

# Uppsala and Berkeley: Two essential laboratories in the development of modern photoelectron spectroscopy

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## ABSTRACT

The development of modern photoelectron spectroscopy is reviewed with a special focus on the importance of research at Uppsala University and at Berkeley. The influence of two pioneers, Kai Siegbahn and Dave Shirley, is underlined. Early interaction between the two centers helped to kick-start the field. Both laboratories have continued to play an important role in the field, both in terms of creating new experimental capabilities and developing the theoretical understanding of the spectroscopic processes.

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## I. INTRODUCTION

The importance of photoelectron spectroscopy in contemporary science and technology cannot be overestimated. Here, we will describe how the field developed from the start in Uppsala and how particularly it expanded after the discovery of core-level chemical shift. A collaboration had already been established between the groups in Uppsala and Berkeley in the field of  $\beta$ -spectroscopy. This activity switched over to photoelectron spectroscopy and Berkeley very soon established itself in the forefront of the field. The technique is now rapidly spreading in the USA and worldwide. Here, we discuss how the activities in Uppsala and Berkeley were linked but also how they took different directions at the two laboratories. The development is covered from the early beginnings of the technique to the introduction of synchrotron radiation, leading to widely used electron spectroscopy methods and tools.

## II. EARLY ELECTRON SPECTROSCOPY: NUCLEAR PHYSICS AND $\beta$ -SPECTROSCOPY

Kai Siegbahn (Nobel Prize 1981) initiated modern electron spectroscopy. He was the son of Manne Siegbahn (Nobel Prize 1924),

who got the prize for his work in the field of x-ray spectroscopy. Kai Siegbahn graduated from Stockholm in 1944 on a thesis titled “Studies in Beta Spectroscopy.” As a young scientist, he also worked on the first electron microscope in Sweden. At this time, nuclear physics was the hottest research field and Kai soon placed himself in the front line. One very important development in order to improve the studies of  $\beta$ -particles was made by Kai Siegbahn with the introduction of a doubly focusing magnetic field spectrometer, which resulted in a very large increase in the transmission of the instrument.<sup>1</sup>

In 1954, Kai Siegbahn got a professorship in Uppsala. There, he started a number of new activities, among these, one was electron spectroscopy. The new type of  $\beta$ -spectrometer was the basis for a fruitful collaboration between Uppsala and Berkeley. This story began around 1960 when an improved version of an “iron-free” spectrometer with cooled coils was developed in Uppsala.<sup>2</sup> The instrument could measure electrons at “lower energies.” At this time, this terminology was interpreted as lower than about 3.5 MeV. Kai Siegbahn had good contacts with researchers at Berkeley, where he

also spent a sabbatical period in 1961. As a result of this collaboration, a decision was made to build two identical instruments. One of these to be placed in Uppsala at the “Diös institute,” and the other instrument, to be shipped to Berkeley.

The Diös laboratory was inaugurated in September 1962. The Berkeley instrument was installed and commissioned by the staff from Uppsala and Berkeley. Dr. Carl Nordling and Kai Siegbahn led the Swedish delegation. A further participant from Uppsala was Stig Hagström, who was a graduate student at that time. From the American side, Jack Hollander was the project leader. In Fig. 1, a photograph from the inauguration of the Diös institute in September 1962 is shown, and Fig. 2 displays a sketch of the instrument.<sup>2</sup>

The instrument in Berkeley arrived in late 1961 and a “field-free” laboratory was built at Strawberry Canyon, which was reasonably far from the big accelerators. In a review article,<sup>3</sup> Dave Shirley and Charles Fadley have described this step of the development of electron spectroscopy at Berkeley:

In the 1960s, nuclear physics was still the historical focus of the Lawrence Radiation Laboratory (now, the Lawrence Berkeley National Laboratory, or more simply, the Berkeley Lab). There were various electron spectrometers in the laboratory, used for studying electrons emitted in radioactive decay, but they were relatively simple instruments. Then, our nuclear spectroscopists learned from Kai Siegbahn, during one of his visits to Berkeley, of a new double focussing magnetic spectrometer that he planned to build. As a

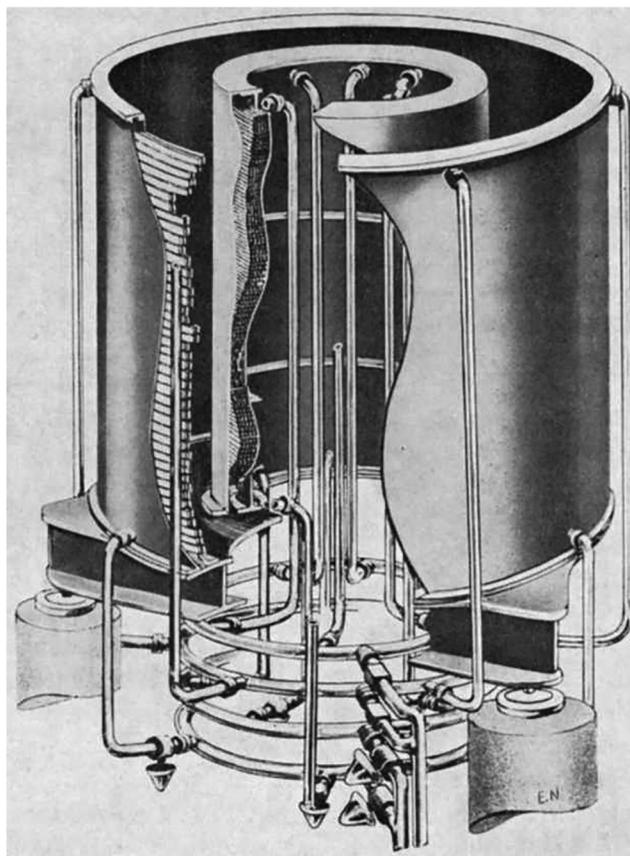
result, two of these iron-free spectrometers were built in Uppsala, with one going to Berkeley for nuclear physics research under the direction of Jack Hollander. To house this machine, a magnetic field-free laboratory building was built, fabricated entirely of wood, with aluminum screws and nails, and located in Strawberry Canyon some distance from the accelerators, all to minimize extraneous field effects on this sensitive device. The construction projects were completed, and the “field-free spectrometer” was used for nuclear physics research, beginning in the early 1960s.

In 1978, one of us (S.S.) made an interview with Prof. Carl Nordling concerning the installation of  $\beta$ -spectrometer in Berkeley. And, he gave an interesting comment, revealing that scientific work can be connected to larger or smaller mishaps:

-If we then discuss disappointments I have experienced; you know yourself that failures show up in research as on an assembly line. This applies to all research that has not been degenerated into routine activities. And, in the case of such



**FIG. 1.** Inauguration of the Diös institute in Uppsala. In the first row: Prof. Kai Siegbahn (third from the left in the front row), and on his right side: the rector of Uppsala University, the donor Anders Diös, and finally, Dr. Carl Nordling (Photo courtesy of Upplandsmuseet).



