



## Electron spectroscopy using ultra brilliant synchrotron X-ray sources



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### ARTICLE INFO

#### Article history:

Available online 27 April 2015

#### Keywords:

Photoelectron spectroscopy  
Synchrotron radiation  
Broadening mechanisms

### 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.

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### 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

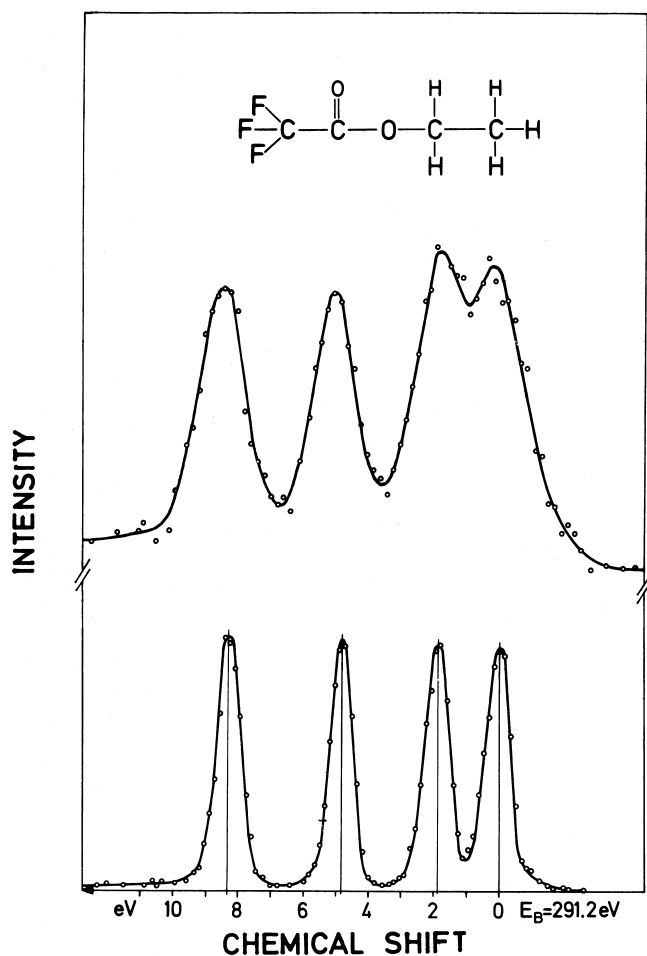
the implementation of various multi-detection techniques. There are also opportunities to incorporate an analysis of the spin state of the photoelectrons. Much of the development can be explained by improved detectors, better electronics, more stable power supplies and the dramatic improvement of the 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.

In the lower part of Fig. 1 we show the corresponding spectrum recorded a decade later, this time from the gas phase molecule [6].

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**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  $MgK_{\alpha}$  radiation to excite the spectrum. The lower spectrum from Ref. [6] was obtained in the gas phase using monochromatized  $AlK_{\alpha}$  radiation for excitation.

In this case a hemispherical electrostatic analyser was used. Furthermore, the spectrum was excited by monochromatized  $AlK_{\alpha}$  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.

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  $-CH_3$  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 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

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