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The ESCA molecule—Historical remarks and new results

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ABSTRACT

The C 1s photoelectron spectrum of ethyl trifluoroacetate (CF_3—CO—O—CH_2—CH_3), also known as the 'ESCA molecule', is the most illustrative showcase of chemical shifts in photoelectron spectroscopy. The binding energies of the four carbon atoms of this molecule spread over more than 8 eV with energy separations ranging from 1.7 to 3.1 eV owing to different chemical environments and hence different charge states of these atoms. The paper discusses history and importance of this spectrum in the field of photoelectron spectroscopy starting from the time of invention of the ESCA technique. The main focus of the paper is a 'revisit' of this spectrum using the most modern experimental and computational tools. Large geometrical changes, different for each ionization site, and the presence of two conformers of ethyl trifluoroacetate influence the spectral lineshapes of all four C 1s lines. These effects are carefully modeled by theory and investigated in the experimental spectrum.

1. Introduction

The first core electron spectra were obtained by Prof. Kai Siegbahn (Nobel Laureate 1981) and his students Carl Nordling and Evelyn Sokolowski in 1957 [1,2]. Already in this pioneering period a chemical shift of the core level binding energies was indicated. However, these early results did not attract the interest one might have expected. Instead, five years later Siegbahn's group found two clearly shifted core electron lines associated with atoms of the same element and in the same molecule. The studied molecule was sodium thiosulphate,[1] which contain two sulphur atoms in different chemical environments. This result was indisputable and lead to a very hectic period of research activity in Siegbahn's laboratory in Uppsala. Only three years later the group published the first of the two famous monographs – ESCA Atomic Molecular and Solid State Spectroscopy Studied by means of Electron Spectroscope [3].

The cover of this volume had a picture of a C 1s core photoelectron spectrum of ethyl trifluoroacetate (CF_3—CO—O—C_2H_5), see Fig. 1. The molecule had been synthesized by the group in order to give an illustrative example of what could be learned from core photoelectron spectroscopy. It contained four carbon atoms in different chemical environments and carbon 1s binding energies decreasing from the CF_3 end and onwards. At this time the group could study only solid samples. Therefore, the sample was prepared by freezing out the liquid as a thin layer on a backing. In addition to the broadening induced by the excitation source and the electron spectrometer, various solid-state broadening effects were present.

Nevertheless, one could clearly see the four chemically shifted core electron lines. This was a beautiful and very striking example of how the core–electron binding energy shifts could probe the chemical environment. In particular, the shifts roughly followed the electronegativities of the substituents on each carbon atom. Therefore, the charge distribution within the molecule could be observed. Soon it was possible to make models where the charge distribution in the ground state was correlated to the core-level binding energy. At this time very little was known about final-state effects and the theory for photoionization of molecules was by no means developed. Only very crude electron-structure calculations were published for molecules. The combination of electronic binding energy data and the emerging calculated energies of higher and higher quality would later boost the field of quantum chemistry.

The cover of the volume [3] was certainly well chosen. The monograph had a very large impact, and the cover spectrum was soon to be known and referred to as that of the ESCA molecule. The number of groups working on electron spectroscopy increased very rapidly into a large community. In 1968, Siegbahn's group had expanded greatly and they produced a second monograph, dealing exclusively with studies of free molecules in the gas phase [4].

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[1] There is a small story about this. There were two members of Siegbahn's group working with a spectrometer on a Sunday and they had run out of samples. Therefore, they went to the photographic lab of the department of physics and found a fixation salt, sodium thiosulphate. In fact, this is a very interesting example of serendipity.

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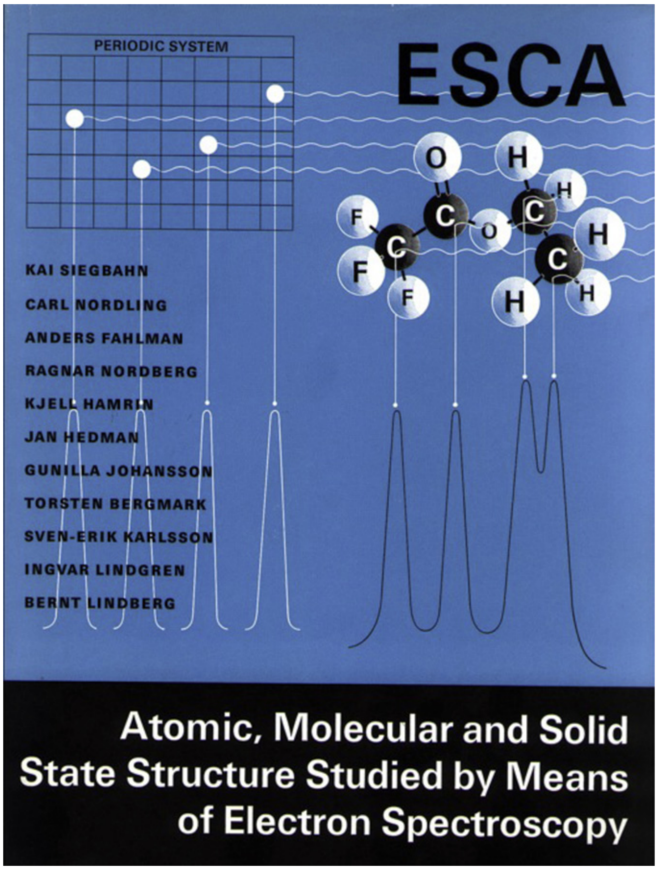

Fig. 1. The cover of the ESCA monograph 1967.

