cycloaddition reaction of two ethylenes. The ethylenes are allowed to approach each other in parallel planes along a symmetry plane (σ_1 in Fig. 5). The important MO's are those encompassing bonds that are made or broken in the reaction and that are symmetric (S) or antisymmetric (A) with respect to the symmetry element characteristic of the reaction. As shown in Fig. 6, the HOMO's of the reactants and products correlate not with each other but with high-energy MO's; that is, as reaction progresses this MO is transformed to a product MO having the same symmetry characteristics. At the transition state, which has some intermediate structure, this MO has high energy. The result is a high electronic energy barrier that precludes reaction, and this reaction is therefore termed symmetry-forbidden. By contrast, the comparable reaction of ethylene with butadiene (Fig. 7) involves occupied reactant MO's that correlate with occupied product MO's (Fig. 8). The result is a smooth conversion of orbitals without additional electronic barriers to reaction; the reaction is symmetry-allowed.

The results of orbital symmetry correlation diagrams lend themselves to alternative formulations that are frequently easier to apply. One is the perturbation charge-transfer approximation that involves only Fukui's frontier orbitals. Another treats the transition states in terms of their aromatic bonding character. This approach has its beginnings in the 1939 work of M. G. Evans, who recognized the relationship between the transition state for the reaction of ethylene with butadiene and the electronic structure of benzene. The idea was later generalized by M. J. S. Dewar and constitutes a simple and equivalent representation of the orbital symmetry approach. A characteristic feature in these methods is a cyclic orbital system having the stabilization of filled electronic shells for $4n$ or $4n + 2$ (n is an integer) electrons, depending on the phase relationships of the interacting orbitals. This concept of aromaticity goes back to the pioneering work of the late Erich Hückel, who first recognized the almost magical properties of some cyclic systems of $4n + 2$ electrons. His simple MO method, now generally known as the Hückel MO (or HMO) method, was used by Fukui in his early work, and an extension (the extended Hückel theory) was developed by Hoffmann and has received much use. The properties of the $4n$ and $4n + 2$ electronic cycles allowed Hoffmann and Woodward to formulate their orbital symmetry results as a set of simple rules.

An important feature of the frontier orbital and orbital symmetry approaches is that one can often derive the important results without involved computations. Even in these days of large high-speed computers and sophisticated quantum mechanical calculations, the essential features of this chemistry can be derived from the nodal properties of orbitals and their associated symmetries. The nodal properties in turn can often be related to the simplest form of electron-on-a-circle exercises familiar to most chemistry students. In a broad sense, this view of reactions has provided understanding and predictions for a large class of reactions, now called pericyclic reactions, that involve an electronic cycle in some form. The examples include many rearrangement reactions, additions, and eliminations. Frontier orbitals and orbital symmetry have generated other ideas and concepts and have led to new organic and organometallic structures. The reaction classification scheme of Woodward and Hoffmann has spawned new reactions that have entered the active repertoire of the synthetic chemist. More recent work of Roald Hoffmann is showing that the same ideas can also be applied to inorganic compounds and reactions.—ANDREW STREITWIESER, JR.

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The 1981 Nobel Prize in Physics

The 1981 Nobel Prize in Physics was awarded to three scientists. Half of the prize went to Kai M. Siegbahn at the University of Uppsala. The other half was awarded to Nicolaas Bloembergen of Harvard University and Arthur L. Schawlow of Stanford University.

Electron spectroscopy has been employed in the past decade by chemists and physicists for a wide and growing range of applications. These include basic research in molecular chemistry and surface physics, chemical characterization of atmospheric particulate matter in environmental studies, and analysis of the performance of catalysts in industrial processes. The success of this technique is due largely to the pioneering work of Kai M. Siegbahn, professor at the Physics Institute of the University of Uppsala, Sweden. During the 1950's and 1960's, Siegbahn and his collaborators in Uppsala combined instrumentation development with scientific discovery to transform electron spectroscopy from a laboratory method of limited use into a practical and powerful research tool. In recent years, many commercial electron spectrometers have become available, and electron spectroscopy is now applied in various forms at university and industrial research laboratories throughout the world. Appropriately, Siegbahn's "contribution to the development of high-resolution electron spectroscopy" has been recognized by the award of half of the 1981 Nobel Prize in Physics.