**FIG. 2.** Sketch of the “iron-free” instrument. Reprinted with permission from Siegbahn *et al.*, Nucl. Instrum. Methods 27, 173, Copyright 1964, Elsevier. One can notice the coil system and the cooling tubes. The beta particles had energies up to 100 keV and quite large currents could exist in the coils. The instrument was produced in two exact copies, one for Uppsala and one for Berkeley.

failures, you should not be disappointed. But I would nevertheless like to mention one moment when I felt really disappointed. This was when we had mounted an ESCA-instrument at the Berkeley laboratory in the USA.<sup>4</sup> Kai Siegbahn and I had travelled with the instrument to the special laboratory that was built on the beautiful slope above the Californian coast. We connected the instrument and, in the presence of an expectant cohort of researchers, we started to record a spectrum that we believed was “foolproof”. But we did not get any sign of a signal! This was really a moment of disappointment. To our luck we could soon rehabilitate us, only by reversing the current direction in the magnets. We had tried to focus positrons instead of electrons! (Translated from Swedish by S.S.).

It can be added that the contacts between Berkeley and Sweden were already established. At the end of the 1930s, Manne Siegbahn, after having created the Nobel institute in Stockholm, sent one of his students, Sten von Friesen, to the laboratory of Earnest Lawrence in order to learn how to build a cyclotron. Von Friesen later moved to Lund, and it was his accelerator-based nuclear physics research that eventually led to the establishment of MAX-lab, the Swedish National synchrotron radiation laboratory in Lund.

### III. BIRTH OF ESCA

It is interesting to note that modern photoelectron spectroscopy was practically impossible before 1955. The photoelectric effect was identified already by Heinrich Hertz,<sup>5</sup> but it turned out that it was very difficult to observe dispersed spectra from the emitted electrons. The theoretical description was made already in 1905 by Albert Einstein.<sup>6</sup> However, a general interpretation of an electron spectrum could be made only after the “golden years of quantum mechanics” 1925–1930. There were some early efforts to experimentally study an electron spectrum; the best known is Robinson’s paper from 1925.<sup>7</sup> In this study, a gold sample was illuminated by radiation from an x-ray tube and the outgoing electrons were dispersed using a homogeneous magnetic field. Only the x-ray edges of gold were observed. The main obstacles for progress were that the vacuum technology was poor, the focusing of the photoelectrons was poor, and last but not least, the necessary detectors were not developed.

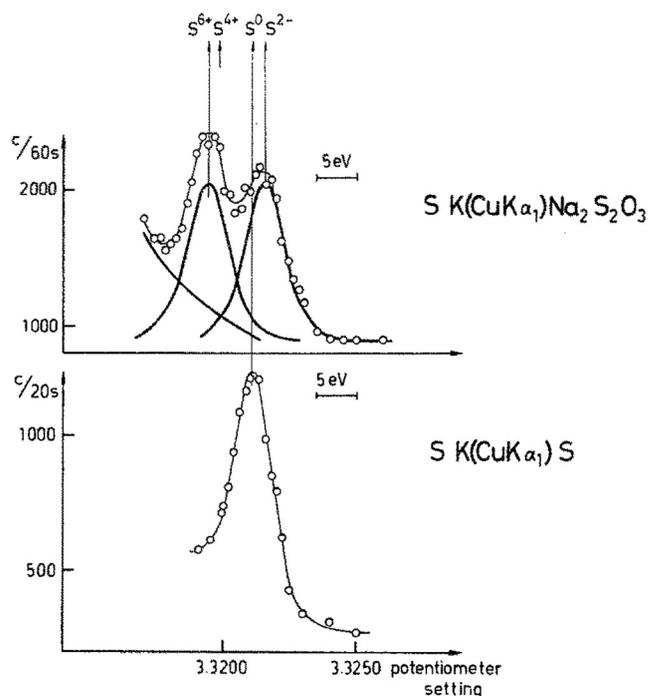
The first modern photoelectron spectra were recorded by Kai Siegbahn and his group in Uppsala in the years 1954–1958.<sup>8,9</sup> The group had developed an “iron-free” electron spectrometer, which was placed in an arrangement of Helmholtz coils to compensate for the earth magnetic field. As a detector, a Geiger tube covered by a very thin carbon membrane was used. An x-ray tube with anode materials such as Mo or Cu was used to give the photoemitted electrons sufficiently high kinetic energy to be analyzed. In fact, due to the detector, no electrons with energies lower than 4 keV could be observed. The first photoelectron spectrum showing lines corresponding to atomic energy levels was published in *Physical Reviews* in 1957.<sup>10</sup> The excitation was achieved by using an x-ray tube with a molybdenum anode (Mo  $K\alpha_1$  17 479.0 eV and Mo  $K\alpha_2$  17 374.1 eV). This activity has been recently reviewed by two of the

authors of this report, in collaboration with one of the pioneers; Evelyn Sokolowski.<sup>11,12</sup>

### IV. GAME CHANGER: THE DISCOVERY OF THE CORE-LEVEL CHEMICAL SHIFT

During a relatively long period, photoelectron spectroscopy was performed only by this small group in Uppsala. The main aim was to produce core-level binding energies, which provided important input when studying inner conversion processes in  $\beta$ -spectroscopy. The impression was that the field was largely explored and the group did not produce very many papers until 1963. But this year, an important discovery was made, namely, that the sulfur 2p core-level binding energies showed large shifts depending on the chemical state of the sulfur atoms. At that time, Stig Hagström had joined the group and the first chemical shift was recorded by him and Carl Nordling. The first unambiguous observation of a chemical shift was made on sodium-thiosulfate, where the two chemically inequivalent sulfur atoms within the same molecule were shifted by more than 5 eV.<sup>13</sup> This shift was much larger than expected, see Fig. 3.

