that the optimum ratio between real and accidental (« false ») coincidences is obtained for relatively low count rates. The most favorable way to achieve this reduction of intensity is to have a very brilliant photon source where the intensity is reduced by operating the monochromator at very high resolution. If one then can combine this with high-resolution, high transmission electron spectrometers, there are very good opportunities for coincidence measurements [66].

5. Doppler effects.

The resolution in gas-phase electron spectroscopy studies, performed using gas cell sample at room temperature, are ultimately limited by the translational Doppler broadening. Doppler-free sample environments, like molecular beams or gas jets have been used [67], but the advantage of narrower line widths come at the cost of low sample densities. Translational Doppler is not only a disadvantageous effect but can i.e. be deployed to access useful information of the dissociating molecules [68]. For example, when considering a homonuclear diatomic molecule like O_2 , the kinetic energies of the electrons emitted from an atom moving towards the detector are blue-shifted while the kinetic energies of the ones from an oxygen atom moving away from the detector are red-shifted [69]. Such a “Doppler labeling” of the electrons have also been observed in other systems than diatomic molecules [70,71].

When a photoelectron is emitted from an atom with a momentum $\mathbf{K}$, the emitter receives a recoil “kick” $-\mathbf{K}$ due to the momentum conservation. Simon et al. [72] demonstrated this recoil effect by ionizing the K shell of Ne atoms with linearly polarized hard X-rays. Due to the anisotropy parameter of the 1s photoionization, the direct photoelectron emission drives a preferential motion of the Ne ions along the axis of the electron spectrometer (in the geometry of the experimental setup used). Thus, the Auger electrons are emitted from recoiling ions moving towards the detector or away from it. This is an Auger Doppler effect analogous to the one described in Ref. [69]. In the present case the splitting increases with the photon energy.

Recoil effects are also seen in molecules. In this case the recoil momentum is distributed between the translational, vibrational, and rotational degrees of freedom. See e.g. the recent reviews by Kukuk et al. [73] and Thomas and Ueda [74].

In a polyatomic system, the kick of the emitted electron displaces the emitter, which in turn can lead to an excitation of vibrational modes not following the Franck-Condon principle, like asymmetric stretching and bending modes in the C 1s ionization of the CF_4 molecule [75]. In the case of a diatomic molecule, 1/3 of the available recoil energy goes to the vibrational excitation and 2/3 into rotation, assuming an isotropic electron emission in the

molecular frame. Kukk et al. have measured the C 1s photoelectron spectrum of CO over a wide range of photon energies, up to 1500 eV [76]. The main focus of the article was to study the scattering of the photoelectron, which is discussed more in detail below. The measured data also show the effect of the recoil excitation which yield intensity ratios of the $v = 1$ and $v = 0$ vibrational peaks different from the Franck-Condon values. The data fit nicely with the theoretical models taking into account the recoil effects. Only at the highest energies, the experimental data points are systematically below the theoretical predictions.

Recoil excitation of the rotational degrees freedom of the molecule are seen as broadenings and small energy shifts the photoelectron lines, since in the soft X-ray regime the rotational structure is usually not resolved [77]. The rotational heating due to the recoil is closely related to the rotational Doppler effect, analogous to the translational Doppler effect and is seen as blue- or red-shifted photoelectron energies depending on whether the electron emitter moves towards the detector or away from it, due to the rotation. The effect is very small and the first experimental observation of the rotational Doppler broadening was only made in 2011 by Thomas et al. in the valence photoelectron spectrum of the N_2 molecule [78].

Recently, it was realized that the recoil induced rotational excitation and the rotational Doppler effects can be used to disentangle the contributions of the atomic orbitals of the

Fig.11. a) The high resolution electron spectrum of the 5σ orbital in HCl . The rotational envelope of the $v=3$ vibrational sub-state consists of a narrow Cl contribution σ_{Cl} (blue solid line) and a broad pedestal related to the H contribution σ_H (black solid line). b) Simulated curves of the Rotational Doppler broadening D (FWHM), and the shift Δ as a function of the kinetic energy of the emitted photoelectron. Reprinted by permission from Macmillan Publishers Ltd: [Nature Communications] Miron et al. [79], copyright (2014).