Electron spectroscopy (or, more precisely, photoelectron spectroscopy) is based on the high-resolution analysis of the kinetic energy distributions of electrons emitted from solid, liquid, or gaseous substances upon irradiation with a beam of monoenergetic x-rays or ultraviolet radiation. In recent years, monochromatized synchrotron radiation from electron storage rings has also become important as a tunable photon source. The physical quantity measured is the electron binding energy, B, which is given by Einstein's relation

$$h\nu = B + K$$

where $h\nu$ is the (known) photon energy and K is the (measured) photoelectron kinetic energy. Chemical information is obtained from chemistry-induced changes in the binding energies. In principle, all electron orbitals from the K shell out to the valence levels can be studied. When x-ray excitation is employed, the technique is usually referred to as x-ray photoelectron spectroscopy

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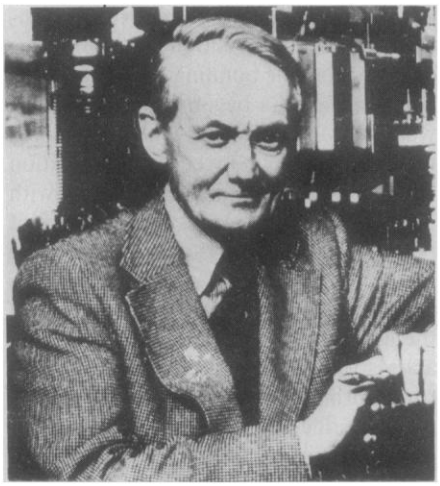
(XPS); when ultraviolet light is used, it is called ultraviolet photoelectron spectroscopy (UPS). The generic acronym ESCA (electron spectroscopy for chemical analysis), which was coined by the Uppsala group, mainly refers to x-ray photoelectron spectroscopy.

The photoelectric effect was discovered in 1883 by Heinrich Hertz, who found that substances irradiated by ultraviolet light may emit electrons. The history of the development of photoelectron spectroscopy is closely intertwined with some of the most fundamental theoretical advances of early 20th-century physics: Einstein's interpretation of the nature of the photoelectric effect, Bohr's structure of the atom, Planck's quantum theory, and Moseley's x-ray spectra of the elements. All of these were known by World War I. But it has often happened in science that great advances have had to wait until long after most of the theoretical ingredients were known, because the experimental tools were not yet at hand. This was the case with photoelectron spectroscopy. During the period between the two World Wars, a number of physicists observed photoelectron spectra. One of them was H. Robinson, who for many years worked in Rutherford's laboratory at Manchester; although many interesting observations related to values of the atomic constants were made by Robinson and his colleagues, their work was constantly plagued by inadequacies of the experimental apparatus. After World War II, the chemists R. G. Steinhardt and E. J. Serfass at Lehigh University sought to use photoelectron spectroscopy for chemical analysis, but did not achieve experimental conditions suitable for studying subtle chemical properties. Until the 1950's the electron-optical quality of the electron analyzers was so poor that photoelectron spectroscopy was useful only in phenomenological studies of the interactions of radiation with matter, rather than as a sensitive probe of electronic structure.

The work of Kai Siegbahn is a superb example of how an astute and talented practitioner of experimental science can recognize the potential of a field and the long-standing constraints on its realization, and can successfully overcome those constraints. Siegbahn had already developed a new theoretical principle of electron optics; using this principle, he constructed several generations of novel electron spectrometers of extremely high precision and resolving power. He eventually overcame the limitations of technique that had prevented photoelectron spectroscopy from becoming a practical science. Along the way, he made several important discoveries that gave to the technique an unanticipated power and generality.


Wide World Photo

Kai M. Siegbahn

In his work, Kai Siegbahn combined elements of precision x-ray spectroscopy, for which his father, Manne Siegbahn, had been awarded the Nobel Prize in 1925, with those of the emerging field of nuclear spectroscopy, in which he did his own doctoral research in the middle 1940's. The fundamental advances that gave the critical impetus to photoelectron spectroscopy were achieved by Siegbahn and his colleagues at Uppsala in the late 1950's. Since then, the Uppsala group have made numerous contributions to the state of the art of photoelectron spectroscopy and its applications. Two seminal books on ESCA were published by Siegbahn and his co-workers in 1967 (*1*) and 1969 (*2*).