Also this volume had the C 1s spectrum of ethyl trifluoroacetate on the front page. It is interesting to note that this was not a new gas phase recording, but the same result from condensed molecules as had been presented earlier. We have talked to some of the (now retired) scientists in the group of Siegbahn, who explained that the reason was that using a non-monochromatized Mg Kα X-ray source the spectrum did not show better resolution for a gas phase sample, compared to the earlier condensed-phase result.

However, the next published result for the molecule was obtained four years later. The instrument development advanced rapidly with monochromatization of the X-rays. On one hand, this severely lowered the photon flux, but simultaneously introducing a multi-channel detection made experiments feasible. The first gas phase electrostatic electron spectrometer with a quartz crystal monochromator and multidetection of electrons was ready by 1972 [5]. In this publication a much better version of the spectrum was presented, also shown in Fig. 2.[2]

The instrument development and electron spectroscopy advancement have progressed further with the use of synchrotron radiation as excitation source. The instrument in Ref. [5] gave a resolution of about 400 meV at best. For comparison, nowadays the level of accuracy reaches a few meV at the best beamlines using the most modern electron spectrometers. This makes it possible to observe the effects of lifetime broadening of the core levels, vibrational fine structure, molecular field splitting (in the case of spin–orbit split core levels) and also more subtle effects like partial delocalization of core holes and conformational equilibrium in the sample gas.

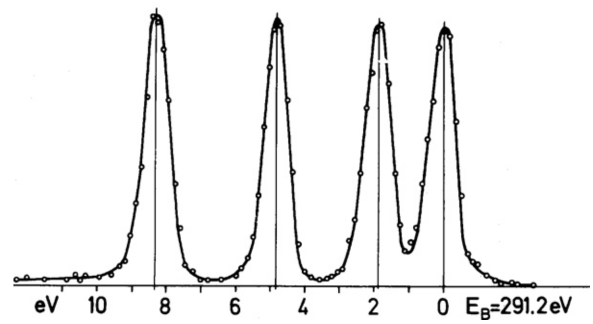

Fig. 2. The C 1s photoelectron spectrum of ethyl triflouroacetate recorded with monochromatized Al Kα X-rays.
From Ref. [5].

Presently, the most recent and advanced beamline for molecular physics studies in the gas phase is the PLEIADES beamline at the SOLEIL synchrotron radiation facility in France. We decided to make a new study of this so-called 'ESCA molecule'. The purpose is to give the community of electron spectroscopists an up-to-date logo for the activities, and to present a modern analysis of the spectrum. The new spectrum is shown in Fig. 3.

The instrumental resolution is about 10 times better than in the case of Fig. 2. The individual peaks are, however, much broader than expected given such a good resolution, indicating additional properties not observed earlier for this molecule. We notice that the most striking difference to the result in Ref. [5] (Fig. 2) is that lines have different heights and different line profiles.

Based on gas phase electron diffraction data and supported by vibrational spectroscopy data, Lestard et al. [13] concluded that ethyl trifluoroacetate exists in a conformational equilibrium with two strongly dominating conformations that are designated as *anti–anti* and *anti–gauche* (see Scheme 1).

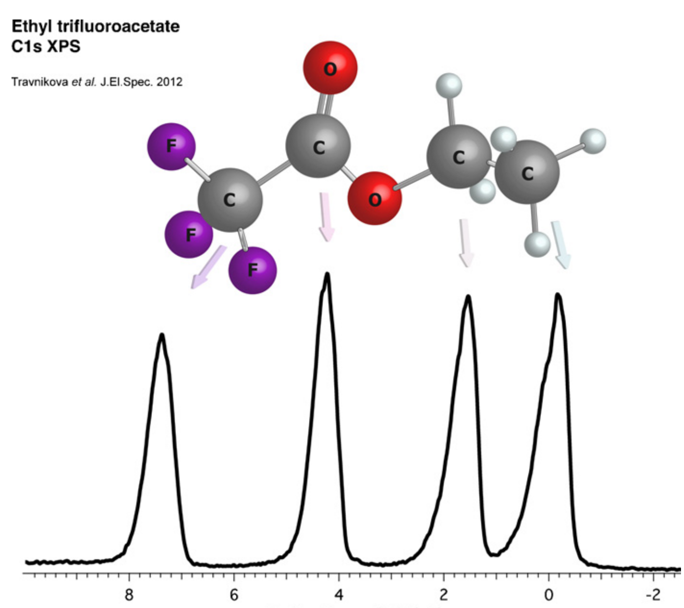

Fig. 3. The C 1s photoelectron spectrum of ethyl trifluoroacetate recorded at a photon energy of 340 eV at the PLEIADES beamline at the SOLEIL synchrotron laboratory. The zero of the *x*-axis is the vertical energy of the C_{CH_3} peak, which corresponds to 291.47(1) eV on the binding energy scale.

[2] This figure has been grossly reproduced during the years and one of the authors of the present paper (SS) was a co-author. He notes that the figure is very often shown in papers, textbooks, presentations and reports; most often without reference to the source.