delocalized molecular orbital ionized [80], especially when the contributing atoms have a large mass difference like in the hydrogen chloride molecule [79]. Fig.11 a) shows an example of a rotational envelope of the $v=3$ vibrational sub-state of the vibrational sequence related to 5σ photoionization of the HCl molecule [79]. The peak has a clearly asymmetric shape due to the underlying rotational structure related to the angular momentum transfer (photon spin S) from the X-ray photon to the molecule creating the R and P branches ($\Delta J=\pm 1$) but also a broad, weak pedestal related to the rotational Doppler induced excitation (presented as brown stars and black solid line). The origin of this pedestal, discussed for the first time in a theoretical paper by Sun et al. [77], is the small H contribution of the 5σ molecular orbital. There is a certain probability that the fast photoelectron leaves from the hydrogen end of the molecule, and thus the H receives most of the recoil. The angular momentum $\mathbf{J}$ received by the hydrogen atom in the emission of a photoelectron with momentum $\mathbf{K}$ is $\mathbf{J} = \mathbf{R} \times \mathbf{K}$, where $\mathbf{R}$ is the distance between the H atom and the center of mass (CM) of the molecule. Since the CM is very close to chlorine atom, the angular momentum transfer is significantly larger when the electron is emitted close to the H atom.

Fig. 11b) shows a simulation of the Rotational Doppler contribution to the broadening and to the line position. The effect is small close to the photoionization threshold, but at sufficiently high energies it is even larger than the translational Doppler contribution [77]. A recent study of angularly resolved photoelectron spectrum of N_2 molecule shows that the rotational Doppler effect is very sensitive to angular effects, leading to different line profiles for final states with different photoelectron emission anisotropy [81].

Thomas pointed out that an important factor has so far been missing in photoelectron emission recoil models [82]. If the molecular geometry changes significantly, the Coriolis coupling between the rotational and vibrational modes transfers energy from rotations to vibrations or vice versa. This correction is small but, when including this effect in the case of previously published C 1s photoionization data of CO [76], the agreement between theory and experiment at high energies was improved.

6. Interference phenomena in soft x-ray photoelectron spectroscopy

Since more than 40 years there has been a discussion on the localized or delocalized character of core hole states. The problem became very visible when Bagus and Schaefer 1971 made one of the first *ab-initio* calculations of the O1s core ionization energy [83]. In this report it was found that the total energy of the core ionized system was lowered if the core hole state was allowed to break the symmetry of the molecule giving an ionization energy much closer to the experimental value found in [30]. The concept of a localized core hole was established and became the standard procedure in quantum mechanical calculations of core ionized systems. This turned out to be a very good approximation in most cases. If correlation is included in the calculations the symmetry can be kept, but the procedure becomes very much more involved.

As pointed out above, it has been possible to observe sub-structures in a few molecular spectra showing evidence of a *gerade-ungerade* splitting of the core levels [45]. With the use of third-generation synchrotron radiation facilities it was possible to partly resolve this splitting [84] in the case of the C1s level of acetylene. So far it has only in a few cases been possible to identify such a splitting, most reports have concerned C₂H₂ [47,85] and N₂ [46]. In section 3.5 above we showed the result from ref. [47]. The splitting is strongly dependent on the internuclear distance and apart from the two mentioned molecules very few other cases have revealed measurable splittings. The splitting in ethene and ethane are e.g. only 10 meV and 1 meV, respectively. Hence, the splittings are very small compared to the lifetime broadening, and also to the vibrational splittings. The *gerade ungerade* splittings of the C1s or N1s core levels are not complicated to calculate. In fact, already Snyder gave a value of 0.1 eV (close to the modern values) in the case of the N1s core level in N₂. He used Koopmans' energies and a limited database as compared to modern standards [86].