The main reason for early difficulties in obtaining information about materials by photoelectron spectroscopy had to do with the extreme sensitivity of the spectral distribution of the emerging photoelectrons to the thickness of the sample. (This would ultimately prove to be one of the analytical strengths of the technique.) Electrons undergo scattering on their way out of the material and lose smaller or larger amounts of kinetic energy. Thus a group of initially monoenergetic electrons (of kinetic energy $K = h\nu - B$) emerge from the sample with degraded kinetic energies. Under conditions of moderate instrumental resolving power, they are observed only as a broad electron energy distribution, which is essentially impossible to interpret in terms of discrete atomic binding energies. However, the electron energy losses are quantized—that is, on their way out, the electrons transfer energy to the sample only in discrete amounts—so that there is a significant probability that no energy loss occurs. Therefore, in addition to the broad lines observed previously, a sharp zero-energy-loss peak should be contained in the photoelectron spectra. In order to resolve these sharp lines, however, the electron spectrometer must have sufficiently high resolving power that the lines stand out from the intense continuum of electrons that have suffered energy loss. This was not the case for any instruments used in the work done before Siegbahn's entry into the field.

An alternative analytical method that was developed in the 1920's for the study of the interior of atoms also overshadowed the photoelectron spectroscopy of the day. This was x-ray emission spectroscopy, by which studies are made of the radiation emitted when electrons move from one inner atomic level to another. Because the x-ray spectra are not sensitive to the surface thickness of samples, the method could be applied successfully to bulk elemental analysis. It did not, however, give detailed information about chemical structure.

The idea of applying electron spectroscopy to the study of atomic phenomena occurred to Siegbahn in the late 1940's during his work on the beta-ray spectroscopy of radioactive nuclei. He considered the possibility of using a strong x-ray source to expel electrons, rather than the radioactive, cyclotron-produced sources he was studying. By the end of the 1940's his work in high-resolution beta-ray spectroscopy had developed to the point where he could record spectra with tenfold higher accuracy than was possible earlier. This advance was achieved through his development of a new two-dimensional focusing principle and construction of a large (50 centimeters in radius) prototype spectrometer, which came to be known as a double-focusing spectrometer. The electron-optical resolving power was sufficiently high that he observed for the first time the inherent line widths of some of the classic internal-conversion electron lines of nuclear spectra (ThB, F, and I lines). His next advance was a double-focusing instrument that was iron-free, that is, in which the correct field form ($\rho^{-1/2}$, where ρ is radius) was produced by a system of coils without iron pole shoes.

The advantages of an iron-free configuration are that it is possible to achieve very high resolving power because the field form can be constructed with high accuracy; it is feasible to measure relative magnetic field strengths with extremely high accuracy; and one can rely on the accuracy of the field form at very low energies. These are just the ingredients necessary to obtain meaningful photoelectron spectra by x-ray excitation of atoms. In Siegbahn's words (*3*), "Looking back then on earlier attempts along these directions I realized that electron spectroscopy for atoms could never become competitive with ordinary x-ray emission and absorption spectroscopy unless I were able to achieve such a high resolution that really well-defined electron lines were obtained with line widths equal to or close to the inherent atomic levels themselves."

The first iron-free double-focusing spectrometer was completed in Uppsala in 1954 and shortly achieved a resolving power close to 10^{-4}—almost a tenfold improvement over contemporary iron instruments. The decisive step in photoelectron spectroscopy was taken in the same year, when Siegbahn and his coworkers Carl Nordling and Evelyn Sokolowski began to record x-ray–produced photoelectron spectra with the new instrument. The first of two major discoveries was made: the electron spectra contained, in addition to the broad (energy-loss) lines observed previously, a number of strong and extremely narrow lines that had not been observed before. These were the zero-energy-loss XPS lines. An important aspect of this finding, which would greatly facilitate analysis of the lines, was that the discrete character of electron energy-loss processes produces an intensity minimum, or valley, between the principal XPS line and the continuous energy distribution. Thus the sharp lines could readily yield precise values of the electron binding energies. This discovery paved the way for the new form of high-resolution spectroscopy known as ESCA. Electron spectroscopy could now compete successfully with x-ray spectroscopy as an analytical technique. During the late 1950's, Siegbahn, Nordling, and Sokolowski made very high precision studies of the electron binding energies of almost all the elements of the periodic system.