Kai Siegbahn immediately realized the importance of this observation and in a short time, the group in Uppsala had

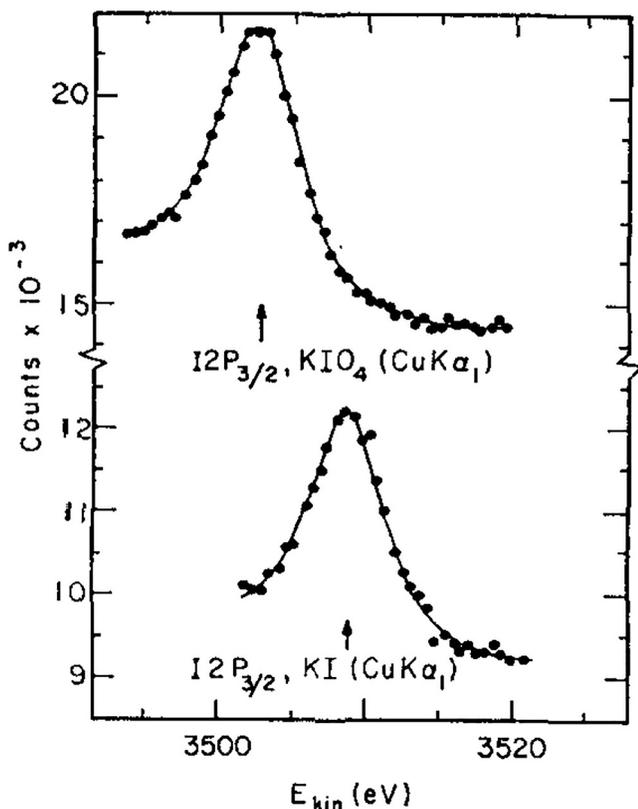


**FIG. 3.** First unambiguous observation of the core electron chemical shift: The S2p photoelectron spectrum of  $\text{Na}_2\text{S}_2\text{O}_3$ . Reprinted with permission from Hagström *et al.*, *Phys. Lett.* 9, 235, Copyright 1964, Elsevier. The two sulfur atoms have different chemical environments and the spectrum shows two distinct lines shifted by more than 5 eV. The excitation was obtained using  $\text{CuK}\alpha$  x-ray radiation.

expanded a lot. In a few years, an impressive number of samples had been analyzed and the first attempts to model the chemical shift using, e.g., Pauling electronegativities were rather successful. In the year 1967, the group could publish the first monograph of the field, “Electron Spectroscopy for Chemical Analysis ESCA.”<sup>14</sup> In the following three years, several new spectrometers were built in Uppsala, optimized to analyze electrons with energies up to a few keV, and they also included gas phase samples. A second monograph “ESCA applied to free molecules” was presented in 1969.<sup>15</sup>

Rather soon, photoelectron spectroscopy also started at Berkeley. The starting point occurred when Stig Hagström came as a postdoc to Berkeley. He pointed out that the previously acquired  $\beta$ -spectrometer could be modified for this purpose, as described by Shirley and Fadley,<sup>3</sup>

Our interest in photoelectron spectroscopy started in 1965. Stig Hagstrom, a recent Ph.D. from the Uppsala group, who was in Berkeley as a postdoc., pointed out to one of us (DAS) the possibility of doing photoelectron spectroscopy with the field-free spectrometer.



**FIG. 4.** Photoelectron peaks from the  $I2p_{3/2}$  level in  $KIO_4$  and  $KI$ . Reprinted with permission from Fadley *et al.*, *J. Chem. Phys.* **48**, 3779 (1968). Copyright 1968, AIP Publishing LLC.

Charles Fadley constructed an x-ray tube, and a suitable Geiger counter was provided with the necessary carbon window. Very soon, the team started to produce real photoelectron spectra. They published chemical shift measurements from  $Eu$  and  $I$  compounds, using a  $Cu$  anode for the excitation of the spectra.<sup>16,17</sup> Figure 4 shows the observed large shifts for the  $I2p$  level between  $KI$  and  $KIO_4$ . For  $Eu$ , they also saw very large shifts between the  $Eu^{2+}$  and  $Eu^{3+}$  states.

Shirley and his group also gave very important contributions which advanced the understanding of spectroscopy. For example, they explored the role of multiplet effects in core-level spectra,<sup>18</sup> and advanced the understanding of the role of atomic and extra-atomic relaxation effects.<sup>19</sup> They also demonstrated the relation between core-level binding-energy shifts and properties like proton affinity and Lewis basicity.<sup>20</sup>

## V. INTRODUCING MONOCHROMATIZED $AlK_{\alpha}$ RADIATION IN PHOTOELECTRON SPECTROSCOPY

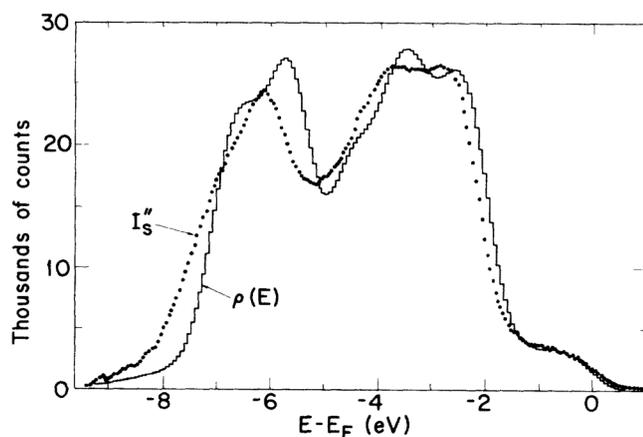
By the end of the 1960s and the beginning of the 1970s, electron spectroscopy research exploded worldwide and several producers of electron spectrometers showed up on the market. A particularly important step was when one started to excite the spectra by monochromatized  $AlK_{\alpha}$  x rays. A monochromator improves the spectrum in many respects. The bremsstrahlung continuum is filtered out, which significantly reduces the background, and thereby, the noise level. One is also removing other x-ray transitions and x-ray satellites, which otherwise create additional features in the spectra. The  $AlK_{\alpha_{1,2}}$  transition is a doublet due to the 0.4 eV spin-orbit splitting of the 2p level. Also, the natural width of the 1s level is about 0.4 eV. Thus, the inherent width of the  $AlK_{\alpha_{1,2}}$  profile is almost 0.8 eV. Using a sufficiently good monochromator, a slice of this characteristic x-ray profile can be cut out. A major challenge, however, is that any type of monochromator significantly reduces the x-ray intensity. Therefore, it is important to make the x-ray source and the monochromator arrangement as efficient as possible.

Here, we note, in particular, two early developments which brought the field forward. For solids, the breakthrough came with the Hewlett-Packard 5950A ESCA Spectrometer. Kai Siegbahn was involved in the design, which was completed in 1971.<sup>21</sup> The spectrometer was equipped with a monochromator consisting of three bent quartz crystals. In order to improve the intensity, one used the concept of dispersion compensation. The sample is placed on the Rowland circle of the monochromator such that the  $AlK_{\alpha}$  line is dispersed over the sample. Since the energy of the incident photons varies across the sample, the kinetic energy of the photoelectrons originating from a certain energy level will show a corresponding variation. The electron optics of the electron spectrometer is then constructed such that it has a matching dispersion but in the opposite direction. This implies that photoelectrons, corresponding to a specific binding energy, but emitted at different positions at the sample, will still end up at the same position at the 2D-detector. In this way, the spectrum will appear as if it was excited by a narrow x-ray line, although the complete  $AlK_{\alpha}$  line is used for excitation. This concept requires a carefully placed and flat solid sample. The dispersion compensation was essential in order to obtain sufficient

intensity in the spectra. The concept had been developed in Kai Siegbahn's group in Uppsala, and it is described in detail in the first ESCA monograph.<sup>14</sup> The first photoelectron spectrometer with a monochromator was built in Uppsala already in the beginning of the 1960s. This was a permanent magnet electron spectrometer equipped with an x-ray monochromator for  $\text{CuK}\alpha_1$  (8 keV) and  $\text{MoK}\alpha_1$  (17.5 keV).<sup>22</sup> The task to construct the monochromator was given to Anders Fahlman who was a graduate student in Kai Siegbahn's group. In connection with this work, a fellow graduate student, Bertil Grennberg, brought up the idea of making the dispersion of the spectrometer opposite to that of the monochromator crystal.<sup>23</sup> In this spectrometer, however, the monochromator was only used to filter out the  $\text{K}\alpha_1$  lines.