By studying inner valence levels one might get much larger g-u splittings. A recent study presents the photoionization cross-sections of the C 2s – derived molecular orbitals in C₂H₂, C₂H₄, and C₂H₆ [87]. It has been observed that the oscillation period of the g - u intensity ratio depends strongly on the carbon - carbon distance, and it has been possible

to determine bond lengths in these compounds with an accuracy of 0.01 Å. When studying inner-valence shells, one soon faces the fact that the one-electron picture is not valid and that the spectra show rather intense satellite structures due to many-body effects. These effects are also influencing the cross-sections. It is still a challenge to reproduce these effects theoretically. However, it is clear that the oscillations in the cross-sections carry quantitative information on the orbital composition and many-body effects, as well as on the bond lengths.

The g-u symmetry can have a very large impact on the spectroscopic observations. This was realized in the 1960's by Cohen and Fano who published a study where also the importance of coherence was pointed out [88]. In a recent study [89] of interference of core photoelectrons the statement of Cohen and Fano was formulated as: *In addition, a system of two indistinguishable, and hence inversion-symmetric emitters such as a homonuclear diatomic molecule, where each electron has an equal probability of being located at and hence of being emitted from either atomic site, is also a source of spatial coherence.*

From this notion it seems possible to use delocalized core hole states in order to perform "double slit" experiments to shed light on quantum optics. However, the situation is more involved since, as the authors of this reference also point out: *The molecular double-slit experiment, however, differs in this respect. Here, photoelectron scattering or diffraction, a coherence effect in momentum space widely exploited in surface science, acts as an extra source of interfering waves and governs the angle-dependent photoelectron intensity in the molecular frame.*

Zimmermann et al. [89] compared the cross-section oscillations in the case of N 1s photoionization of N₂ and C 1s photoionization of CO. Their experimental setup was based on a set of time-of-flight spectrometers, which allowed them to detect the electron emission in the molecular frame. The coincidence between the electrons and ions made it possible to study electron emission from oriented molecules. They could observe if the C or O ends pointed towards the electron analyser. In the first case the detected electrons originated either from direct emission or from a single scattering by the O atom. In the other case one detects electrons which have passed the O atom or which have undergone a double scattering event. These results for CO were used to understand the more complicated situation for N₂. In this case the N 1s cross-section exhibits oscillations due to

two phenomena: Two-centre “double-slit” coherent emission from the partially delocalized core electrons and photoelectron scattering i.e. one-centre self-interference.

In connection to a beautiful multi-coincidence study of O_2 , Schöffler et al. discussed the complexity of a molecular double slit experiment [90]. If the g-u splitting is smaller than the lifetime width of the core hole state, the Auger- and photoelectrons form an entangled system. This implies that the excitation and de-excitation processes have to be treated simultaneously. The authors conclude: *The experiment, along with the accompanying theory, shows that observation of symmetry breaking (localization) or preservation (delocalization) depends on how the quantum entangled Bell state created by Auger decay is detected by the measurement.*

Very recently, Guillemin et al. demonstrated how to obtain information about core-hole localization via post-selection of the fragmentation pathway in connection to the S 1s ionization of CS_2 [91]. When the S 1s orbital of linear CS_2 is ionized, and the core-hole is delocalised, the ion is left in a coherent superposition of states, where either the “left-hand side” or “right-hand side” S atom has a core hole. The lifetime of the S 1s level is very short, about 1 fs, and the highly excited state decays via a sequence of Auger decays which eventually lead to multiply charged states. It can be assumed that the Auger decay is local (at least in the first steps), but since the initial core-hole is delocalized, also the Auger decay must conserve the symmetry, keeping the coherence between “left” and “right”. During of the Auger decay cascade, the molecule starts to dissociate, and the delocalized nature of the initial core-hole state is seen when analyzing the three-body dissociation dynamics via Dalitz plots and Newton diagrams. Guillemin et al. noticed that there are two pathways; concerted (simultaneous emission of fragments S^+ , C^+ , and S^{2+}), and sequential (in the initial step producing S^{2+} and CS^{2+} . The latter decays later on to C^+ and S^+ . The concerted process is related to a delocalized core-hole leading to a coherent superposition of electronic states, driving the dynamics of the system to a completely symmetric dissociation (simultaneous cleavage of all bonds). We observe a symmetric distribution of S^+ and S^{2+} ions in the coincidence measurement.