The second major discovery, which was to establish ESCA (XPS) as a powerful and unique tool in chemical research, was the chemical shift. Siegbahn, together with Nordling and Stig Hagström, observed in 1964 that in the spectra of certain substances, more than one photoelectron line was produced in the location where only one elemental line was expected. For example, sodium thiosulfate ($Na_2S_2O_3$) exhibited two well-resolved *K*-shell photoelectron lines for the element sulfur. Because the chemical structure of the thiosulfate ion was known, the origin of the two lines was quickly recognized: in this ion the two sulfur atoms are chemically nonequivalent, one being in the -2 formal oxidation state and the other in the $+6$ state. The chemical shifts are caused by different electron densities in the vicinity of the atom. This observation gave rise to the idea of correlating the electron binding energy with chemical oxidation state, which in turn provided the basis and incentive for the development of increasingly realistic correlations and theoretical interpretations from which chemical information can be obtained. Thus, it became possible to use ESCA to identify not only the atoms in a substance but also the chemical environments in which these atoms exist. Siegbahn and his group were in the forefront of these developments.

During the past decade, the applications of electron spectroscopy have grown enormously in both breadth and depth. The direct relation of the technique to electronic structure has made it the method of choice for studying certain electron correlation effects in bound and continuum states of atoms. Photoelectron cross sections and angular distributions yield unique information about orbital symmetries in free and adsorbed molecules. Diffraction can affect the angular distributions of photoelectrons emitted from molecules and solids, yielding information about structural parameters. Resonant photoemission has been observed in a variety of contexts and promises to grow into a subject of interest itself. Of overwhelming importance, however, is the multitude of applications of electron spectroscopy to the characterization of materials of scientific and commercial importance. Because of its high surface sensitivity and universal applicability, ESCA has been used to study the elemental composition and chemical state of many industrially important surfaces. Although much of the information about such uses of ESCA is not available for proprietary reasons, it is safe to estimate that it has been employed for the study of high-technology materials with annual sales volumes of several billion dollars.

It is of interest to note that the 1981 Nobel award to Kai Siegbahn is the fourth time that a father and son have both received the Nobel Prize. The first time was in 1915, when W. H. Bragg and his son W. L. Bragg jointly received the prize for their work on x-ray crystallography. In 1906 J. J. Thomson received the award for his discovery of the electron; his son G. P. Thomson received it in 1937 for his discovery of electron diffraction. And in 1922 Niels Bohr received the award for his work on atomic structure, while his son Aage Bohr received it in 1975 for his work on nuclear structure.—JACK M. HOLLANDER and DAVID A. SHIRLEY

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Laser Spectroscopy Shares Prize

The Royal Swedish Academy of Sciences announced on 19 October that Nicolaas Bloembergen of Harvard University and Arthur L. Schawlow of Stanford University would share half of the 1981 Nobel Prize in Physics for development of laser spectroscopy. The physics community and, in particular, those in laser research laud the award of this high honor in recognition of the achievements of Bloembergen and Schawlow. Their contributions in physics have been wide-ranging, timely, and continuous. Bloembergen's interests and research have included nuclear and electronic magnetic resonance, solid state masers and lasers, and especially nonlinear optics and spectroscopy, while Schawlow's research activities have spanned radio frequency, optical, and microwave spectroscopy, nuclear quadrupole resonance, superconductivity, and especially lasers and high-resolution laser spectroscopy.

Their innovative ideas and unequaled experimental skills have dominated the field of laser spectroscopy in the past two decades and have been an inspiration to those in laser research. Both are celebrated teachers, possessed of a characteristic flair and combination of talents that have marked them as outstanding scientists and gifted lecturers. And both have instilled a passion for first-class work in a host of brilliant young students


Wide World Photo

Nicolaas Bloembergen


Wide World Photo

Arthur L. Schawlow

and co-workers, who have gone on to make their mark in quantum electronics and physics. Both have also contributed much to the well-being of science as active members of scientific societies at home and abroad, and as consultants to industrial and government research organizations.