Dave Shirley immediately realized the potential of HP 5950A spectrometer. At an early stage, he traveled the short route to the Hewlett Packard Site in Palo Alto, bringing a gold single crystal. This led to a landmark spectrum of the valence band of gold.<sup>24</sup> The quality of the data made it possible to analyze the spectrum in detail. In this paper, the still much used "Shirley model" for removing the inelastic scattering contribution was introduced. In this way, he produced a high-resolution spectrum that could be compared to the calculated DOS (density of states) functions from different band structure calculations. This was a time when band theory developed rapidly. Different approaches were used for handling the wave functions, different types of exchange potentials were employed and the importance of relativistic effects was still not clear. Dave Shirley was then able to assess how well different calculations reproduced the spectrum. One such comparison is shown in Fig. 5.

Somewhat later, Dave Shirley got one of the first Hewlett-Packard instruments to his laboratory and the Berkeley group became one of the leading groups in the field with many ground-breaking results. Important investigations were published

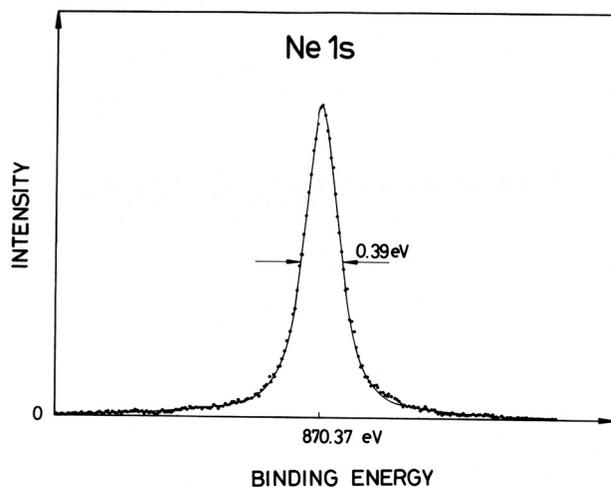


**FIG. 5.** Comparison between a background corrected valence band spectrum (dots) for Au and a broadened DOS function obtained from a relativistic Kohn–Kohn–Rostoker (KKR) (line) calculations by Connolly and Johnson. Reprinted with permission from Shirley, *Phys. Rev. B* **5**, 4709 (1972). Copyright 1972, American Physical Society.

for different types of semiconductor systems.<sup>25</sup> The group also made important contributions to the understanding of electron screening and correlation effects.<sup>26,27</sup>

Using dispersion compensation, good intensity could be obtained for solid samples using a fixed, water-cooled, anode. The samples had to be produced as plane surfaces of a dimension of a few mm. Obviously, it was not possible to use this scheme for monochromatized studies of gas phase samples. For such studies, it was necessary to build a monochromator with no entrance slit, but instead, based on fine focusing of an electron beam onto a small spot on the anode surface.<sup>28</sup> In Uppsala, such a project was initiated in 1971 by Kai Siegbahn and his graduate student Ulrik Gelius. The electron beam had to have a very high power, and therefore, a water-cooled anode in the form of a rotating disk was constructed. The rotation was achieved by an air pressure motor (with no magnetic material), put on an axis with seals that isolated the pressurized cooling water from the vacuum. The device was also differentially pumped. A focusing electron gun of the Pierce type generated a suitable spot on the rotating anode. A monochromatic beam was achieved by using a spherically bent quartz crystal. The sample (a gas cell) was placed on the opposite side of the Rowland circle.

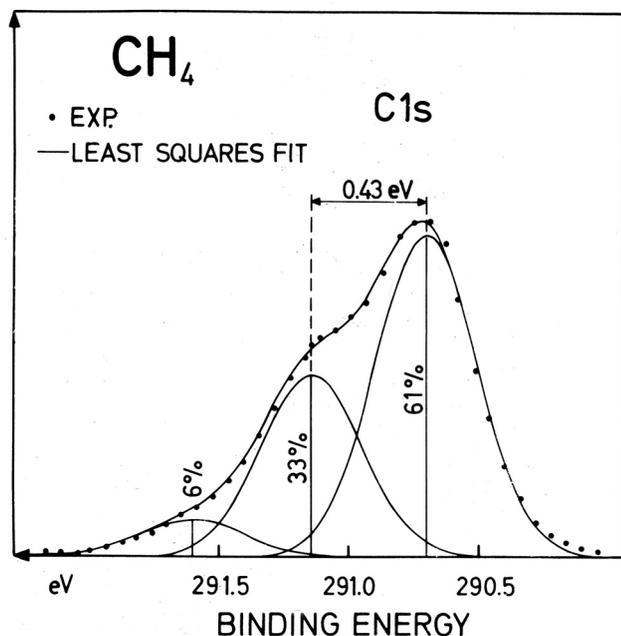
This construction gave enough intensity of monochromatized  $\text{AlK}\alpha$  radiation for studying the gas phase samples. Finally, the instrument was – as in the case of the HP 5950A spectrometer – provided with a multi-detection system for the photoelectrons. Several improvements were achieved: The resolution was improved with a factor better than 2. The signal-noise ratio was improved by a factor >100, and the multi-detection system increased the information ratio by a large factor.



**FIG. 6.** Core photoelectron spectrum of the Ne1s level. Reprinted with permission from Gelius *et al.*, *Chem. Phys. Lett.* **28**, 1 (1974). Copyright 1974, Elsevier. In Ref. 29, a value of 0.23 eV was given for the natural linewidth. However, at this time, no detailed computer-based fitting was possible. A better fit to the same data gave the value of 0.27 eV, see note in Ref. 30.

For the first time, the lifetime widths of core hole states could now be directly measured from the line profiles in photoelectron spectra. Figure 6 shows the 1s photoelectron spectrum from neon. The analysis gave a Lorentzian width of 0.27 eV, while the total width was 0.39 eV.