The other process, sequential fragmentation, results from a localized core-hole state. The Auger decay happens locally without a symmetry conserving mirror image counterpart,

and thus the dynamics of the system different. The first step of the fragmentation is in this case asymmetric. Experimentally, this demonstration requires a tender X-ray light source with a suitable time structure, The measurements in Ref. [91] were performed at the LUCIA beamline [92] at the SOLEIL synchrotron facility. An 8-bunch mode was used. A double momentum imaging spectrometer was used to record the multiple coincidences between the photoelectron and the three ions.

As another example of controlling interference effects in core processes, we describe a recent study using UFD of the oxygen molecule. The oxygen atoms were considered as nanoscopic slits [81]. The neutral molecule is excited with soft x-ray synchrotron radiation, either to an ultra-fast dissociating electronic state or to a bound Rydberg type excited state in which the de-excitation takes place within the molecule. An electron-ion coincidence experiment was set up to measure the momentum exchange between the Auger electron and the molecular or atomic ion. If an electron is ejected shortly after the excitation, before the molecule has had time to dissociate, the recoil is distributed between both atoms (as an analog to a macroscopic case with two open slits). If the Auger electron is ejected after the UFD, only one of the two oxygen atoms receives the recoil, which is seen in the coincidence experiment as a change in the momentum of the ion. The recoil labels the «path» from which the electron originates. In the 2D plots presented in Fig. 12, showing the correlation between the resonant Auger electron energy and the emission angle in the molecular frame, the differences between these two situations are seen. In the case of excitation to the molecular (Rydberg) state the molecular frame is fixed relative to the spectrometer and a double slit pattern is visible. In contrast, for the excitation to the σ state the UFD the emission originates from a single atom. No interference pattern is visible in this case. The observed linear energy dispersion is due to the Auger Doppler effect [69].

Fig. 12. Correlation maps between the kinetic energy of the Auger electrons and the cosine of the emission angle with respect to the molecular axis θ [81]. Panels (a) and (b) show experimental data and theoretical simulations for the resonant Auger electrons emitted after an $O1s^{-1}4p$ Rydberg excitation, and panels (g) and (h) present experimental and theoretical results related to an $O1s^{-1}\sigma^*$ excitation, respectively. Reprinted by permission from Macmillan Publishers Ltd: [Nature Photonics], advance online publication, Aug 2015 (doi: 10.1038/nphoton.2014.289)

When Cohen and Fano theoretically discussed interference effects in photoionization they considered valence levels [88]. The first direct observation of this type was realized only in 2011 in a photoemission study of H_2 , N_2 , and CO [93]. In this study the vibrationally resolved valence photoelectron lines in a range of photon energies were measured, and a figure showed the intensity ratios of the vibrational peaks as function of the excitation energy. If the vibrational bands could be described by the Franck-Condon principle, the ratio should remain constant. In contrary, they observed that the vibrational ratios show an oscillatory behavior due to interference effects.

Photoelectron scattering has since a long time been used for structural investigations of solid samples, like extended X-ray absorption fine structure (EXAFS) and similar methods. These effects must also be taken into account when interpreting photoelectron spectroscopic data, also for free molecules.

Scattering induced cross-section oscillations was demonstrated by Söderström et al. [94], when they reported the ratios of the C 1s photoionization cross sections of chlorinated versus methyl carbons in chloroethane molecules ($\text{CH}_3\text{CH}_{3-x}\text{Cl}_x$). The oscillations were shown to extend several hundred eVs above the C 1s ionization threshold. This shows that the stoichiometry of a sample cannot be directly derived from the observed intensities of core electron peaks. The observed oscillations of the relative photoionization cross sections were found to be well described by state-of-the art XAFS codes. Fig. 13 shows an example of the relative cross-sections of mono- and trichloroethane, taken as an intensity ratio of the main C1s photolines for the chlorinated carbon C_{Cl} and the methyl carbon C_{H} , respectively. By studying such ratios the purely atomic contributions to the photon energy dependence of the cross-sections, as well as effects due to a varying transmission of the experimental set-ups are avoided. The spectra show a rich vibrational structure especially in the C_{H} peak, which is located at the low binding energy side of the spectrum. The heavy chlorine atoms “damp out” the vibrations and since they are **more electronegative** than the hydrogen atoms, they cause the C_{Cl} peak to shift to higher binding energies.