At this time, prior to learning the individual citations for the Nobel Prize, it is worth noting the citations accompanying the highest award of the Optical Society of America, the Frederick Ives Medal, recently presented to Bloembergen and Schawlow. Bloembergen's award in 1979 was given "in recognition of his achievement in establishing the theoretical framework of nonlinear optics; his sustained innovative contributions to the exploration of all aspects in the field of nonlinear optical phenomena; and his successes in the role of teacher and interpreter of science." Schawlow was cited in 1976 "in recognition of his pioneering role in the invention of the laser, his continuing originality in the refinement of coherent optical sources, his productive vision in the application of optics to science and technology, his distinguished service to optics education and to the optics community, and his innovative contributions to the public understanding of optical science."

Nicholaas Bloembergen was born on 11 March 1920 in Dordrecht, The Netherlands. He received the Phil. Cand. (1941) and Phil. Drs. (1943) degrees from the University of Utrecht, and the Ph.D. degree (1948) from the University of Leiden. He began his long association with Harvard University and his career in the United States in 1946 and 1947 as a part-time research assistant and continued as a member of the Society of Fellows (1949 to 1951). In 1951, he was awarded an honorary A.M. degree by Harvard and appointed associate professor. He has held the rank of Gordon McKay professor of applied physics from 1957 to the present, was Rumford professor of physics from 1974 to 1980, and became Gerhard Gade university professor in 1980. Bloembergen became a U.S. citizen in 1958. He married Huberta Deliana Brink in 1950, and they have three children.

Bloembergen has also served as Guggenheim fellow and visiting professor at the Ecole Normale Supèrieure (Paris) in 1957; visiting professor at the University of California (Berkeley) in 1965; Lorentz guest professor at the University of Leiden in 1973; Raman visiting professor, Bangalore, India, in 1979; Alexander von Humboldt senior U.S. scientist, Munich; and visiting professor, Collège de France (Paris) in 1980.

Bloembergen's list of publications includes two books (*1*) and over 200 papers in scientific journals on topics in nonlinear optics, quantum electronics, solid state masers, and magnetic resonance. Together with his co-workers, he developed a rigorous theory of nonlinear polarizability, the extension of Maxwell's equations to include nonlinear source terms, and the interaction of multiple waves in the bulk and at the boundaries of nonlinear media. This latter work led to the extension of the laws of reflection and refraction.

No less important have been his subsequent contributions to the experimental development of this field. The experimental work, which was pursued with a series of students and collaborators, included virtually the entire domain of nonlinear optics as it is known today: the exploration of effects predicted by the theory for the mixing of multiple waves; the determination of the effect which partial coherence in a laser beam has on nonlinear interaction; measurements of the dispersion of the nonlinear susceptibility in semiconductors; determination of stimulated Raman emission, avoiding self-focusing; dielectric breakdown phenomena and their interpretation; coherent anti-Stokes Raman spectroscopy; stimulated Brillouin and Rayleigh scattering; processes of optical radiation damage due to defects; two-photon Doppler-free spectroscopy of sodium; the use of interference technique for the measurement of nonlinear susceptibilities in highly dispersive media; and, most recently, the investigation of collision-free processes of multiphoton dissociation.

For these many contributions, Bloembergen has received many honors. He is a member of the National Academy of Sciences; fellow of the American Academy of Arts and Sciences; correspondent of the Koninklyke Nederlandse Akademie van Wetenschappen, Amsterdam; fellow of the American Physical Society; fellow of the Dutch Physical Society; fellow of the Institute of Electrical and Electronics Engineers; fellow of the Optical Society of America; and honorary fellow of the Indian Academy of Sciences.