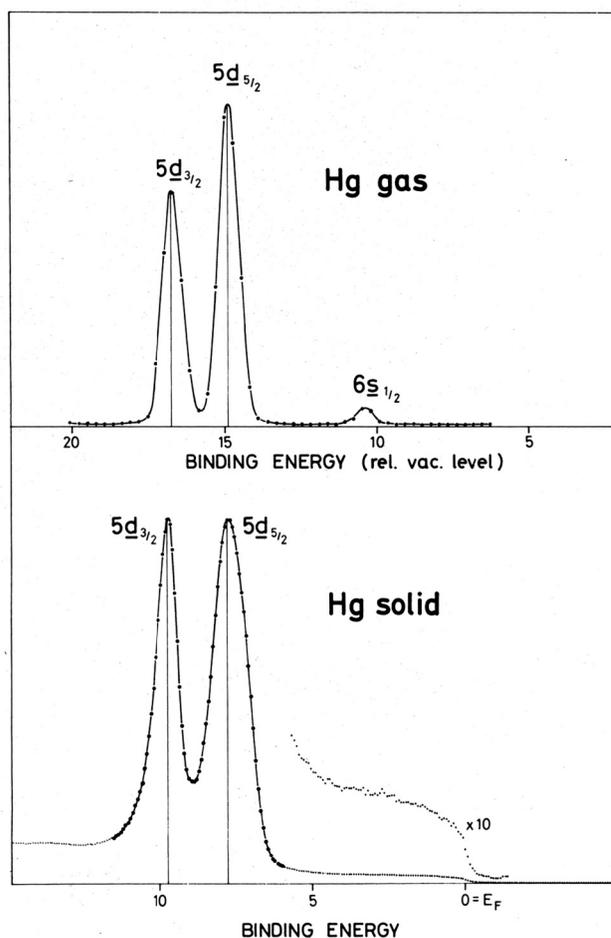
Another observation was that there was a vibrational progression in the C1s spectrum from CH<sub>4</sub>, see Fig. 7 (Ref. 29). At this time, the general opinion was that core hole states should not show dynamical fine structure. There was no overlap between the core orbitals, and therefore, these were considered to be nonbonding. You can find this argument, e.g., in the second (red) ESCA book from Siegbahn's group. On page 55 in Ref. 15, we can read what was the general knowledge at the time: *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.* The real understanding of the core hole dynamics was not achieved until a better understanding of the screening effects had been developed. This was a field where Dave Shirley made essential contributions. It can also be added that the vibrational progression in C1s of CH<sub>4</sub> is influenced by more sophisticated effects such as a Fermi resonance that have been cleared out by Karlsen and Børve.<sup>31</sup> The experimental and theoretical study of core-level line profiles is very demanding and can only be performed using the most modern electron spectroscopy based on synchrotron radiation beamlines and modern theoretical techniques.<sup>32</sup>



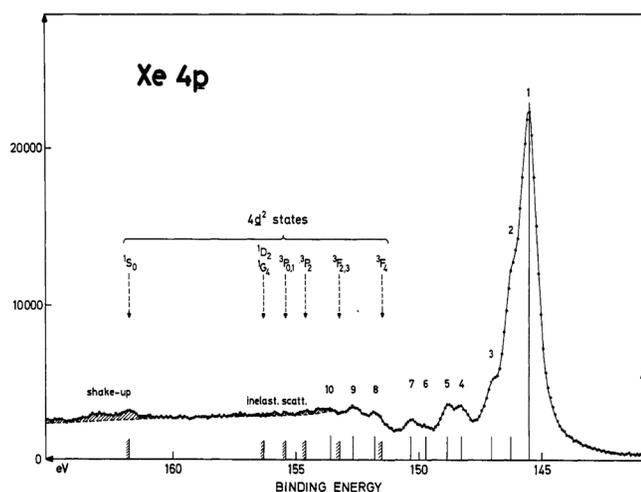
**FIG. 7.** C1s photoelectron spectrum of methane. Reprinted with permission from Gelius *et al.*, Chem. Phys. Lett. **28**, 1 (1974). Copyright 1974, Elsevier. This was the first core photoelectron spectrum showing vibrational sublevels, see text.

In 1974, an HP5950A instrument was delivered to Uppsala and there were then two world-class electron spectrometers (one for solids and surfaces, and one for gas samples) in the laboratory. Two of the authors of this report (N.M. and S.S.) responsible for these instruments were Ph.D. students. The experimental opportunities were, for instance, used to directly compare gas phase and solid state photoelectron spectra. In one of these studies, the core and valence electron spectra of water and ice were compared.<sup>33</sup> In another study, it was possible to directly show how the band structure of the solid metal was related to the orbital structure of the atom, see Fig. 8 (Ref. 34).

The direct comparison between core-level data for the free atom and the metallic state of mercury<sup>34</sup> also became the starting point of an extensive experimental and theoretical activity focusing on core-level screening effects and chemical shifts in solids. The chemical shifts between the free atom and the solid were calculated



**FIG. 8.** 5d and 6s levels of mercury. The upper spectrum: gas-phase. The lower spectrum: solid mercury. Reprinted with permission from Svensson *et al.*, J. Electron Spectrosc. Relat. Phenom. **9**, 51 (1976). Copyright 1976, Elsevier.



**FIG. 9.** 4p region of the core photoelectron spectrum of Xe. The super Coster-Kronig effect is energetically allowed for the Xe  $4p_{1/2}$  state, but not for the Xe  $4p_{3/2}$  state. The former forms a wide continuum, whereas the latter generates a large number of correlated states. Reproduced with permission from Svensson *et al.*, *Phys. Scr.* **14**, 141 (1976). Copyright 1976, IOP Publishing Ltd.

for all metallic elements in the periodic table, a model for understanding the chemical shifts in alloys was derived and a theory for surface core-level shifts was derived.<sup>35</sup>

The immense reduction of the background in the spectra made it possible to observe in detail, the correlation states in core-level spectra. This was first observed for Xe atoms, see Fig. 9 (Ref. 36). In earlier studies, no fine structure was observed and only an anomalously small “ $4p_{1/2}$ ” intensity was reported. The monochromatized result showed that the correlation is very strong between the 4p single core hole states and  $4d^2$  derived states. It should be noticed that the super Coster-Kronig (CK) effect is only possible for the  $4p_{1/2}$  single hole state. The “ $4p_{3/2}$ ” line is split into a large number of correlated states, whereas the  $4p_{1/2}$  state is not at all possible to observe. The lifetime of the  $4p_{1/2}$  single core hole is extremely short due to CK interaction.

## VI. SYNCHROTRON RADIATION REVOLUTION

In the 1970s, it became evident that synchrotron radiation had the potential of revolutionizing the field of photoelectron spectroscopy. Dave Shirley and Kai Siegbahn, both played important roles in this development, but in very different ways. The Shirley group started to work at SSRL, Stanford, already in the middle of the 1970s, which turned into a very successful activity. There were important results produced relating to the valence electron structure of solids,<sup>37</sup> temperature effects in photoemission,<sup>38</sup> and the structure of adsorbed molecules.<sup>39</sup> Dave Shirley also promoted the field in general, and, in particular, he became very important for the establishment of the advanced light source (ALS) at Berkeley.