The systematic studies of mono-, di-, and trichloroethanes [94,95] highlight nicely certain facets of the photoelectron cross-section in gas phase molecules. Firstly, when the C 1s photoionization cross section ratio of chlorinated carbon and methyl carbon was plotted against the electron's momentum, the period of the oscillations was found to be consistent with the carbon-chlorine bond length. Secondly, the amplitude of the oscillations increased progressively with the increasing number of chlorine atoms in the molecule. Thirdly, at high photon energies, the cross-sections approach different asymptotic values, indicating a higher probability for shake processes for more chlorinated carbon atoms. As can be seen from Fig.13, the monochloroethane approaches a value of 0.96 while the trichloroethane seems to stay well below the stoichiometric ratio 1 (approximately 0.8). A fourth facet is that the intramolecular scattering strongly affects the photoionization asymmetry parameter β , even far from the ionization threshold [95]. It was also noted that even at high energies the β is below 2 and is smaller for the more chlorinated molecules.

Fig. 13. The left panel shows the intensity ratios of the main C 1s photolines, shown in the right panel of monochloroethane (black) and trichloroethane (blue). The figure is based on the same raw data as in [94]. Diamonds and circles denote the experimental points. In the left panel the solid lines show the theoretical simulations made using multiple scattering calculations. In the right panel the solid line represents the fitted line-shapes obtained using *ab initio* calculated Franck-Condon factors.

A systematic study by Ueda et al. of the central atom 1s ionization (one-centre emission) of gas-phase CH₄, CF₄, and BF₃ demonstrated how the electron diffraction can be accurately studied using oscillating vibrational ratios (v-ratio) as a function of the photon energy [96]. The ratios are not affected by the rapidly decreasing photoionization cross section and do not require accurate normalizations and calibrations of instrumental effects. Fig. 14 shows the B 1s photoelectron spectra measured with a) 225 eV and b) 570 eV photons. BF₃ is a planar molecule, and the main vibrational structure originates from the excitation of the totally symmetric stretching mode. The peaks in the spectrum a) have highly asymmetric line shapes due to post collision interaction of the outgoing photo- and Auger electrons. However, due to the low kinetic energies of the emitted electrons almost no recoil activated vibrational modes are visible. Spectrum b), however, shows a significant contribution of recoil activated modes. Fig. 14 c) shows the deviations from the Franck-Condon factors due to the scattering. The intensities of selected A'₁ vibrational peaks $v = 3 - 6$ divided by the intensity of the most intense peak $v = 2$ are plotted together with theoretical values [96]. At least the first two maxima are well reproduced in each of

these plots. At higher energies there seem to be discrepancies, but the experimental error bars are quite large.

Fig. 14. B 1s photoelectron spectra of BF₃ measured with a) $h\nu = 225$ eV and b) $h\nu = 570$ eV [96]. Experimental data points are indicated by diamonds. The total fit, including all the totally symmetric stretching A₁' peaks, the recoil activated peaks and the linear background is denoted with a thick solid line. The individual A₁' peaks are indicated by thin solid lines. The shaded area shows the sum of all the recoil-activated vibrations. c) Examples of v-ratios of the vibrational peaks $v = 3 - 6$ at the energies marked with vertical bars in b) divided by the intensity of the $v = 2$ peak (marked with an arrow). The magenta colored dotted line shows results from time-dependent DFT calculations. The black curve denotes the results of static-exchange DFT calculations. The circles with error bars indicate the experimental data points. The horizontal grey lines show the ratios between the Franck-Condon factors.

6. Summary

We have discussed the development of core-level photoelectron spectroscopy since the start of the technique in the laboratory of Kai Siegbahn in Uppsala. The importance of instrument development and its connection to scientific achievements is emphasized. In

particular the use of synchrotron radiation has led to completely new opportunities. A number of recent examples are given where new effects have been revealed by the improved brilliance of the photon sources and the much increased spectral resolution in the experiments. The examples are mainly taken from atoms and molecules in the gas phase, since in these cases the different effects can be most accurately separated.

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