He is the recipient of the Oliver E. Buckley Prize for Solid State Physics (1958); the Morris Liebmann Memorial award of the Institute of Radio Engineers (1959, with C. H. Townes) in recognition of contributions to the maser art; the Stuart Ballentine Medal of the Franklin Institute (1961, with H. E. D. Scovil) for the invention and subsequent development of the three-level solid state maser; the National Medal of Science (1974), awarded by the President of the United States "for pioneering applications of magnetic resonance to the study of condensed matter and for subsequent scientific investigations and investigations concerning the interaction of matter with coherent radiation"; the Lorentz Medal (1978) awarded every 5 years by the Dutch Academy of Sciences; and the Half-Moon trophy of the Netherlands Club of New York (1972) in recognition of an outstanding Dutch immigrant.

Arthur Leonard Schawlow was born in Mount Vernon, New York, on 5 May 1921. His family moved to Canada in time for him to receive all of his education in Toronto. He obtained his B.A. in 1941, M.A. in 1942, and Ph.D. in 1949 under the guidance of Professor M. F. Crawford at the University of Toronto. He achieved early recognition for his research on atomic spectroscopy, and distinguished himself in certain Toronto circles as a clarinetist playing Dixieland jazz at a time when his idols were Benny Goodman and "Jelly Roll" Morton. In 1949 he became a research associate at Columbia University, and there began a long and fruitful association with Charles H. Townes (Nobel laureate in 1964). In 1951 Schawlow joined Bell Telephone Laboratories as a research physicist, and he spent 1960 as a visiting associate professor at Columbia University. Since 1961 he has been professor of physics at Stanford University, where he served as chairman of the Department of Physics from 1966 to 1970. In 1978 he was appointed the J. G. Jackson and C. J. Wood Professor of Physics. He married Aurelia Townes in 1951, and they have three children.

Schawlow was co-author with Townes of the book *Microwave Spectroscopy* (*2*) and the seminal paper on "Infrared and optical masers" (*3*). He has published almost 200 papers in scientific journals on atomic, molecular, and solid state spectroscopy, lasers, quantum electronics, fluorescence, and nonlinear laser spectroscopy. With his co-workers, he has developed extremely sensitive techniques of Doppler-free spectroscopy using laser saturation, two-photon absorption, polarization labeling, optogalvanic spectroscopy, as well as wave meters for precise wavelength measurements. While this work has mainly centered on the basic understanding of the interaction of light and matter, he has enthusiastically promoted the practical applications of this knowledge to industry, communications, and medicine.

Schawlow gave the AAAS Holiday Science Lectures in Philadelphia (1965), Salt Lake City (1966), and Durham (1967) and was the Richtmyer lecturer of the American Association of Physics Teachers (1970). He was also Cherwell-Simon lecturer, Oxford University (England) in 1970; H. L. Welsh lecturer, University of Toronto, in 1976; Hoxton lecturer, University of Virginia (1977); and W. V. Houston lecturer, Rice University (1978). He has appeared on the 21st Century programs with Walter Cronkite, and on the Experiment series with Don Herbert, as well as on films for Canadian and British television networks.

Among his many honors, Schawlow is a member of the National Academy of Sciences; fellow of the American Academy of Arts and Sciences; fellow of the American Physical Society, of which he is president this year; fellow of the Optical Society, of which he was president in 1975; fellow of the Institute of Electrical and Electronics Engineers; fellow of the American Association for the Advancement of Science; fellow of the Society of Photo-Optical Instrumentation Engineers; and fellow of the Institute of Physics (Great Britain). He has received honorary doctorates from the University of Ghent in Belgium, the University of Bradford in England, and the University of Toronto.

Schawlow was awarded the Stuart Ballantine medal by the Franklin Institute (1962, with C. H. Townes) and the Thomas Young Medal and Prize of the Physical Society and the Institute of Physics (1963, with C. H. Townes) for the first paper on "Infrared and optical masers"; the Morris Liebmann Memorial Award of the Institute of Electrical and Electronics Engineers (1964) for his pioneering and continuing work with optical masers. He was the recipient of a senior postdoctoral fellowship from the National Science Foundation for 1970 and 1971, recipient of the Geoffrey Frew fellowship of the Australian Academy of Science in 1973, and was named California Scientist of the Year in 1973. In 1977, Schawlow was awarded the third Marconi International Fellowship for his collective contributions to science, especially the laser, and this was presented in Stockholm by the King of Sweden.

—BORIS P. STOICHEFF

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