Also, Kai Siegbahn realized that synchrotron radiation was an interesting tool. In collaboration with the Nobel laureate Wolfgang Paul, he started a project to construct an electron spectroscopy

beamline at the Bonn synchrotron. The idea of a Swedish synchrotron radiation facility also started in the middle of the 1970s. This project was initially pushed by P.O. Nilsson in Gothenburg. Kai Siegbahn, however, did not support this idea. Instead, he claimed that the Uppsala-Bonn project would cover Sweden’s need for synchrotron radiation for a long time. This was, of course, a total misjudgment of the strength of the development of the field. It can also be mentioned that the Uppsala-Bonn project collapsed. In spite of this, Kai Siegbahn’s role in the development of the field turned out to be very important.

The Swedish synchrotron radiation facility was funded, although at a very low budget. A 550 MeV storage ring (MAX I), also used as a pulse stretcher for photonuclear research, was taken into operation in 1985. In spite of the fact that the budget for the storage ring was very lean, the synchrotron radiation research at MAX I took off in a very good way. There were several reasons for this. The accelerator team managed to reach a good performance of the machine, despite the economic constraints. Another important factor was that an experienced and motivated user community already existed in Sweden, not the least in Uppsala. Several young researchers, who had graduated from Kai Siegbahn’s group, had already gained experience at various synchrotron radiation facilities in the world. At the same time, they carried on the strong tradition of instrument development from Kai and Manne Siegbahn.

Thanks to the foresight of the Swedish research council (NFR) and the Wallenberg Foundation, a few beamline projects were immediately funded at a very good level. The funding was also quite flexible which made it possible to take on new developments within these projects. Uppsala was an excellent place for such activities. As a consequence of Kai Siegbahn’s interest in instrument development, there were very skilled construction engineers and technicians and there was a very good workshop in the department. Furthermore, based on the instrument development in Kai Siegbahn’s group, a company, Scienta AB, had been established in Uppsala. The original focus of Scienta AB was on large photoelectron spectrometers with rotating anodes for  $AlK_{\alpha}$  radiation. One of the researchers who was very important for the completion of this instrument was Ulrik Gelius. Rather few instruments of that type were built, the instruments were too costly to become the basis for a large commercial activity. However, this meant that crucial competence was built. In particular, two important researchers, Björn Wannberg and Peter Baltzer, from the department, who had been involved in several new developments gradually moved over to the company. At this time, it also became increasingly hard to fund technical staff within the university system. Several technicians and engineers who had previously been employed on research grants at the university could instead be employed by the company. With time, several new Ph.D.’s from the department also became employed by Scienta AB.

As soon as MAX I was funded, the Uppsala group proposed to build an advance beamline for the studies of solids and surfaces. The proposal was funded which led to the build-up of Beamline 22 at MAX I.<sup>40</sup> At that time, the only option was to place the beamline at a bending magnet. A modification of the SX-700 monochromator concept was introduced, such that a rather large fan of the radiation from the bending magnet could be used. In this way, the x-ray flux on the sample could be increased, although it was spread

out over a line focus. For this reason, a new electron spectrometer was built, which could efficiently use the line focus produced by the monochromator. By optimizing all parts of the beamline together, a very competitive system was developed and the beamline was one of the most advanced for the studies of solids and surfaces at that time.

The electron spectrometer became a preprototype for the Scienta SES-200 electron spectrometer. The spectrometer development continued and the final prototype for the SES-200 spectrometer was built at the Department of Physics in Uppsala, in collaboration with Scienta AB.<sup>41</sup> This spectrometer used a multidefection system and a flexible electron lens, which could be used to optimize transmission, spatial resolution, or angular resolution. This spectrometer development was, e.g., recognized by the American Physical Society, when awarding Björn Wannberg the 2008 Joseph F. Keithley Award “for advances in the development of angle-resolved electron analyzers for photoelectron spectroscopy”. The SES-200 spectrometer was a great success and was soon used at many beamlines and most synchrotron radiation facilities in the world, and became a game changer for the company.

The Uppsala group was also heavily involved in the build-up of a second advanced beamline for the studies of gas phase samples at MAX I, also based on an SX-700 monochromator. This beamline used a very short, small-gap, in-vacuum undulator. The undulator and the monochromator were provided by a Finnish consortium, whereas the Uppsala group provided an advanced electrostatic electron spectrometer.<sup>42,43</sup> It was possible to study core levels up to about 500 eV with high resolutions. The resolution in the spectra was improved by a factor of 3–4 in comparison with earlier measurements. For the first time, the Resonant Auger effect could be demonstrated in the VUV range.<sup>44</sup> Also, the molecular field splitting of S2p lines was demonstrated.<sup>45</sup>

Furthermore, Joseph Nordgren’s group in Uppsala had developed a very compact, portable, high-resolution x-ray emission spectrometer.<sup>46</sup> This was used at several synchrotron radiation facilities in the world. This activity became very important for the development of soft x-ray RIXS (resonant inelastic x-ray scattering) both at Berkeley and in Sweden. At MAX I also, it was demonstrated for the first time that it was possible to measure x-ray emission spectra for adsorbed atoms and molecules.<sup>47</sup>

Based on the success of these beamline projects and the fact that there were many experienced spectroscopists involved, and in spite of the rather modest performance parameters of the MAX I accelerator, MAX-lab managed to place itself in the absolute forefront in several important research areas. The synchrotron radiation research reached a very strong position in Sweden and laid the ground for the next step in the development of MAX-lab. Although Kai Siegbahn did not promote this development at all, it is interesting to note that much of this happened as a direct result of Kai Siegbahn’s activity.

## VII. THIRD-GENERATION FACILITIES

Based on the success of the first- and second-generation synchrotron radiation facilities, it was realized that a new generation of storage rings could be constructed, where the electron beam properties were optimized to produce very brilliant x-ray beams using

undulators and wigglers in the straight sections. At Berkeley, David Shirley played a very important role, when he as Berkeley Lab director during the 1980s proposed the construction of advanced light source (ALS). ALS was funded in 1987. The construction started the year after and on 22 October 1993, Dave Shirley could cut the ribbon at the inauguration of the facility. Three other soft x-ray synchrotron radiation facilities were funded at an early stage. These were ELETTRA in Trieste, Italy, BESSY II in Berlin, Germany, and MAX II in Lund, Sweden.

The Max II project was approved in 1991. There were a number of reasons for the successful funding of the MAX II facility. The machine physicists at MAX-lab had presented an innovative design, which made it possible to reach the necessary small electron beam emittance in a storage ring with a circumference of only 90 m. It is clear that the success of the spectroscopy activities at MAX I was essential in order to get the project funded. Sweden had also a strong activity in crystallography, not the least protein crystallography, based on activities at different synchrotron radiation facilities in the world. However, this community was divided in the beginning when it came to supporting the funding of the MAX II facility. This changed later, when the facility had been funded.

Also, in this case, a few beamline projects were funded at an early stage and at a very good level. Again, Uppsala became heavily involved in this work. In fact, Uppsala researchers were strongly engaged in three of the first four soft x-ray beamlines at MAX II. Beamline I411 was constructed for electron spectroscopy on gases, neutral clusters, liquids, and outgassing (dirty) surfaces.<sup>48</sup> Researchers from Uppsala and Linköping were responsible for this project, also with substantial support from Finland. Another of these projects was BL I511,<sup>49</sup> which was totally led by Uppsala. This was a spectroscopy system with a rotatable chamber, incorporating an x-ray emission spectrometer as well as an SES-200 electron spectrometer. This set-up allowed the studies of emission spectra from surfaces for different directions of the x-ray polarization. Especially, for the x-ray emission spectra, this possibility became very important, since it made it possible to select different symmetries for the final states in the x-ray emission spectra.

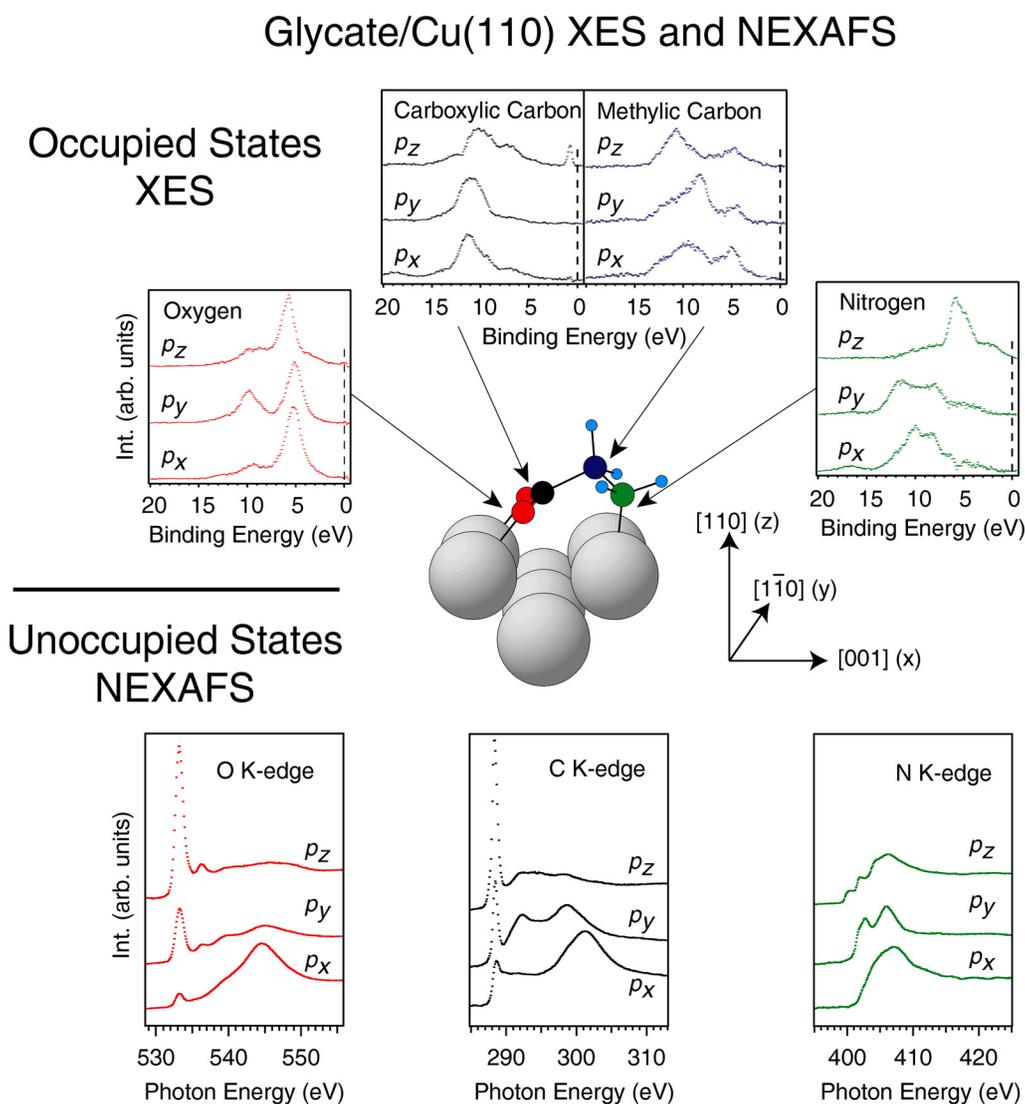
The MAX II project was built on a much lower budget than, for instance, ALS. One consequence of this was that the build-up took a somewhat longer time. It also started somewhat later. Tempted by the unique opportunities at ALS, several Uppsala researchers became immediately active at the Berkeley facility. Actually, the time window between the start of the operation of ALS and MAX II created a unique opportunity to move dedicated MAX II end-stations to the ALS and kick-start the science program. This led to very lively and successful activities, and again, to a close collaboration between Uppsala and Berkeley.

Surface science on metallic single crystals and surface chemical bonding was advanced by placing the dedicated MAX II I511 surface science experiment by the Uppsala group at Jo Stöhr’s IBM beamline 8 of the ALS, expanding a collaboration that had started already at SSRL.<sup>50</sup> Several researchers from Uppsala were more or less permanent at ALS for quite some time; among them were Anders Nilsson, and one of the authors (A.F.), who was a Ph.D. student at the time, with Dave Shirley as his Uppsala faculty opponent in 1999. Thus, polarization dependent surface science with the linearly polarized soft x-rays of beamline 8 became possible,<sup>51</sup>

where sample orientation and the direction of observation could be adjusted independently through the rotatable mounting of the hemispherical photoelectron spectrometer SES-200 and the compact transportable soft x-ray spectrometer developed previously by Joseph Nordgren and Ralf Nyholm.<sup>46</sup>

The research spanned from surface chemical bonding derived from x-ray emission and x-ray absorption with atom specific, chemical state and orbital symmetry sensitive information, as exemplified for Glycate/Cu(110) in Fig. 10 (Ref. 52), to the aspects of electron correlation from resonant photoemission.<sup>53</sup>

Using high-resolution electron spectroscopy, it was shown how vibrationally resolved adsorbate core-level spectra give important information on the structure and electronic structure of adsorbate systems. For CO adsorbed on Ni(100), it was shown that the very broad O1s lines can be explained by vibrational effects, see Fig. 11 (Ref. 54). Since the vibrational fine structure could be resolved, it was also possible then to determine the adiabatic core-level position. Furthermore, it was shown that vibrational splitting and the shape of vibrational progression for the C1s line were characteristics of the specific adsorption site, see Fig. 12 (Ref. 54).



**FIG. 10.** Adsorption structure of the amino acid glycine on Cu(110). A complete atom-specific and orbital symmetry selective separation of the unoccupied and occupied valence electronic structure has been accomplished by polarization-dependent x-ray emission and x-ray absorption. Reprinted with permission from Nilsson *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **110**, 15 (2000). Copyright 2000, Elsevier.

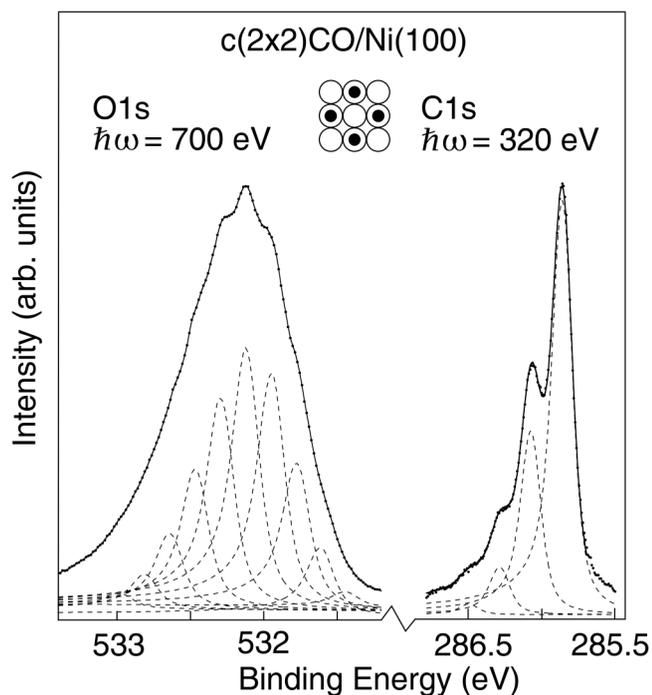


FIG. 11. C1s and O1s photoemission spectra of  $c(2 \times 2)\text{CO}/\text{Ni}(100)$ . Vibrational fine structure due to intramolecular stretch; C1s  $217.8 \pm 2.2$  meV, O1s  $173 \pm 8$  meV. Adiabatic transitions at  $285.8 \pm 0.1$  eV (C1s) and  $531.4 \pm 0.2$  eV (O1s). Reprinted with permission from Föhlisch *et al.*, Phys. Rev. Lett. **81**, 1730 (1998). Copyright 1988, American Physical Society.

The group of Joseph Nordgren installed their dedicated spectrometer for resonant inelastic x-ray scattering as part of the SpectroMicroscopy Facility<sup>55</sup> at beamline 7 of the Advanced Light Source. Fundamental insights for resonant x-ray—matter interaction were gained: The interplay of the effective scattering duration time, resonance detuning, lifetime interference, and symmetry selection rules advanced the conceptual aspects of resonant inelastic x-ray scattering.<sup>56–58</sup> Liquid phase RIXS investigations with thin membrane windows were initiated,<sup>59</sup> and for functional oxides and highly correlated solids, electronic structure properties and charge transfer excitations have been identified.<sup>60</sup>

Berkeley scientists, with a strong focus on angle-resolved photoelectron spectroscopy, have continuously developed beamline 7 based on the next generation of the hemispherical analyzer Scienta R4000. In 2009, Eli Rotenberg, from the Lawrence Berkeley National Laboratory received the Kai Siegbahn prize, at Uppsala University, established in honor of Kai Siegbahn, the founder of the journal “Nuclear Instruments and Methods A” (NIMA). The prize was given for the creation of ARPES “Electronic Structure Factory” end-station at the advanced light source and its artful application to the understanding of quantum electronic properties of nano-phase and reduced dimensionality materials. From 2016 on, the Microscopic and Electronic STRucture Observatory (MAESTRO) continues these capabilities by employing two Scienta R4000 spectrometers.

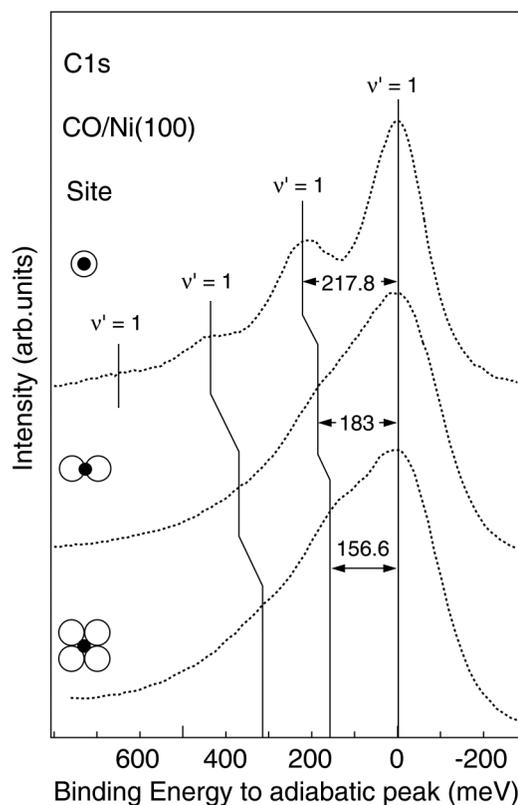


FIG. 12. Vibrational fine structure as a function of substrate coordination. The C1s line is shown for CO molecules adsorbed at the top, bridge, and hollow sites. Reprinted with permission from Föhlisch *et al.*, Phys. Rev. Lett. **81**, 1730 (1998). Copyright 1988, American Physical Society.

Independently, Charles Fadley (UV Davis) employed a modified hemispherical Scienta SES-200 analyzer in combination with brilliant undulator radiation to create optimum conditions for photoelectron diffraction (XPD) and holography as a probe of atomic structure and magnetic order, and the use of soft x-ray standing waves to study buried interfaces. This advanced photoelectron spectrometer/diffractometer at the Advanced Light Source Beamline 9.3.2<sup>61</sup> followed his conceptual framework of x-ray photoelectron diffraction (XPD) and holography as a powerful approach to atomic level structure determination.<sup>62</sup> Charles Fadley received an honorary doctorate from Uppsala University in 2014 for his research on condensed matter, materials, and surface/interface physics, as well as molecular physics.

## VII. FINAL COMMENTS

The authors of this paper have all been Ph.D. students in Uppsala, engaged in research in the field of electron spectroscopy. Our work has been focused on instrument development as well as the development of the basic understanding of the spectroscopic techniques—following the track started by Kai Siegbahn and Dave

Shirley—and we have continued the cooperation between Uppsala and Berkeley. We are grateful for the work of the pioneers described in this article.

## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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